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Photochromic molecular materials for the controlled organization of nanoparticles

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Abstract

The displacement of polystyrene nanoparticles promoted by bulk azo mass transfer using interferential light illumination will be discussed. For this a variety of different push pull small azo molecules were synthesized and characterized, changing the polarity, hydrophobicity and bulky groups around the azo moiety. These small dyes appear to orientate quicker than similarly reported azo polymers, because of the lack of entanglement of the azobenzene group in the polymeric backbone. The dyes were used to form surface relief grating on the thin films due to the bulk mass transfer. This mass transfer was exploited to align polystyrene nanoparticles in the crests and troughs of the gratings. Secondly, the fabrication of azo nano objects will be discussed, here the photochromic studies showed the azo nanospheres had a larger photochemical conversion than their corresponding thin films. These nano objects were then successfully coated with gold nanoparticles by using azo compounds with dithiane or thioacetate ligands that are known to complex gold. The hybrid structure was proved by Raman spectroscopy where surface enhanced resonance effects have been evidenced upon excitation in the gold localized surface plasmon bands. Such assemblies, following a reverse architecture with the azo situated in the core and not on the exterior of the metallic nanoparticle, represents the first example of high-payload photochromic nanoparticles.

Keywords

Photochromic materials, photo organization, nanoparticles, nanohybrids, polystyrene nanoparticles, gold nanoparticles.

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Abbreviations

AFM = atomic force microscopy

AuNP = gold nanoparticle

DCM = dichloromethane

FTIR = fourier transform infrared

HRMS (EI) = high resolution mass spectrometry (electron ionization)

IR = infrared

MALDI-MS = matrix-assisted laser desorption ionisation mass spectrometry

NaDBS = sodium dodecylbenzenesulfonate

NMR = nuclear magnetic resonance

NR = nanorods

NS = nanospheres

PDDA = polydiallyldimethyl ammonium chloride

PM IRLD = polarized modulated infrared linear dichroism

PS = polystyrene

PVP = polyvinylpyrrolidone

SEM = scanning electron microscopy

SERS = surface enhanced Raman spectroscopy

SRG = surface relief gratings

TEM = transmission electron microscopy

TERS = tip enhanced Raman spectroscopy

THF = tetrahydrofuran

TOAB = tetraoctylammonium bromide

UV = ultra violet

Vis = visible

Preface

Photochromism can be defined as a reversible photochemical conversion between two species, exhibiting different absorption spectra. After the photochemical conversion, the species can either thermally or photochemically convert back to their initial state. A variety of different photochromic molecules exist, including compounds containing azo groups. These molecules can photoisomerize from the *E* to the *Z* state in the presence of light. When processed as materials, the azo compounds can undergo dramatic matter reorganization under polarized illumination. Several groups have exploited these phenomena to move macroscopic objects. The use of polarized illumination gives rise to surface relief gratings due to photoinduced mass transfer that will be further discussed in this thesis.

Since the discovery of surface relief gratings by Tripathy and Natansohn in 1994, the mass migration on azo thin films has been thoroughly studied but never harnessed to displace nanometer-sized objects. Nanoparticle research has exploded over the past two decades, because of their unique properties based on quantum or structural confinement effects and the possibility to incorporate multiple functionalities. Such properties can be used in applications such as data storage, phototherapy, and bioimaging among others. However, in order to fully utilize these properties, it is desired that nanoparticles could be organized into a specific configuration. To date, several methods have been developed to organize nanoparticles onto substrates, including dip-pen lithography, stamping, or self-assembly. Self-assembly is the most promising method of organizing nanoparticles although imperfections and instability toward ambient conditions are likely to occur. In this thesis, we will discuss about the synthesis and the use of azo photochromic materials to organize different nanoparticles by means of polarized light.

In Chapter 1, we will discuss what a photochrome is, the different types of photochromes and the way photochromic materials have been used to move external objects; Highlighting the importance of using an azo photochromic material to move external objects. Later, in Chapter 2, the criteria and synthesis of our desired azo molecules, and their photochromic properties in solution and thin films will be discussed. These thin

films will be used to organize different nanoparticles and will be further mentioned in Chapter 3. In Chapter 4, the synthesis of different photochromic nanohybrids will be discussed and their ability to organize different nanoparticles onto their exterior. Finally general conclusions and perspectives will be discussed in Chapter 5.

Chapter 1

Photochromes as photoactivable actuators

1.1 Photochromes

Photochromic materials undergo a reversible transformation between two states, *A* and *B*, by absorption of an electromagnetic radiation.¹ The resulting photo-induced reaction of the initial system *A* yields a new system *B* that has a distinct absorption spectrum (Figure 1.1). After the photoinduced chemical change, the newly formed species *B*, can convert back to *A* thermally or photochemically. Such reversible photochemical conversion can be utilized in applications such as photochromic lenses² and more recently as molecular switches,^{3–5} DNA scissors,^{6,7} nanomechanics,⁸ optical data storage,^{9,10} multi-photon devices,^{11–15} electro-chemical writing¹⁶ and phototherapy.^{17,18} Although the applications of photochromes are getting more complex, the core structure of the photochromes remain the same. There are four main classes of photochromes involving different mechanisms for the phototransformation and the back conversion reaction: diarylethenes, spiropyranes and spirooxazines, stilbenes and azo molecules. All of them are presently subject to intense research efforts for a variety of applications that depend on several critical parameters such as the speed of response under irradiation, the stability of the created species, the reversibility of the photoreaction and the absence of fatigue over multiple cycles of irradiation.^{1,9,19–22}

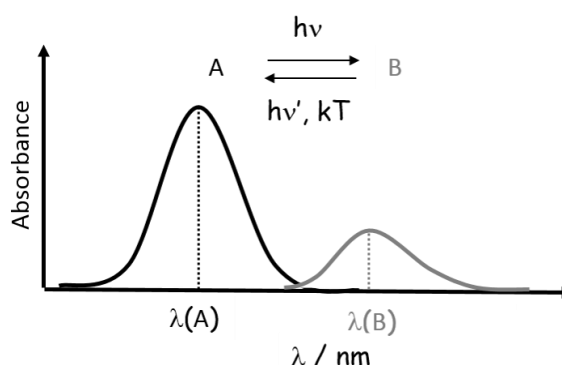


Figure 1.1. UV-vis absorption transforms from species *A* into species *B* upon light absorption.

1.1.1 Diarylethenes

In diarylethenes materials, a photoinduced 6π electrocyclization gives rise to a conrotatory mechanism following the Woodward-Hoffmann rules, providing closure of the central ring with both hydrogen atoms positioned in antiparallel fashion. Among the antiparallel and the parallel conformers, only the antiparallel conformers, displaying the reactive carbon atoms close enough, are amenable to photoreact. When the ring is closed, the compound becomes planar and fully conjugated, hence the compound absorbs in the visible range in contrast with the open form that is colorless. By irradiating at a longer wavelength than the initial irradiation (usually > 600 nm), retrocyclization occurs, causing ring opening and reversion of the system to its original state. Diarylethenes, when properly functionalized, exhibits two thermally stable states, and are thus dubbed “P-type photochromes”, where a photochemical conversion is required to revert back to its initial state.

Figure 1.2 shown below illustrates nicely the pioneering work led by the group of Prof. Irie at Rikkyo University and Tokyo University on diarylethene photochromic crystals. The dithienylethene compounds in the presence of UV light close the ring, forming a conjugated system that can revert back by visible irradiation and whose color depends on the π -conjugation path extension and the chemical nature of the substituents (Figure 1.2).^{19,23}

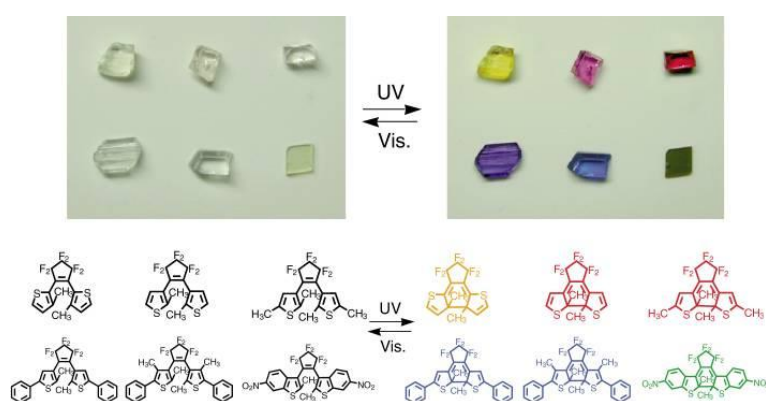


Figure 1.2. Irie's dithienylethenes crystals. Reprinted with permission of ref 23 © IUPAC.²³

With a similar type of molecule, 1,2-bis[4-methyl-2-(2-pyridyl)thiazolyl]-perfluoro cyclopentene, Piard et al from École Normale Supérieure de Cachan, showed the

effect of the photochromic properties when going from solution to solid state. Here, in solution the molecule exhibited large photochromic behaviour with very little fluorescence in the open ring form. The properties of the molecule drastically change when in a crystalline form, where no obvious sign of photochromism was observed while the molecule was extremely fluorescent in its open form. To try and balance the properties of this molecule between solution and bulk state, nanoparticles were formed through laser ablation and showed to have both fluorescent and photochromic properties.²⁴ This example emphasizes the differences between solution, bulk state and nanometric scale materials.

1.1.2 Spiropyrans/ Spirooxazines

Spiropyrans or spirooxazines are photochromic materials that upon light absorption also undergo a 6π electrocyclization reaction. Their peculiar behavior is related to the C-O bond breaking, leading to the pyrane or oxazine ring opening and the generation of the photomerocyanine form. Such geometry changes from the spiro arrangement to a planar one is accompanied by the appearance of strong absorption in the visible range due to the extensive π -conjugated backbone of the photomerocyanine define in Figure 1.3. Ring closure usually occurs by thermal conversion or by light absorption. Because of their possible thermal back reaction, spiropyrans and spirooxazines belong to the class of T-type photochromes (Figure 1.3).^{1,2}

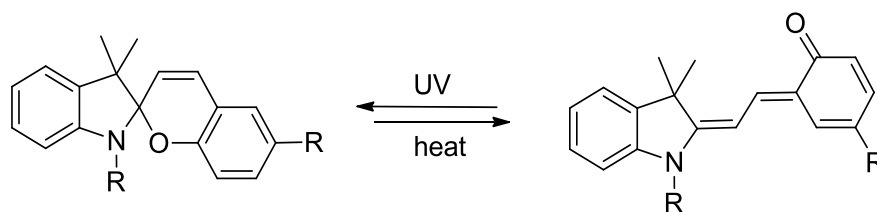


Figure 1.3. The reaction scheme of spirooxazine.

1.1.3 Azobenzene and Stilbenes

Azobenzene and stilbene molecules are a class of T-type photochromes that undergo *E-Z* photoisomerization from the more stable *E* isomer to the usually thermally unstable *Z* state. Once in its *Z* form the molecule can close its ring, similarly to the diarylethenes, depending on the substituents on the aryl ring or revert back to its *E* isomer. In the case of stilbenes, isomerization occurs around the central --C=C-- bond

while it involves the --N=N-- bond for the azo derivatives. Over the past two decades, azo molecules have more specifically been studied because of their ability to migrate over space and move external objects. This unique properties of mass transfer triggered by light has made azobenzene a photochrome of choice for the studies reported in this thesis (Figure 1.4).²⁵⁻²⁷

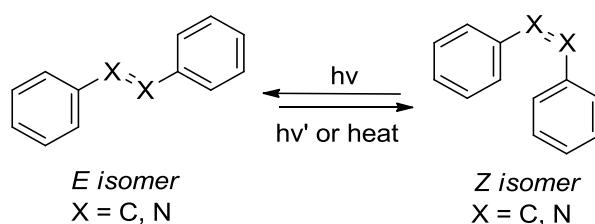


Figure 1.4. The reaction scheme of azobenzene ($X = \text{N}$) and stilbene ($X = \text{C}$) molecules.

1.2 Azobenzene materials

Azobenzene molecules have been revealed as attractive photochromes because of their easy synthetic pathway, the large impact of the substituents onto their photo- and thermal isomerization reactions, the large change in geometry from the *E* isomer (4-4' distance: 1 nm) to the *Z* isomer (4-4' distance: 0.59 nm), the large change in dipole moment, and finally their ability to respond to polarized light and induce material anisotropy and/or deformation.^{28,29} In this context, azobenzene moieties have been substituted in the para positions with a vast choice of electron donating and accepting groups leading to increased charge transfer along the conjugated azo core. The resulting molecules (and materials) display colorful properties and strong absorption in the visible range, opening new optical application fields in both the linear and non-linear optical regimes.^{25,26,30,31}

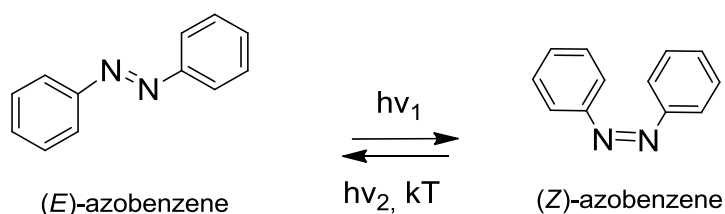


Figure 1.5. Photoisomerization reaction for azobenzene molecules.

1.2.1 Photoisomerization in azo materials

Photoisomerization of azo molecules has for a long time been a subject of debate. Two limit mechanisms are nowadays admitted: rotation for pseudo-stilbene like (or push-pull) azobenzenes, namely those containing a strong push-pull character, or inversion for the aminoazobenzene-like and centrosymmetric compounds.³² The rotational mechanism usually proceeds after a $\pi\pi^*$ transition while the inversion mechanism operates from a $n\pi^*$ electronic state (Figure 1.6).³³

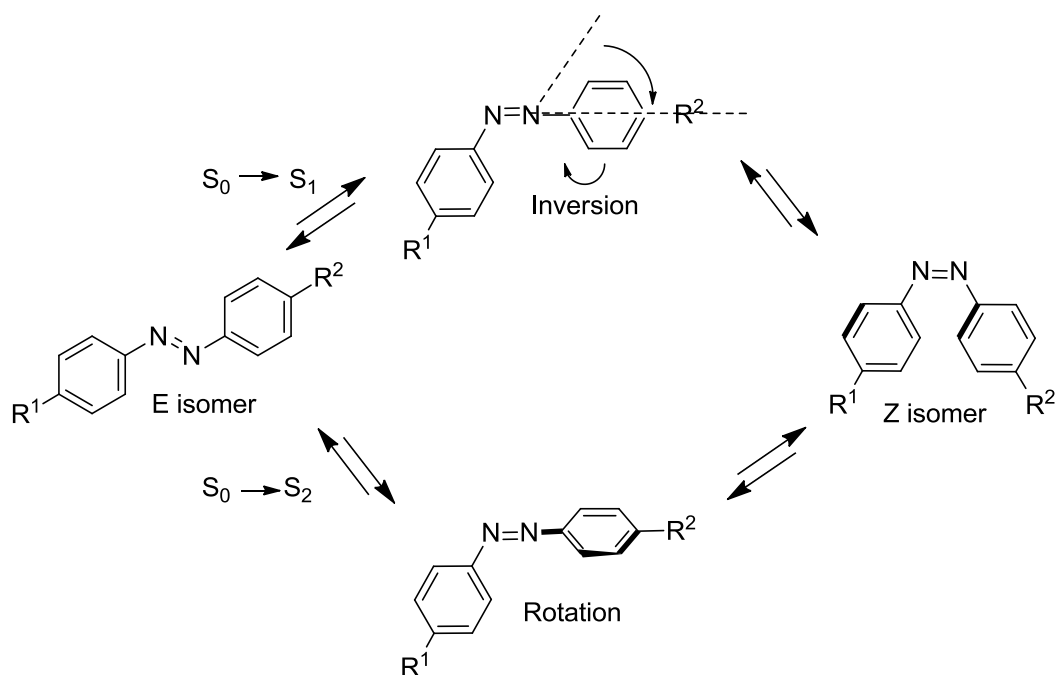


Figure 1.6. Rotational and inversion mechanism for photoisomerization.

For push-pull azo compounds, the $\pi\pi^*$ transition occurs at a lower energy compared to the $n\pi^*$ transition that is hidden under the $\pi\pi^*$ transition due to its low oscillator strength. In this case, the *E* and *Z* absorption maxima for the $\pi\pi^*$ transition occur in the same region, allowing for continuous photoisomerization between the *E* and *Z* isomer using a single excitation wavelength.²⁵

1.2.2 Photomodulation of properties in the solid state

Azo molecules have been studied for their potential as molecular switches opening new prospects in the field of optical memories. However, such devices require solid state photoisomerization, stable photoinduced species, fast rate of photoconversion and possibility to perform multiple on-off cycles. In 1995, Natansohn³⁴ and Tripathy²⁶

simultaneously discovered that azobenzene molecules mixed in a polymer matrix could form thin films and that the surface of such thin films could be modulated using light interferences. The change in topography yielded very regular diffraction gratings that were out of phase with the irradiation pattern: the ridges of the grating corresponded to the area where the electric field was smaller while the valleys corresponded to the area where the electric field was the strongest (Figure 1.7).^{31,35} Two decades later, it has been accepted that this surface pattern is due to the mass migration of the azobenzene units due to a continuous cycle of photoisomerization. However, the exact mechanism is still unknown. Some explanations of this mechanism include: pressure gradient,³⁴ photomechanical effects,³⁶ optical field gradient theory,³⁰ random-walk photoinduced molecular diffusion,³⁷ entropy-driven sample deformation,³⁸ and more torque inducing dipole electric interaction.³⁹ This migration occurs until the compound has totally migrated away from the excitation light. Most of the studies associated with mass migration had previously dealt with the specific case of azobenzene polymers. The difficulty with polymers relies on the size distribution of polymers that in turn influences the macroscopic viscosity and consequently the microscopic velocity of the polymer chains. Other studies have been done with azo liquid crystal polymers,^{10,40} sol gels,⁴¹ hydrogen and halogenated bonding polymers⁴² and small molecules.⁴³ In this context, the group has studied the behavior of small molecule-based azo materials and showed strong dependence of the bulkiness of the substituents on the magnitude of the thin film deformation. Such studies will be extended to the organization of a large number of nanoparticles as reported in Chapter 3 using the formation of surface relief gratings.

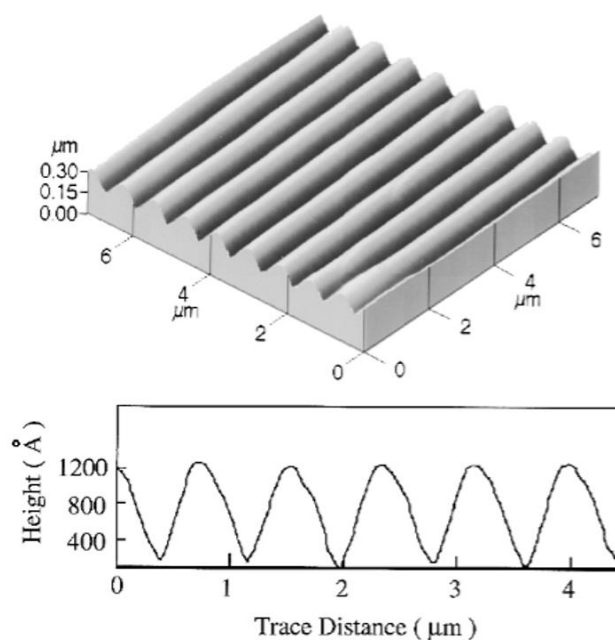


Figure 1.7. Atomic force microscopy (AFM) image of a surface relief grating (SRG) on azo polymers illustrating the mass migration of azo thin film. Reprinted with permission of ref 26 © AIP Publishing LLC.²⁶

Another example of photomechanical migration includes the use of azo liquid crystal polymers synthesized by Prof. Ikeda's group from the Tokyo Institute of Technology.^{15,44} Here the sample incorporates one or two acrylate groups that was cured to form a polymer thin film. The self-supported thin film was irradiated in the UV range using linearly polarized light and the sample rolled-up in the polarization direction. When the irradiation was stopped, the thin film reverted back to its original flat shape. Further irradiation steps using a light with different linearly polarizations led again to film deformations along the irradiation axis. These studies show how the orientation or the migration of azo polymer chain can be tuned by light to yield large deformation of matter (Figure 1.8).

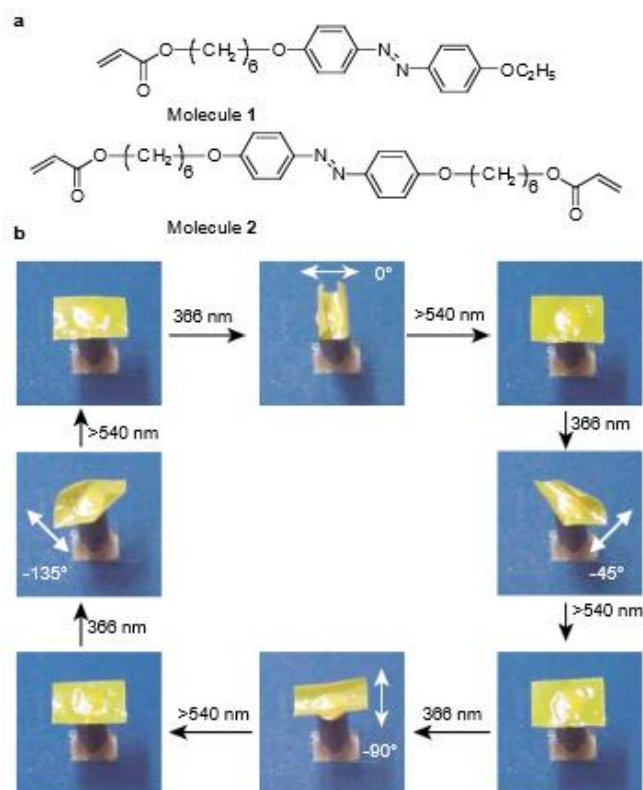


Figure 1.8. Molecular motions activated in a liquid crystal polymer thin film. The film can roll up along the direction of polarization of the impinging beam ($\lambda_{\text{max}} = 366 \text{ nm}$). The thin film can be unrolled when the irradiation wavelength is higher than 540 nm. Reprinted with permission of ref 44 © Nature Publishing Group.⁴⁴

Later, Ikeda et al. extrapolated that light could be used as a driving force to displace a thin film made of azo liquid crystals over space. In this elegant experiment, an azo thin film bent into a ring with dimensions of 18 mm x 3 mm, a thickness of 20 μm and a diameter of 3 mm could be rolled by using alternative cycles of UV and visible light exposures (Figure 1.9).⁴⁵

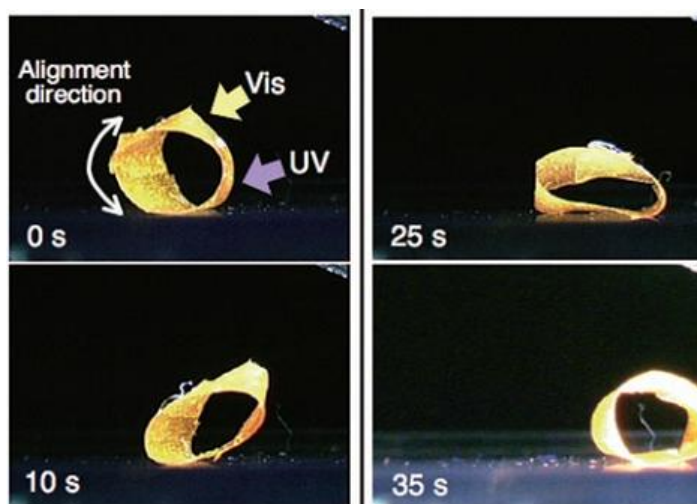


Figure 1.9. Illustration of the rolling motion of an azobenzene liquid crystal polymer using UV and visible lights as driving forces. Reprinted with permission of ref 45 © John Wiley and Sons.⁴⁵

1.2.3 Photoactivable actuators

Due to the electronic and mechanical properties of the azo molecules and their ability to migrate in the presence of light, it was thought that these properties could be exploited to move, sort or organize other external objects. The photoinduced azo mass flow could in turn be used to position nano objects into configurations that could be valorized for specific photonics applications. As a result of the large geometry change between the *E* and *Z* isomers, and an even larger change in the dipole moment, the hydrophilic and hydrophobic properties of the material can change, allowing for the hydrophobicity of the azo material to be controlled by irradiating the surface with UV or visible light. Prof. Ichimura's group from the Tokyo Institute of Technology reported the first studies involving the hydrophilic and hydrophobic properties of the azo molecules to displace droplets of substances with distinct hydrophobicity.⁴⁶ This was realized by synthesizing a thin film of O-carboxymethylated calix [4] resorcinarene that had p-octylazobenzene moieties incorporated into the structure. Here the droplet (oil, water, etc.) migrated by irradiating the surface with UV light ($\lambda_{\text{max}} = 365 \text{ nm}$), initiating the photoisomerization and yielding a high population of the *Z* isomers on the surface. Since the *Z* isomers had a larger dipole moment than that of the *E* isomers, the photoisomerized material became more polar and exhibited a higher surface energy than that before irradiation. A part of thin film was irradiated with blue light ($\lambda_{\text{max}} = 436 \text{ nm}$) resulting in the photochemical conversation of the *Z* isomer to the *E* isomer, resulted in the droplet moving to the side with higher surface

free energy (the side with the higher content in *Z* isomers) (Figure 1.10). Other studies performed by Delorome et al.⁴⁷ and Hamelmann et al.⁴⁸ showed that the contact angle of the droplet (water or oil) changed when the surface was photochemically converted to the *Z* or *E* isomer. Figure 1.11 shows azo thin films that move droplets upon irradiation.

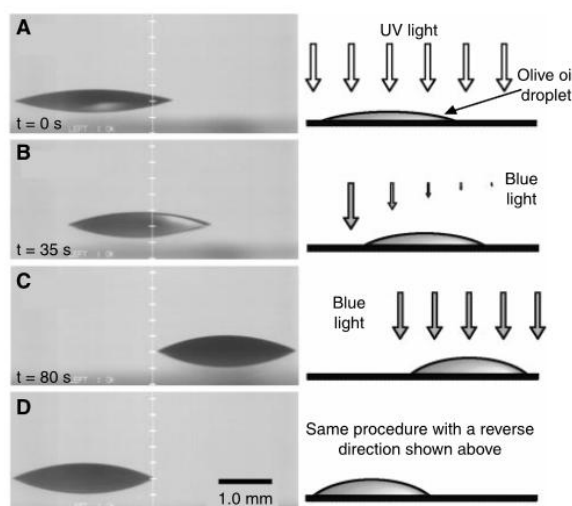


Figure 1.10. Azo thin films used to migrate droplets of fluids (a) deposition of a droplet onto a thin film, (b) the thin film was irradiated for 35 s with UV light forming a larger population of *Z* isomers, (c) part of the thin film was irradiated with blue light forming *E* isomers, here the droplet moves towards the *Z* isomer, (d) droplet was migrated back to its original position by the same reverse procedure. Reprinted with permission of ref 46 © The American Association for the Advancement of Science.⁴⁶

Photochromic materials have also been used to control the motion of other objects. For example, Prof. Feringa's group from the Groningen University has used liquid crystals doped with a stilbene derivative to control the rotation of a microscale glass rod⁴⁹ while Prof. Irie's group has showed that a diarylethene crystal could kick silica microspheres in the presence of light ($\lambda_{\text{max}} = 365 \text{ nm}$).²³ A last example through the studies of Kurihara's group illustrated the translation of $5 \text{ }\mu\text{m}$ polystyrene microparticles using a liquid crystal thin film doped with an azo small molecule.²⁷ The thin film was irradiated with UV light and the PS microsphere migrated away from the *E* isomer and towards the *Z* isomer. However, in order to withstand the weight of the microspheres, film thicknesses greater than $50 \text{ }\mu\text{m}$ had to be used, resulting in a larger volume of photochromic molecules being used. To try and reduce

the volume of material being used, it was thought that the displacement of nanoparticles using the azo thin film could be performed.

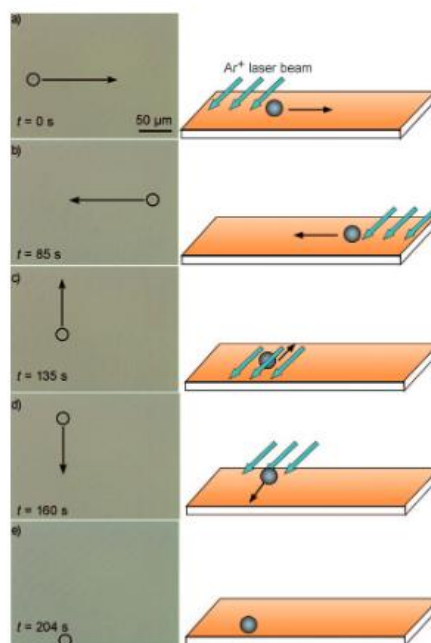


Figure 1.11. Translation of a polystyrene microsphere ($\phi = 5 \mu\text{m}$) using an azo thin film. Reprinted with permission of ref 27 © John Wiley and Sons.²⁷

When narrowing the size of the particle, a variety of new and interesting properties can be observed, due to the larger surface-to-volume ratio and confinement effects of nanoparticles compared to bulk materials.⁵⁰ One problem when going from one nanoparticle to several nanoparticles is uncontrollable aggregation.¹⁸ In order to control this aggregation, photochromic molecular materials will be used to organize nanoparticles.

1.3 Hybrid photochromic nanomaterials

Hybrid nanomaterials with inorganic and organic components are continually being explored due to their unique optical and electronic properties that have shown promising potential in fields such as optoelectronics and photonics.⁵¹ In order to utilize these properties, the hybrid nanomaterial has to be able to organize into a specific configuration.⁵² To date, a lot of traditional hybrid nanomaterials involve an inorganic core with the photochromic ligand surrounding the exterior.^{21,53–55} Different metallic species involving Fe, Si, Cd, Ag, and Au elements on the nanoscale have been studied incorporating a photochromic ligand onto the exterior. One of the most

popular examples of a hybrid photochromic nanosystem was shown by Klajn et al. and incorporated an azobenzene moiety into the monolayer of gold nanoparticles (AuNPs, $\varnothing = 5.6 \pm 0.6$ nm).⁵³ To avoid undesirable aggregation, additional alkylthiol ligands were introduced into the monolayer as spacers. When the AuNPs were irradiated with UV light, due to the large change in dipole moment, causing decreasing stabilizing solvation interactions the AuNPs collapsed together into 150 nm-wide aggregates that could be followed by a red shift in the surface plasmon resonance (SPR) band and a color change from red to blue. This aggregation phenomenon was reversible when the Z forms of the azo units relaxed back to their *E* isomers, and the solution turned red again. The azo-functionalized AuNPs were incorporated in thin films and surface patterning was performed using a mask (Figure 1.12). After irradiation, a pattern was formed due to areas composed of aggregated (blue) and non-aggregated (red) nanoparticles and remained visible for 16 to 24 h. Visible light irradiation could rapidly erase it in a reversible way. This example shows the benefits of using hybrid nanoassemblies, especially incorporating gold nanoparticles enabling the absorption to be monitored through the energy of the localized surface plasmon resonance (LSPR) band. For these reasons, the later part of this thesis will focus on using azo materials to organize different AuNPs.

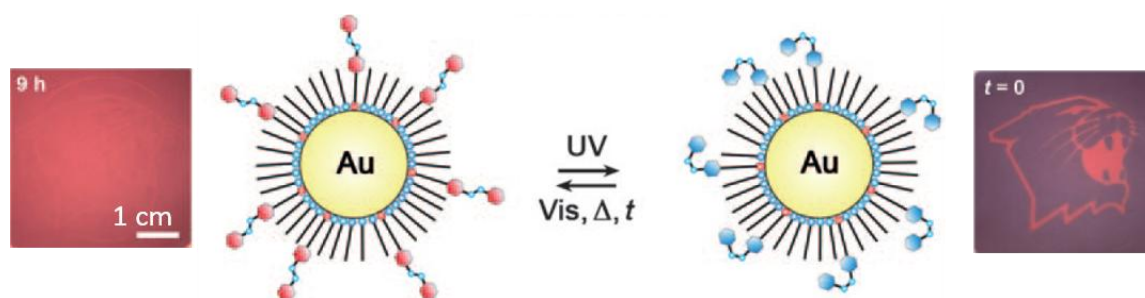


Figure 1.12. Surface patterning performed by using azo coated AuNPs. Adapted with permission of ref 53 © John Wiley and Sons.⁵³

The architecture with a metallic core is generally used for applications in the fields of data storage, biosensing, and phototherapy, where a chemical interaction with the grafted ligands occurs. But what happens if the architecture is reversed, i.e. if the core is made of an azo compound while the surface is coated with gold or metallic nanoparticles? One example includes polymer spheres coated with AuNPs, which showed enhanced catalytic properties, due to the optical coupling of the AuNPs

within close proximity of each other.⁵² Another example involves fluorescent polymer nanorods where iron nanoparticles have been dispersed throughout the nanorod.^{56,57} Here a magnet could be used to control the location of the iron nanoparticles during fabrication. Previous studies in our group have reported the use of small molecule-based fluorescent nanospheres (fluorescent organic nanoparticles) to organize iron nanoparticles onto their surface.⁵⁸ However, this reverse architecture is still unexplored at the level of photochromic units. Very little has been done with nanoassemblies obtained following a reverse approach, even though their potential is huge because of to the high load of photoactive units constituting the core and their ability to further complex nanoparticles and induce unprecedented optical couplings.

1.4 Objectives

The main objective of this work is to synthesis a new class of push pull azo molecules, which are capable of forming amorphous thin films and nano objects. The photochromic properties of these molecules in solution and thin films will be studied, to better understand the effect of the bulky substituents and the effect the dipole moment has on the photochromic properties of these push pull azo molecules. Anisotropy studies of the thin films will be performed by measuring the birefringence level and the dichroism as the molecules orientate orthogonal to the direction of the polarized light. Different nano objects will then be synthesized using the azo molecules and their photochromic properties will be studied and compared to the photochromic properties of the corresponding azo molecule in solution and thin films, highlighting the benefit to working on a nanoscale. The photochromic properties of these azo materials will then be utilized to organize different materials into a specific configuration. This will be done by depositing nanoparticles into the surface of an organic photoactive material, such as azo thin films or azo nanorods/ nanospheres and by using polarized light as a driving force to move and control the precise positioning of the nanoparticles. The extension of this migration can be tuned through structural changes of the azo compounds that directly impact the photochromic properties of the azo compounds.

Chapter 2

Synthesis and characterization of photochromic push-pull azo compounds

2.1 Molecular Engineering

Photochromic azo materials have been explored due to the efficient and permanent mass migration that occurs when the compounds are subjected to interferential illumination. Under continuous irradiation, cycles of *Z-E* isomerisation results in molecular motion due to the large change in geometry between both isomers and their ability to reorientate, and consequently to move under polarized irradiation. Depending on the molecular structure, isomerization from *E* to *Z* and from *Z* to *E* can be induced by defined excitation wavelengths enabling reversible photoisomerization as shown in Figure 2.1. In addition, *Z* to *E* isomerization can occur thermally at room temperature as the *Z* isomer is usually less stable than the *E* isomer. The rate constant of this conversion is noticeably dependent on the electron donating and electron accepting substituents on the azobenzene moiety. For example, an azobenzene without substituents will have a longer lifetime (i.e. 12 h) compared to that of a push-pull azo compounds characterized by lifetimes in the second range.^{59–61}

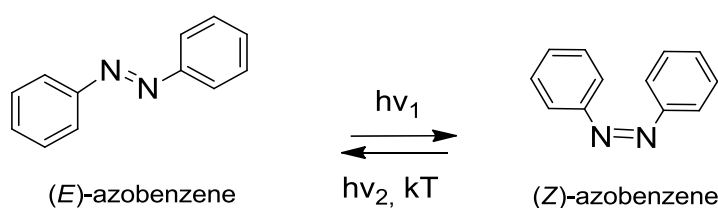


Figure 2.1. Photoinduced and thermal isomerization of azobenzene.

There are three general sub-classes in azo materials (in the *E* isomer) : symmetrical (and thus apolar) azobenzene, 4-aminoazo benzene, and pseudostilbene-type (push-pull and thus polar) molecules (Figure 2.2). The appearance of a strong charge transfer along the N=N bond induces a bathochromic shift of the $\pi\pi^*$ transition that can be measured by UV-vis absorption spectroscopy.²⁵

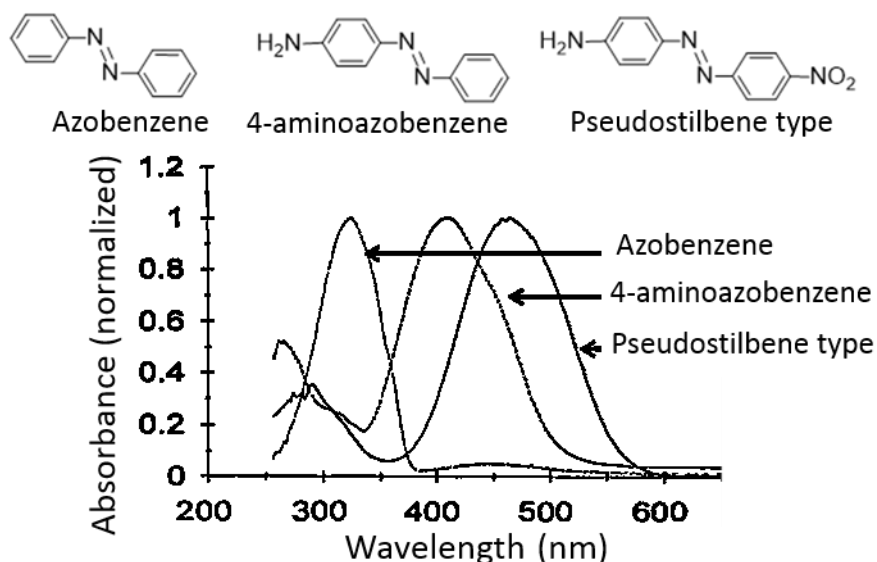


Figure 2.2. UV vis absorption spectra of three types of azomolecules: azobenzene, 4-aminoazobenzene, and pseudostilbene type. Adapted with permission of ref 25 © NRC Research Press.²⁵

In the case of symmetric azobenzene molecule, the lowest lying electronic transition corresponds to the $n\pi^*$ one, which is symmetry forbidden, as confirmed by its weak oscillator strength. By substituting the 4- position of the azobenzene moiety by an electron poor or an electron rich group, the energy of the $\pi\pi^*$ transition is reduced and the resulting band overlaps with the $n\pi^*$ band. This permits the use of a single wavelength to induce continuous photoisomerization between the *E* and *Z* isomers. By substituting the 4- and 4'- positions of the azobenzene unit with an electron donating and an electron accepting moieties (push-pull system), the intense $\pi\pi^*$ transition displays the lowest energy and overlaps the weaker $n\pi^*$ transition occurring at slightly higher energy. The benefit of this last series is that the back thermal photoisomerization is quicker due to the significant thermal instability of the *Z* isomer. Since fast, efficient, and continuous photoisomerization at room temperature upon one excitation wavelength is desired for the targeted photochromic materials, we devised push-pull azo derivatives containing in the 4- and 4'- positions a triphenylamino moiety and various electron withdrawing groups ($X = \text{CO}_2\text{Me}$, CN , NO_2). In this way, we could evaluate the effect of the charge transfer magnitude on the photoisomerization reaction and migration in the solid state.⁶²

One of the most explored pseudo-stilbene type azo compounds for mass transfer investigations in solid state is the nitrophenyl-4'-[[2-(methacryloyloxy)ethyl]ethyl-

aminolphenyldiazene also called DR₁ (Figure 2.3).^{63,64} By using photochromic azo polymers functionalized with DR₁ (pDR₁M), efficient mass transfer occurred under polarized light but required quite a long time to reach saturation. Compared to azo liquid crystalline polymers, no cooperative effects for pDR₁M could operate and polymer chain entanglement reduced the azo mobility. To overcome this problem, the main goal of the current research project was to design and synthesize a variety of push-pull azo materials displaying more efficient migration response to an impinging excitation. In this context, small push-pull molecules are of particular interest with respect to azo polymers for several reasons. Firstly, the synthesis of the push-pull azo dye is reproducible and the size of the azo molecules is perfectly defined, providing reliable results, unlike other azo polymers that have generally a broader range of molecular weight. Secondly, no chain interactions, slowing down the migration, take place since the molecules are simply forming materials without any additional matrix.^{10,42,59} Thirdly, small push-pull azo molecules allow for a better mechanistic understanding of the photochemical isomerization, since their structures can finely be tuned and the effects of bulkiness and polarity can be investigated in an independent manner.

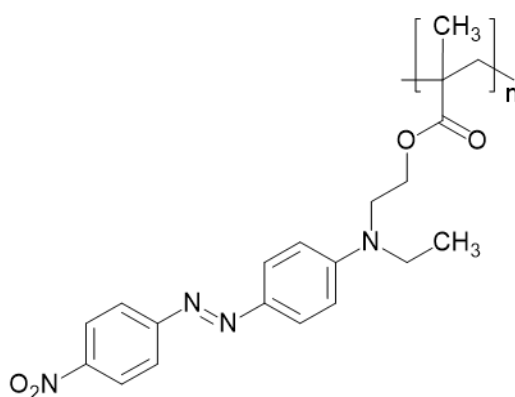


Figure 2.3. Molecular structure of poly[4-nitrophenyl-4'-[[2-methacroyloxy)ethyl] ethyl-aminolphenyldiazenel] (pDR₁M).

Crystallization of small azo molecules in the solid state is common because of strong π - π packing between the aromatic moieties. When this happens, the molecules are unable to migrate as the photoisomerization is blocked. Furthermore, strong light scattering occurs, leading to considerable loss of absorption efficiency. To avoid the formation of crystalline materials, and investigate the hydrophilic and hydrophobic

interactions developed later with aqueous suspensions of nanoparticles, various bulky substituents (CF_3 = 3, 5-bis(trifluoromethyl)phenyl, tBu = 4-tert-butylphenyl, Carb = 4-bis(4-tert-butyl) carbazolyl phenyl) were incorporated into the amino branches (Figure 2.4). Upon variation of the substituent bulkiness, the influence of the free volume on photoisomerization and photomigration could be investigated independently of the variation of polarity. The introduction of bulkier substituents on the azo molecules has been shown to improve the photoinduced migration of the molecules processed as thin films.^{65,66}

The overall design of the small push-pull molecules retained for these studies are shown below in Figure 2.4. To summarize, a series of azo derivatives containing different electron withdrawing groups (X) and triphenylamino moiety substituted with different bulky groups has been synthesized.⁶⁷

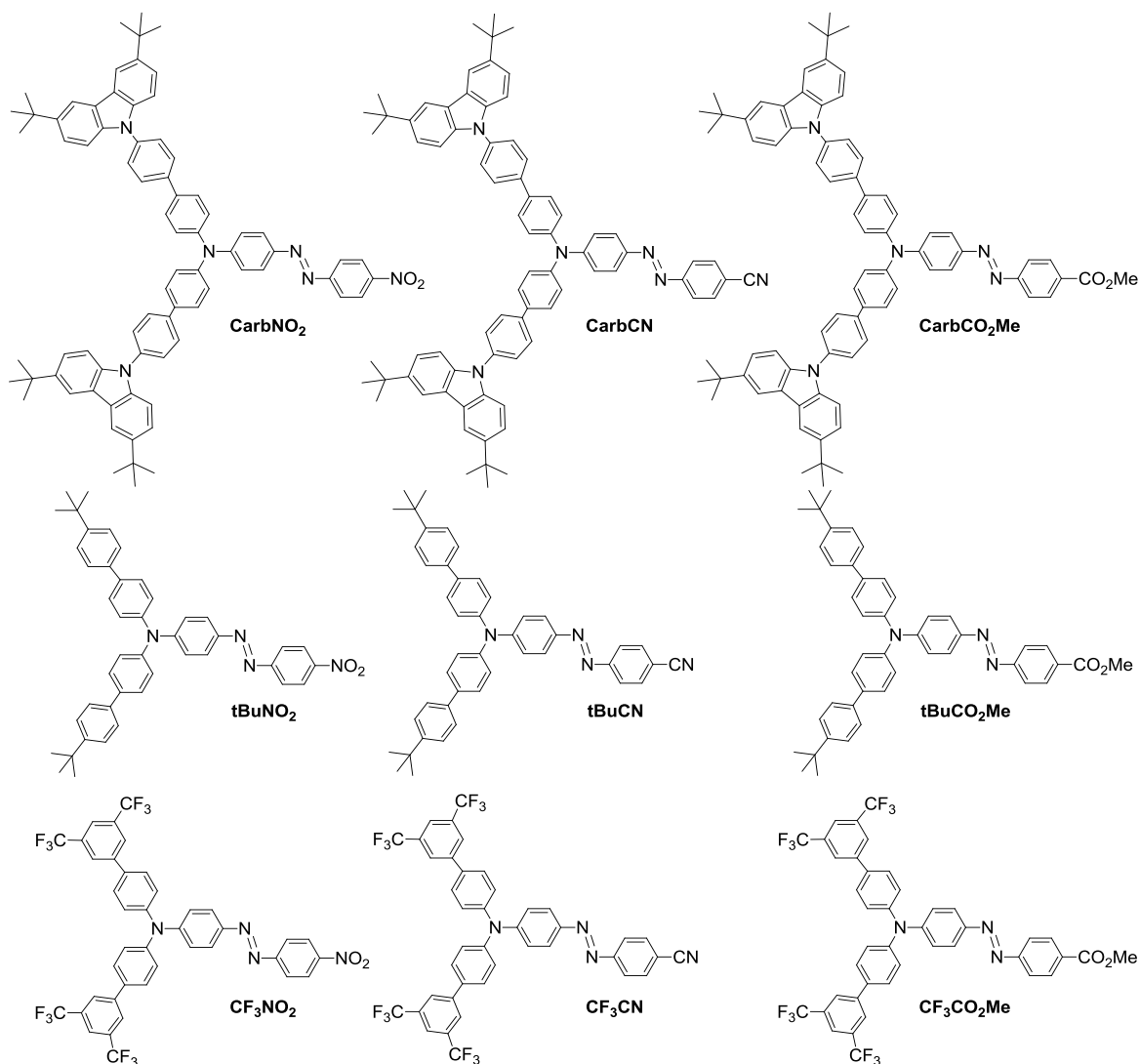


Figure 2.4. Molecular structures of the push-pull azo compounds designed and synthesized in the present work.

2.2 Synthesis and characterization of small push-pull azo compounds

The compounds indicated in Figure 2.4 were synthesized and their ability to photoisomerize was studied. We report here below the main synthetic steps and UV-visible absorption measurements performed in solution.

2.2.1 Synthesis of small push-pull azo compounds

Two synthetic pathways can be followed to yield the desired push-pull molecules (Figure 2.5). The first method incorporates the bulky substituents (CF_3 , *t*Bu, Carb) on the triphenylamino core before undergoing an azo coupling reaction.⁶⁶ The second method involves the synthesis of the azo moiety prior to the incorporation of the bulky substituents on the triphenyl amino core.⁶² In both approaches, the bulky substituents were incorporated on the triphenyl amino core via a Suzuki-Miyaura cross coupling reaction,⁶⁸ which provides an efficient method to form C-C bond between aromatic cycles. To this aim, we used the following boronic acids: 3, 5-bis(trifluoromethyl)benzeneboronic acid, 4-*tert*-butylbenzeneboronic acid, and 4-bis(4-*tert*-butyl)carbazolylbenzeneboronic acid. The first two compounds were commercially available from Aldrich whereas the 4-bis(4-*tert*-butyl)carbazolylbenzene boronic acid had to be synthesized.

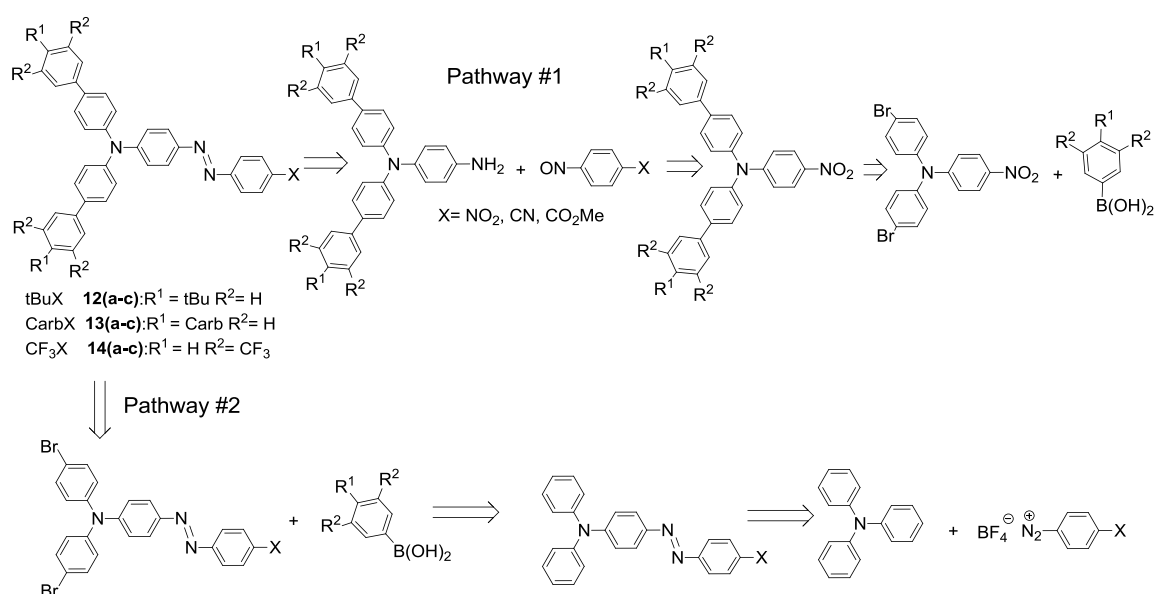


Figure 2.5. Retrosynthesis of the desired azo compounds.

The synthetic pathway toward the 4-bis(4-*tert*-butyl)carbazolylbenzene boronic acid (**4**) is shown in Figure 2.6. First, a Friedel Crafts alkylation reaction was done using aluminum trichloride as a catalyst to promote the aromatic electrophilic substitution. Carbazole and aluminum trichloride catalyst were dispersed in dry dichloromethane and cooled to 0 °C. *Tert*-butyl chloride was then added dropwise to avoid polyalkylation. This reaction was stirred for 24 h to produce 4-bis(4-*tert*-

butyl)carbazolyl (**2**) in 20 % yield. The reason for the low yield was due to the strong Lewis acid adduct formed between the nitrogen atom of the carbazole and the catalyst, which could be avoided by protecting the nitrogen atom before alkylation. However since the commercial products were cheap, our approach appeared to be more economical in terms of synthetic efforts. An Ullman coupling reaction was then done by dissolving (**2**) and 4-bromo-1-iodobenzene in nitrobenzene and heating the reaction to 190 °C to activate the Cu catalyst. 4-bromo-1-iodobenzene was chosen over 1, 4-dibromobenzene to limit as much as possible di-substituted by-product. Once the reaction was complete, nitrobenzene was removed through azeotropic distillation with water, and 4-bis(4-*tert*-butyl)carbazolylbenzene bromide (**3**) was purified to yield a white powder in a 93 % yield. 4-bis(4-*tert*-butyl)carbazolylbenzene bromide (**3**) was dissolved in tetrahydrofuran, and the solution was deoxygenated with argon and cooled to -78 °C. Carefully, 1.1 eq of *n*-butyl lithium was added dropwise to the solution to avoid warming up the reaction mixture. The resulting solution was stirred for 1 h at -78 °C for the lithium insertion to happen and then triisopropyl borate was added dropwise to -78 °C solution where a metal-borate exchange occurred. The solution was warmed to room temperature over 3 h, and chilled to 0 °C as the isopropoxy groups were cleaved in the presence of 1 mol L⁻¹ HCl (aq). After extraction with diethylether and precipitation in hexane, 4-bis(4-*tert*-butyl)carbazolylbenzene boronic acid (**4**) was collected as a white powder in a 40 % yield; this is significantly lower than the previously reported yield (83 %) for this particular boronic acid.¹⁴ This low percent yield might be a result of the instability of the lithium intermediate, so the reaction time at -78 °C was reduced to 30 min, resulting in an increased yield of 80 %.

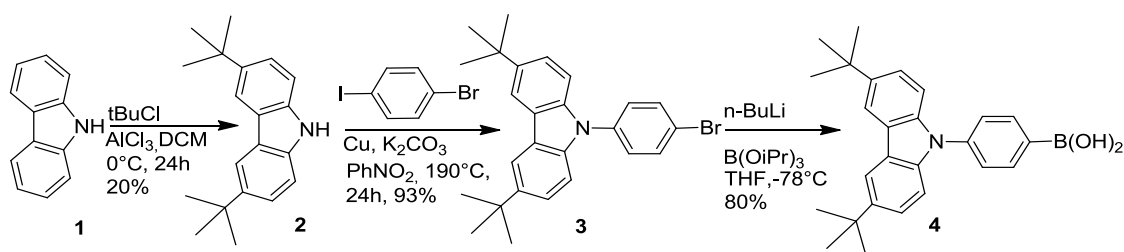


Figure 2.6. Synthetic pathway for the synthesis of tBu carbazole boronic acid (4**).**

With all the targeted boronic acids in hand, the first synthetic methodology was followed. This method advantageously allowed the electron withdrawing group to be

introduced in the last step (Figure 2.7). This synthetic pathway has been previously followed with the 4-*tert*-butylbenzene boronic acid in high yields. Generally, the Suzuki-Miyaura coupling reaction was performed using tetrakis(triphenylphosphine) palladium (0) $\text{Pd}(\text{PPh}_3)_4$ as a catalyst and provided the nitro compound (**6**) in a 96 % yield. Compound (**6**) was attempted to be reduced to the corresponding amine (**7**) using hydrazine $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ and 10 % Pd on activated charcoal as catalyst. A color change from yellow to colorless indicating the completion of the reaction should have occurred due to the decrease in charge transfer by replacing the nitro with the amino group. Unfortunately, the reaction failed even with an excess of hydrazine or Pd/C catalyst, which prompted us to adopt the second synthetic strategy.

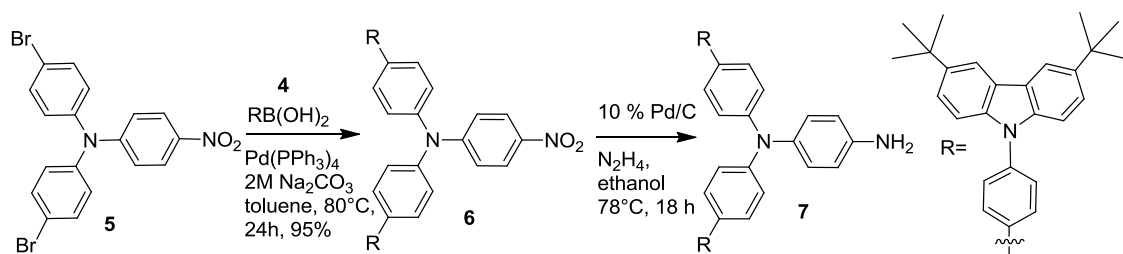


Figure 2.7. Synthetic pathway to tBu carbazole phenyl amine (7).

The second method to synthesize the desired push-pull azo compounds was investigated (Figure 2.8). Briefly, the desired diazonium tetrafluoroborate salts (**9 a-c**) were synthesized using a previously reported method.⁶⁹ The salt was dissolved in water and coupled to triphenylamine in dichloromethane using sodium dodecylbenzenesulfonate (NaDBS) as a surfactant to promote an organic phase transfer. Thanks to the stability of these salts, the azo coupling could take place at room temperature for 24 h. As formation of the azo bond occurred, the solution color changed from pale yellow to red. The red compounds (**10 a-c**) were purified and brominated in the para position of the triphenyl amino branches using 2 eqs of *N*-bromosuccinimide. Heat was required to get electrophilic substitution because of the electron withdrawing character of the azo bond reinforced by the presence of strong electron deficient atoms (X). These compounds (**11a-c**) were collected and a Suzuki-Miyaura coupling reaction was performed with the preferred boronic acid, as previously described, to yield the final compounds (**12-14 a-c**). For full experimental procedures and characterizations, see **Appendix A**.

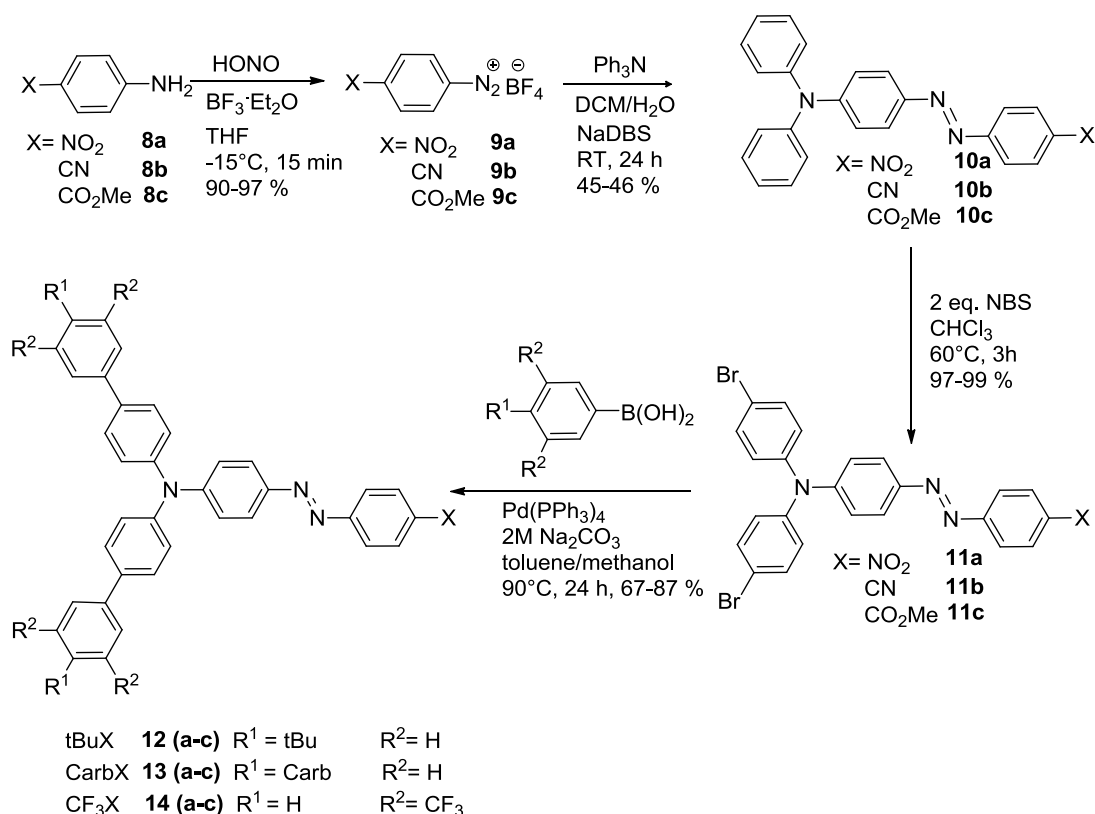


Figure 2.8. Synthetic pathway for the formation of a series of push-pull azo dyes (12-14 a-c).

2.2.2 Absorption of azo dyes in solution

The solutions were prepared in the dark to avoid undesirable photoisomerization caused by the surrounding light, the concentrations of the dyes were adjusted between $3 - 5 \times 10^{-5} \text{ mol L}^{-1}$. As shown in Figure 2.9, all compounds absorb in the visible and UV range, these absorption bands are due to the $\pi\pi^*$ electronic transition. The $\pi\pi^*$ electronic transition in the visible range is due to the charge transfer between the amino core to the bulky substituents and the electronic transition in the visible range is due to the charge transfer between the amino core and the different electron withdrawing groups ($\text{X} = \text{CO}_2\text{Me}, \text{CN}, \text{NO}_2$).

In Figure 2.9, the absorption spectra comparing the CarbX, tBuX, and CF₃X series illustrates the direct influence that the strength of the different electron withdrawing groups has on the maxima of these transitions. By increasing the strength of the X group ($-\text{CO}_2\text{Me} < -\text{CN} < -\text{NO}_2$), the $\pi\pi^*$ transition becomes more red shifted, between 10 - 30 nm, due to the decrease in the energy between the $\pi\pi^*$ transitions. A

second absorption band at a higher energy, highlights the charge transfer between the triphenyl amino to the peripheral biphenyl units, this was based on previous TD-DFT computations done in the group.⁷⁰ Here the energetic maxima changes based on the peripheral group, CF₃X ($\lambda_{\text{max}} \sim 350$ nm) in comparison to tBuX ($\lambda_{\text{max}} \sim 330$ nm), this again is due to the decrease in the energy levels between the $\pi\pi^*$, due to the electron density being more dispersed with a dye with a stronger withdrawing group, such as the CF₃ group. In the case of the CarbX series a third absorption band is observed ($\lambda_{\text{max}} \sim 350$ nm), this is due to the $\pi\pi^*$ transition present in the carbazolyl moiety. The molar absorption coefficients were compared, and seem to have no significant influence when changing the strength of the X group. All absorption bands and molar absorption coefficients are reported in Table 2.2.

The absorption spectra of the dyes were compared, keeping the electron withdrawing group the same and varying the peripheral substituents, to observe the effects of the more energetic transitions, involving the charge transfer between the triphenyl amino core to the peripheral biphenyl units (Figure 2.10). By incorporating a better electron withdrawing group, such as the CF₃ group, the electron density was into the biphenyl branches, resulting in a red shift of the absorption maxima in the UV range, due to the decrease in energy levels between the $\pi\pi^*$ transition with the triphenyl amino core and the peripheral branches. Conversely, this also yields a blue shift in the absorption maxima in the visible range due to the increase in energy levels between the $\pi\pi^*$ transition with the triphenyl amino core and the X group.

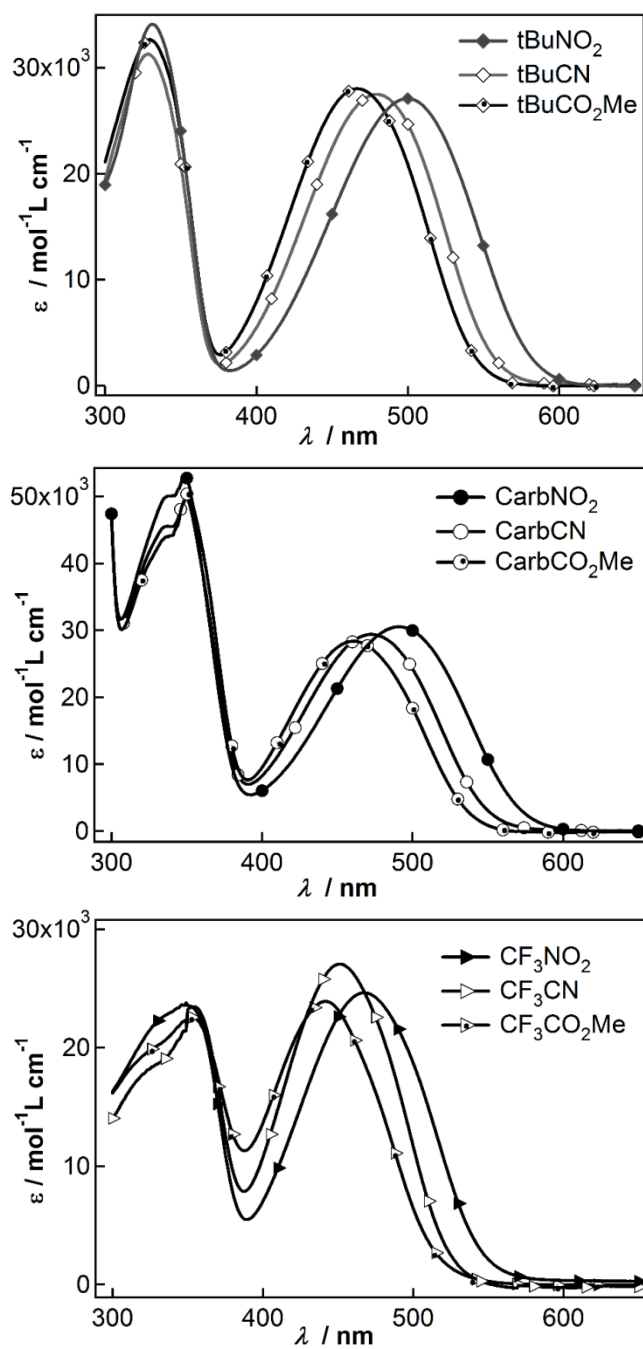


Figure 2.9. UV-Vis absorption spectra of the push-pull azo molecules in toluene varying the electron withdrawing group (X).

Compounds		μ_E^a	$\lambda_{\max} \text{ abs (nm)}^b$	ρ^c	$k_{ZE}^{db,d}$
		(D)	($\epsilon \text{ (mol}^{-1}\text{Lcm}^{-1}\text{)}$)	(%)	(10^{-5} s^{-1})
12a	tBuNO ₂	10.49	499 (27100), 331 (34100)	35	70.8
12b	tBuCN	9.62	479 (27500), 328 (31300)	45	13.0
12c	tBuCO ₂ Me	4.91	468 (27500), 328 (31300)	38	6.7
13a	CarbNO ₂	8.16	493 (30500), 349 (52700), 338 (50100)	40	46.0
13b	CarbCN	7.20	473 (29400), 349 (49800), 338 (45500)	48	9.2
13c	CarbCO ₂ Me	2.70	461 (28500), 351 (50400), 335 (45500)	43	5.2
14a	CF ₃ NO ₂	4.75	468 (24600), 348 (23600)	36	17.5
14b	CF ₃ CN	3.92	451 (27100), 354 (23500)	49	6.2
14c	CF ₃ CO ₂ Me	2.01	441 (23900), 353 (22600)	34	2.9

Table 2.2. Photochromic properties of the desired push-pull compounds. ^aDFT calculations in the gas phase (B3LYP, 6-31G(d)). ^b In toluene solution. ^c Minimum conversion yield (ρ) assuming no absorption from Z isomer at the irradiation wavelength of $\lambda_{\text{irr}} = 488 \text{ nm}$, $P = 8 \text{ mW.cm}^{-2}$, $\rho = \left[\frac{(A_0 - A_{\text{pss}})}{A_0} \right] \times 100$. ^d Back thermal conversion rate constant of the Z-E using a monoexponential fit involving the decay: $[E] = [E]_0 + ([E]_{\text{pss}} - [E]_0) e^{-k_{ZE}t}$.

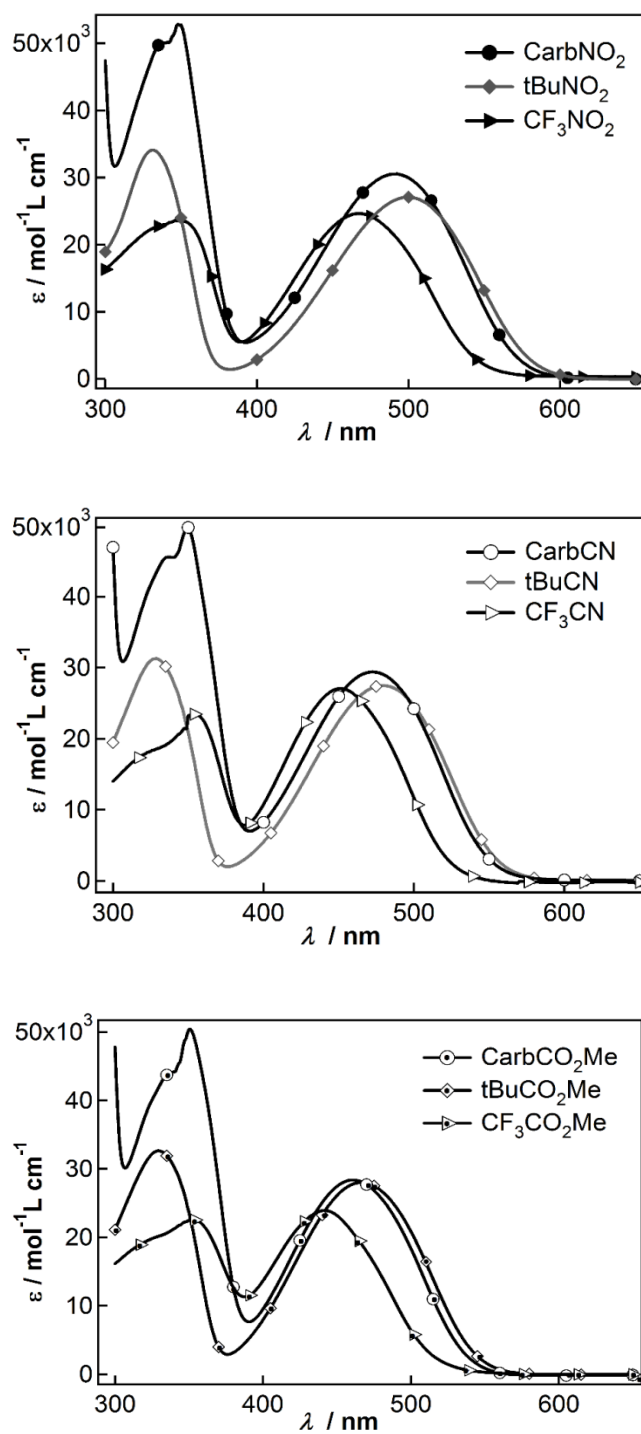


Figure 2.10. UV-Vis absorption spectra of the desired push-pull azo molecules varying the bulky substituent dissolved in toluene.

2.2.3 Photoisomerization of azo dyes in solution

The photoisomerization reactions between the *E* and *Z* azo isomers have been studied, providing information about the back thermal rate constants k_{ZE} and the minimum photoconversion yields ρ_{EZ} (simply noted later ρ) as a function of the X group and bulky substituents on the biphenyl moieties. The solutions were irradiated in the visible band, using a mercury-xenon lamp excitation source with a 488 ± 2 nm narrow bandpass filter at a power of $8 \text{ mW} \cdot \text{cm}^{-2}$, for an acquisition time of 10 s before each absorption spectrum was collected. A series of such spectra was collected continuously until the photostationary state was reached. At this point, the minimal amount of *E* isomer was present in the solution. For comparison, the absorption spectra before irradiation have been normalized and all further spectra traced with regard to the initial state (Figure 2.11). During irradiation, the bands in the visible region mainly decreased while no other bands appeared. This behavior is due to the *E*→*Z* photoreaction where the *Z* isomers display a molar absorption coefficient ten times lower than those of the *E* isomers,^{1,63,70} and absorb approximately at the same wavelengths as those of the *E* isomers. This particular feature is to be related to pseudo-stilbene type character for all azo molecules, the $\pi\pi^*$ absorption band maxima of the *E* and *Z* isomers occur at approximately the same wavelengths. The minimal photochemical conversion yield ρ , calculated using the formula indicated below (Equation 2.1), assumes no absorption from the *Z* isomer, giving a rough approximation of the chemical conversation from the *E* to the *Z* isomer. In equation 2.1, A_o and A_{pss} correspond to the absorbance before irradiation, where there is the maximum *E* isome present and the absorbance at the photostationary state, where the minimal about of *E* is present.

$$\rho = \left[\frac{(A_o - A_{pss})}{A_o} \right] \times 100 \quad (2.1)$$

At the photostationary state, the back thermal relaxation was monitored in the dark by observing the recovery of absorbance as a function of time, as the *Z* isomers thermally converts back to their more stable *E* isomers (Figure 2.12). Such evolution could be fit using a monoexponential mathematical law since the reaction is a unimolecular process (Equation 2.2). Where $[E]_0$ and $[E]_{pss}$ represents the absorbance of the *E* isomer before irradiation and at the photostationary state.

$$[E] = [E]_0 + ([E]_{pss} - [E]_0) e^{-k_{ZE}t} \quad (2.2)$$

The minimum photochemical conversion yields appear in the same range of 34 - 49 %. When comparing the back thermal relaxation kinetics, this latter occurs faster for compounds containing stronger electron withdrawing groups. In the case of compound tBuNO₂, the rate constant of the back thermal relaxation was k_{ZE} was $70.8 \times 10^{-5} \text{ s}^{-1}$, drastically larger than that for compound tBuCO₂Me valued at $6.70 \times 10^{-5} \text{ s}^{-1}$. When comparing azo compounds with the same electron withdrawing group, for example -NO₂, the rate constants increased for more electron donating bulky substituents : $k_{ZE}(\text{CF}_3) = 6.70 \times 10^{-5} \text{ s}^{-1} < k_{ZE}(\text{Carb}) = 13.0 \times 10^{-5} \text{ s}^{-1} < k_{ZE}(\text{tBu}) = 70.8 \times 10^{-5} \text{ s}^{-1}$. We suspected that more polar compounds characterized by strong charge transfer and showing less thermal stability, would relax faster to the initial *E* forms. These observations were indeed supported by calculations of the dipole moments in the gas phase for the *E* isomers using density functional theory (DFT). The values of the dipole moments display indeed the same evolution as that found for k_{ZE} (Table 2.1). In the same way, the minimum photochemical conversions yield ρ of the series tBuX, CarbX and CF₃X show lower values for azo compounds substituted with stronger electron withdrawing groups like NO₂. This is due to the increased thermal instability of the *Z* isomers that cannot accumulate after having been photogenerated.

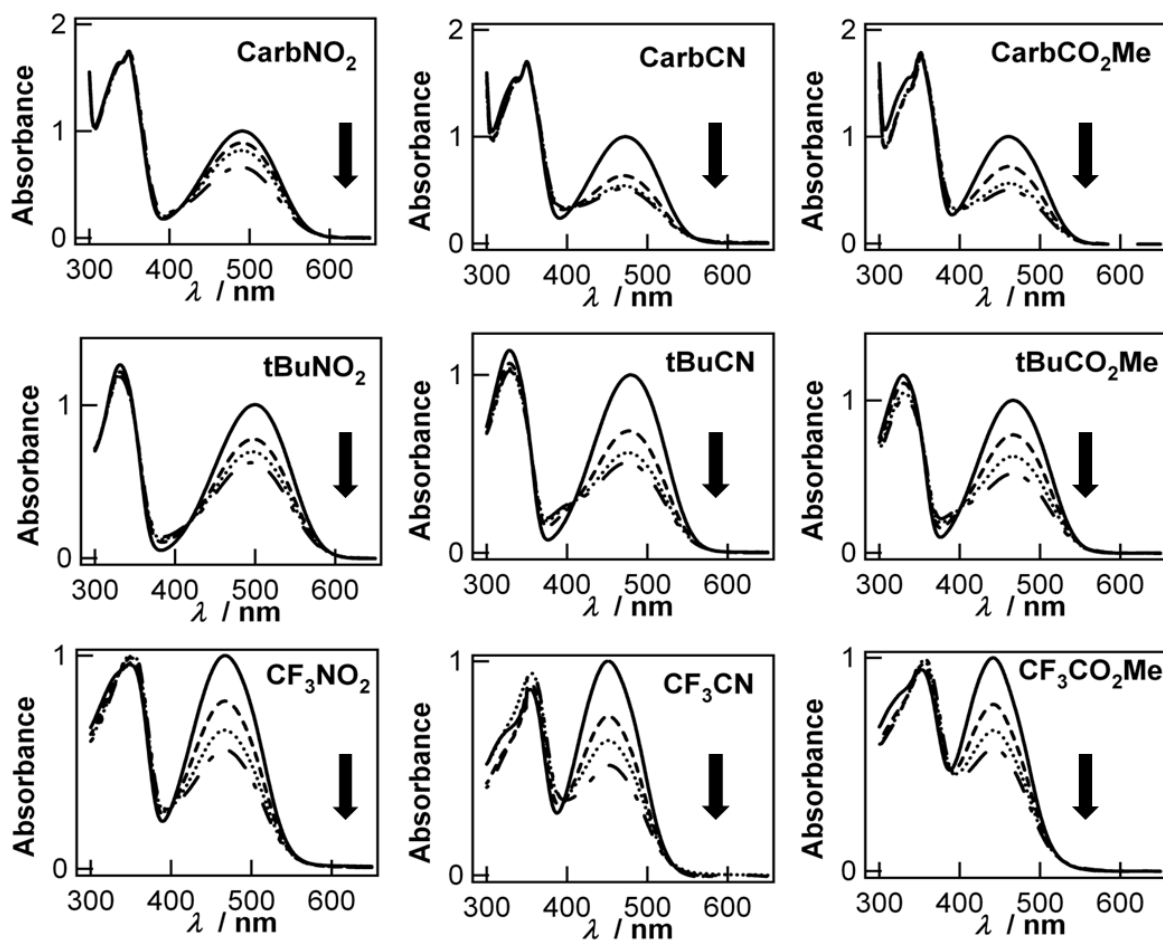


Figure 2.11. UV-vis absorption spectra for the azo push-pull series dissolved in toluene, normalized to an absorbance of 1, were irradiated at 488 nm, $P = 8 \text{ mW.cm}^{-2}$ in intervals of 10 s until the photostationary state was reached.

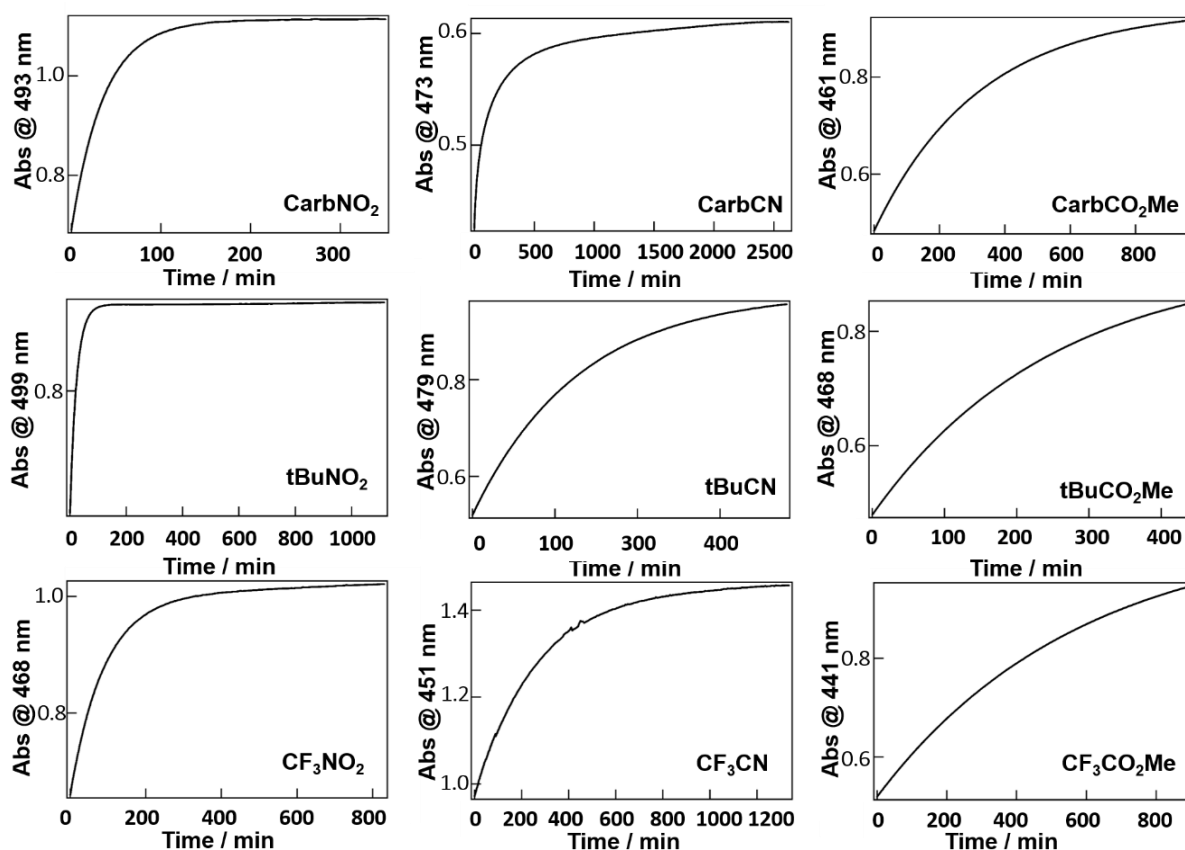


Figure 2.12. Back thermal relaxation curves of azo compounds dissolved in toluene, where the absorption at a certain wavelength was monitored over time after the photostationary state was reached.

2.3 Thin films

In order to fully exploit the photochromic properties of the azo compounds in the solid state, thin films were prepared and characterized using UV-vis and Raman spectroscopy, along with different anisotropic studies.

2.3.1 Thermal properties

The azo compounds were designed having different bulky groups in the peripheral branches of the amino core to prevent the molecules from aggregating together. This in turn avoids undesirable crystallization when solutions of azo compounds are spin-casted on glass substrates. Almost all compounds, but two of them (CF_3NO_2 and CF_3CN), formed glassy thin films from chlorinated solutions. Such properties are related to the amorphous characteristics of the compound, namely their glass transition temperatures T_g identified by differential scanning calorimetry. They were

measured over the temperature range of 25 – 250 °C after a first heating and cooling cycle to reset the material thermal history. All compounds but CF₃NO₂ and CF₃CN exhibit neither crystallization nor recrystallization peaks, proving stable glassy state after cooling. The T_g values of all compounds are reported in Table 2.2. They dramatically increase with the bulkiness of the peripheral groups (CarbX: 190 – 200 °C; tBuX: 110 – 120 °C; CF₃X: 60 – 70 °C). The molecular volume, calculated for each bulky substituent using DFT, increased in the following order: from CF₃ ($V_{\text{mol}} = 351.48 \text{ cm}^3 \text{ mol}^{-1}$) < tBu ($V_{\text{mol}} = 454.55 \text{ cm}^3 \text{ mol}^{-1}$) < Carb ($V_{\text{mol}} = 808.24 \text{ cm}^3 \text{ mol}^{-1}$). These results show that the fluorinated moiety compared to the methyl one induces less steric crowding. Interestingly, no specific influence of the electron withdrawing group could be noticed as very similar T_g were found for a given substituent.

2.3.2 Preparation of thin films

Azo thin films were prepared by spin casting a 2 % wt. solution of compounds in chloroform at an acceleration of 500 rpm and spun at a rate of 1000 rpm for 2 min. In such experimental conditions, the thickness of the thin films was in the 200 - 300 nm range. The electronic transitions and vibrational spectra of the resulting azo thin films were studied, providing information about the photochromic properties of the azo thin films. When comparing the general absorption bands in the visible range of the thin films to those of the corresponding solutions, a minor red shift was observed due to the way the molecules pack in the solid state (Table 2.3).

Compounds	T_g (°C) ^a	$\lambda_{\text{max}}(\text{abs})$ (nm)	ρ^b (%)	k_1^c (10^{-5} s^{-1})	f_1^c	k_2^c (10^{-5} s^{-1})	f_2^c
CarbNO ₂	202	498, 349, 339	20	3.9	95	40	5
CarbCN	201	475, 350, 332	29	2.8	85	23	15
CarbCO ₂ Me	187	459, 349, 336	30	2.2	96	21	4
tBuNO ₂	118	508, 328	8.5	6.5	85	69	15
tBuCN	117	483, 327	16	3.7	90	19	10
tBuCO ₂ Me	89	468, 328	17	3.6	93	18	7
CF ₃ NO ₂	62	478, 345	17	5.1	85	40	15
CF ₃ CN	68	456, 353	17	1.6	93	11	7
CF ₃ CO ₂ Me	65	444, 357	17	0.7	96	6.7	4

Table 2.2. Photochromic properties of the azo push-pull compounds processed as thin films that were formed from spin casting a chloroform solution of the azo compound onto pre cleaned glass slides. ^a DSC measurements in aluminum cap using a 20 °C min⁻¹ thermal gradient. ^b Minimum conversion yield (ρ) assuming no absorption from Z isomer: $\rho = \left[\frac{(A_0 - A_{\text{pss}})}{A_0} \right] \times 100$. ^c Back thermal relaxation rate constant of the Z-E using a biexponential fit involving the decay: $[E] = [E]_0 + a_1 e^{-k_1 t} + a_2 e^{-k_2 t}$, with f_i designating the rate constant averaged fraction $f_i = \frac{a_i k_i}{\sum_j a_j k_j}$.

2.3.3 Photoisomerization of azo dyes in the solid state

The photochromic properties of thin films were studied. Irradiation of the thin films was performed by exciting the molecules at 488 nm, until the photostationary state was reached following the same conditions as those described for azo solutions. The corresponding absorption spectra are represented in Figure 2.13. The back thermal relaxations from the Z to E isomers were characterized by monitoring the recovery of the absorbance band in the visible range (Figure 2.14). Biexponential modeling was performed and previous studies have emphasized the presence of two main rate constants: a fast relaxation rate constant, often referred as the homogeneous contribution assigned to the Z→E isomerization, and a slower relaxation rate constant, referred as an inhomogeneous contribution due to the distribution of the free volume or physical space to adapt the photoinduced Z isomers. The best fit of the absorbance recovery required the use of a biexponential mathematical law shown below (Equation 2.3), with f_i designating the rate constant-averaged fraction $f_i = \frac{a_i k_i}{\sum_j a_j k_j}$ of the total recovery of E species.

$$[E] = [E]_0 + a_1 e^{-k_1 t} + a_2 e^{-k_2 t} \quad (2.3)$$

The minimal photochemical conversion yields ρ for the thin films ranges from 17 - 30 % at the photostationary state, significantly lower than in solution to the geometrical constraints in thin films. The larger value was found to associate with the CarbX series. This can be accounted by the molecular volume provided by the Carb bulky groups in the amino branches ($V_{\text{mol}} = 808.24 \text{ cm}^3 \text{ mol}^{-1}$) and the related free volume, created after photoisomerization once an azo molecule has photoisomerized, in comparison to those for tBuX ($V_{\text{mol}} = 454.55 \text{ cm}^3 \text{ mol}^{-1}$) and CF_3X compounds ($V_{\text{mol}} = 351.48 \text{ cm}^3 \text{ mol}^{-1}$). Among all thin films, tBuNO₂ compound displayed the lower ρ value at 8.5 %. As already stated for the photochemical reaction in solution, this feature can be explained by the instability of the tBuNO₂ Z isomer, relaxing back to its more stable E isomer so quickly that it was hard to build up a large population of the Z isomers. This assumption was confirmed by the fast back thermal relaxation rate constants found for tBuNO₂ to be of $69 \times 10^{-5} \text{ s}^{-1}$ and $6.5 \times 10^{-5} \text{ s}^{-1}$. These values are significantly lower than those for azo solutions and result from the spatial constraints surrounding the azo moiety. When comparing the thermal back relaxation of the compounds within the same series (CarbX, tBuX, CF_3X), no significant difference could be observed for the rate constants, except for the NO₂ dyes. For the latter considered as the most polar compound, a much quicker conversion from the Z to the E forms occurred. When comparing the thermal relaxation rate constants of the thin films to those in solution, it was noticed that the fast rate constant was found to be very similar to those in solution. This suggests that the molecules immobilized as thin films have just enough free space to relax the same way that the molecules relax in solution. After the first set of molecules have relaxed, the second set of molecules takes longer because free space around the azo molecules is now missing.

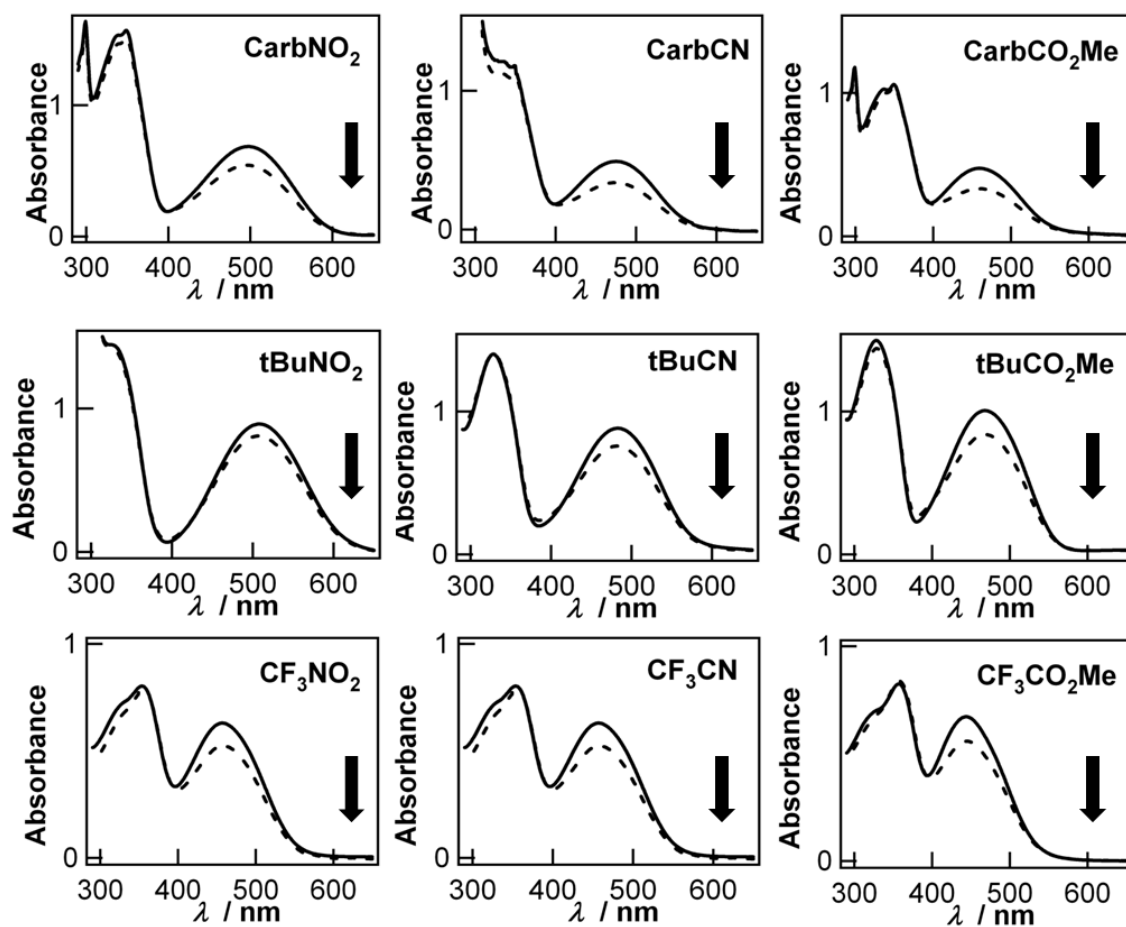


Figure 2.13. UV-Vis absorption spectra for the azo push-pull series processed as thin films and irradiated at 488 nm, $P = 8 \text{ mW. cm}^{-2}$ until the photostationary state was reached.

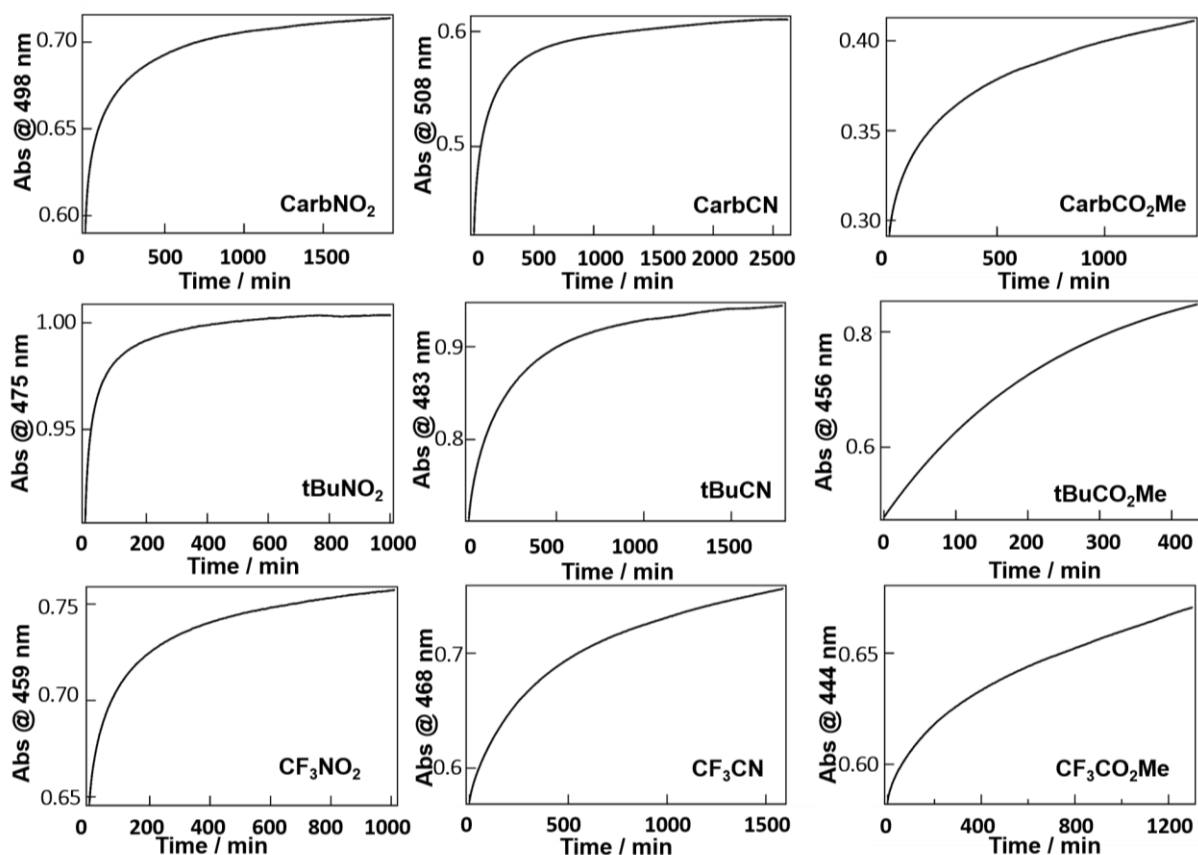


Figure 2.14. Absorbance evolution of the back thermal relaxation curves of azo thin films after irradiation at 488 nm to the photostationary state.

2.3.4 Raman spectroscopy of thin films

The thin films were characterized by Raman spectroscopy to provide vibrational information about the molecules (Figure 2.15). For all compounds, the characteristic bands are located in the $1000 - 1800 \text{ cm}^{-1}$ spectral range. Full characterizations of these compounds are shown below (Table 2.3). The main vibrational stretches include the -N=N- stretch at 1425 cm^{-1} , and the vibration issued from the coupling between the -N=N- and $\phi\text{-N}$ stretches at 1395 cm^{-1} . In addition, the C=C stretches in the aromatic rings are found at 1495 cm^{-1} and 1588 cm^{-1} while the ring deformations can be assigned to the bands at 1107 cm^{-1} and 1136 cm^{-1} . The Raman vibrational spectra of the different compounds show very little change due to the additional vibrational stretches related to the X group (CO_2Me , CN , NO_2). The -NO_2 antisymmetric and symmetric stretches are located at 1521 cm^{-1} and 1341 cm^{-1} respectively, the -CN vibrational stretch at 2230 cm^{-1} and eventually the carbonyl vibrational stretch of the CO_2Me ester group at 1725 cm^{-1} .

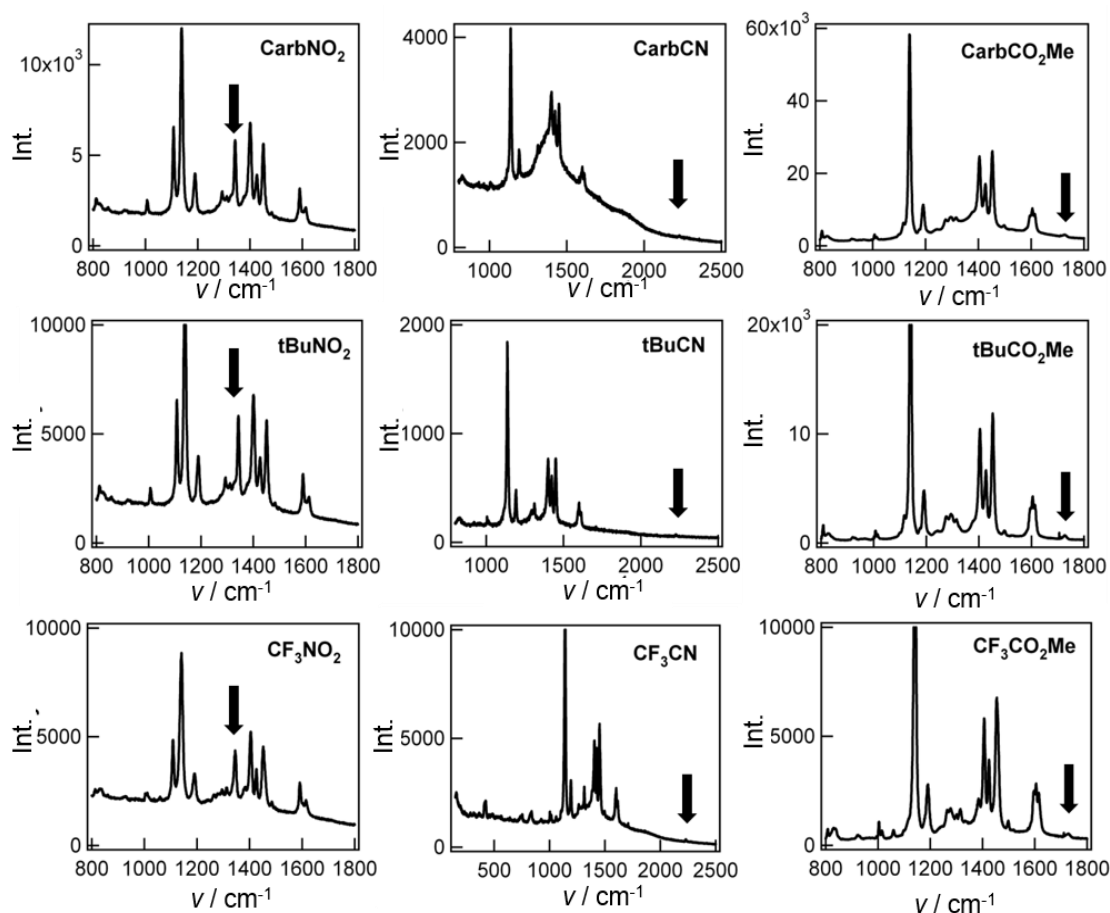


Figure 2.15. Raman spectra of thin films of the push pull azo compounds CF_3X , tBuX and CarbX with an excitation at $\lambda = 785 \text{ nm}$. Acquisition time was of 10 s. The characteristic stretches of each compound are indicated by the black arrow.

Raman normal mode	$\nu \text{ (cm}^{-1}\text{)}$
<i>deform</i> ($-\text{C}=\text{C}-$)	1107
<i>deform</i> $\text{C}-\text{C}=\text{C}$	1136
$\nu (\phi-\text{N}-)$	1278
$\phi-\text{N}=\text{}$	1294
$\text{N}-\phi$	1323
$\nu_{\text{sym}} (-\text{NO}_2)$	1341
$-\text{N}=\text{N}-$ coupled to $\phi-\text{N}$	1395
$-\text{N}=\text{N}-$	1425
$-\text{N}=\text{N}-(\text{Ph})$	1448
$\text{Ph}-\text{C}=\text{C}-\text{C}$	1495
$\nu_{\text{antisym}} (-\text{NO}_2)$	1521
$\nu_{\text{para}} (\text{C}=\text{C})$	1588
$\nu (\text{C}=\text{O})$	1725
$-\text{CN}$	2230

Table 2.3. Assignments of the main vibrational bands upon Raman spectroscopy of thin films of azo compounds CF_3X , tBuX and CarbX .

2.4 PM-IRLD of thin films

Azo molecules are known to undergo photoinduced reorientation under polarized irradiation. Upon exciting the thin films with a linearly polarized laser, photoisomerization occurs first and is followed by spatial reorientation of the azo units in a perpendicular direction with respect to that of the impinging polarization. The probability of exciting a molecule is directly proportional to $\cos^2 \theta$,^{71,72} where θ is the angle between the direction of the linearly polarized light and the transition dipole moment of the azo molecule, that is parallel to the main azo axis for rod-like molecules like the investigated azo compounds. This spatial reorientation leads to anisotropic properties of the thin films, which can be probed experimentally through polarized modulated infrared linear dichroism (PM-IRLD). Such PM-IRLD technique had already been reported for studying azo functionalized polymers.^{71,73} However, none of the studies has dealt with molecular materials made of non-covalently linked small molecules. To see if there were any correlation between the degree of orientation and the ability of azo units to migrate, PM-IRLD was used to monitor the individual vibrational modes of the azo molecules during a cycle of orientation followed by a cycle of relaxation.

2.4.1 PM-IRLD setup

The setup for PM-IRLD experiments is shown below (Figure 2.16). The IR beam was provided by a Thermo Scientific Nicolet 6700 infrared instrument and directed outside the spectrometer compartment. The focussed IR beam passed through a photoelastic modulator (modulated at selected wavenumbers such as 1350, 1700 and 2400 cm^{-1}) before reaching the sample and being recorded by a MCT-A detector. The thin film was irradiated with a 532 nm laser operating at a power of 80 mW. cm^{-2} . After a series of mathematical treatments, the PM-IRLD characteristic data were expressed as $\Delta A = A_{\parallel} - A_{\perp}$, where ΔA is the differential absorbance between the absorbance parallel ($A_{\parallel}$) and perpendicular ($A_{\perp}$) to the direction of the incident polarized light. The differential IR absorption spectra are obtained in real-time with a temporal resolution of 1 spectrum per min. Before irradiation, $\Delta A = 0$ since the orientation of the azo molecules in the thin film is isotropic. Upon irradiation, ΔA becomes negative for all modes oscillating in a direction perpendicular to that of the exciting polarization while ΔA becomes positive for modes that possess a strong

component parallel to the input polarization. During the relaxation cycle, the linear dichroism slowly relaxes back towards an isotropic state. Nevertheless, for some compounds, the induced level of anisotropy appears very stable, giving rise to remnant linear dichroism over a long time.

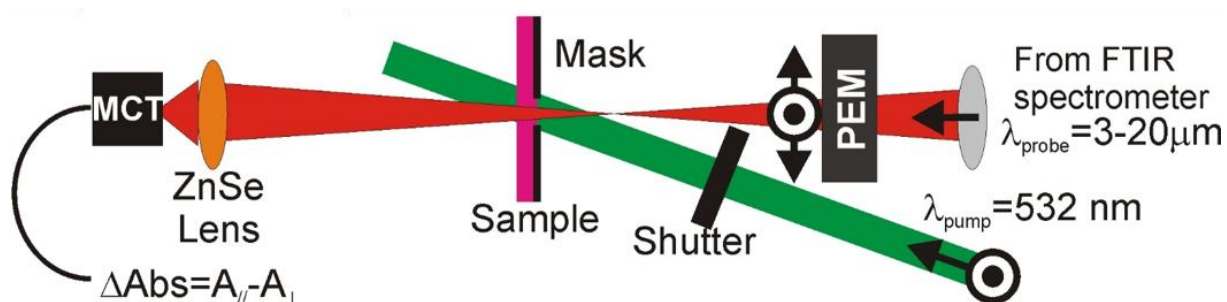


Figure 2.16. Setup for the PM-IRLD experiments.

2.4.2 Fourier transform infrared (FTIR) spectroscopy

Briefly, the thin films were prepared by spin-coating a 4 % wt. solution of the desired compound in chloroform onto different NaCl plates at a 700 rpm rotation speed for 2 min. The thicknesses of the resulting thin films were measured using atomic force microscopy and ranged from 300 - 450 nm. Fourier transform infrared (FTIR) spectra of the thin films were then obtained (Figure 2.17). Below, the FTIR spectrum for tBuNO_2 with a thickness of 450 nm is shown. For all other compounds, the spectra have been reported in **Appendix B**.

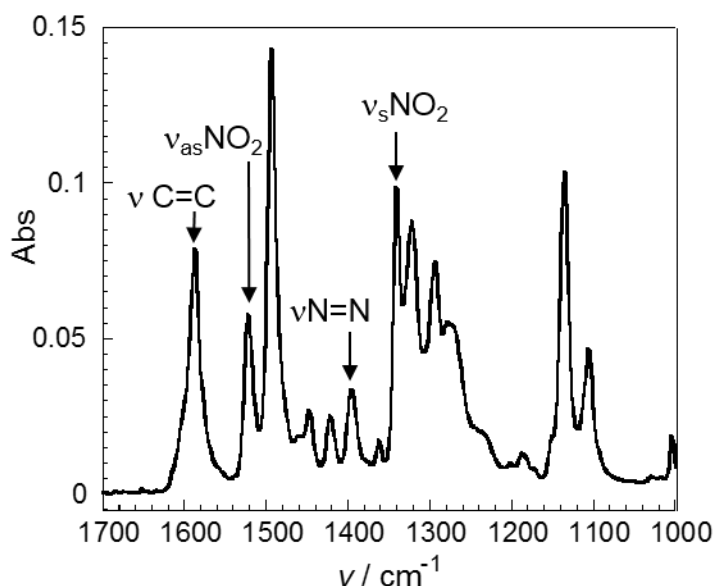


Figure 2.17. FTIR spectrum of tBuNO₂ thin film.

The main stretches to look at in the spectrum are listed in the table above. The --N=N-- stretch was assigned to the vibration at 1425 cm^{-1} while the one resulting from the coupling between the --N=N-- and $\phi\text{--N}$ stretches appear at 1395 cm^{-1} . The --NO_2 asymmetric and symmetric stretches were located at 1521 cm^{-1} and 1341 cm^{-1} respectively. In addition, the C=C stretches in the aromatic rings in the aromatic ring are found at 1495 cm^{-1} and 1588 cm^{-1} and the ring deformation can be assigned to 1107 cm^{-1} and 1136 cm^{-1} .

2.4.3 Polarized modulated infrared linear dichroism spectroscopy

Differential spectra were collected every minute for 125 min. Before irradiation, 5 spectra were obtained, showing a flat line that indicating isotropically oriented molecules ($\Delta A = 0$). The samples were then irradiated for 60 min with a linearly polarized laser operating at 532 nm ($P = 80\text{ mW. cm}^{-2}$). During irradiation, the recorded differential absorbance became negative for almost every vibrational stretch of the azo molecule, except for the asymmetric stretch of the NO_2 group at 1521 cm^{-1} (Figure 2.18). This lets us suggest that the main symmetry axis of the azo molecule orientates perpendicular to the direction of the polarized light. The positive differential absorbance of the asymmetric NO_2 stretch suggests that the molecule orientates parallel to the polarized light. The relaxation was monitored for 60 min and a spectrum was collected every minute. The differential absorption spectra for

tBuNO₂ compound, illustrating the common behaviour of the investigated azo series, are shown in Figure 2.18. They correspond to the systems before irradiation, right after 60 min of irradiation and 60 min of relaxation. The sensitivity of this technique can be noted as the resulting ΔA signals could detect the orientational events that are ten times less intense than those measured by FTIR spectroscopy. For instance, the absorbance of the –N=N– elongation vibration for tBuNO₂ in FTIR was equal to 0.0245, in comparison to the $\Delta A = 0.00245$, thus highlighting the extreme sensitivity of PM-IRLD to probe photoinduced dichroism.

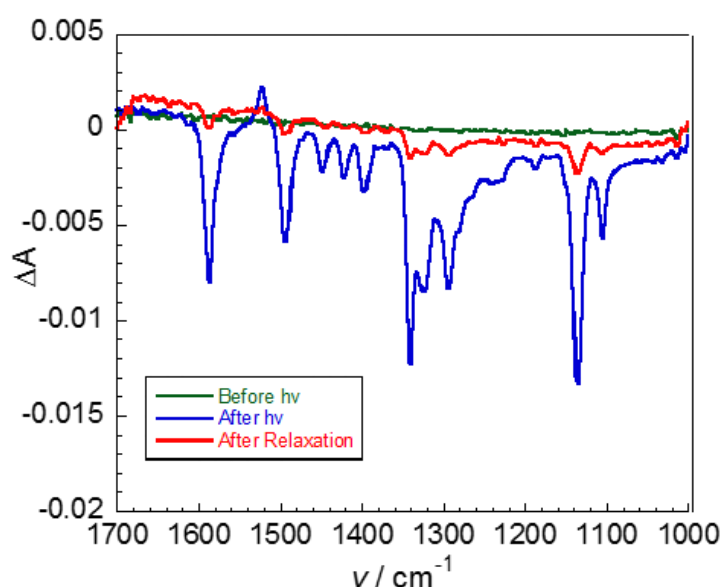


Figure 2.18. Differential infrared absorption spectra for tBuNO₂ before irradiation, after 60 min of irradiation, and after 60 min of relaxation.

2.4.4 Dynamic curves of PM-IRLD

From the individual linear dichroism spectra shown in Figure 2.18, the dynamic absorbance evolutions of particular molecular vibrations were monitored over time (Figure 2.19). First, they were obtained by integrating certain regions, and normalized using the initial absorbance ($\int \frac{\Delta A}{A_0}$). Typical dynamic measurements for tBuNO₂ compound again is shown in Figure 2.19, by selecting several vibrational modes such as the NO₂ symmetric and antisymmetric vibrations, along with the –N=N– and C=C elongation modes. The dynamic curves show that for the first 5 min, the ΔA value remains at 0, this is in agreement with the isotropic samples ($A_{\parallel} = A_{\perp}$). The laser was then turned on and instantly the molecules orientated. The sample was irradiated

for 60 min, and the dynamic curve showed no sign of photobleaching as the $\int \frac{\Delta A}{A_0}$ values remain constant. Finally, the light was turned off and the relaxation was monitored, showing that up to 84 % molecules disoriented back to their initial state. All the dynamic curves are summarized in **Appendix B**.

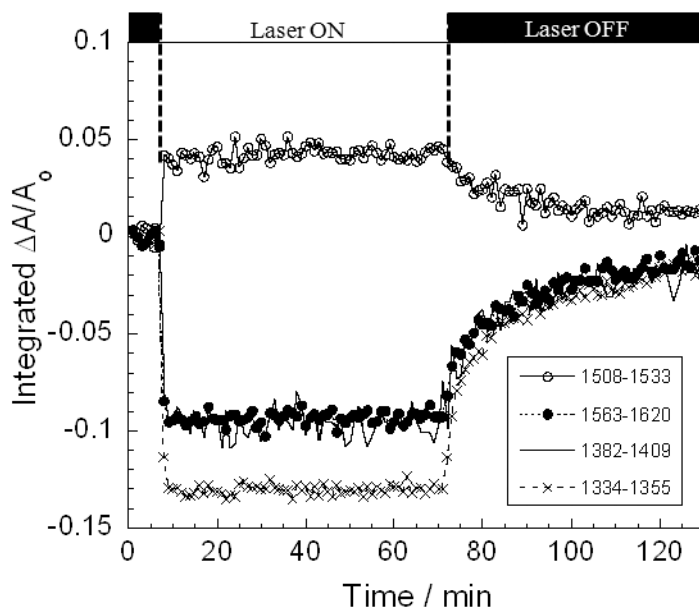


Figure 2.19. Dynamic curves of selected vibrational modes ($\nu\text{C}=\text{C}$: 1563 - 1620 cm^{-1} , $\nu_{\text{as}}\text{NO}_2$: 1508 - 1533 cm^{-1} , $\nu\text{N}=\text{N}$: 1382 - 1409 cm^{-1} , $\nu_{\text{s}}\text{NO}_2$: 1334 - 1355 cm^{-1}) of the tBuNO_2 for a cycle of orientation (60 min) and relaxation (60 min).

The experimental data $\int \frac{\Delta A}{A_0}$ and the percentage of relaxation have been studied for the $-\text{N}=\text{N}-$ vibration of all compounds. The results after 60 min of irradiation are summarized in Table 2.4, giving an idea of the degree of orientation. When comparing different integrated vibrations, it was observed that the larger the bulky substituents, the larger the degree of orientation reaching up to a value of 0.15 (see **Appendix B** for the comparison of other vibrations). The percentage of relaxation also appears to be larger for azo compounds containing a stronger electron withdrawing group as more molecules thermally relax out of the planes parallel or perpendicular with respect to the initial direction of the light polarization. Noticeably, once the $-\text{CO}_2\text{Me}$ containing azo thin films have been oriented, very little relaxation could be observed (7.9 - 35 % against 41 – 84 % for the nitro compounds).

Compound	Degree of orientation $(\int \frac{\Delta A}{A_0})$	Relaxation (%)
tBuNO ₂	-0.098	84
tBuCN	-0.073	61
tBuCO ₂ Me	-0.079	35
CarbNO ₂	-0.152	41
CarbCN	-0.143	18
CarbCO ₂ Me	-0.014	7.9
CF ₃ NO ₂	-0.152	60
CF ₃ CN	-0.083	57
CF ₃ CO ₂ Me	-0.110	24

Table 2.4. Summary of the degrees of orientation $\int \frac{\Delta A}{A_0}$ and the percentages of relaxation for the- N=N- bond of the series of azo compounds CF₃X, tBuX and CarbX.

2.5 Birefringence of thin films

Another way to evaluate macroscopic photoinduced anisotropy is to measure the resulting birefringence. In general, such measurement is done at a single wavelength, opening the possibility of measurements with good temporal resolution. The access to such temporal resolution is of interest to gain precise information about the rate of the orientation/relaxation processes, as well as to probe the level of orientation after multiple cycles.

2.5.1 Birefringence setup

Birefringence studies on the thin films were performed to determine the absolute photoinduced birefringence $\Delta n = n_{//} - n_{\perp}$, where $n_{//}$ and $n_{\perp}$ are the refractive indices along the two orthogonal directions with respect to the input polarization direction. A birefringence setup was designed to measure the birefringence dynamically with a time resolution of 100 ms (Figure 2.20). First, a 632.8 nm He-Ne

laser was aligned to probe the sample. The propagating light passed through a polarizer, set at a $+45^\circ$ angle, then the polarized light passed through the sample, followed by a second polarizer, set at -45° , and was eventually detected by a photodiode. Prior to irradiation, the azo molecules in the thin films have no preference in direction, therefore Δn was zero. Upon irradiation using a 532 nm linearly polarized laser oriented at 0° ($P = 80 \text{ mW} \cdot \text{cm}^{-2}$), the azo compounds orientated in a perpendicular fashion with regard to the 532 nm polarization direction. This photoinduced orientation changes the polarization of the He-Ne light, resulting in an increase in intensity to the photodiode. The birefringence studies were conducted by performing cycles of 200 s of irradiation followed by an additional period of 200 s of relaxation (Figure 2.21). The absolute birefringence Δn , could be calculated by knowing the thickness of the film d and the wavelength of the probe laser ($\lambda = 632.8 \text{ nm}$) and Equation 2.4, where δ_{corr} was the corrected phase shift that was experimentally measured with a Babinet-Soleil compensator.

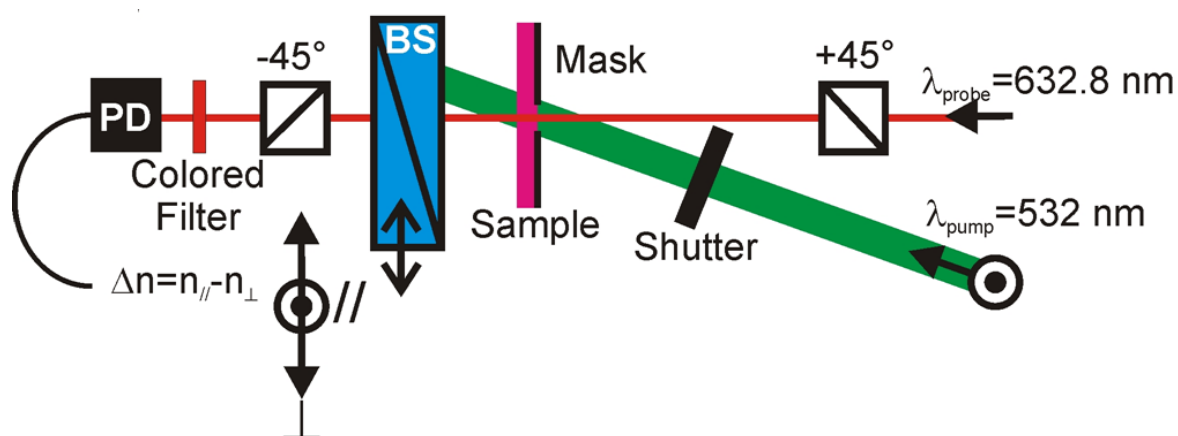


Figure 2.20. Optical setup for dynamical birefringence measurements.

$$\Delta n = \frac{\delta_{corr} \lambda}{2\pi d} \quad (2.4)$$

2.5.2 Birefringence on thin films

Several trends were noticed when conducting the birefringence studies (Figure 2.21). First, the relaxation was again quicker for azo compounds containing a stronger electron withdrawing group. Second, when comparing thin films made of small push-pull azo compounds to a reference azopolymer (pDR₁M), it was noticed that the small molecules orientated 4 to 10 times faster than the pDR₁M polymer (Table 2.5). Third,

the Δn values seemed to be related to the terminal group on the amino branches, as Δn was found around -0.015 for the CF_3X compounds, and -0.025 for the tBuX and CarbX compounds. However, when comparing these values with the Δn ones obtained with the azo polymer ($\Delta n = -0.05$), the azo molecular thin films present a significantly lower birefringence level. Here, we show a direct correlation between the free volume of the azo compounds with both the rate of orientation and the maximum induced birefringence. The available free volume can yield faster rates but faster rate in orientation tends also to be accompanied by a faster rate in relaxation, hence the level of final induced birefringence is reduced.

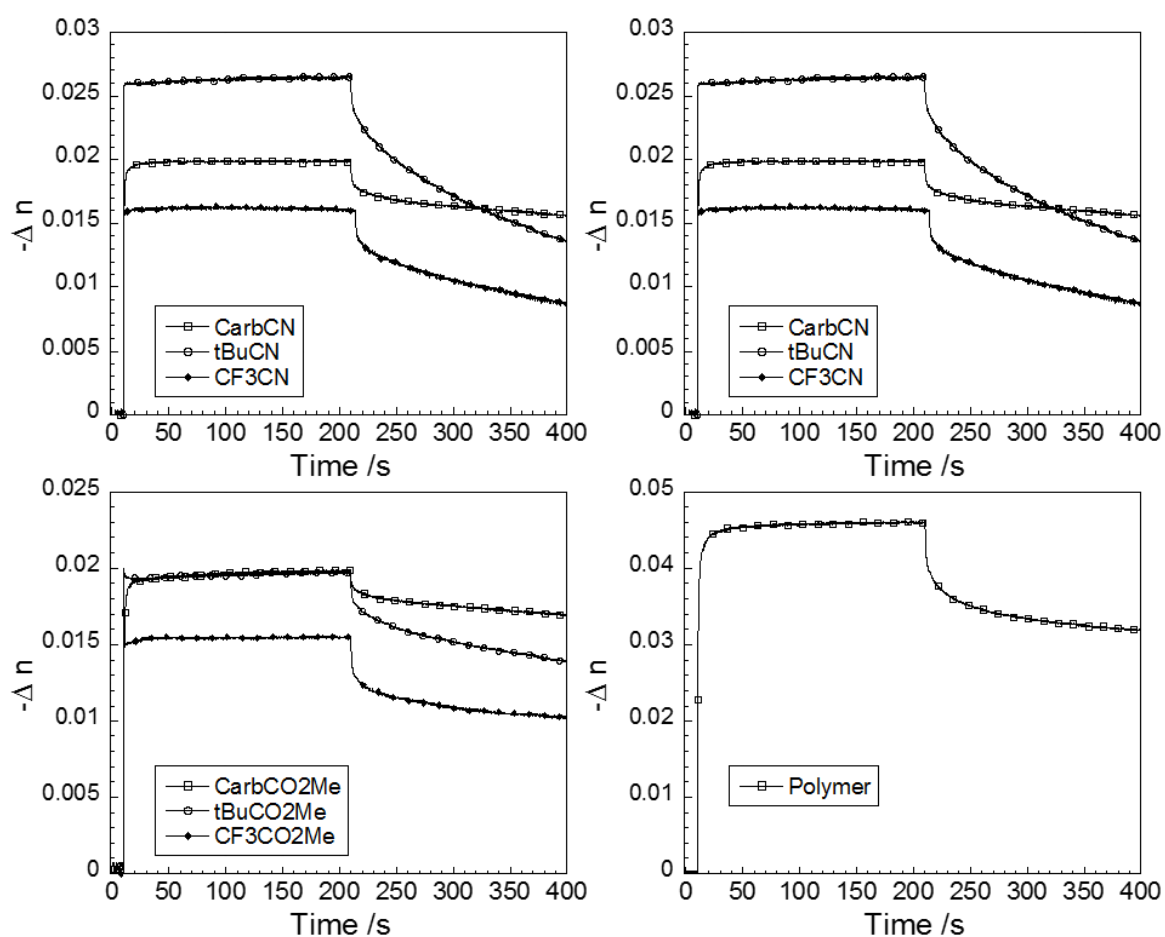


Figure 2.21. Birefringence curves for the series of azo thin films.

Compound	Thickness (nm)	$-\Delta n_{\max}$	Orientation (s)	Remanence (%)
tBuNO ₂	453	0.0253	2.1	35.1
tBuCN	580	0.0268	0.4	49.0
tBuCO ₂ Me	520	0.0197	6	69.7
CF ₃ NO ₂	430	0.0155	0.4	40.6
CF ₃ CN	520	0.0159	3.4	53.6
CF ₃ CO ₂ Me	350	0.0154	22.1	66.0
CarbNO ₂	480	0.0317	9	72.9
CarbCN	380	0.0198	11.4	78.4
CarbCO ₂ Me	555	0.0198	57.8	85.2
pDR ₁ M	500	0.0460	48.5	69.1

Table 2.5. Birefringence characteristics for molecular and polymer azo thin films after irradiation at 532 nm.

2.6 Photo-orientation cycling and reversibility

To show that photo-orientation can be repeated with a good stability, successive cycles of orientation/relaxation have been performed on the thin films. tBuNO₂ and CarbCO₂Me thin films were selected since they display the fastest and slowest orientation rates. They were again compared against pDR₁M thin film used as a reference sample. By respecting the same setup used in the previous birefringence studies, the thin films were irradiated with a 532 nm laser ($P = 100 \text{ mW} \cdot \text{cm}^{-2}$) for 200 s followed by a relaxation cycle during 200 s. Ten cycles were recorded for each compound (Figure 2.22). These cycles showed identical levels of birefringence after each irradiation cycle, meaning that no visible photobleaching occurred.

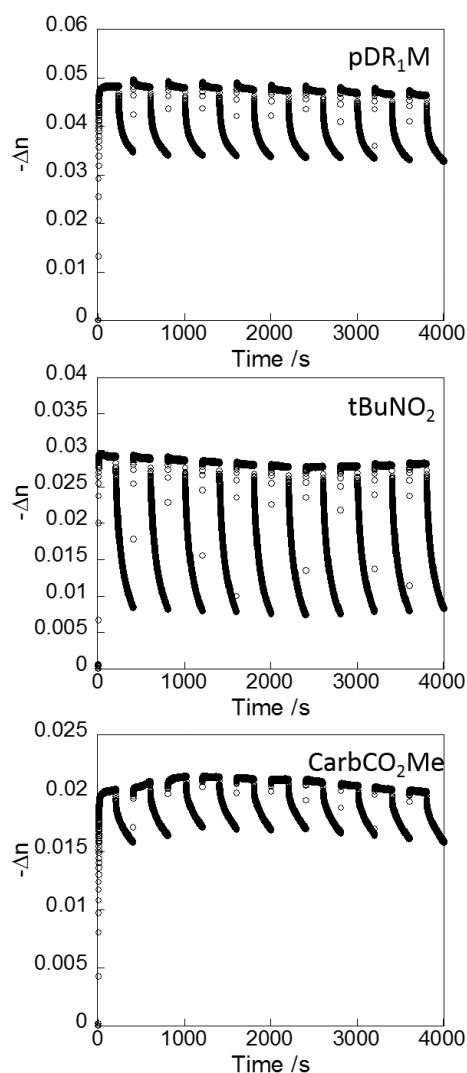


Figure 2.22. Birefringence evolution upon cyclic irradiation, relaxation sequences for pDR₁M, tBuNO₂, CarbCO₂Me.

In order to show that the thin films are rewritable after relaxation, irradiation with circularly polarized light was performed to erase the induced birefringence (Figure 2.23). The experiments reported in Figure 2.23 consist of two successive cycles of irradiation (100 s), relaxation (100 s) and erasure (100 s) until reaching a birefringence level of zero. pDR₁M, tBuNO₂, and CarbCO₂Me thin films were irradiated for 100 s, and it was observed that the molecules orientate perpendicular to the linearly polarized light; the molecules then relaxed, and the percentage of their remnant orientation varied from $86 \pm 5\%$ (CarbCO₂Me) to $69 \pm 5\%$ (pDR₁M) down to $35 \pm 5\%$ (tBuNO₂). The orientation of the molecules was then erased and a second

cycle was performed. These studies showed that in the case of the small push-pull azo molecules they orientate quicker, in comparison to a similar polymer, and still exhibits full rewritability.

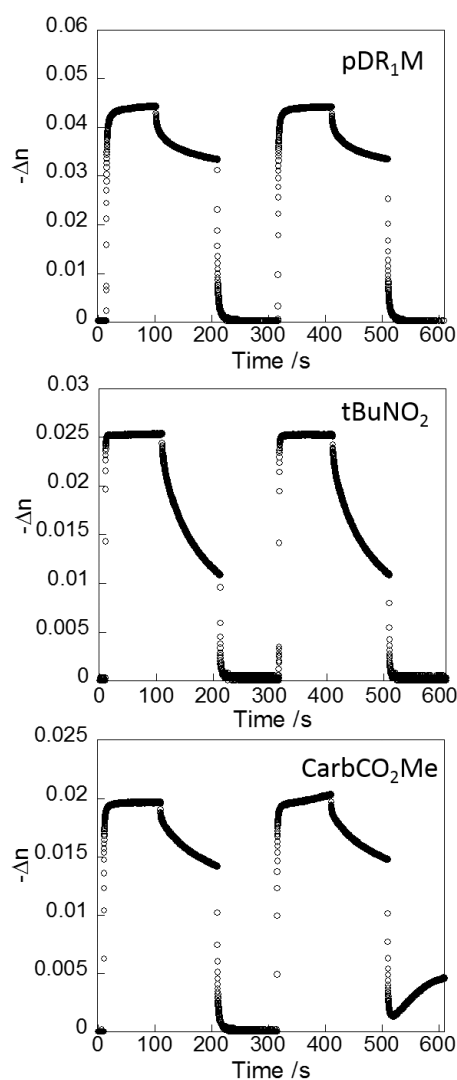


Figure 2.23. Birefringence measurements during cycles of irradiation, relaxation and erasure sequences for pDR₁M, tBuNO₂, CarbCO₂Me.

2.7 Conclusions

A variety of push-pull azo molecules were synthesized and characterized in solution and in thin films. The photochromic studies of these compounds showed that the photoisomerization reaction in solution was driven by the nature of the electron withdrawing group substituted in *para*-position the azobenzene moiety. However, in the solid state, the photoisomerization reaction was more driven by the free volume

produced by the bulky substituents. PM-IRLD measurements also showed the direct effect exerted by the electron withdrawing group on the remanence. The birefringence studies highlighted not only that larger degrees of birefringence could be obtained by using bulkier substituents, but also proved that small push-pull azo molecules orient significantly faster than a similar azo polymer.

Chapter 3

Organizing nanoparticles using azo thin films

3.1 Surface relief gratings

Ever since the independent discovery of the formation of surface relief gratings (SRGs) on azopolymer thin films by two separate groups in 1995,^{26,74,75} the photoinduced mass transportation in azopolymers has been extensively explored.^{34,36} Several types of azo materials have been investigated including azopolymers, liquid crystals, and small molecules.^{15,36,44,66,72,76,77} Spin casting the materials onto the substrate is the most common method of deposition, resulting in isotropic orientation of the azo molecules with a thickness being relatively homogenous and proportional to the concentration and the speed of spin casting the material. The inscription of SRGs onto the azo thin film results from the projection of an interference light pattern onto the photosensitive surface. Under selected polarization and irradiance of the desired pattern, a substantial surface mass migration occurs, due to continuous cycles of photoisomerization. This photoinduced migration is due to the gradient of light intensity and to the polarization of the impinging pattern at the surface of the film. The yield of photoisomerization is distinct in the different parts of the interference pattern, leading to local mass migration in directions that mimic the interference pattern. Experimentally, it has been shown that the surface relief gratings were shifted by half a period with respect to the interference field. Such π phase shift suggests that the molecules migrate away from the more intense illuminated regions, building-up towards area with weaker light intensity (Figure 3.1).^{31,35} The fundamental processes explaining the nature of the photoinduced migration is still not clear-cut. Its origin results from several effects including light-dependent pressure gradient and different photomechanical effects,³⁶ optical field-gradient theory,³⁰ random walking photoinduced molecular diffusion,³⁷ entropy-driven sample deformation,³⁸ and torque inducing dipole electric interactions.³⁹ Many of these mechanistic studies were applied to the peculiar case of azopolymers thin films, which allows for an inaccurate comparison as the average molecular weight of the polymer chains, their steric crowding as well as the azo polarity influence the migration efficiency. Furthermore, several of these studies show how polarization effects are material dependent, as

observed in glassy polymers and liquid crystalline polymers. To try and more accurately study the photomechanical migration of the azo materials, new molecules were synthesized with the aim to prevent and minimize any entanglements due to polymer backbone or intermolecular interactions through hydrogen bonding.^{42,78,79} In this way, the group of Shirota et al. at the University of Osaka and our group devised a variety of glass forming small azo molecules with glass transition temperatures varying from 68 to 200 °C.^{66,80} These related studies showed that the compounds exhibiting the higher glass transition temperatures migrated well beneath the T_g points, confirming that the mass migration was photoinduced by the azo photoisomerization reaction and not by secondary thermal effects. Instead of looking at these compounds in terms of T_g , it was suggested that the migration should be discussed in terms of free volume.⁶²

In previous projects conducted in our group, different bulky substituents were introduced into the peripheral branches of the triphenylamino core giving rise to a mass migration in the pseudostilbene-like azo molecules.⁶⁶ By inducing a large free volume around the azo moiety, the aim was to enable the azo molecule to photoisomerize more efficiently. Therefore, the series of small push-pull molecules was expanded to the molecules synthesized in Chapter 2, in order to utilize the photoactivable mechanical properties of the azo molecules to ultimately move and control the position of nanometer-sized objects. To this endeavor, surface relief grating patterning on the azo thin films was an important preliminary step in order to confirm the possibility of enabling photoinduced forces.

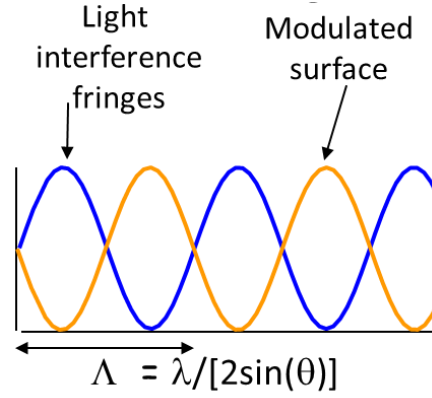


Figure 3.1. Schematic illustration of the interference pattern light (blue) and the resulting surface relief pattern (orange). X axis: periodicity, Y axis: surface topography and light intensity.

3.2 Optical setup for the fabrication of surface relief gratings

The surface relief gratings (SRGs) were formed by projecting an interferential light pattern onto the surface of thin films. The interferential light pattern was formed by means of a two-arm interferometer (Figure 3.2). First, the light of an Ar ion laser ($\lambda_{\text{pump}} = 488 \text{ nm}$) was passed through a half waveplate, to adjust the output polarization of the laser irradiation, then through a polarizer set at a 45° angle. The linearly polarized light was cleaned using a spatial filter, and the laser beam was split in two beams of equal intensities using a 50: 50 beam splitter. Both beams were eventually recombined on the surface the thin films. The polarizations of the individual beams were set to $+45^\circ$ and -45° . The resulting interferential light pattern yields SRGs with a sinusoidal shape (as measured later by atomic force microscopy) whose real-time formation was monitored using a He-Ne probe laser beam ($\lambda_{\text{probe}} = 632.8 \text{ nm}$). Detection of the first-order diffracted beam $I_{\pm 1}$ indicates the presence of a SRG and can be used to calculate the diffraction efficiency of the resulting grating.

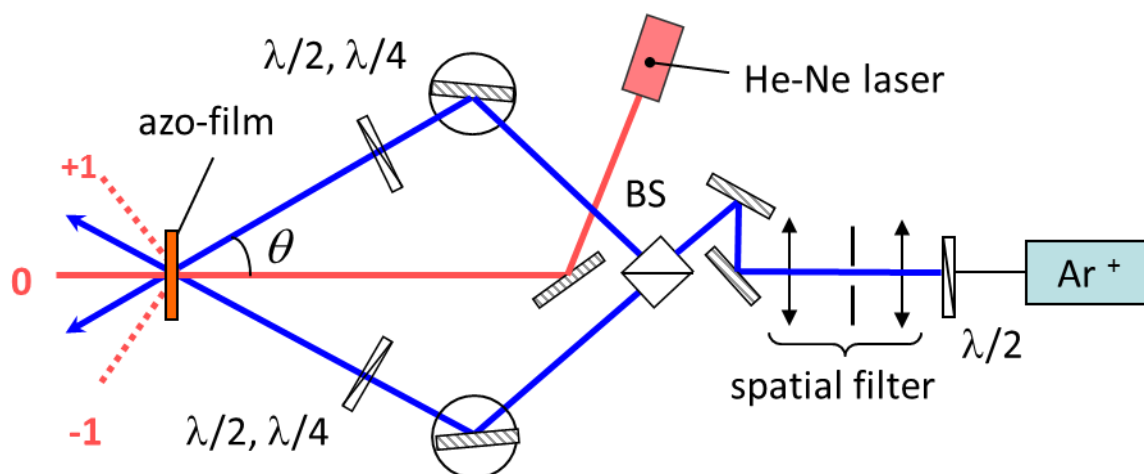


Figure 3.2. Optical setup for the formation of the surface relief gratings.

3.3 Formation of surface relief gratings

The thin films were irradiated with an interferential light pattern resulting from the combination of the -45° and $+45^\circ$ polarized beams that were previously split (160 mW cm^{-2} / beam). This polarization configuration has shown to be the most efficient one, due to the field gradient of the interferential light pattern along the grating vector direction, enabling a large mass migration. During the formation of SRGs, the diffraction efficiency $\eta = I_{\pm 1}/I_0$ was monitored to see how the grating diffracts the incoming He-Ne beam. The resulting SRGs were characterized by atomic force microscopy (AFM) (Figure 3.3) and the AFM images for all thin films made of distinct azo compounds are shown in Figure 3.3. We have then compared all series to see the effect exerted by the bulky substituents on the SRG amplitude. In the case of the $-\text{CO}_2\text{Me}$ series, the peak-to-trough amplitude (h) of the SRGs increased as the bulky substituent increased: $\text{CF}_3\text{CO}_2\text{Me}$ ($h = 150 \text{ nm}$) $<$ tBuCO_2Me ($h = 260 \text{ nm}$) $<$ CarbCO_2Me ($h = 300 \text{ nm}$). The heights h of the SRGs were compared to the thicknesses d of the thin films in Table 3.2. Instead of considering the height itself, we took into account the h/d ratio allowing us to normalize the SRG amplitude with respect to the initial amount of material. A correlation between the h/d ratio, and the bulky substituents could be evidenced: CF_3X ($h/d = 0.5 - 0.8$) $<$ tBuX ($h/d = 1.1 - 1.3$) $<$ CarbX ($h/d = 1.5 - 2$). For substituents containing bulkier groups, the SRG amplitude as well as the h/d ratio appeared to be the larger. In the case of the CF_3X thin films, the h/d ratio ranges from $0.5 - 0.8$, meaning that less than half the

molecules on the thin films undergo migration under interferential light. In contrast, the CarbX species exhibit the highest h/d ratio. Reduced migration abilities of the CF₃X species by a factor of two could be noticed due to partial crystallization of the molecules, impeding any photoisomerization reaction and thus migration. Moreover, the maximum absorption wavelengths of the CF₃ compounds ($\lambda_{\text{max}}(\text{abs}) = 445 - 477$ nm) were significantly red shifted compared to the irradiation wavelength, diminishing the photon absorption probability and consequently the extent of photoisomerization.

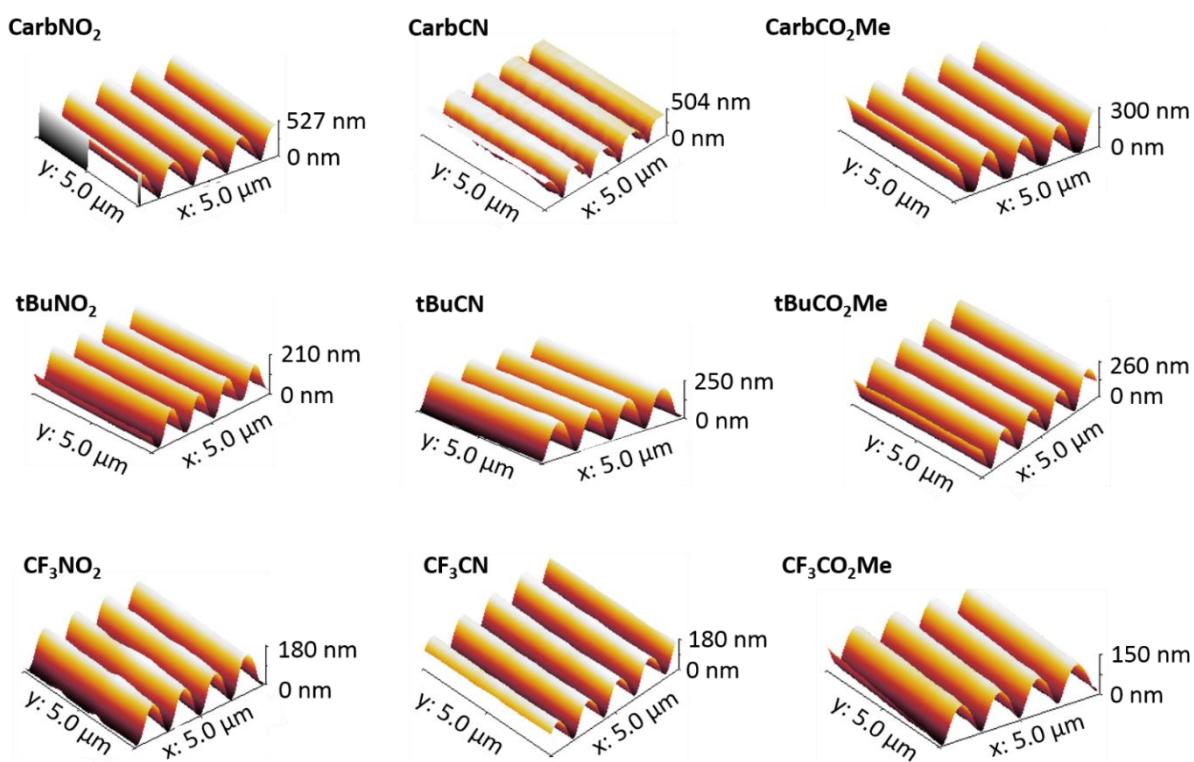


Figure 3.3. AFM characterization of SRGs formed over thin films made of azo molecules.

To confirm the existence of correlation between the migration ability and the free volume induced by the bulky substituents in the peripheral branches, the h/d ratio was plotted against the glass transition temperatures (T_g) (Figure 3.4). These latter are directly related to the bulkiness of the compounds: CF₃X ($T_g = 62 - 68$ °C) < tBu ($T_g = 89 - 118$ °C) < Carb ($T_g = 187 - 202$ °C). Larger migration efficiency was then observed for azo materials with higher T_g s, showing that this mass migration is induced by the sterically demanding photoisomerization reaction. Indeed, the higher

the T_g values, or the larger the molecules, the more efficient the migration, due to large free volume created around each azo moiety.

Compound	SRG height h (nm)	Thickness of thin films d (nm)	Ratio h/d
CarbNO ₂	527	297	1.8
CarbCN	504	246	2.0
CarbCO ₂ Me	300	196	1.5
tBuNO ₂	210	202	1.1
tBuCN	250	204	1.2
tBuCO ₂ Me	260	193	1.3
CF ₃ NO ₂	180	234	0.8
CF ₃ CN	180	275	0.7
CF ₃ CO ₂ Me	150	298	0.5

Table 3.2. Thickness d of the thin films, SRG amplitude h and h/d ratio measured by AFM microscopy.

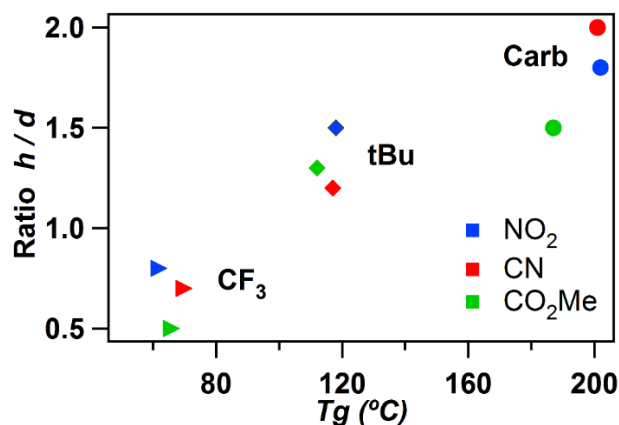


Figure 3.4. Evolution of ratio h/d as a function of the glass transition temperatures T_g . Reprinted with permission from ref 67. Copyright 2014 American Chemical Society.

3.4 Migration of nanoparticles using the formation of SRGs

3.4.1 Surface deformation

Now that the azo thin films have shown to efficiently deform into periodic arrangements in the presence of polarized light, the goal is to deposit polystyrene (PS) nanoparticles onto the surface of thin films and try to exploit the migration properties of the azo thin films to spatially organize different nanoparticles. For such a purpose, commercially available polystyrene nanoparticles were used. Their diameter $\phi = 200$ nm was chosen smaller than the periodic pitch of the gratings $\Lambda = 1.1 \mu\text{m}$. A 2.6 wt. % aqueous solution of suspended PS nanoparticles was diluted by a factor of a 100 and a droplet was deposited onto the surface before the SRGs were formed. The aqueous PS nanoparticle suspension was critical to avoid dissolution of the thin films. However, when a hydrophobic organic thin film comes into contact with water, its surface may strongly deform as a result of strong surface tension effects developed between the hydrophilic glass substrate, the hydrophobic thin film and the hydrophilic water droplet. To gain insight into such effects, a droplet of ultrapure water (Millipore) was deposited onto the surface of all thin films and dried over 60 min. AFM measurements showed nano- to micrometric features, resulting from the surface deformation due to the hydrophilic/ hydrophobic surface tension (Figure 3.5). Such effects were minimized and even absent in the case of the CarbNO₂ thin film, likely due to the largely polar structure of the azo organic backbone.

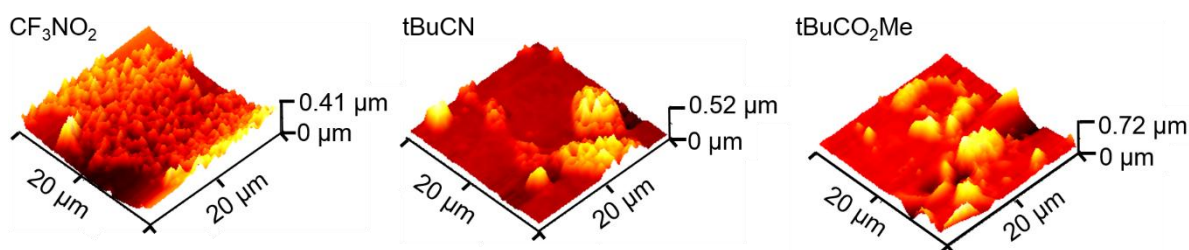


Figure 3.5. AFM images of azo thin films after exposure to a water droplet for 60 min. Reprinted with permission from ref 67. Copyright 2014 American Chemical Society.

3.4.2 Deposition of polystyrene nanoparticles

The thin films were prepared by depositing a 2 wt. % azo solution prepared in chloroform onto clean glass films, silicon wafers or glass slides coated with indium

tin oxide (ITO), a transparent semi-conducting material. These latter two materials were chosen to correlate scanning electron microscopy (SEM) and AFM measurements to get a clear description at the nanometer scale. After the thin films were prepared and dried overnight (18 h) at room temperature, 10 μL of the previously prepared diluted solution of polystyrene nanoparticles were deposited onto the surface of the azo thin film. This solution was left for 60 min before the droplet was removed to avoid unnecessary nanoparticle aggregation. AFM imaging of the PS nanoparticles deposited onto the surface of the CarbNO₂ thin films was performed and confirmed the 200 nm height of the PS nanoparticles and their dispersion (Figure 3.6).

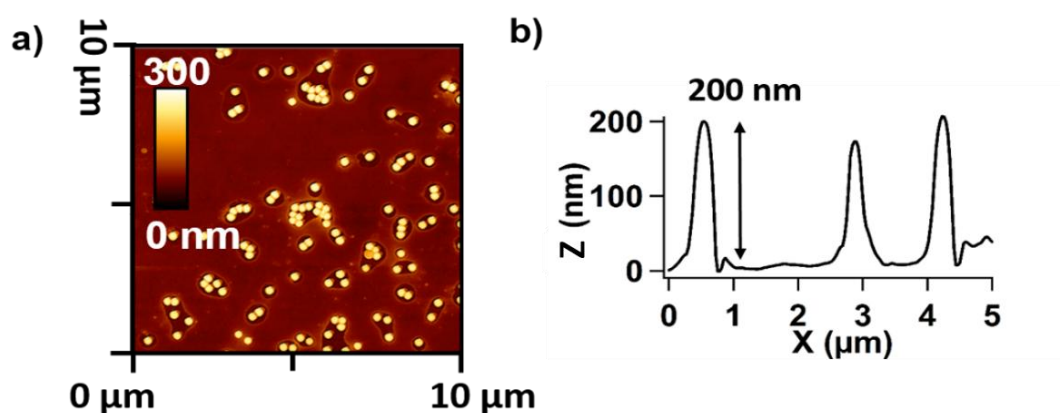


Figure 3.6. (a) AFM image of polystyrene nanoparticles (0.026 wt. % in water) deposited onto the surface of CarbNO₂ thin film and (b) cross section of the sample. Adapted with permission from ref 67. Copyright 2014 American Chemical Society.

The sample was irradiated with an interference pattern and further characterized using both SEM and AFM. When comparing the sample with and without polystyrene nanoparticles, the samples present similar surface relief gratings with the periodic spacing equal to 1.1 μm . The diffraction efficiency η increased from 18 % for CarbNO₂ SRGs without nanoparticles to 24 % for structured thin films with nanoparticles, suggesting additional organization that may involve the nanoparticles. Surprisingly, very few PS nanoparticles appeared visible while the crests lost regularity and presented periodical bumps. The cross section along the crest shows bumps ranging in height from 50 - 100 nm (Figure 3.7), letting us suggest the embedment of nanoparticles under the azo material upon mass migration.

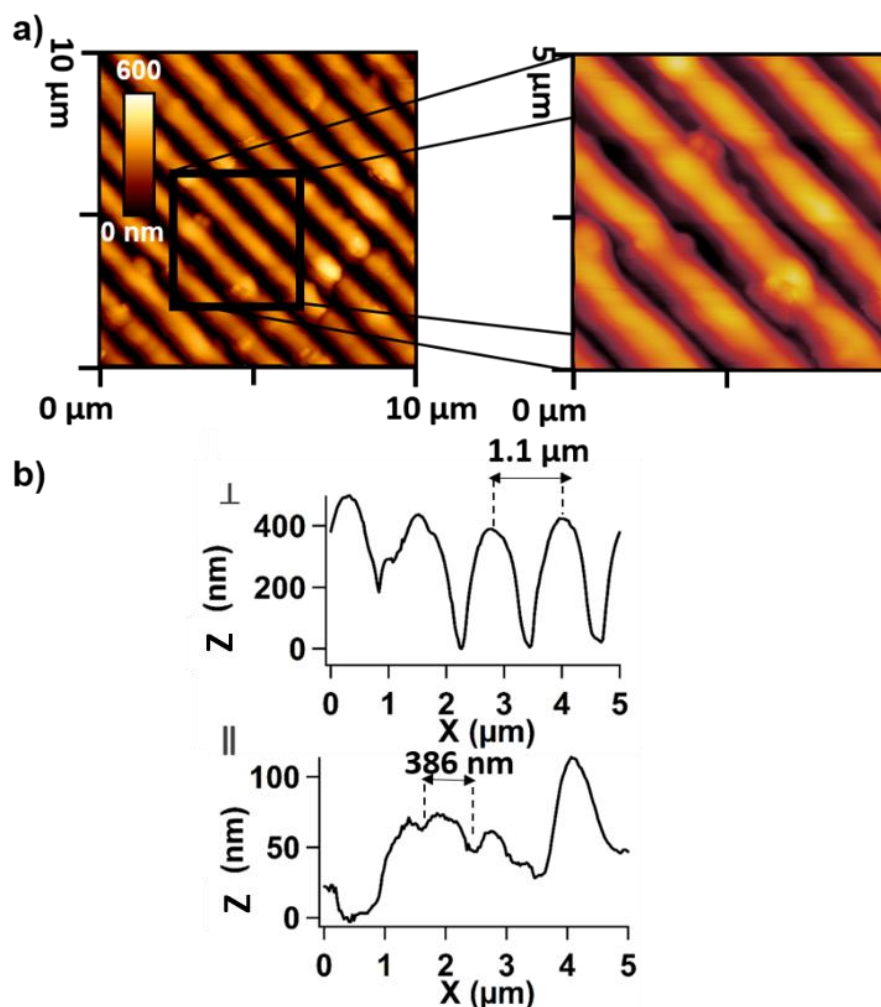


Figure 3.7. AFM image of the surface relief grating formed after the polystyrene nanoparticles have been deposited onto CarbNO₂ thin films. (a) 2D image (b) cross sections orthogonal and parallel to the crests of the SRG. Adapted with permission from ref 67. Copyright 2014 American Chemical Society.

SEM was used to validate this assumption and carried out on thin films devoid of PS nanoparticles (Figure 3.8 a-b); and coated with PS nanoparticles (Figure 3.8 c-f). Using the same conditions as those described in the previous section, PS nanoparticles were deposited over CarbNO₂ thin films spin-cast on ITO substrate, and SRGs were then inscribed. SEM imaging revealed indeed aligned spherical patterns under very regular SRG patterns (Figure 3.8 d), which did not appear for CarbNO₂ thin films in the absence of PS nanoparticles (Figure 3.8 b). Some parts of the surface relief gratings appeared deformed, letting show half engulfed nanoparticles in the azo material. (Figure 3.8 (e) and (f)). At certain points, the nanoparticles were so concentrated that some appear on the surface.

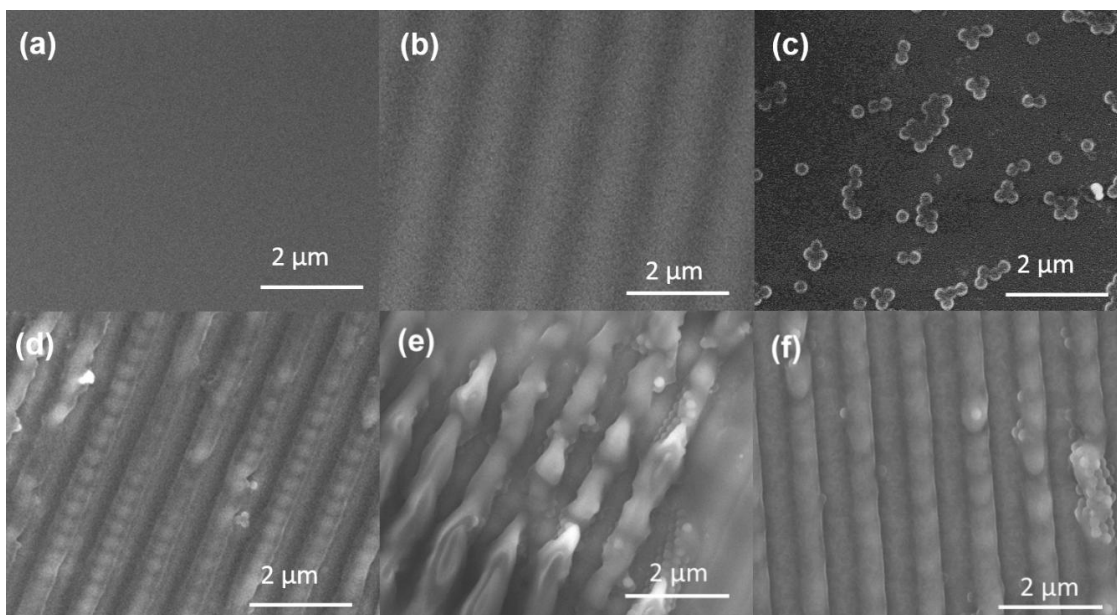


Figure 3.8. SEM images of (a) CarbnO₂ thin film (b) SRGs formed on the surface of CarbnO₂ thin film, (c) polystyrene nanoparticles ($\phi = 200$ nm) deposited on the CarbnO₂ thin film, (d)-(f) SRGs formed after deposited polystyrene nanoparticles onto CarbnO₂ thin film. Adapted with permission from ref 67. Copyright 2014 American Chemical Society.

To characterize the embedded nanoparticles better, commercially PS nanoparticles ($\phi = 200$ nm) doped with a variety of emitting dyes were used. The absorption maxima for these dyes are as follows: 377, 517 and 588 nm, while the emission maxima are centered at 479, 546 and 612 nm, respectively. The normalized emission spectrum of the fluorescence nanoparticles was recorded and compared to the absorption spectrum of CarbnO₂ that has been normalized for the charge transfer band in the visible range. (Figure 3.9). In case the nanoparticle embedment occurs, a decrease in fluorescence is expected, due to the overlapping emission spectrum by the azo absorption spectrum.

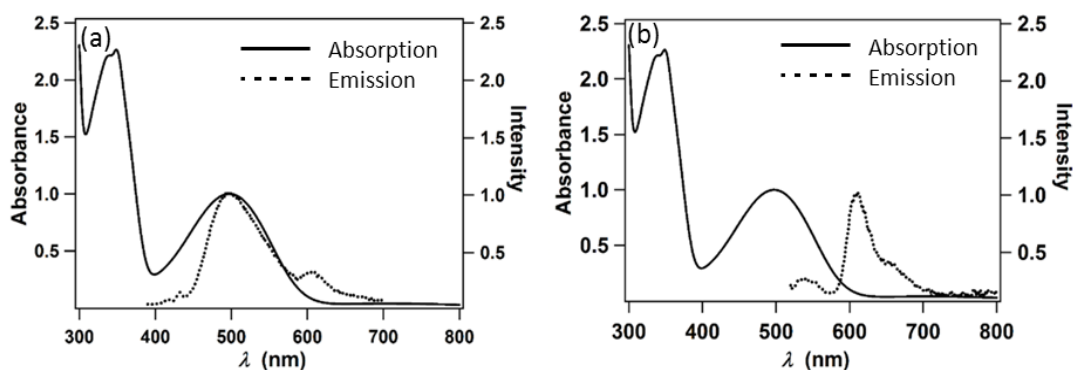


Figure 3.9. Absorption spectrum of CarbNO₂ thin films and emission spectrum of fluorescent nanoparticle suspensions that were excited at (a) 377 nm, and (b) 513 nm. Reprinted with permission from ref 67. Copyright 2014 American Chemical Society.

The fluorescent polystyrene nanoparticles were drop-casted onto the azo surface in the same way as before (10 μ L of an aqueous 0.026 wt. % suspensions), and left to dry for 60 min on a 1 mm-thick microscope glass slide. The surface relief gratings were formed under the same irradiation conditions. An epifluorescence microscope (Nikon, TI Eclipse) equipped with a 60 $\times$ oil immersion objective and an excitation laser source at $\lambda_{\text{exc}} = 513$ nm was used to provide transmission and fluorescence images. The surface of the thin film was observed through a 0.17 mm glass coverslip because of the short working distance of the microscope objective (WD = 0.17 mm), and the risks of thin film dissolution by the oil of the objective. A significant decrease in fluorescence was observed for thin film areas structured as SRGs in comparison to non-structured areas. The fluorescent polystyrene nanoparticles were checked to be photochemically stable upon interferential illumination, to ensure the absence of photobleaching. Therefore, the diminution of the nanoparticle fluorescence signal could only be attributed to an internal filter effect caused by the azo absorption of the fluorophore emission as shown above (Figure 3.10). However, in order for the azo compounds to play the role of a filter, they must wrap around the fluorescent nanoparticles. This tends to confirm the embedment of the nanoparticles into the SRGs, as suggested by the overall weaker fluorescence signal. When looking at the wide-field fluorescence images of samples coated with a low density of NPs, two types of fluorescent spots could be distinguished: bright spots that might be due to nanoparticles on top of the SRG, and dimmer spots, which could be due to the engulfed nanoparticles (Figure 3.10). The corresponding transmission images display protuberances aligned along identical motifs, namely darker lines that are

characteristic of the crests of the azo gratings. The combination of the fluorescence and transmission images revealed that the brightly emissive spots are aligned along the dark lines, confirming that the dimmer spots, more difficult to observe in a transmission mode, correspond to nanoparticles embedded under the crest of the gratings (Figure 3.10 c).

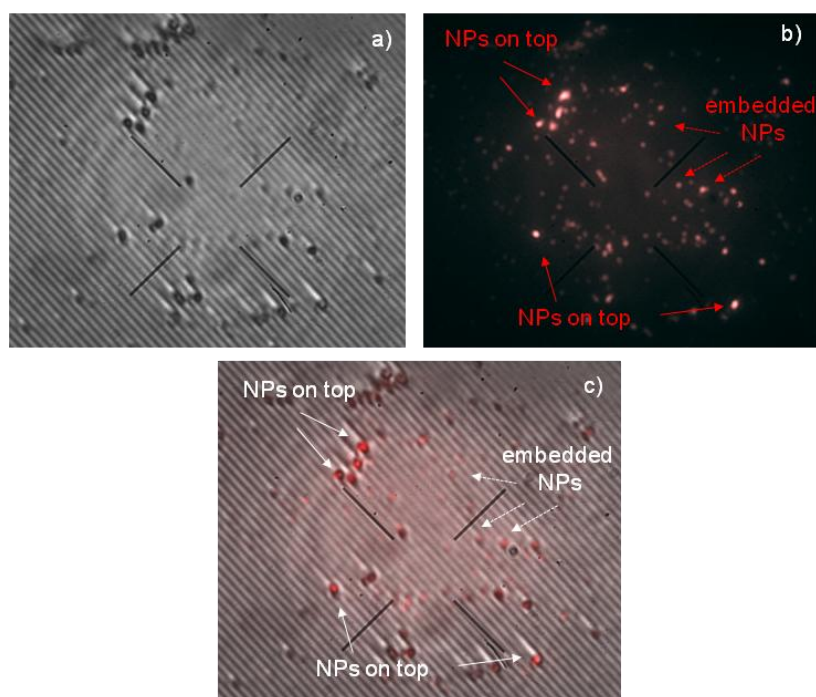


Figure 3.10. Surface relief gratings formed after depositing polystyrene nanoparticles from an aqueous suspension. (a) Transmission image, (b) fluorescence image, (c) combined transmission and fluorescence images. The black bars on the images are the microscope centering tool and are 11 μm large. Reprinted with permission from ref 67. Copyright 2014 American Chemical Society.

Characterization of the nanoparticle embedment was then done by removing the azo material. Careful dissolution of the thin films using a drop of chloroform was unsuccessful since no trace of the nanoparticles remained. The reversible migration of the azo compounds was exploited to erase the SRGs. The surface was exposed to a non-polarized 482 nm light at high irradiance ($P = 360 \text{ mW} \cdot \text{cm}^{-2}$) for 30 min, using an 60 $\times$ oil objective (N.A. 1.4). AFM, transmission and fluorescence images were obtained (Figure 3.11). AFM images display large agglomerations that are 2.5 μm wide and 250 - 300 nm high. Interestingly, the height was close to the diameter of the polystyrene NPs. Even though there was very little evidence of nanoparticles laying

on the surface, it was suspected that these agglomerates correspond to ensemble of fluorescent polystyrene nanoparticles. These latter seem to inhibit the azo material migration and act as ‘glue’ holding the azo compound around them. When looking more carefully at the AFM images, one can distinguish regular features aligned in a direction parallel to that of the crests of the initial SRGs. In these images, the surface relief gratings were formed with the crests aligned horizontally, before erasure transmission/ fluorescence images completed with AFM analyses and evidenced a strong fluorescence signal emitted by the agglomerates. All these observations tend to confirm that the nanoparticles have been displaced and aligned during SRG formation. One question still arises: what happens if we deposit the fluorescent nanoparticles onto already pre-structured gratings?

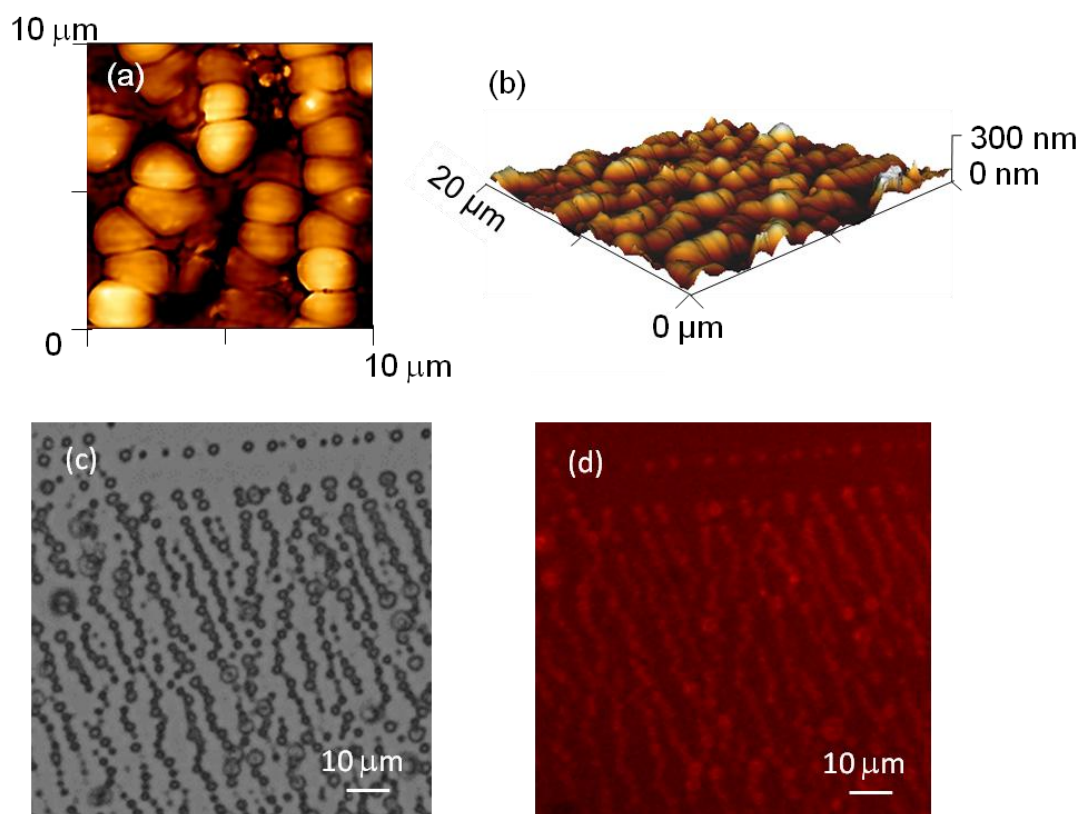


Figure 3.11. Erased surface relief gratings formed after deposition of the polystyrene nanoparticles. (a) AFM image, (b) 3D AFM image (c) transmission image, and (d) fluorescence image ($\lambda_{\text{exc}} = 543 \text{ nm}$) . Reprinted with permission from ref 67. Copyright 2014 American Chemical Society.

3.5 Organization of nanoparticles using pre-structured SRGs

The surface relief gratings (SRG) were previously formed on a CarbNO₂ thin film deposited on an ITO-coated microscope glass slide (1 mm thick glass) enabling both optical and electron microscope imaging. A 0.026 wt. % solution of fluorescent nanoparticles was spin-casted onto the surface relief gratings at a speed of 1000 rpm for 20 min. Fluorescence optical microscopy imaging was used to reveal nice red-emitting lines that suggest the nanoparticle alignment. This was further confirmed by SEM imaging, evidencing clear alignments of nanoparticles. In some places, the alignment comprises of one row of nanoparticles and in other places, it can go up to three rows of nanoparticles, depending on the nanoparticle packing (Figure 3.12).

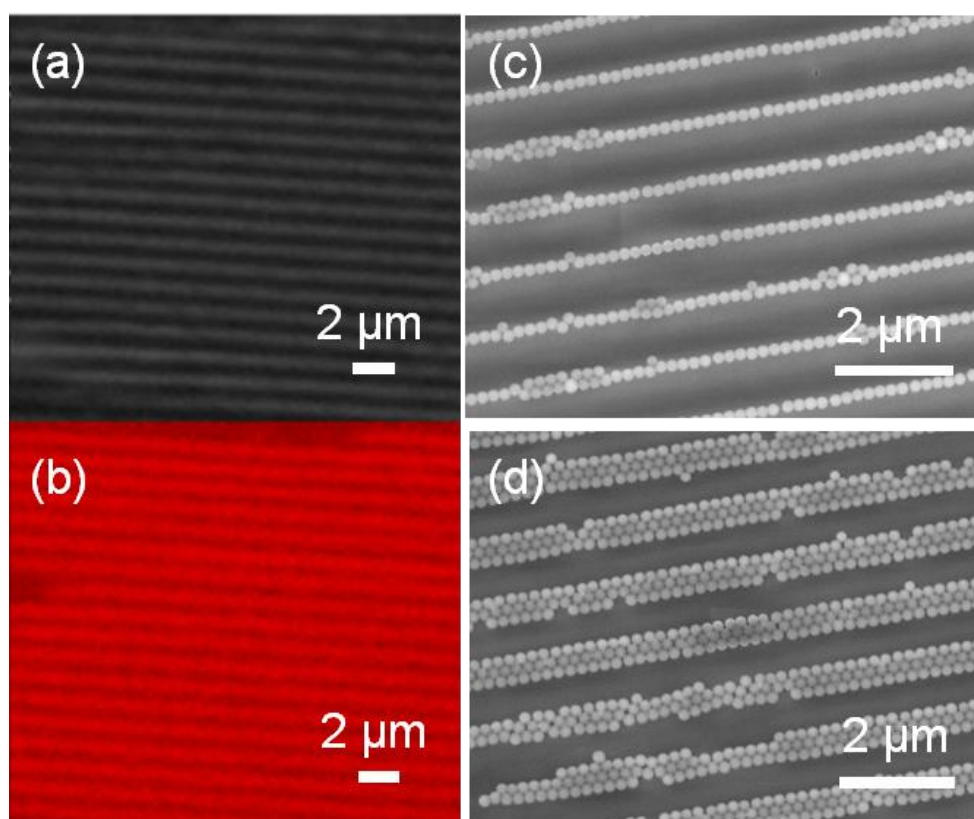


Figure 3.12. Deposited fluorescent nanoparticles ($\varnothing = 200$ nm) onto pre-structured surface relief gratings written on CarbNO₂ thin film. (a) Transmission image, (b) fluorescence image, (c) and (d) SEM images. Reprinted with permission from ref 67. Copyright 2014 American Chemical Society.

To further explore the location of nanoparticles, AFM investigations have been performed (Figure 3.13). They provided evidence that the polystyrene nanoparticles ($\phi = 200$ nm) were located in the valleys of the gratings. Two cross sections, orthogonal (X direction) and parallel (Y direction) to the SRG lines were measured. Along the X direction, the periodic spacing of the grating (large bumps) has not changed and remained equal to $1.1\ \mu\text{m}$. The particles appeared to occupy the valleys of the grating. Along the Y direction, the 200 nm periodic features recall the diameter of the nanoparticles that looked well-aligned along the SRG lines. After such topographically induced alignment, the thin films were irradiated with non-polarized light with the goals to (i) erase the SRG and to (ii) check if the particles remained organized upon erasure of the SRG topography.

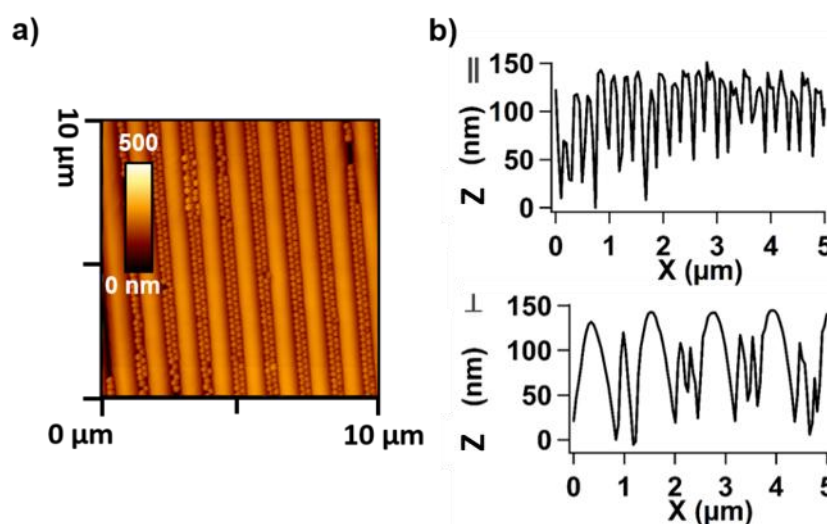


Figure 3.13. (a) AFM image of the polystyrene nanoparticles deposited onto the pre-structured surface relief gratings, (b) cross sections of the image in the X and Y directions. Adapted with permission from ref 67. Copyright 2014 American Chemical Society.

The sample was placed upside down on a cover slip and irradiated with non-polarized white light filtered through a 482 nm (fwhm 35 nm), using a 60 $\times$ microscope oil objective. The irradiation was performed for 30 min ($P = 360\ \text{mW}\cdot\text{cm}^{-2}$). AFM imaging revealed that the nanoparticles remain where they were originally located, whereas the azo grating flattened (Figure 3.14). The cross section of the sample in the X direction showed that the nanoparticles formed rows which were separated by a distance of $1.1\ \mu\text{m}$, identical to the period of the surface relief gratings. The cross section in the Y direction showed again periodic and compact features as already observed before erasure. The average height of these features is measured to be 200

nm in accordance with the diameter of the nanoparticles, showing that a pre-structured azo thin film can be used as an effective template to align small enough polystyrene nanoparticles. At this stage, a new question arises: can the SRG be used as a template to align nanoparticles other than polystyrene ones?

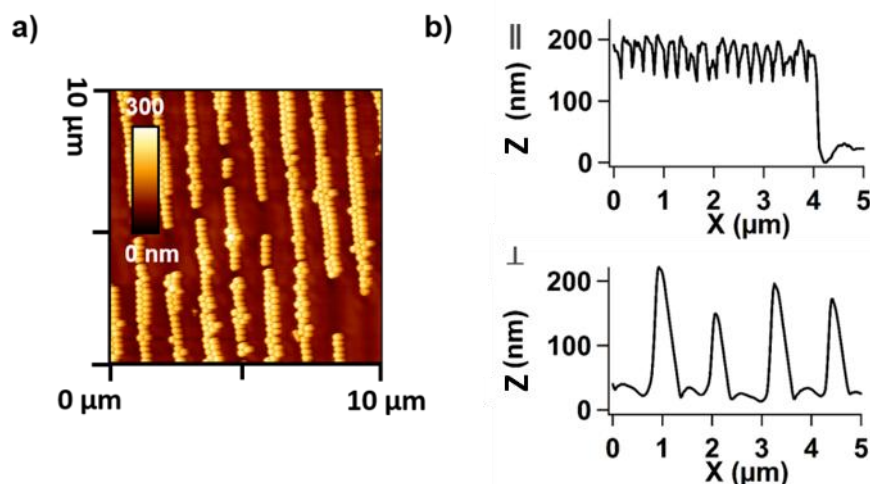


Figure 3.14. (a) AFM image of erased SRGs on which polystyrene nanoparticles had previously been deposited, (b) cross sections of the image in the X and Y directions. Reprinted with permission from ref 67. Copyright 2014 American Chemical Society.

3.6 Tentative organization of gold nanoparticles using structured azo thin films

The organization of conductive nanoparticles that could be arranged as nanowires opens fantastic applications in the fields of transistors, optical sensing and data storage. Examples of conductive nanoparticles include copper, silver, gold (AuNPs) and even iron nanoparticles to name just a few.^{81,82} For this experiment, AuNPs were used because of their conductive properties and simple synthesis using the Turkevich method.^{83–85}

A droplet of a 0.036 wt. % solution (10 μ L) of gold nanoparticles ($\phi = 14.7 \pm 2$ nm) stabilized by citrate ions was deposited onto the surface of a flat CarbNO₂ thin film, and allowed to dry over 60 min, prior to the SRG inscription. This concentration was chosen because the AuNPs are still dispersed (no aggregation). The formation of SRGs was as usual monitored by the growth of the diffraction efficiencies. After irradiating the sample with an interferential light pattern at 488 nm for 12 min ($P = 160$ mW. cm⁻² per beam), no evolution of the diffraction efficiencies could be

observed, which was attributed to the AuNPs acting as filters or to a quenching optical coupling between the gold nanoparticles and the azo compounds. SEM images of the irradiated sample were also obtained (Figure 3.15), and showed relatively dispersed gold nanoparticles that appeared to dissolve the azo thin film, likely due to the citrate. To assert that the lack of formation of the SRG was due to optical coupling with AuNPs, and not just due to the aggregation of the nanoparticles scattering light, the same experiment was performed with a more diluted solution (0.012 wt. %). Similar results were obtained. As a final confirmation to the AuNPs restricting the formation of the SRGs, 10 μL of a 0.22 % wt solution of sodium citrate was added to thin film, dried, and the SRGs were written. The gratings could efficiently form as the first-order diffracted intensity increased, thus proving that the sodium citrate solution did not restrict the formation of the gratings.

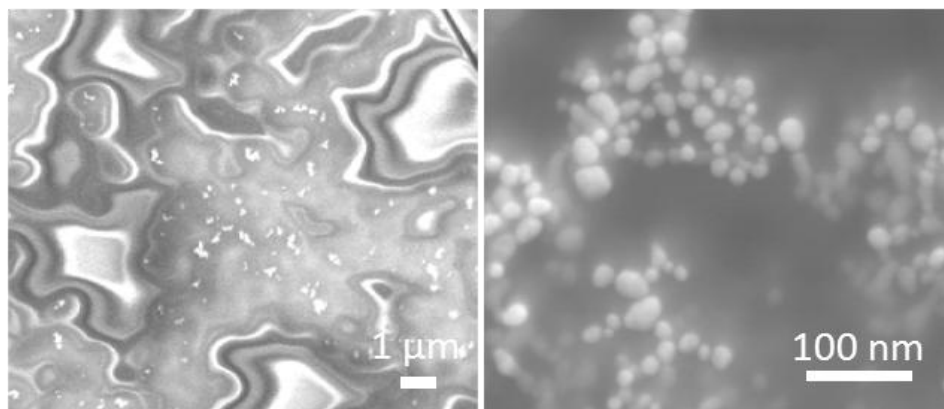


Figure 3.15. SEM images at two distinct magnifications of gold nanoparticles deposited onto a CarbNO₂ thin film, irradiated with an interferential light pattern at 488 nm.

In a last experiment, the gold nanoparticles were deposited onto a preformed SRGs, with the same conditions as those used for the polystyrene nanoparticles. The existence of SRGs is clearly revealed by SEM images (Figure 3.16). However, we could not detect preferential location of the AuNPs in the trough or in the crest while the nanoparticles looked aggregated together. Presumably, the density of the AuNPs and their aggregation state do not allow the colloidal gold nanoparticles to position in the valleys of the SRGs. These tentative experiments showed that the chemical nature and presumably the density/size of the nanoparticles themselves can seriously affect the ability of SRGs to organize nano objects.

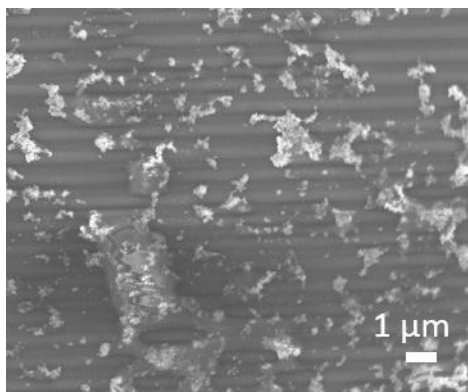


Figure 3.16. SEM images of AuNPs deposited on to a pre-structured surface relief grating.

3.7 Conclusions

Thin films were fabricated out of a variety of push-pull azo derivatives with varying polarity, hydrophobicity and bulkiness. Their photochromic properties were studied and appeared mostly driven by steric constraints in comparison to those in solutions, where the azo polarity induced by a strong charge transfer was the major factor. Polar azo compounds containing hydrophobic groups allowed for the deposition of aqueous polystyrene nanoparticle suspensions onto azo thin films without deforming or dissolving the surface. Comparative experiments with nanoparticles deposited before and after interferential illumination showed that the bulk azo photoinduced mass transport can drag the nanoparticles and organize them under the crests of the periodic surface relief gratings. The formation of more complex organized patterns were obtained after simple optical erasure of embedded polystyrene nanoparticles, paving the way to the fabrication of strongly diffusing systems. The influence of polystyrene nanoparticles in terms of size and material density onto the azo matter flow is currently being studied in order to understand the capillary and tension surface effects developed at such a nanometer scale, thus enabling rewritable nano- and microstructures. Extension of nanoparticle organization has been attempted with gold nanoparticles of various sizes. Any migration was totally blocked, letting us suggest a strong optical coupling between the azo compounds and the gold localized surface plasmon resonance band.

Chapter 4

Hybrid structured nanomaterials

4.1 Hybrid Nanomaterials

We have previously showed that azo thin films could successfully be used to organize polystyrene nanoparticles ($\varnothing = 200$ nm) through the formation of SRGs. However, difficulties were encountered when the PS nanoparticles were changed into gold nanoparticles (AuNPs). To try to organize the AuNPs, a different approach was used, varying the size of the azo photochromic material and reducing it to different nanometer-sized objects. Using this strategy, photochromic nano objects coated with nanoparticles could control further the nanoparticle displacement upon deformation or migration of the azo material. Since, nano objects are desired to migrate AuNPs over space, a high payload of azo compounds is required, hence requiring the fabrication of neat organic nanomaterials coated with AuNPs (Figure 4.1). This is a distinct approach compared to what has previously been done, where AuNPs are coated with azo or other functional ligands.

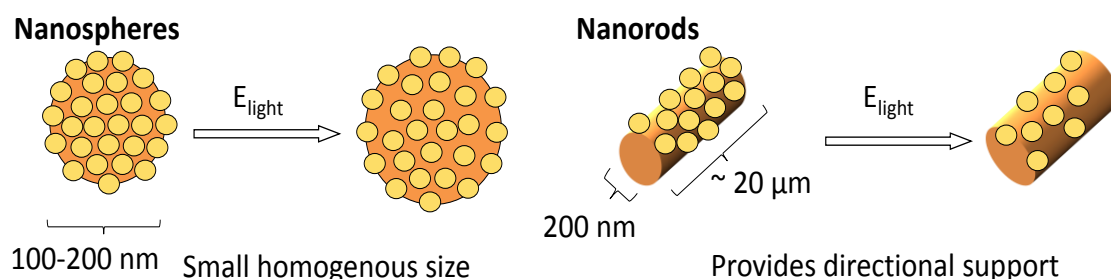


Figure 4.1. Schematic illustration of the reverse approach towards photochromic and plasmonic nanoassemblies.

Since the discovery and interpretation of the specific physical and chemical properties of gold nanoparticles, the fabrication of novel gold-based nanomaterials has been tremendously boosted to address numerous domains of applications among others including oxidative catalysis,⁸⁶ nanolithography,^{87–90} solar cells,⁹¹ biological and chemical sensing,⁹² and more recently photothermal cancer therapy.^{18,93} Change in the size, the shape,⁹⁴ or the chemical coating,⁵¹ drastically influences the optical response of AuNPs and can therefore sign external events or tune their interactions with the

surroundings.^{95–97} Many of these applications are based on the change in color when changing the size of the AuNPs, due to the change in the localized surface plasmon resonance (LSPR) of the particles.

Localized surface plasmon resonance can be described as the collective oscillation of electrons at the nanoparticle surface of AuNPs subjected to light illumination. Such oscillation behaves as a dipole that can radiate an electric field enhanced by several orders of magnitude and is confined at the nanoparticle surface (Figure 4.2).⁹⁸ The energy and the intensity of the SPR band can be tuned by changing the size or shape, the interparticle distance and the chemical surroundings of the AuNPs. By increasing the size of the particle, the oscillation of electrons occurs over a larger space, resulting in a red shift in the SPR band upon energetic stabilization. The optical coupling between two or more nanoparticles placed only a few nm far apart results in ‘hot spots’ that correspond to the local enhancement of the electric field. The electric field gradient created by these ‘hot spots’ is very distance dependent.^{99–101} This LSPR has shown to be useful in applications such as surface patterning, as investigated by Klajn et al. at the Weizmann Institute of Science.

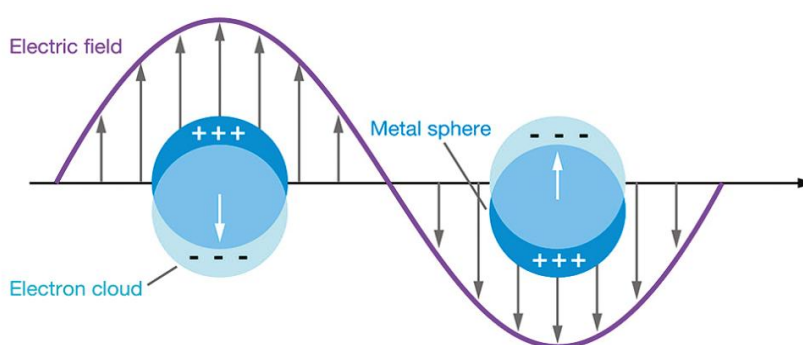


Figure 4.2. Illustration of the oscillation of electrons in AuNP subjected to light illumination. Reprinted with permission of ref 97 © American Chemical Society.
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In this context, 5 nm large gold nanoparticles were coated with a monolayer of alkyl substituted azo dyes. Upon light irradiation in the UV range, the geometry of the azo molecule changed, altering the stability of AuNPs due to a change in the local electric

field. This resulted in a reversible aggregation of AuNPs characterized by red shifted absorption (Figure 4.3).^{53,102}

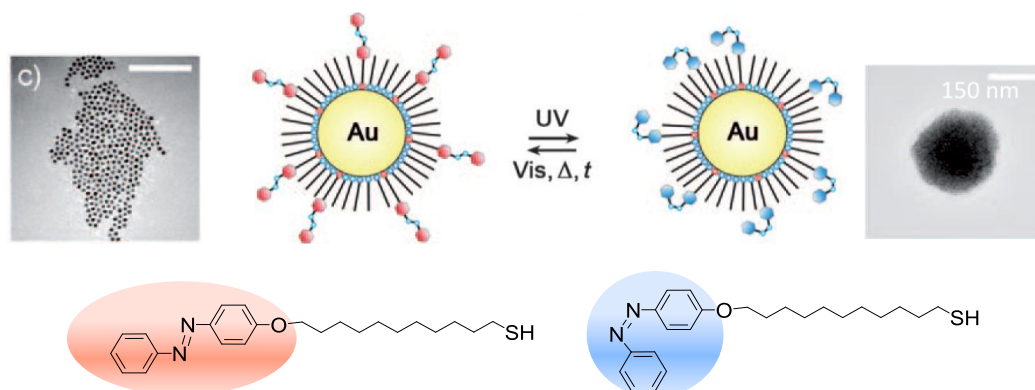


Figure 4.3. Illustration of hybrid nanoparticles made of a gold core coated with azo photochromes as stabilizing ligands. Adapted with permission of ref 53 © John Wiley and Sons⁵³

Incorporating an organic photochrome, such as an azo dye, into the monolayer of gold nanoparticle has been studied over the past decade.^{102–104} However, to the best of our knowledge, very little has been done with the reverse architecture involving an organic core coated with an inorganic layer (Figure 4.1).⁵⁸ In this thesis, we have focused on the fabrication of two types of reverse nanohybrid assemblies: organic nanospheres, and organic nanorods that offer more directional support when trying to migrate the nanoparticles over space.

4.2 Synthesis of precursors

4.2.1 Synthesis of photochromic ligands

The backbone of the azo derivatives must meet several criteria. It must contain a chelating group to coordinate AuNPs, bulky substituents to photoisomerize in the solid state and hydrophobic groups to allow for the formation of organic nanoparticles upon precipitation in water. We thus selected sulfur moieties (disulfide and thioacetate) as chelating groups due to the high affinity of sulfur for gold.^{105–109} The use of disulfide and thioacetate moieties avoids side reactions of thiol oxidation promoted by dioxygen during the synthesis of the final azo compounds. For synthetic reasons, we retained the 4-*tert*-butylphenyl groups as sterically crowded groups to avoid π – π stacking and allows for efficient photoreaction performances in the solid state, as already discussed in the previous chapters. Finally, alkyl chains were

introduced to attach the sulfur moieties to the azo backbone. They reinforce the hydrophobic character brought by the *tert*-butyl moieties to favour the nucleation of organic nanoparticles in water. Their length has been varied to evaluate how the formation of nanospheres and the optical coupling between the dyes and AuNPs can be affected by structural changes.

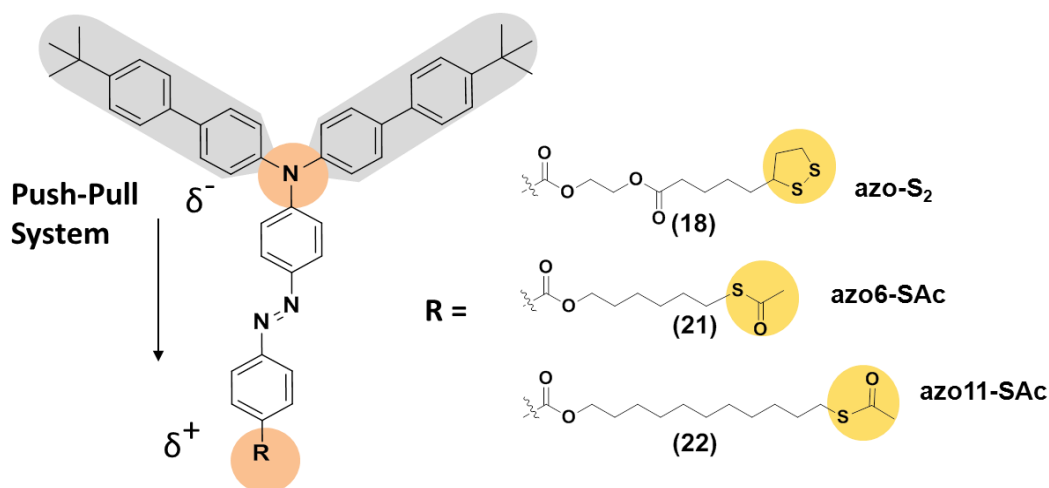


Figure 4.4. Structure of the sulfur base azo molecules (18), (21), (22).

The main backbone was based on the carboxylic acid compound (15) ($t\text{BuCO}_2\text{H}$) that was esterified by various sulfur terminated chains to yield three distinct ester derivatives. To obtain (15), we started from the previously synthesized $t\text{BuCO}_2\text{Me}$ (13c) that was hydrolysed using a 3 mol L^{-1} aqueous KOH solution in refluxing THF for 6 h. After neutralization of the reaction mixture with concentrated hydrochloric acid, and THF removal, the targeted carboxylic acid compound (15) precipitated as a pure red solid (15) in a 98 % yield.

The reaction pathway to the disulfide compound (18) comprised three steps based on esterification reactions (Figure 4.5). Compound (15) was first converted to its corresponding acid chloride derivative (16) in the presence of thionyl chloride in anhydrous dichloromethane for 6 h. After removal of the excess thionyl chloride under reduced pressure, compound (16) was esterified to (17) (70 % yield) using ethylene glycol that bridged the chelating group and the azo molecule. The final product azo-S_2 (18) was obtained as a red powder following a mild esterification (Steglich esterification) in 90 % yield. Typical procedure involved an alcohol (here (17)), a carboxylic acid (here lipoic acid), the coupling agent N,N' -

diisopropylcarbodiimide (DIPC), and 4-(dimethylamino)pyridinium-4-toluene sulfonate (DTPS) as an acid catalyst to avoid accumulation of semi-urea as a terminal by-product.

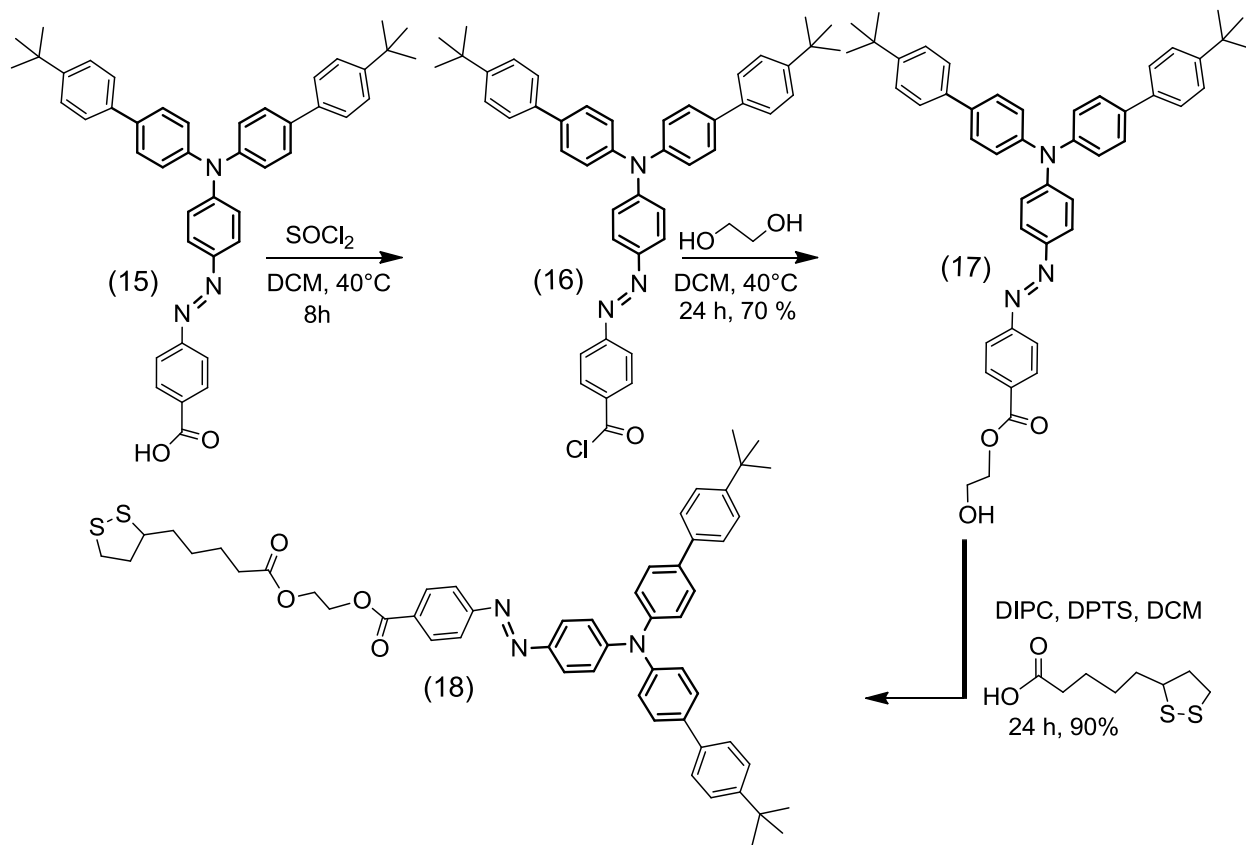


Figure 4.5. Synthetic pathway to azo-S₂ (18).

In parallel, we investigated the synthesis of thioacetate compounds where thioacetate is known to be spontaneously cleaved into thiol in the presence of gold surface and yield tight anchoring. The general synthesis of azo6-SAc (21) and azo11-SAc (22), involving a mild Steglich-type esterification and a nucleophilic substitution, is displayed in Figure 4.6. Briefly, compound tBuCO_2H (15) was reacted with 6-bromohexanol or 11-bromoundecanol, using again DIPC as a coupling agent and DTPS as a catalyst. The corresponding brominated compounds tBuC_6Br (19) and $\text{tBuC}_{11}\text{Br}$ (20) were obtained in 82 - 85 % yields. A substitution ($\text{S}_{\text{N}}2$ type) reaction allowed for the generation of azo6-SAc (21) and azo11-SAc (22) using potassium thioacetate in acetone.

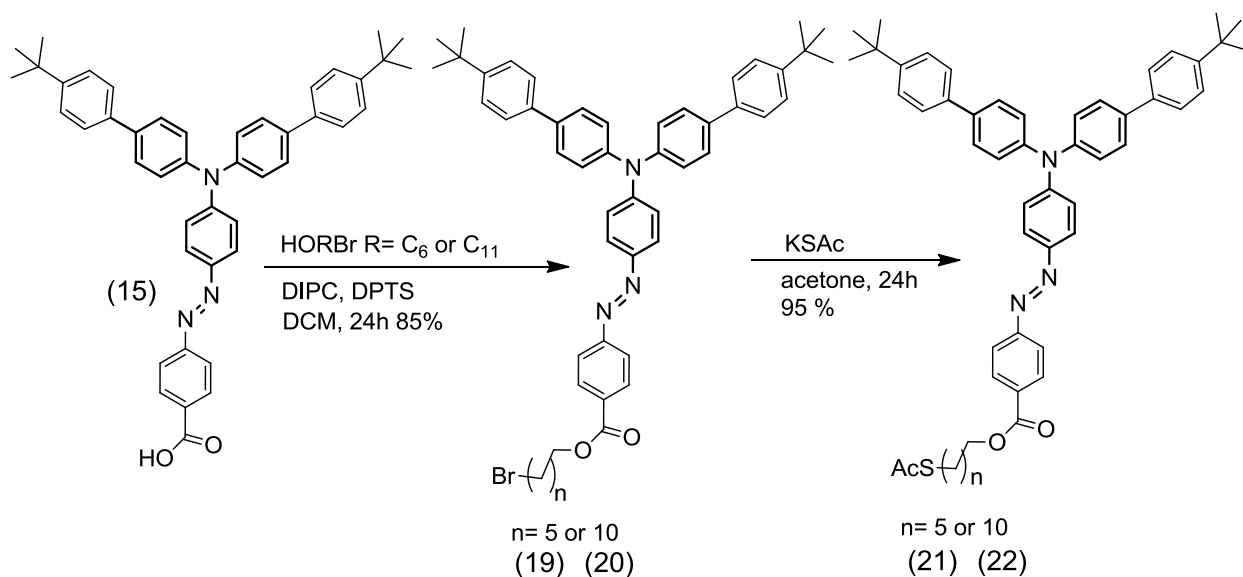


Figure 4.6. Synthetic pathway toward azo6-SAc (21) and azo11-SAc (22).

4.2.2 Photochromic properties in solution

To study the dye photoisomerization, all solutions were initially prepared in the dark so that undesirable photoisomerization caused by the surrounding light was avoided. The concentrations of the dyes in toluene were between $1.5 - 3 \times 10^{-5} \text{ mol L}^{-1}$. All compounds exhibit two absorption bands, one in the visible region ($\lambda_{\text{max}} = 467 - 471 \text{ nm}$) and the other one in the UV region ($\lambda_{\text{max}} = 330 - 331 \text{ nm}$). The absorption band in the visible region is due to the $\pi\pi^*$ transition between the triphenylamino core and the electron-withdrawing group (azophenylester) while the absorption band in the UV region can be ascribed to the charge transfer between the amino core and the biphenyl peripheral branches (Figure 4.7). Very similar absorption maxima in the visible and the UV region were found for all compounds, indicating that the remote sulfur moieties exert weak electronic influence onto the charge transfer mainly located on the push-pull azo backbone.

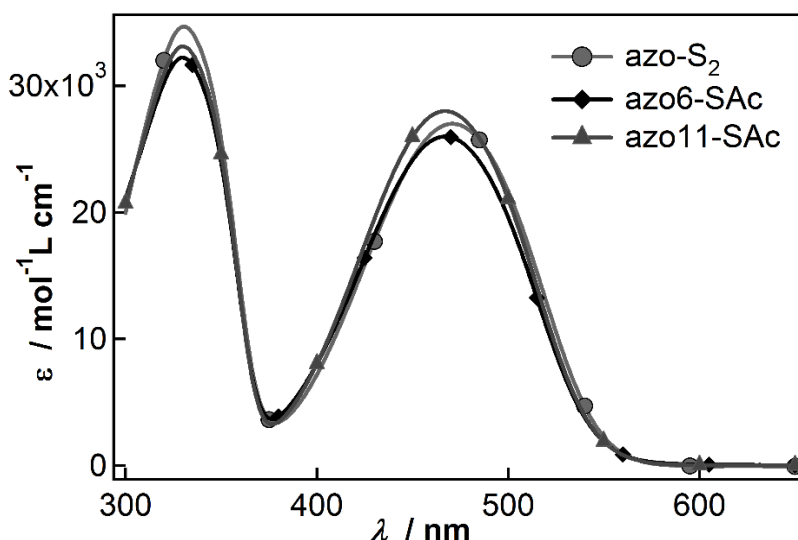


Figure 4.7. UV-vis absorption spectra of compounds azo- S_2 (18), azo6-SAc (21), azo11-SAc (22) in toluene solution with the concentration ranging between $1.5\text{--}3 \times 10^{-5} \text{ mol L}^{-1}$.

The solutions were irradiated with a Mercury-Xenon lamp using a narrow bandpass filter at $488 \pm 2 \text{ nm}$. The evolution of the spectra was recorded after each period of irradiation, showing a decrease in the visible band due to the photoisomerization reaction $E \rightarrow Z$. Once the photostationary state was reached, the solution was left in the dark and the back thermal relaxation was monitored by following the absorption evolution at five significant wavelengths. The UV-vis absorption spectra of the azo11-SAc (22) during the $E \rightarrow Z$ photoisomerization reaction as well as the absorbance recovery of the solution upon back thermal relaxation $Z \rightarrow E$ at $\lambda_{\text{max}} = 467 \text{ nm}$ are displayed in Figure 4.8. The relaxation kinetics were fit using a monoexponential law, providing the rate constants k_{ZE} . Such absorbance evolutions are provided in Figure 4.8 for both the $E \rightarrow Z$ photoreaction and $Z \rightarrow E$ back thermal relaxation for azo11-SAc.

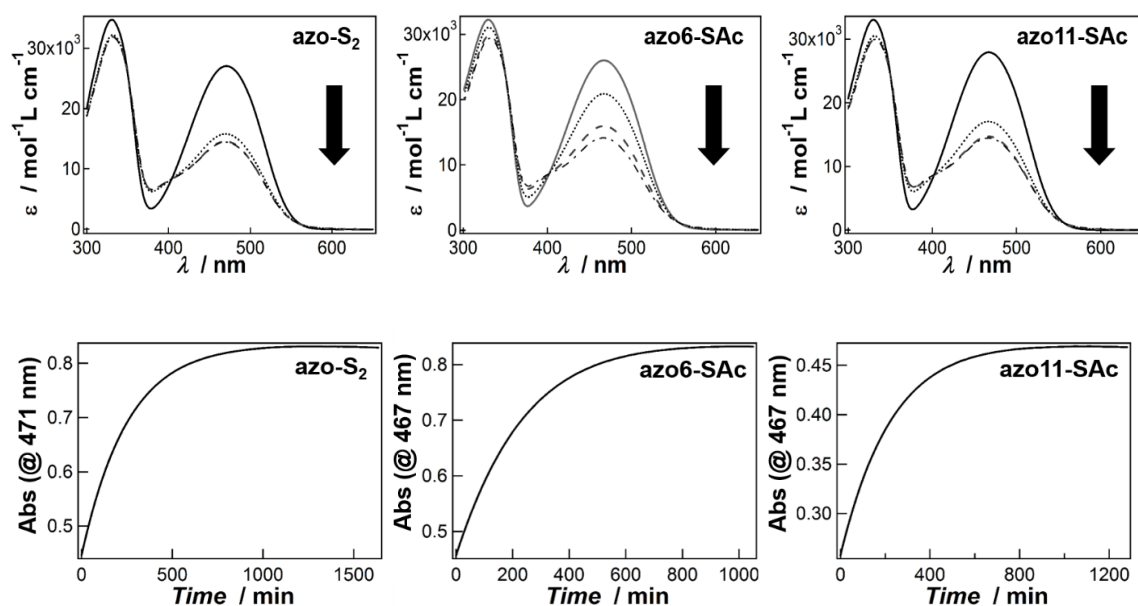


Figure 4.8. Evolution of the solution absorbance for azo-S₂ (18), azo6-SAc (21), azo11-SAc (22) upon irradiation at 488 nm ($P = 8\text{mW. cm}^{-2}$), collected after every 20 s of irradiation (top) and thermal back relaxation (bottom).

The rate constants and the minimum conversion yields for all three compounds are presented in Table 4.1. Here, it is observed the absorbance maxima for azo6-SAc (21) and azo11-SAc (22) are the same at 467 nm. This shows that there is no influence of the length of the chain and the energy of the transition between the amino phenyl core and the ester group. However, there is an extremely minor shift in the absorbance maximum for the azo-S₂ with the λ_{max} absorbing at 471 nm, illustrating that the azo-S₂ compound is slightly less polar. In solution, no significant difference could be observed. The minimum conversion yield is about 46 - 50 % while the thermal back rate constants appear around $7 \times 10^{-5} \text{ s}^{-1}$, which is in agreement with the values obtained with tBuCO₂Me (12c). The kinetics similarity agrees with the weak influence of the sulfur-terminated chain onto the electronic properties of the azo derivatives as no π -electronic conjugation operates (k_{EZ} (azo-S₂) = $6.7 \times 10^{-5} \text{ s}^{-1}$; k_{EZ} (azo6-SAc) = $7.4 \times 10^{-5} \text{ s}^{-1}$; k_{EZ} (azo11-SAc) = $7.6 \times 10^{-5} \text{ s}^{-1}$) (Figure 4.9).

Compounds	Solution ^{b,c}				Thin film ^{c,f}					
	T_g^a (°C)	$\lambda_{\max}$ (nm) (ϵ (mol ⁻¹ Lcm ⁻¹))	ρ^d (%)	k_{ZE}^e (10 ⁻⁵ s ⁻¹)	$\lambda_{\max}$ (nm)	ρ^d (%)	k_1^g (10 ⁻⁵ s ⁻¹)	f_1^g	k_2^g (10 ⁻⁵ s ⁻¹)	f_2^g
azo-S ₂	63	331 (34700), 471 (27000)	50	6.7	328, 479	13	30.1	7.5	5.8	92.5
azo6-SAc	59	330 (32200), 467(26000)	46	7.4	329, 473	14	31.8	2.5	3.5	97.5
azo11-SAc	40	330 (32200), 467(28000)	49	7.6	335, 478	15	25.6	13.5	8.7	86.5

Table 4.4. Thermal, photophysical and photochromic properties of compounds azo-S₂ (18), azo6-SAc (21), azo11-SAc (22) in solutions and thin films. ^a DSC measurements in aluminum cap using a 20 °C min⁻¹ thermal gradient. ^b In a toluene solution. ^c Irradiation wavelength of λ_{irr} = 488 nm. ^d The minimal photochemical conversion (ρ) assuming no absorption from Z isomer at the wavelength of irradiation: $\rho = \left[\frac{(A_0 - A_{pss})}{A_0} \right] \times 100$. ^e Back thermal relaxation rate constant of the Z-E using a monoexponential fit involving the decay: $[E] = [E]_0 + ([E]_{pss} - [E]_0) e^{-k_{ZE}t}$. ^fThin films formed from spin casting a chloroform solution of the azo compound onto pre cleaned glass slides. ^gBack thermal relaxation rate constant of the Z-E using a biexponential fit involving the decay: $[E] = [E]_0 + a_1 e^{-k_1 t} + a_2 e^{-k_2 t}$, with f_i designating the rate constant averaged fraction $f_i = \frac{a_i k_i}{\sum_j a_j k_j}$.

4.2.3 Photochromic properties in thin films

For all compounds, thin films were fabricated by spin-casting a 2 % wt. solution of the dye in chloroform onto cleaned glass slides at a rotation speed of 500 rpm up to 1000 rpm over 2 minutes. Glassy thin films with no apparent trace of microcrystallites were obtained, which is compatible with the glass transition temperatures T_g detected between 40 °C and 63 °C. The large difference between azo6-SAc and azo11-SAc stems from the longer alkyl chains, imparting more flexibility and lower glass transition temperature. After drying at room temperature (no difference was observed for film dried under vacuum), the thin films were irradiated following the same procedure as that described earlier. Compared to solutions, thin films of dyes display a slight bathochromic shift (5-11 nm) due to more polar surroundings caused by the neighbouring push-pull molecules, compared to toluene molecules. Such evolution again agrees with what has previously been observed in Chapter 2. As for photoisomerization, the thin film illumination also conducted to a decrease in the

absorption band in the visible range. Yet, the minimal conversion yields ρ were valued again at 13 - 15 %, much lower than those in the constraint-free solution. The back thermal relaxation kinetics of all compounds required biexponential modeling, featuring two populations of molecules (Table 4.1). As already described in Chapter 2, the slower component has been ascribed to more stabilized Z isomers while the faster component describes Z isomers occupying very constraint space.

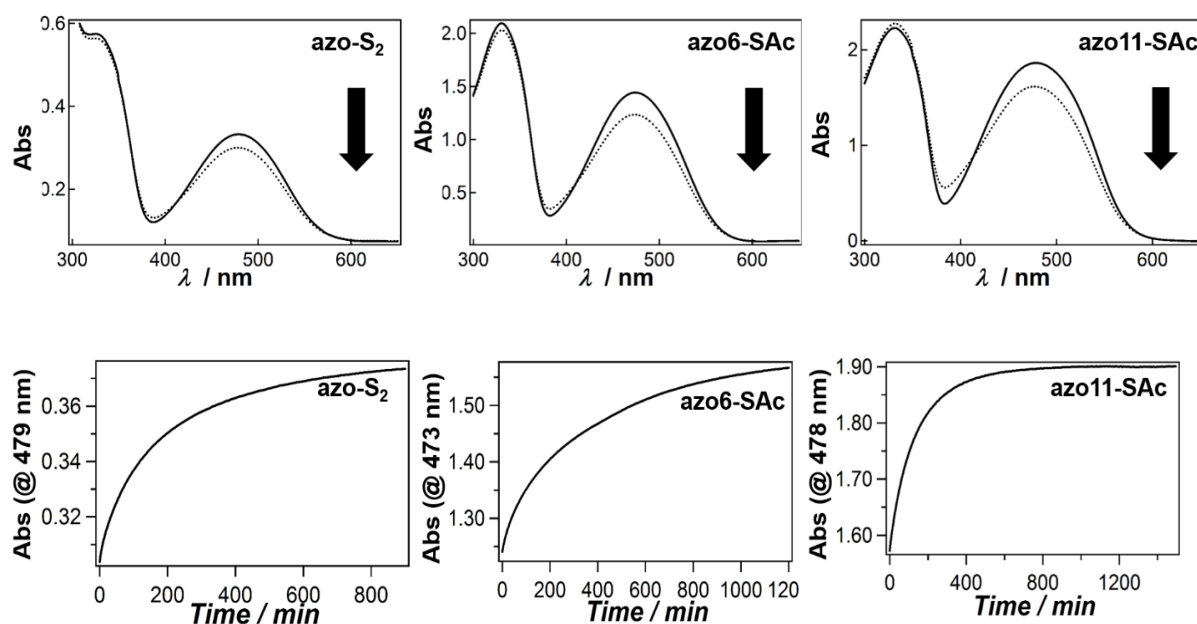


Figure 4.9. Evolution of the thin film absorbance for azo-S₂ (18), azo6-SAc (21), azo11-SAc (22) upon irradiation at 488 nm ($P = 8\text{mW. cm}^{-2}$) until the photostationary state was reached (top), and thermal back relaxation (bottom).

4.2.4 Synthesis of azo-functionalized AuNPs (Au@azo NPs)

First, the synthesis of AuNPs capped with azo molecules was carried out to understand the interactions between the azo ligand and the LSPR band and ascertain the complexation step. Two synthetic pathways have thus been considered: citrate soluble AuNPs and Brust Schiffrin AuNPs. Second, the synthesis of the reverse architecture will be discussed, involving an organic core with inorganic AuNPs surrounding the exterior.

Citrate gold nanoparticles

Gold nanoparticles, ranging in size from 1 - 100 nm, are generally synthesized by reducing HAuCl_4 in the presence of capping organic ligands to ensure colloidal stabilization and passivation toward further reduction and nanoparticle growth. Altering the mode of reduction and the chemical nature of the passivating ligands directly influences the size and the solubility of AuNPs. Turkevich et al. tried to control the size of AuNPs by performing homogeneous reduction of Au^{3+} ions (from HAuCl_4) using sodium citrate under heating.⁸³ This resulted in water-soluble AuNPs, stabilized by a monolayer of citrate ions and ranging in diameter size from about 8 to 40 nm. Frens et al. later optimized Turkevich's method and synthesized AuNPs with a more narrow size distribution, by changing the molar ratio between the gold salt and sodium citrate. They observed that high concentrations of citrate ions led to smaller gold nanoparticles due to highly passivated surfaces, while lower citrate ions concentrations yielded larger gold nanoparticles.¹¹⁰ Once the AuNP surface is stabilized with citrate ions, it can be functionalized further through a ligand exchange provided that the novel complexing units exhibit higher affinity constant than citrate with gold, and are water soluble to ensure homogenous and complete coverage. The most commonly used ligands to perform such exchange comprise thiol, amino or phosphino functions.

We thus adopted Turkevich's method first to generate azo-coated gold nanoparticles, called Au@azo NPs in the following. Briefly, a 2.2 mM aqueous solution of sodium citrate (150 mL) was refluxed for 10 min, then a 25 mM aqueous solution of HAuCl_4 (1 mL) was added and the nucleation of AuNPs started. Aliquots of the solution were removed and stored in the fridge (5 °C).^{85,111} The refluxing solution was cooled to 90 °C and the growth of AuNPs was continued by adding quickly more of the 25 mM gold salt solution. The full experimental procedure is reported in **Appendix A**. The AuNP growth could be followed by spectrophotometry since the LSPR band characteristic of AuNPs first increased in intensity and then undergoes red shift and broadening (Figure 4.10).

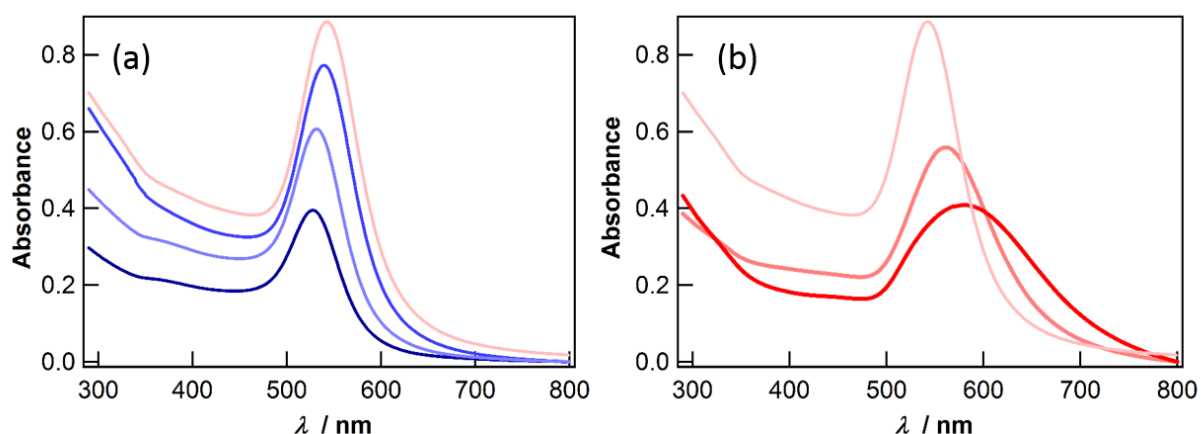


Figure 4.10. Evolution of the UV-vis absorption spectra of the citrate-stabilized AuNPs as a function of the nanoparticle growth (from blue to pink and pink to red indicates the growth of the AuNPs from 5 nm to 60 nm): (a) as the particles begin to grow the intensity of the SPR band increases and bathochromic shift is observed (b).

Azo Citrate AuNPs

The citrate coated gold nanoparticles were reacted with the azo ligands to generate functional Au@azo nanoparticles. To this aim, a solution of citrate AuNPs ($\phi = 14.7 \pm 2$ nm; 1.5 mL of a 0.2 % wt. solution of citrate AuNPs) reacted with azo-S₂ (1 mg dissolved in 1.5 mL dichloromethane) and the resulting mixture was vigorously stirred for 30 min. The coordination of the azo-S₂ ligand was observed through a color change in the top aqueous layer from purple to colorless while the bottom organic layer went from a bright orange to a dark orange. The UV visible spectrum of the Au@azo NPs shows an apparent 25 nm hypsochromic shift of the absorption maximum wavelength in comparison to that of the citrate AuNPs due to the contribution of the azo band centered at 471 nm (Figure 4.11). Over time the nanoparticles became insoluble and precipitated out of the solution. We attributed such a colloidal instability to insufficient azo coverage due to the bulky groups, preventing dense surface functionalization. We thus performed co-functionalization with long alkyl chains to generate nanoassemblies more stable in organic solvents. To this aim, we decided to employ the Brust Schiffrin method to directly incorporating the desired ligand, which avoids an additional ligand exchange.

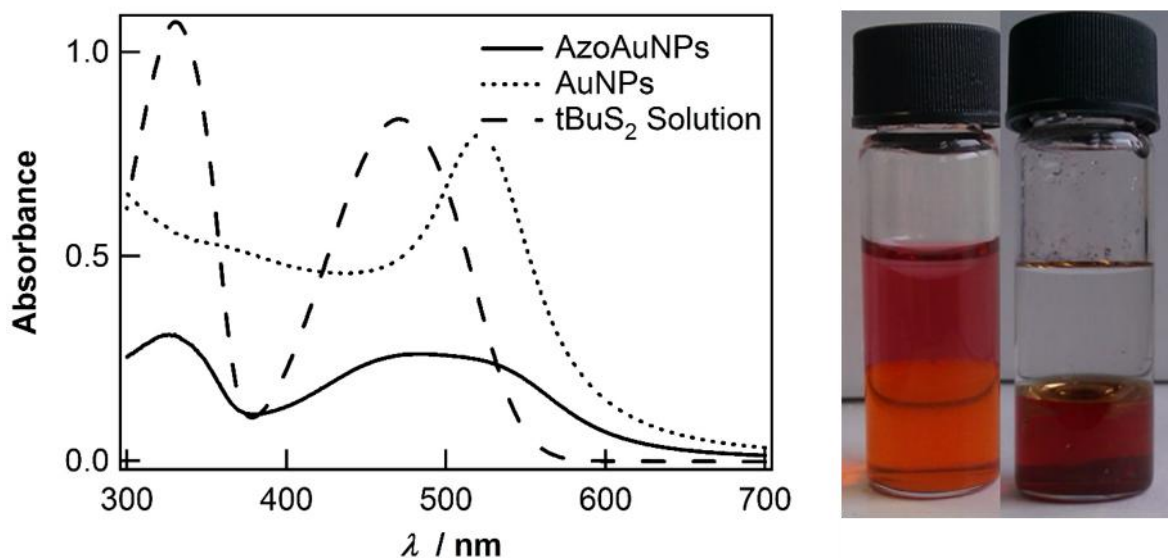


Figure 4.11. UV-vis absorption spectra of citrate-coated AuNPs, azo- S_2 solution, and the azo-coated AuNPs (left) and the phase transfer reaction of the citrate AuNPs to the organic phase (right).

Brust Schiffrin AuNPs

In 1994, Brust, Schiffrin and coworkers reported a versatile and different approach, producing AuNPs that were stabilized by organic monolayers and became soluble in organic solvents. The diameter size of the resulting AuNPs ranged from 1 to 6 nm.¹¹² Gold nanoparticle fabrication processed from a reduction of hydrogen tetrachloroaurate (HAuCl_4) in biphasic conditions. Tetraoctylammonium bromide (TOAB) is mostly used as a phase transfer catalyst to help the transfer of aurate ions into the organic layer containing alkyl thiol agents (usually dodecanethiol). The Au^{3+} ions are then partly reduced by the alkyl thiol reactants, forming first Au^+ polymeric species that are further reduced to the Au^0 by sodium borohydride (NaBH_4), resulting in thiol-stabilized AuNPs. The longer the alkyl chain, the more stable the particle in the organic phase due to van der Waals interactions. The smaller AuNPs are extremely stable under ambient conditions because of the covalent bonds between the thiolate moieties and the AuNPs.

We first prepared an aqueous solution of HAuCl_4 (15.0 mg, 0.044 mmol) dissolved in water (1 mL) and stirred it with a 0.06 M solution of TOAB (115 mg, 0.210 mmol) in toluene (4 mL). After 30 minutes, phase transfer of the tetrachloroaurate ion was observed into the organic layer that became orange while the aqueous layer became

colorless thanks to the ion pair formation $\text{AuCl}_4^- \text{nBu}_4\text{N}^+$. From here, addition of dodecanethiol (20 mg, 0.10 mmol) partly reduced Au^{3+} ions into Au^+ ions and the solution appeared colorless, after which the desired azo ligands (20 mg, 0.05 mmol) were added. The reduction process was continued by adding a freshly prepared solution of NaBH_4 (0.015g, 0.397 mmol) dissolved in water (2 mL). The resulting solution was stirred for 1 h and stored in the fridge, yielding organic soluble AuNPs ranging in size from around 2 to 6 nm (Figure 4.12).

To make sure that there was no excess ligand remaining in solution, the nanoparticles were washed several times. This purification procedure consisted of precipitating Au@azo NPs in absolute ethanol, decanting the alcohol solution that contained any free ligand and redissolving the nanoparticle in toluene. Toluene was evaporated and the resulting nanoparticles were again suspended in absolute ethanol. These purification cycles were done until the sample of Au@azo NPs was deemed pure as revealed by ^1H NMR spectroscopy. The adopted procedure yielded AuNPs with the diameter of the gold core of 1.9 ± 0.4 nm.

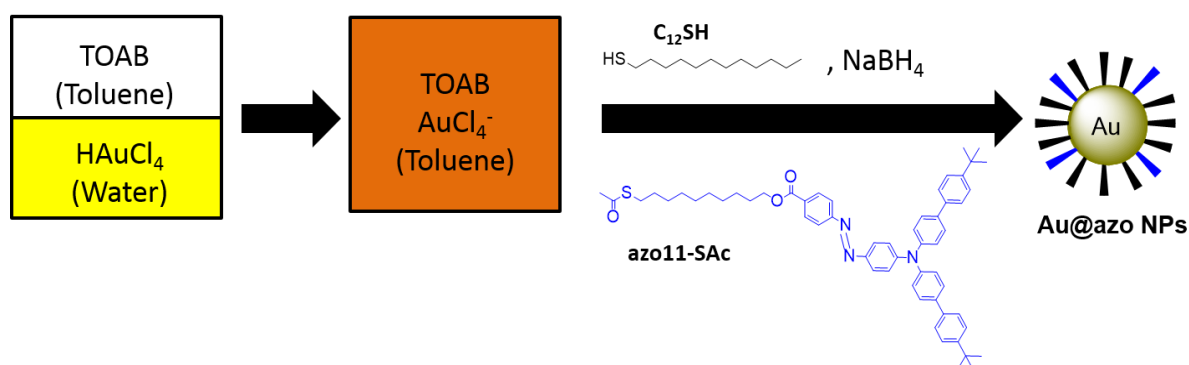


Figure 4.12. Scheme of the synthesis of Au@azo NPs following the Brust-Schiffrin method.

^1H NMR spectroscopy indeed turned out to be an excellent tool to characterize whether or not the ligand is bound to the surface of the AuNPs (Figure 4.13).^{113–115} For any ligand coordinated to gold, the corresponding proton signals dramatically broaden and often shift upfield due to paramagnetic effects caused by the unpaired electrons of gold. As spin dephasing is increased due to spin-spin interactions, the transverse proton magnetization relaxation (T_2 relaxation) is increased and any

characteristic details of the ligand are completely lost. This feature is particularly observed for AuNPs with diameter larger than 3.5 nm. No such feature could be observed for unbound ligands simply mixed with AuNPs. ^1H NMR spectra were recorded on solutions of AuNPs coated with dodecanethiol only (Au@DT NPs), free azo compounds, and Au@azo NPs. Model experiments were also performed on Au@DT NPs mixed with tBuCO_2Me unable to coordinate to gold. For Au@DT NPs, two peaks were observed at 0.78 and 1.18 ppm and correspond to the methyl and methylene protons of the thioalkyl chain. The ^1H NMR spectrum of Au@azo NPs (we considered here azo11-SAc as the azo ligand), additional peaks at 4.27, 7.18, 7.47, 7.52, 7.85, and 8.14 ppm were observed (Figure 4.13 (c)), due to the contribution of the bound azo ligands AuNPs (Figure 4.13 (b)). It is worth noting that no sharp peaks could be observed, illustrating the absence of any free ligand and the efficiency of the purification procedure to generate functionalized Au@azo nanoparticles. Such broadening could be unambiguously ascribed to the coordination of the azo compounds to gold since only sharp peaks were observed for tBuCO_2Me compound, containing no coordinating sulfur unit, even in the presence of AuNPs. Also a minor upfield shift of the peaks could also be observed upon azo coordination to AuNPs due to the change in the species chemical environment. The very large broad peak at around 3.32 ppm was actually due to remaining TOAB molecules that were hard to remove even after several washing cycles.

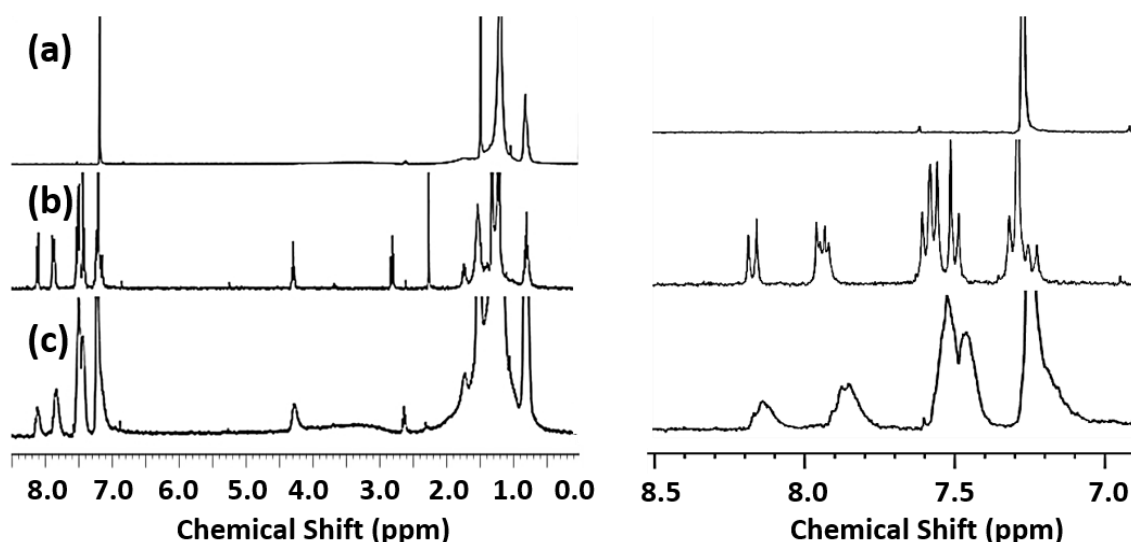


Figure 4.13. ^1H NMR spectra in CDCl_3 of AuNPs coated with dodecanethiol (a), azo11-SAc ligand (b), Au@ azo11-SAc NPs. Left: full range. Right:

magnification of the NMR response of the aromatic protons. Illustrating the broadening of peaks when coordinated to the AuNPs.

Photochromic studies of Au@azo NPs in solution

The photochromic properties of the Au@azo NPs species were studied, to understand the optical effects exerted by AuNPs on the azo ligands. Solutions made of 0.04 wt. % Au@azo NPs in toluene were prepared in the dark. A solution of dodecanethiol coated AuNPs (Au@DT), prepared in the same conditions, served as a model to interpret the spectroscopic features (Figure 4.14). All azo Au@azo NPs display similar absorption spectra with two bands, located at 325 nm and 459 nm, typical of the azo ligands as already mentioned in part 4.2.2. Such bands are indeed absent from the absorption spectrum of model Au@DT NPs. The deviation of the absorption spectra from the baseline, especially above 600 nm, can confidently ascribed to the scattering contribution of gold nanoparticles, which is also observed for the model Au@DT NPs, despite the small nanoparticle size. A slight hypsochromic shift ($\Delta \lambda_{\max} = -5$ nm) and broadening of the visible band could however be observed for compound Au@azo-S₂, that may be assigned to slight azo packing at the nanoparticle surface.

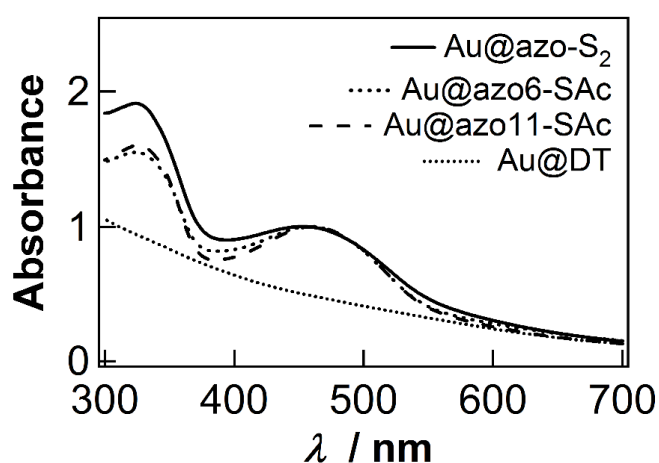


Figure 4.14. UV-vis absorption spectra of the Au@azo NPs and Au@DT NPs in toluene.

The photoisomerization studies were conducted using the same protocol as that previously described in section 4.2.2. Compared to free azo solutions illuminated in the same conditions, the absorption spectra of Au@azo NPs underwent limited decrease. The minimum photoconversion yields were found five times lower than those in solution, namely between 8 and 21 %. Interestingly, there is less difference in the back thermal rate constants k_{ZE} between the free and coordinated azo compounds (k_{ZE} was found around $9\text{-}10 \times 10^{-5} \text{ s}^{-1}$ for the Au@azo NPs against $6\text{-}7 \times 10^{-5} \text{ s}^{-1}$ for the free ligands). As the photoreaction $E \rightarrow Z$ involves excitation of the azo compounds, the existence of any optical interactions between the azo excited states and gold dramatically impacts the extent of photoconversion. We can thus here conclude that the azo excited states are partly quenched by an energy transfer to the gold particles and do not feel the enhancement of the electric field radiated by the gold dipole. By contrast, since the back thermal conversion from Z to E concerns the azo ground state and the rate constants k_{ZE} are hardly influenced by the presence of gold, the azo moieties can be considered as chemically decoupled from the gold core. The dodecanethiol chains act as possible isolating spacers, avoiding $\pi\text{-}\pi$ stacking of the azo moieties that is often detrimental to photoisomerization requiring free volume around the $\text{N}=\text{N}$ bond. Deeper analyses of the photoisomerization characteristics show that compound azo11-SAc exhibits significantly a higher minimum photoconversion yield (21 %, against 9.5 % and 8 % for azo6-SAc and azo-S₂ respectively) and a slightly higher back thermal rate constant ($10.5 \times 10^{-5} \text{ s}^{-1}$, against $9.3 \times 10^{-5} \text{ s}^{-1}$ and $9.6 \times 10^{-5} \text{ s}^{-1}$ for azo6-SAc and azo-S₂ respectively) (Figure 4.15). We ascribe these differences to the longer alkyl chain that enables better electronic decoupling and imparts the molecule with better flexibility so that both isomerization reactions $E \rightarrow Z$ and $Z \rightarrow E$ are more favoured. This evolution shows that azo ligands can serve as molecular rulers to probe the spatial extension of the plasmon coupling in the same way as fluorophores do since the latter compounds are commonly used to investigate the radiative *versus* non-radiative relaxation pathways induced by gold plasmons.¹¹⁶ Finally, we must emphasize the absence of gold nanoparticles precipitation upon irradiation as often reported for symmetric azo derivatives. We have attributed this remarkable feature to the larger dipolar character of the push-pull azo moieties and the lesser difference in dipole moments between the E and Z forms, so that stabilization can be ensured by multifold van der Waals interactions.

Compound	Tg (°C)	Au @ azo NPs			NS			azo NS @ AuNPs			
		$\lambda_{\max}$	ρ (%)	k_{ZE} ($10^{-5}s^{-1}$)	$\lambda_{\max}$	ρ (%)	k_{ZE} ($10^{-5}s^{-1}$)	$\lambda_{\max}$	$\lambda_{\max}$ shift	ρ (%)	k_{ZE} ($10^{-5}s^{-1}$)
azo-S ₂	63	457	9	10.5	480	21	13	510	512	9.2	12.3
azo6-SAc	59	462	8	9.3	477	22	10.5	514	518	8.3	10.3
azo11-SAc	40	462	21	9.6	483	21	11.3	506	511	13	9.47

Table 4.5. Spectroscopic and photochromic properties of azo nanospheres and azo@Au nanoassemblies in water, and Au@azo nanoassemblies in toluene. azo-S₂ (18), azo6-SAc (21) and azo11-SAc (22). Irradiation was performed at 488 nm (P = 8 mW. cm⁻²) while the minimum conversion yield ρ was determined at the photostationary state: $\rho = \left[\frac{(A_0 - A_{pss})}{A_0} \right] \times 100$.

To briefly conclude, a variety of photochromic materials amenable to chelate gold nanoparticles has been synthesized. Their coordination to the AuNPs from the Brust-Schiffrin method was successfully achieved, yielding hybrid nanoparticles with a high functional coverage. The photochromic properties have been found to be partly hindered in the presence of AuNPs due to plasmon coupling in the excited state, recalling the quenched formation of SRGs in the presence of the AuNPs upon interferential illumination. However, the introduction of a C11-long alkyl spacer between the azo moiety and the gold core dramatically decreased the deleterious optical quenching exerted by the surface plasmon. Attempts to lengthen the alkyl chain up to 20 carbon atoms unfortunately failed. We thus adopted a reverse strategy based on the grafting of gold nanoparticles onto photochromic nanoplateforms made of azo compounds, and investigated the behavior of remote photochromes, located in the core far from the gold coating.

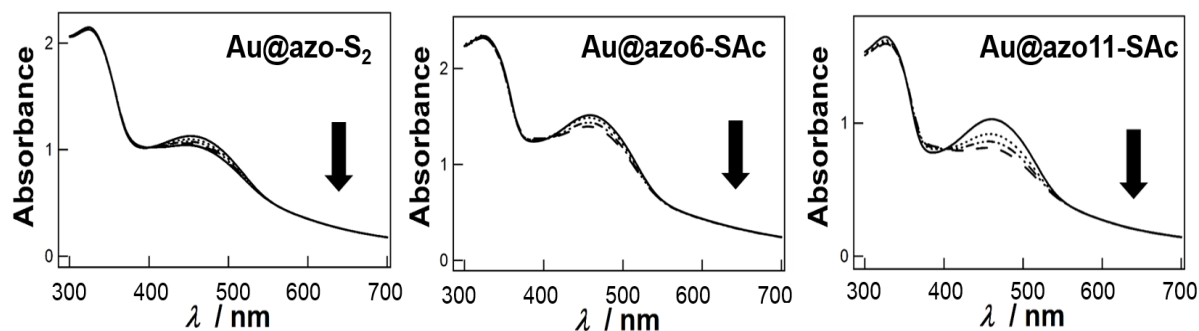


Figure 4.15. Evolution of the UV-vis absorption spectra of toluene solutions of Au@azo NPs upon illumination at 488 nm ($P = 8 \text{ mW} \cdot \text{cm}^{-2}$). Each spectrum is collected every 10 s until the photostationary state was reached.

4.3 Hybrid nanoassemblies

Most of the hybrid functional nanoassemblies are issued from the surface functionalization of inorganic nanoparticles with organic units. As showed in the previous part, all three sulfur derivatized azo compounds do photoisomerize in neat thin films. We thus exploited a strategy developed in the group, dealing with the fabrication of organic nanoplateforms coated with inorganic nanoparticles. Such a strategy, here referred to as reverse strategy, has been applied to the elaboration of magnetic and fluorescent core-shell nanoassemblies where the core comprised fluorescent dyes terminated with phosphonic acids and the shell consisted of superparamagnetic iron oxide nanoparticles tightly complexed to the core. In the present case, the presence of gold-capping functions within the azo backbone allowed us to generate novel nanoassemblies made of a photochromic core and a shell of gold nanoparticles. The benefits of the reverse approach rely on the high number of photoactive units (more than 10^5 per nanoassembly) that can be incorporated into the organic nanosphere, and the large number of AuNPs that can be chelated to the exterior. Strong interactions are thus expected and should be easily detectable.

4.3.1 Synthesis of photochromic nanospheres

Organic Nanospheres (NS)

Organic nanoparticles can be obtained from a nano-precipitation method.¹¹⁷ Briefly, this approach consists in the addition into water of a water-miscible solution of hydrophobic dyes. Generally, a supersaturation regime is followed due to the

hydrophobicity of the dyes. Numerous nuclei thus form and merge into larger nanoparticles. Such mechanism, called nucleation-aggregation process, recalls that followed during formation of polymer nanoparticles. The formation of organic nanospheres obeys the same mechanisms as those reported for polymer nanoparticles.¹¹⁸

In order to fabricate azo nanoparticles, we followed to the following protocol. A stock solution of the azo dyes (0.2 wt. %) was prepared in spectroscopy grade THF that is miscible with water. In the dark, 50 μ L of this stock solution were added into a Millipore water (2.5 mL) and stirred with a vortex to yield a turbid solution (Figure 4.16). Transmission electron microscopy imaging performed on carbon-coated copper grids (lacey or holey-type) showed remarkable spherical nanoparticles with no crystalline feature. The amorphous character of the azo nanoparticles is to be related to the absence of melting point measured by thermal scanning calorimetry. Such measurements indeed revealed the presence of glass transition temperatures between 40 °C and 67 °C (Table 4.1). Dynamic light scattering (DLS) and zeta potential measurements have been used to complete the nanosphere characterizations by providing their hydrodynamic diameter and the surface potential. The diameter size distribution was found to be centered at 90 ± 30 nm for azo-S₂, 125 ± 48 nm for azo6-SAc, and 139 ± 20 nm for azo11-SAc (Figure 4.17). For a given concentration and added volume of the stock solution,¹¹⁹ previous studies have shown that the size of the nanoparticles increases with the hydrophobic character of the organic dyes. The notable size increase from azo-S₂ to azo6-SAc and azo11-SAc can indeed be related to the more hydrophobic character of thioacetate compared to disulfide moieties, and to the longer alkyl chain for azo11-SAc. All three types of nanospheres have approximately the same zeta surface potential valued at -40 mV. Such values do not result from surface ionization of the nanoparticles but from contaminants such as fatty carboxylic acids also present in water as previously reported by Roger and Cabane.¹²⁰

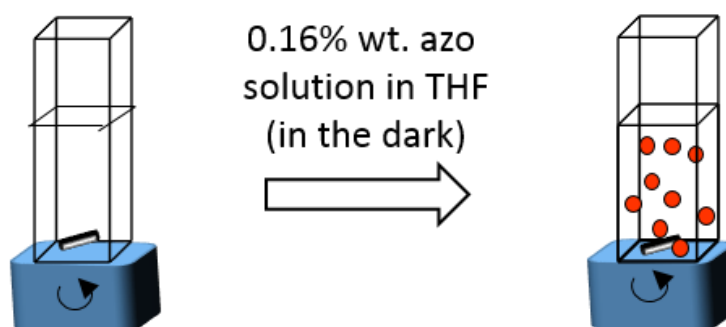


Figure 4.16. Schematic process to form organic nanoparticles.

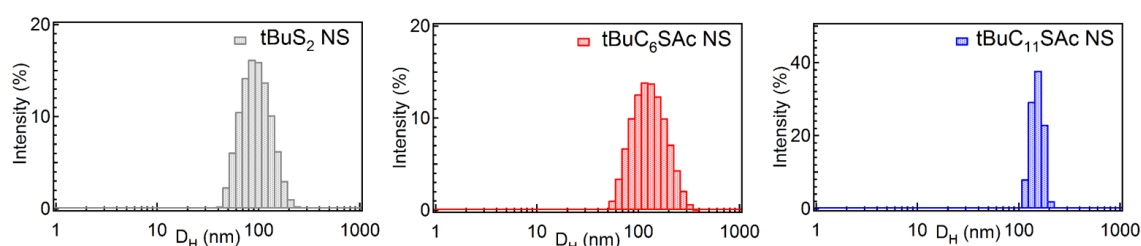


Figure 4.17. DLS size measurements of organic nanoparticles.

Organic Nanospheres coated with AuNPs

Hybrid photochromic nanoassemblies comprising a gold shell of AuNPs were prepared using a similar procedure as that previously described. This time, the photochromic nanospheres were formed by adding the organic dye solution into a freshly prepared solution of aqueous soluble citrate AuNPs ($\phi = 15 \pm 3$ nm, 0.2 wt. %) (Figure 4.18). The solution was stirred from a few hours to several days to let the ligand exchange process occur. More concentrated solutions of AuNPs did not allow us to clearly distinguish hybrid nanoassemblies, mostly masked by the large excess of gold NPs. Using a 0.2 wt. % solution of AuNPs provided approximately the right number of AuNPs per organic nanosphere (~ 250 AuNPs / nanosphere with a diameter of 120 nm, assuming complete coordination of only one layer of AuNPs).

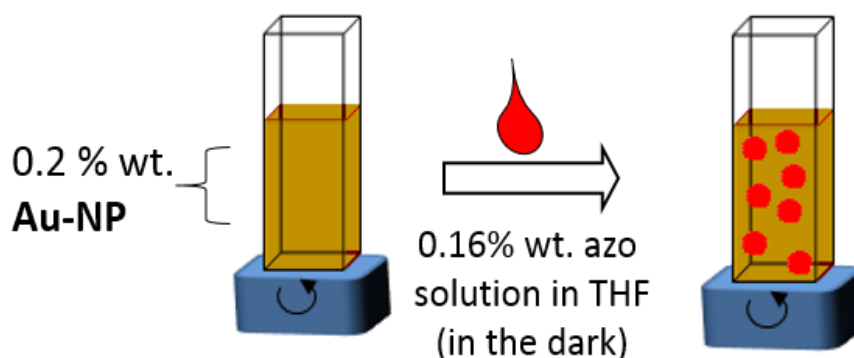


Figure 4.18. Schematic process to form hybrid nanoassemblies azo@Au upon injection of an azo concentrated solution into a suspension of gold AuNPs.

TEM imaging showed grainy nanoassemblies with highly contrasted 15 nm large nanoparticles organized in a round geometry (Figure 4.19). The dimensions of the core template recall those of the organic nanospheres. All these features let us conclude that self-assembling of gold nanoparticles efficiently operate at the surface of the photochromic nanoparticles thanks to the presence of coordinating sulfur moieties. We can notice at several places the formation of nanoassembly clusters due to the bridging ability brought by the AuNPs. Full coverage was actually obtained within 2 h, in the case of the thioacetate –SAc group or up to 1 week in the case of the disulfide –S₂ group causing slower ligand exchange.

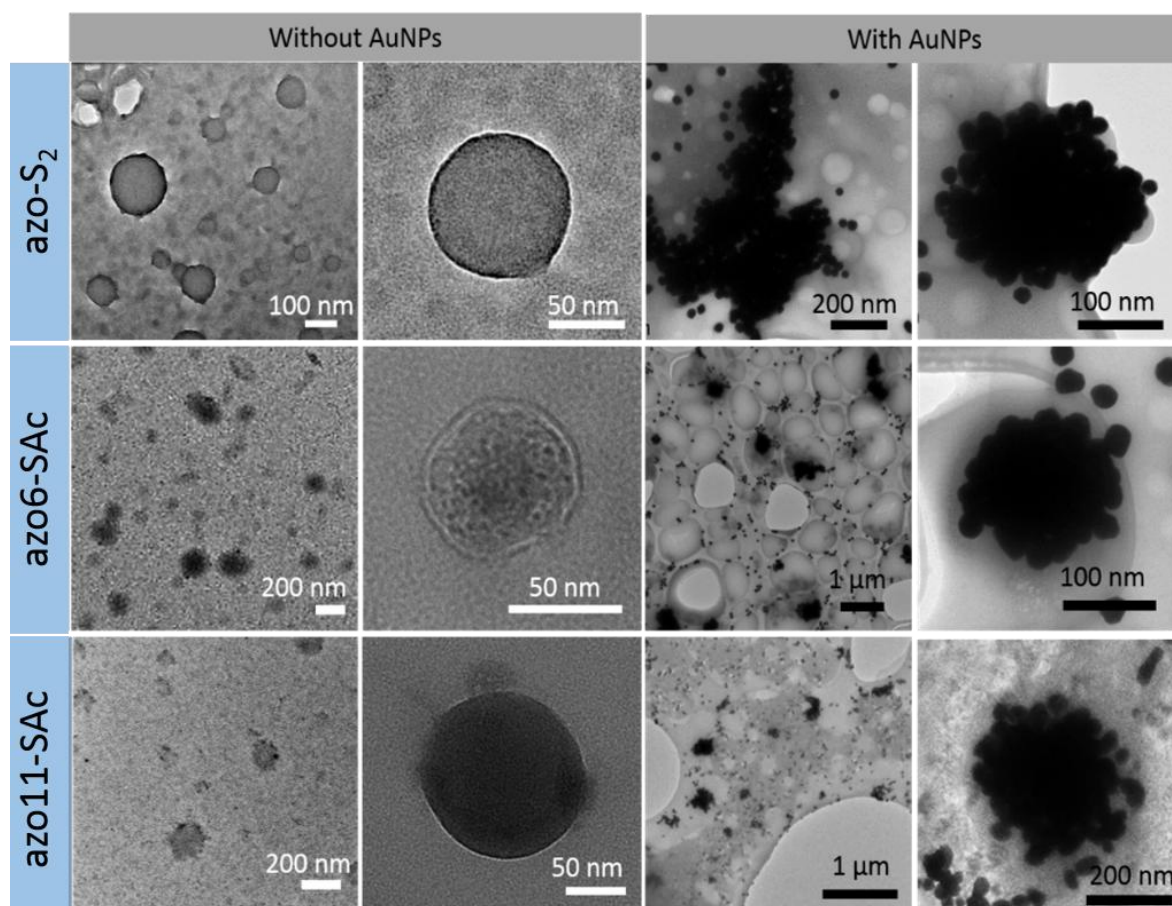


Figure 4.19. TEM images of the different organic nanospheres without and with AuNPs.

DLS measurements confirmed the coordination of AuNPs to the photochromic nanospheres as all of them but azo11-SAc displayed increased hydrodynamic diameter and broader size distribution (102 ± 47 nm (azo-S₂@AuNPs) to 156 ± 99 nm (azo6-SAc@AuNPs) to 137 ± 77 nm (azo11-SAc@AuNPs) (Figure 4.20). The surface potential of the hybrid nanoassemblies was measured at -40 mV in accord with the negative charge brought by the stabilizing shell of citrate ions.

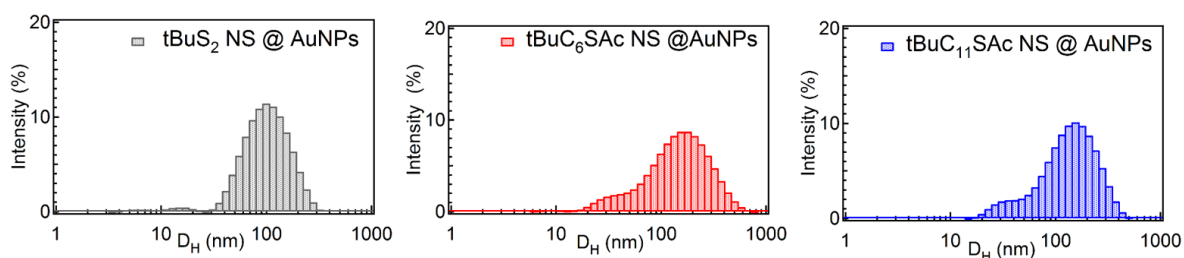


Figure 4.20. DLS of the hybrid organic nanospheres @ AuNPs

4.3.2 Structural characterizations of nanospheres

To characterize the gold NP attachment onto the organic nanospheres and infer mutual optical interactions, Raman microscopy was used since it offers a high spatial resolution (i.e. $\sim 1 \mu\text{m}$) together with a unique sensitivity to the vibrational fingerprints of the molecules of interest. As reported in Chapter 3, azo compounds exhibit characteristic vibrational modes $1400\text{-}1500 \text{ cm}^{-1}$ ascribed to N=N and C=C bonds. As illuminated AuNPs are responsible for the dramatic enhancement of the excitation and scattered electric fields in their vicinity, their presence close to organics can amplify the intensity of the scattered Raman signal by five orders of magnitude. To perform excitation, various wavelengths from the near infrared to the visible ranges are commonly used. In our case, four irradiation wavelengths have been employed: 785 nm or 633 nm (far from the AuNP LSPR absorption band), 514 nm (matching the absorption maximum wavelength of the AuNP LSPR band), and 488 nm close to the azo absorption band. All Raman investigations were performed on both model systems (azo nanospheres) and hybrid nanoassemblies (azo@Au NPs) (Figure 4.21). At 785 nm and 633 nm, the vibrational stretches of the azo material composing the core of the hybrid nanospheres were hardly observed. Excitation at 488 nm induced a photoreaction causing irreversible damages of the nano object which was burned by the laser. We thus privileged the use of a laser excitation at 514 nm, the laser power for the Raman experiments was set at 0.1 % of the maximum energy, namely 10 W. cm^{-2} , with an exposure time of 1 s and 10 accumulations. The Raman spectra of azo@Au nanoassemblies clearly indicate the presence of azo moieties due the vibrational bands in the $1400 - 1500 \text{ cm}^{-1}$ range. Such bands are significantly enhanced by a factor of 15 (azo-S₂) to 30 (azo6-SAc) to 70 (azo11-SAc) in the case of azo@Au nanoassemblies compared to the azo nanospheres alone. These enhancements suggest that optical coupling exists between the AuNPs and azo core, albeit weaker than expected and whose origin requires immediate proximity of the AuNPs to the azo surface.

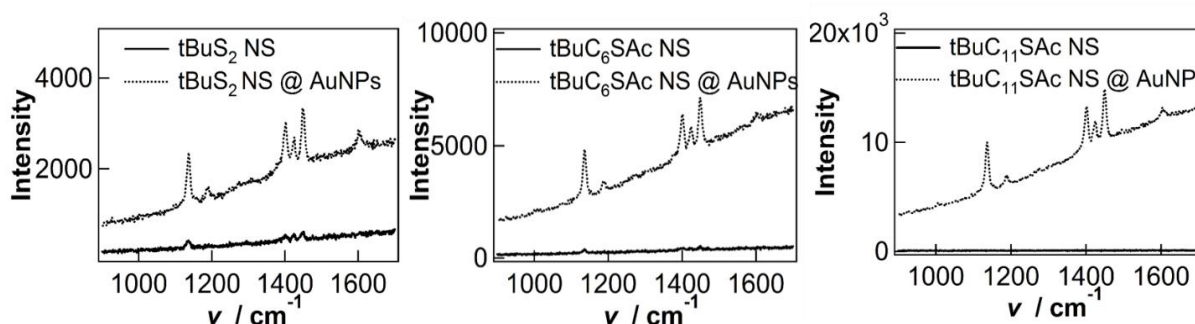


Figure 4.21. Raman spectra of the organic azo nanospheres and hybrid nanoassemblies azo@Au using a 514 nm laser excitation.

4.3.3 Photochromic properties of nanospheres

Before studying the photochromic hybrid nanoassemblies, we have investigated the response of the azo nanospheres and their ability to deform under polarized light. All solutions were prepared in the dark. Their absorption maxima were found at around 480 nm, namely 10 nm red-shifted compared to those of azo ligands in toluene solution, and identical to those in thin films. These results suggest that the electronic influence of the surrounding water molecules is negligible. Irradiation with a white light source equipped with a 488 ± 2 nm narrow band filter ($P = 8 \text{ mW} \cdot \text{cm}^{-2}$). The absorption spectra of the azo nanospheres were collected every 20 s until the photostationary state was reached (Figure 4.22). From here, the sample was left in the dark and the back thermal relaxation was monitored by recording over time the absorbance at the maximum absorption wavelength in the visible range (Figure 4.23). A second cycle (irradiation-relaxation) was performed to investigate the photoreaction reversibility. Kinetics of the back thermal reaction could be surprisingly fitted using a monoexponential rate. All kinetics and photoconversion data are presented in Table 4.5. At the photostationary state, the minimal photochemical conversion yield of the nanospheres was found between 21 and 22 %, less than in solution (~ 50 %) but much higher than in thin films (13 – 15 % only, see Table 4.1). The photoirradiated nanospheres relaxed to their initial state following a monoexponential law with a rate constant of around $10.5 - 13 \times 10^{-5} \text{ s}^{-1}$, almost identical to the fastest component in thin films. This remarkable result contrasts with the reported observation of a fluorescence multidecay in fluorescent nanoparticles, which was ascribed to the heterogeneous assembling of fluorophores.¹²¹ The monoexponential law, adapted to the analyses of the thermal $Z \rightarrow E$ relaxation for the nanoparticles, let us suggest that

the azo geometries are randomly distributed and the azo photochromes are imparted with higher degrees of freedom in nanoparticles than in thin films. Two structural parameters could thus be evoked: the high surface-to-volume ratio encountered in nanoparticles and the larger free volume around each chromophore due to quick dye nanoreprecipitation in solution. As observed latter in the part devoted to the fabrication of novel hybrid nanoassemblies (section 4.3.5.1 on azo@PVP@Au nanoassemblies) comprising a polymer shell around the azo nanospheres, photoisomerization at the interface of the nanoparticle and water plays a major role. Finally, we could interestingly note that the larger the alkyl chain, the higher the photochemical conversion yield, which tends to correlate with the larger free volume induced by large alkyl groups. The sample was irradiated again until the photostationary state was reached and the back thermal relaxation was monitored. The same absorbance measurements from one cycle to another were obtained, illustrating that the samples are rewritable and the results are reproducible.

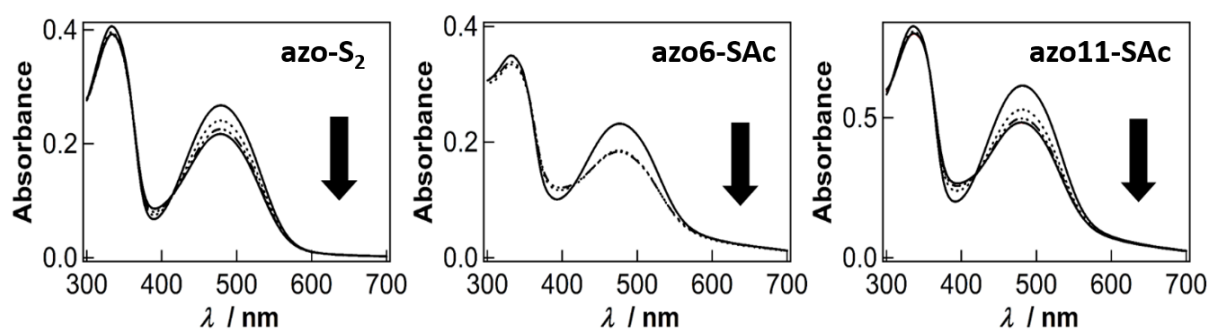


Figure 4.22. Nanospheres composed of azo-S₂, azo6-SAc and azo11-SAc upon illumination at 488 nm ($P = 8 \text{ mW} \cdot \text{cm}^{-2}$). Each spectrum was obtained every 10 s of irradiation until the photostationary state was reached.

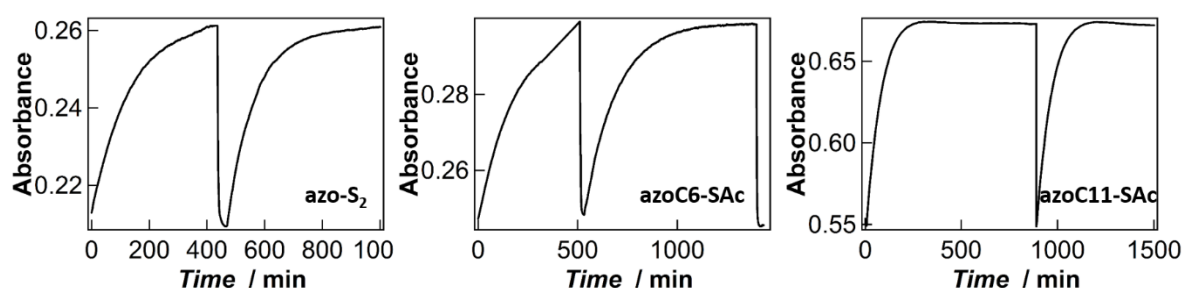


Figure 4.23. Evolution of the absorbance spectra of the organic nanospheres in solution monitored at the maximum absorption wavelength for two successive

back thermal relaxation steps, following each an irradiation step thermal relaxation.

The photochromic properties of the hybrid nanoassemblies have been studied using the same conditions as before (Table 4.5). To ensure first that the azoNS@Au was being observed, the absorption spectra of the citrate AuNPs, the azoNS, the nanospheres and the AuNPs, were compared with the azoNS@Au (Figure 4.24). Here, the difference between the absorption of the azoNS, the citrate AuNPs plus azoNS, and the azoNS@Au, indicates that the hybrid systems are formed, due to the minor change in the λ_{max} value between all spectra. The corresponding absorption spectra display the two bands typical of the azo moiety with the charge transfer band in the visible range masking the LSPR band, supposed to peak at 528 nm. The apparent absorption maxima in the visible range thus appeared between 506 and 514 nm (Figure 4.25). Upon irradiation, the band characteristic of the azo charge transfer decreased in intensity, albeit to a lesser extent than for neat organic nanospheres. The minimum photoconversion yields ρ reached only 8 to 13 % against 21 %, which recalls the optical coupling observed within the Au@azo NPs. It is worth noting that ρ shows larger values for azo11-SAc while azo6-SAc and azo-S₂ photoisomerize to the same extent at 8 - 9 %. We propose here that the longer C11 chain partially acts as a spacer between the AuNPs and the azo moiety, hence the optical coupling between the azo and gold plasmons is reduced. Finally, no real influence of the gold nanoparticles was again observed on the back relaxation rate constants whose values were found between 9.5 and $12 \times 10^{-5} \text{ s}^{-1}$. In order to go deeper in the photoisomerization process, we have investigated the shape change of nanoparticles upon irradiation.

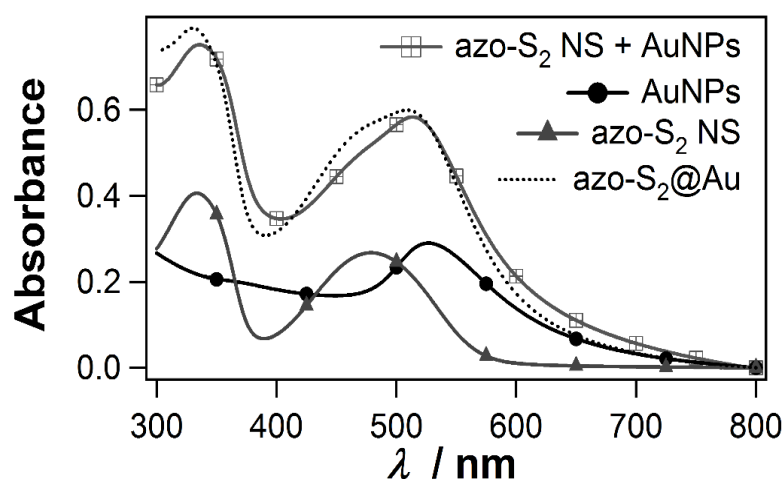


Figure 4.24. UV vis spectra of the AuNPs, the azoNS, the azoNS@ AuNPs, and the calculated azoNS + AuNPs in Millipore water.

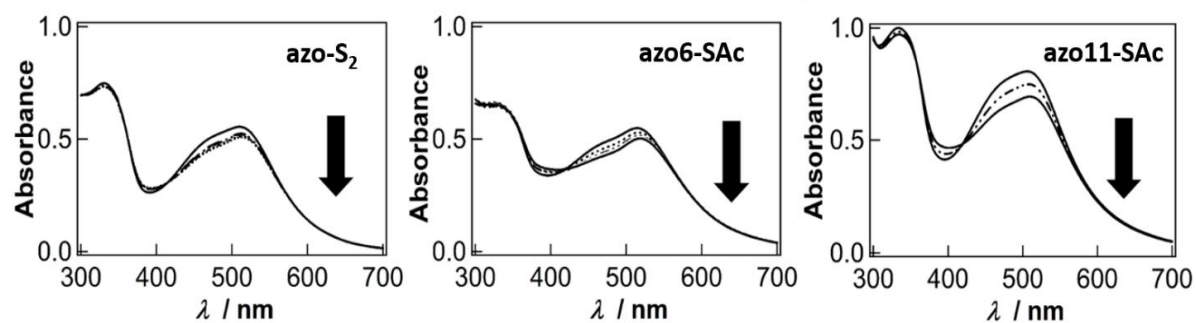


Figure 4.25. UV-vis absorption spectra of azo@Au NPs in Millipore water and subjected to irradiation at 488 nm ($P = 8 \text{ mW} \cdot \text{cm}^{-2}$). Each spectrum was obtained every 10 s of irradiation until the photostationary state was reached.

4.3.4 Photodeformation of nanospheres

DLS measurements were performed after irradiation of water suspensions of azo nanospheres and hybrid nanoassemblies. When comparing the average size of the organic nanospheres with and without AuNPs, before irradiation and after irradiation, most of the diameter distributions shifted to narrow values, except for that related to azo11-SAc that slightly widened. It is observed that the diameter of the azo-S₂ and azo6-SAc nanospheres are smaller (Table 4.6).

Compound	Diameter of NS (dark)	Diameter of NS (after irradiation)
----------	--------------------------	---------------------------------------

azo-S ₂ NS	90 ± 30 nm	60 ± 24 nm
azo6-SAc NS	125 ± 48 nm	96 ± 50 nm
azo11-SAc NS	139 ± 20 nm	160 ± 76 nm
azo-S ₂ NS@ AuNPs	102 ± 47 nm	70 ± 29 nm
azo6-SAc NS@ AuNPs	156 ± 99 nm	101 ± 50 nm
azo11-SAc NS @ AuNPs	137 ± 77 nm	126 ± 34 nm

Table 4.6. DLS measurements of the azo NS and the azo NS @ AuNPs before and after irradiation with a 488 nm light source operating at a power of 8 mW. cm⁻², these samples were irradiated for 2 min.

In order to investigate the possible deformation of photochromic nanospheres under polarized light as already reported for azo-functionalized polymeric nanoparticles, we irradiated the samples with linearly polarized light using an Ar⁺ laser at 488 nm, operating at a power of 470 mW. cm⁻². We deposited a droplet (15 µL) of azo nanospheres (azo11-SAc) directly onto TEM grid to enable further highly resolved imaging. Since we had no wide-field microscope equipped with a laser source, we placed the grid vertically on a glass plate covered with parafilm so that the grid and the drop could adhere vertically without falling. Irradiation was thus performed with normal incident light for 30 min until the droplet dried. TEM imaging (Figure 4.26) revealed that the once spherical nanospheres deformed into croissant like geometries. The lack of directional deformation originates from the free moving nanoparticles in solution. Due to the optical coupling between the dyes and the AuNPs with a diameter of 15 nm, this experiment was not performed on the AuNPs coated species.

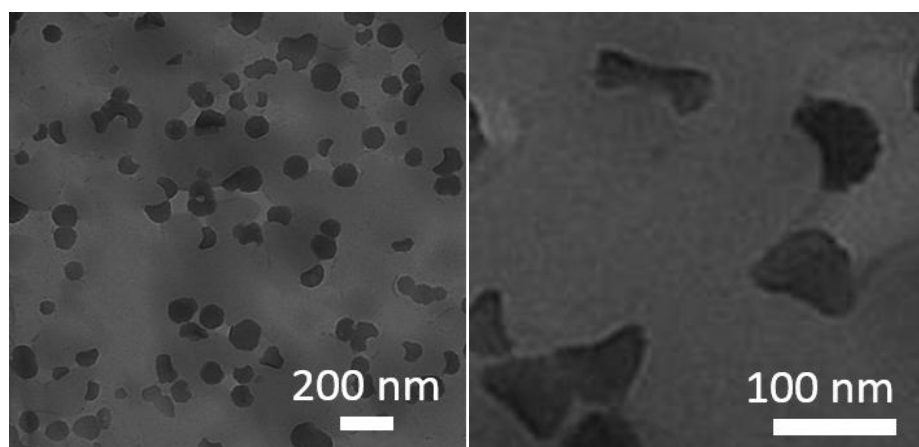


Figure 4.26. TEM images of the azo11-SAc nanospheres irradiated with linearly polarized light at 488 nm and a power of 470 mW. cm⁻² using an Ar⁺ laser source.

4.3.5 Other methods to incorporate AuNPs on the surface of the nanospheres

4.3.5.1 PVP polymer coated nanospheres

In order to get rid of the LSPR bands responsible for the quenching of photoisomerization, attempts to reduce the size of the coordinated AuNPs were performed. To this aim, we resorted first to the seeding method consisting in nucleating AuNPs directly on a template, here the azo nanospheres. We thus used a method involving polyvinylpyrrolidone (PVP),¹²² a photoactive polymer that is able to undergo photo-oxidation in the presence of gold nanoparticles (Figure 4.27).

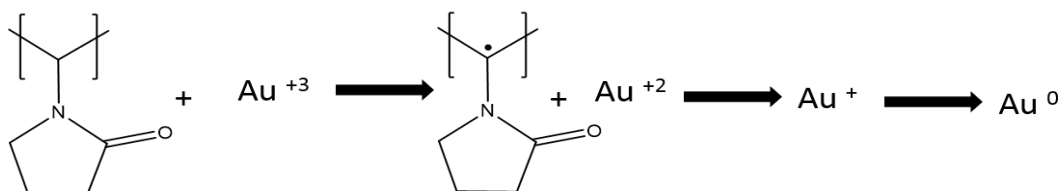


Figure 4.27. Photo-oxidation mechanism of PVP in the presence of gold salts.

The protocol thus consisted in forming first azo nanospheres by adding a 0.2 wt. % azo solution into a 0.008 wt. % aqueous solution of polyvinylpyrrolidone (PVP) (2.5 mL) (MW = 40,000 g mol⁻¹). The subsequent addition of 0.001 g of HAuCl₄ followed by light irradiation at 365 nm initiated a radical reaction with PVP reducing the gold salt into Au⁰ and AuNPs at the vicinity of PVP. Since PVP exhibits polar groups, stabilization of the newly formed AuNPs was achieved upon interacting with the polymer chains (Figure 4.28).

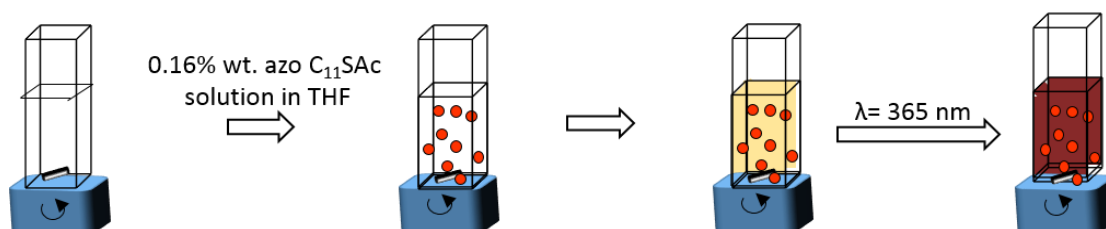


Figure 4.28. Scheme of precipitating the organic nanospheres into a solution of PVP. After addition of HAuCl₄ and irradiation at 365 nm, the AuNPs from directly on the surface of the nanospheres.

The surface potential ζ of the azo nanospheres in the presence of PVP was found almost neutral at + 5 mV (against -40 mV in the absence of PVP), suggesting the

interaction of the polymer with the nanosphere surface. After gold reduction, the surface potential of azo@PVP@Au nanoassemblies was measured to be + 37 mV, as a result of non-reduced Au^{3+} ions left in the solution.

The generation of gold nanoparticles was monitored by UV-vis absorption spectroscopy (Figure 4.29). Upon irradiation, the visible band, initially corresponding to the azo intramolecular charge transfer, increased in intensity and underwent a significant bathochromic shift 479 nm to 514 nm. These spectroscopic changes feature the growth of AuNPs, large enough to exhibit LSPR band.

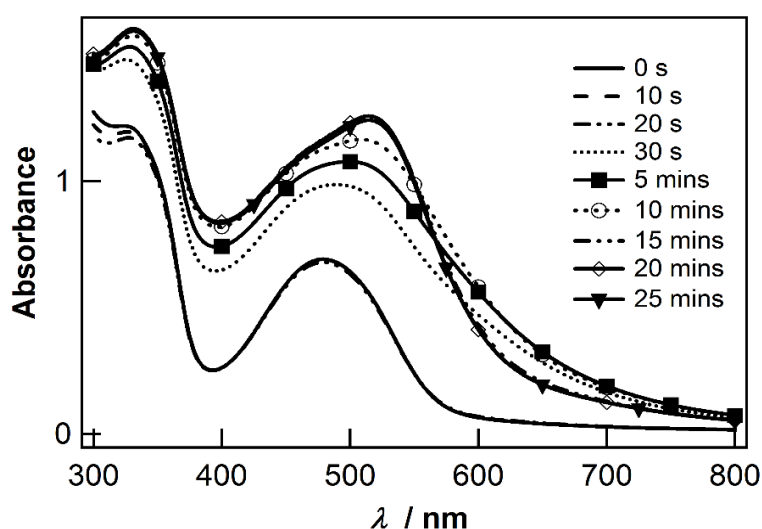


Figure 4.29. UV-vis absorption spectra of solutions of PVP-coated azo11-SAc nanospheres containing HAuCl_4 salt upon irradiation at 365 nm for 25 min ($P = 190 \text{ mW} \cdot \text{cm}^{-2}$).

TEM imaging on azo@PVP nanoassemblies showed spherical nano objects, with less defined edges compared to those of azo nanospheres. A more grainy structure, spotted with darked dots, could be observed for azo@PVP@Au nanoassemblies, as a result of the coordination of ultra-small gold NPs (2 nm) and larger gold NPs (up to 10 nm) exhibiting surface plasmons (Figure 4.30).

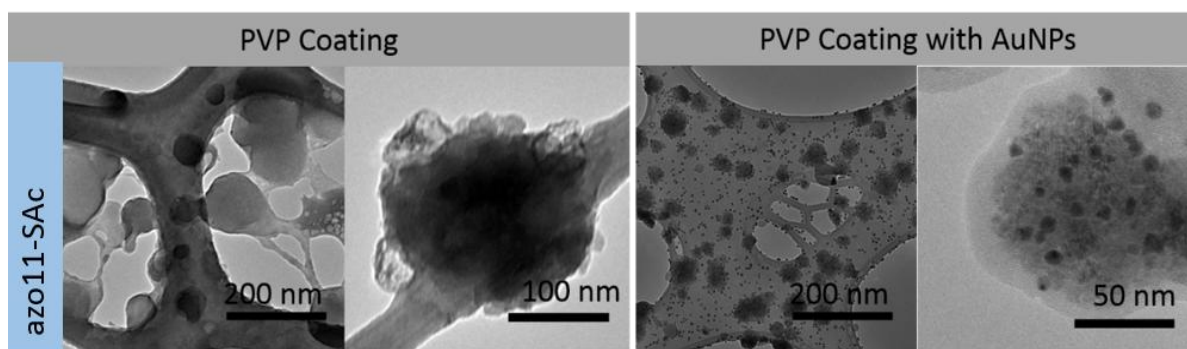


Figure 4.30. TEM images of azo11-SAc@PVP and azo11-SAc@PVP@Au nanoassemblies.

We thus compared the photoisomerization behavior of these novel nanossemblies with that of the previous azo@Au hybrid nano objects. All conditions were kept identical except that the sample was irradiated for 240 s (Figure 4.31). The photostationary state was reached after 60 s and the minimum photochemical conversion yield ρ was estimated at 3.6 %. This value is drastically lower than that found for the previous architecture ($\rho = 13$ %). The reduced photochemical conversion could be due either to the PVP coating around the nanospheres, or to the gold NPs surrounding the nanoassemblies. We thus studied the photochromic behaviour of the azo@PVP nanosystems in absence of AuNPs (Figure 4.32).

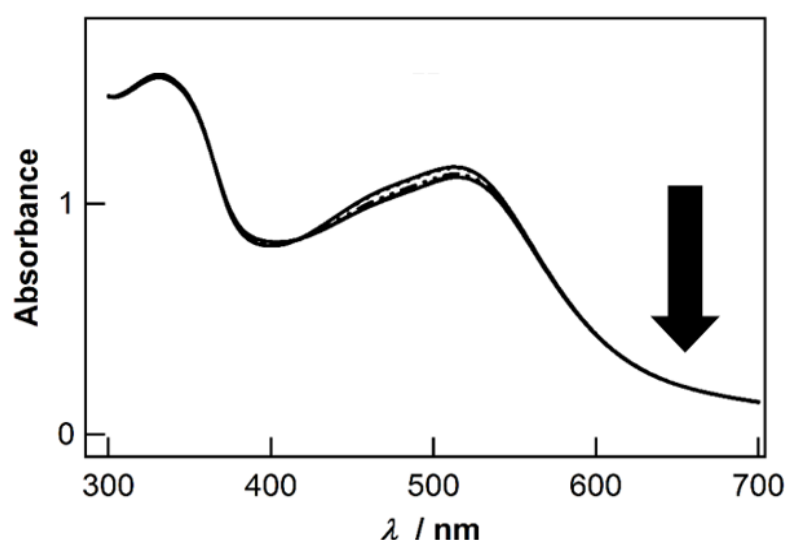


Figure 4.31. UV-vis absorption spectra of azo@Au@PVP nanoassemblies in water upon irradiation at 488 nm ($P = 8 \text{ mW} \cdot \text{cm}^{-2}$). Each spectrum was obtained every 10 s until the photostationary state was reached.

Again, only limited conversion ($\rho = 4.7\%$) was found for neat azo nanospheres. The PVP coating seems thus to be the prevailing photoisomerization quenching phenomenon rather than an optical coupling between plasmons and azo transition moments since AuNPs are quite distant. These latter indeed contributed to only 1.1 % to the decrease of photoconversion. These studies point out the fact that azo dyes located at the nanoparticle surface contribute the most to the photoisomerization reaction in neat photochromic nanoparticles.

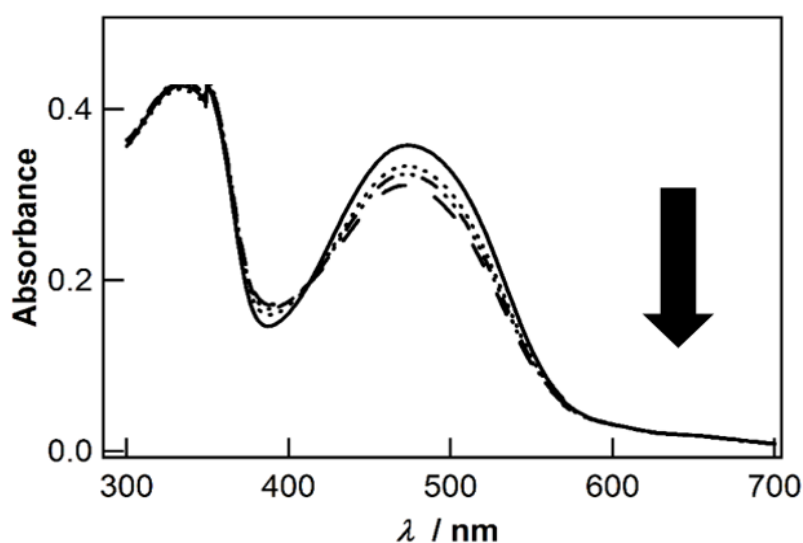


Figure 4.32. UV-vis absorption spectra for azo@PVP@Au nanoassemblies in water upon irradiation at 488 nm ($P = 8 \text{ mW} \cdot \text{cm}^{-2}$). Each spectrum was collected every 10 s until the photostationary state was reached.

4.3.5.2 TOAB coated nanospheres

The second method used to coat azo nanospheres with ultra-small gold nanoparticles was based on the observation that azo organic nanospheres become insoluble in solvents immiscible with water (toluene, dichloromethane, diethyl ether) once they have been formed. We exploited such physicochemical properties and the organo-soluble gold nanoparticles (TOAB-AuNPs) prepared by a phase transfer method (see section 4.2.4) to fabricate novel hybrid assemblies through a ligand exchange mechanism favoured by the sulfur terminated chains at the azo nanospheres surface. A toluene solution of freshly synthesized TOAB AuNPs ($4.3 \pm 2 \text{ nm}$, 1 mL of a 2.4 wt. % solution) was added to aqueous suspensions of azo11-SAc nanospheres (2.5 mL) and the resulting biphasic mixture (orange in the aqueous layer and purple in the toluene layer) was vigorously vortexed for 24 h. We observed a color change of the

organic layer to an orange color as most of the nanospheres were transferred into the organic layer. The aqueous layer turned very pale orange. Both solutions were analyzed by TEM. To our surprise, clean nanoassemblies were only observed from the aqueous layer. No *free TOAB AuNPs* could be observed as logically expected from the hydrophobic surface of *AuNPs* (Figure 4.33).

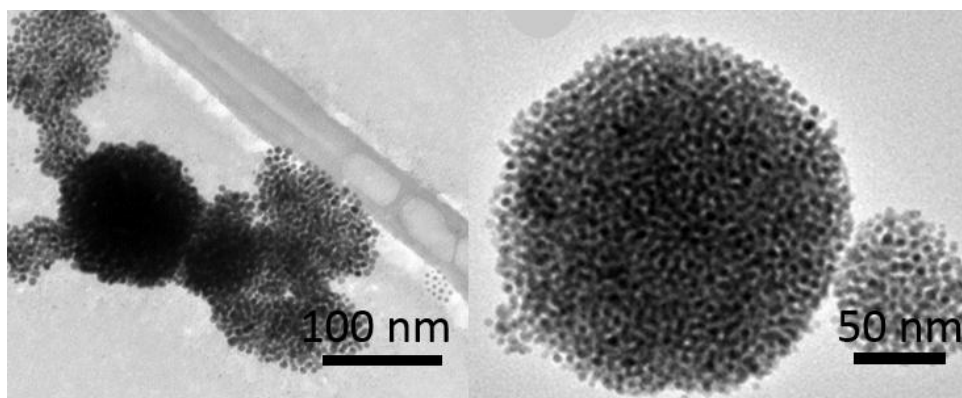


Figure 4.33. TEM images of the azo11-SAc nanospheres with TOAB AuNPs in the aqueous phase.

By contrast, TEM images of the toluene solution displayed essentially gold nanoaggregates and no azo nanospheres. We suspected that the TOAB salt transferred along with gold nanoparticles dissolved entirely the azo nanospheres. This was indeed confirmed by a brief experiment where TOAB was added to a solution of azo nanospheres, these latter disassembled (Figure 4.34).

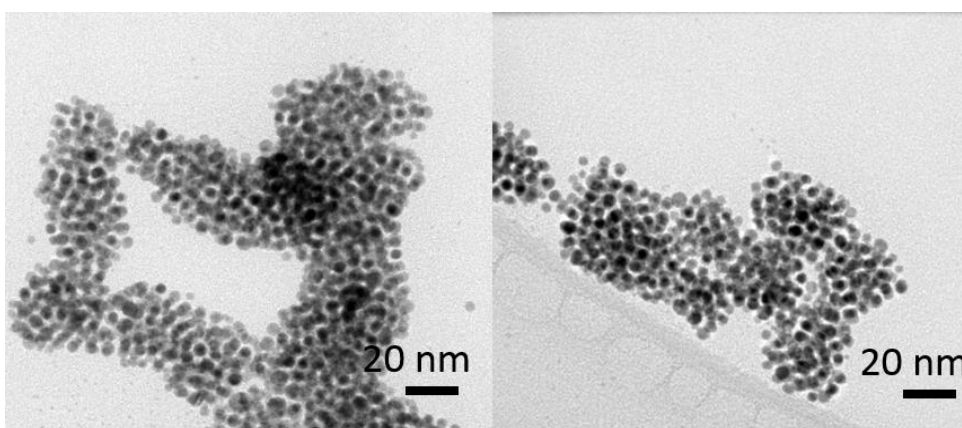


Figure 4.34. TEM images of the azo11-SAc nanospheres with TOAB AuNPs in the organic phase

UV-vis spectroscopy analyses of the aqueous layer showed the prevailing presence of a gold plasmon band, centered at 539 nm, coming from the assembling of small nanoparticles at the azo nanosphere surface. Indeed, no such plasmon band could be observed for TOAB-Au nanoparticles, alone masking any azo contribution (Figure 4.35). Photoisomerization studies of this sample were attempted. However, the solution was too diluted to observe any significant change.

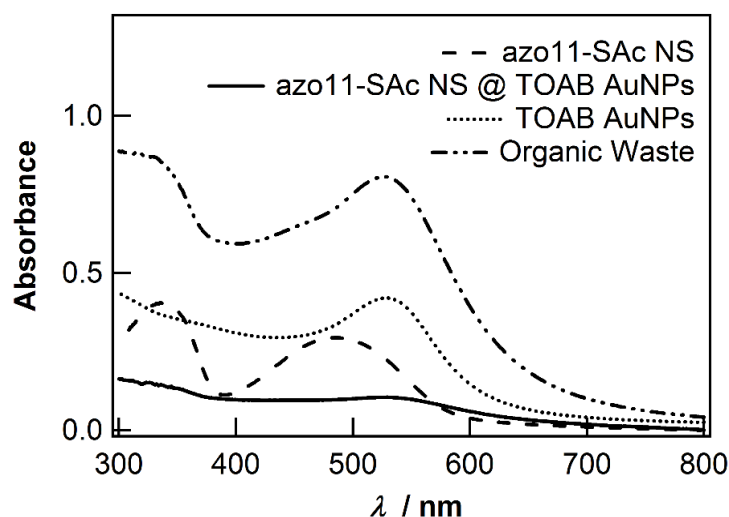


Figure 4.35. UV vis absorption spectra of azo11-SAc nanospheres with and without TOAB AuNPs in the aqueous phase after ligand exchange in biphasic conditions.

4.3.6 Conclusion and perspectives

A variety of photochromic nanospheres has been synthesized and characterized. These nanospheres display higher photochemical conversion in comparison to that of the corresponding thin films due to the large surface-to-volume ratio, hence a large number of azo dyes at the surface can photoisomerize. These photochromic nanospheres were then used to assemble as a shell a variety of gold nanoparticles. The photochromic properties of the resulting hybrid nanomaterials appeared drastically reduced due to optical coupling between the azo excited states and the plasmon band, both located close in energy. The use of a longer spacer between the azo moiety and the sulfur-terminated chain amenable to chelate gold NPs, known to weaken optical coupling, led to significant increase in the photoconversion yield. In absence of AuNPs, the organic nanospheres could be deformed by linearly polarized light while

the deformation was impaired in the presence of gold coating, due to a probable optical coupling between the AuNPs and the azo nanospheres.

4.4 Hybrid photochromic nanorods

In Chapter 3, we showed that the directional organization of azo compounds could be achieved by using interferential illumination. To see if these nano objects could be directional organized as well, we self-assembled the azo molecules to fabricate micrometric-long nanorods using hollow templates. Allowing the deformation of large 1D-nano objects to more easily be followed under isotropic and polarized illumination.

4.4.1 Synthesis of nanorods

Numerous nanorods or nanotubes have been synthesized in the literature using alumina or a polycarbonate templates that are loaded with polymers, ion salts or nanoparticles, and further subjected to specific treatments to obtain mono- or multicomposite plain or hollow materials. Though polymeric and metallic nanorods have long been studied, very little has been done with small organic molecules that present distinct wettability with the template walls compared to those of polymers.^{56,123} To address the fabrication of organic nanorods out of azo compounds, we have used 60 μm -thick alumina membranes displaying a pore size of 200 nm. A variety of azo compounds (azo models tBuCO₂Me, tBuCN and thioderivatives azo-S₂, azo6-Sac, azo11-SAc to chelate gold nanoparticles) has been used to test their ability to yield clean nanorods after the membrane dissolution. Three loading techniques were explored: melting, dipping or drop-casting. Loading the template with melt compound was performed by pressing an alumina membrane onto azo melts obtained from azo powder deposited on glass plates and heated up to their glass transition temperature using a heating plate. After a 30 min contacting period, the template was cooled to room temperature and any excess compound on the surface of the template was buffed away using a diamond paper. Dissolution of the template, carried out over 18 h in a 3 mol L⁻¹ KOH solution, failed to entirely remove alumina due to strong cohesion of the organic nanomaterials between the walls. The second loading method involved template dipping into a 4 wt. % azo solution prepared in chloroform. Unfortunately, no proper loading occurred with insufficient material impregnation.

Finally, the third method consisted in drop casting a 4 wt. % azo solution prepared in anisole onto an alumina template, followed by slow solvent evaporation overnight. Anisole was used as a solvent because the azo compounds are highly soluble, the resulting materials exhibit weak crystalline character and the boiling point is higher than that of chloroform, allowing for better material penetration into the pores of the membrane. After the excess compound on the surface of the template was buffed away using a cotton swab, the organic nanorods could be successfully recovered by dissolving the template in a 3 mol L⁻¹ KOH solution or in a 1 mol L⁻¹ phosphoric acid solution (2 mL per template). This dissolution occurred between 24- 48 hours, then the solution was diluted by adding Millipore water (2 mL) and dialyzed against Millipore water (molar weight cut-off membrane: 6 - 8,000 g mol⁻¹). The water container was regularly changed until neutralization of the solution (Figure 4.36). In order to analyze the fabricated nano objects, a drop of the nanorod suspension was dispersed onto a silicon wafer. After water evaporation, the organic nanorods were characterized using SEM. Generally, all organic nanorods displayed a diameter of 200 nm and a length ranging from 10 to 40 μ m. When the alumina template was dissolved in 1 mol L⁻¹ phosphoric acid instead of potassium hydroxide, the nanorods appeared deformed (Figure 4.37). We have so far no particular explanation to support this observation that encouraged us to retain the alkaline dissolution as the method of choice. More interestingly, the surface quality and the length of the nanorods strongly depended on the azo structures. For strongly polar azo compounds like those substituted by nitro or cyano moieties, the resulting nanorods appeared shorter and displayed corrugated surfaces due to remaining chunks of undissolved alumina. Instead, azo ester derivatives gave longer nanorods and smoother surface. This was also true for azo-S₂ that contains an ester group and a hydrophobic disulfide group. By contrast, azo6-SAc and azo11-SAc failed to provide nanorod surfaces devoid of alumina debris. Such features, also observed for other polar series of push-pull molecules (-NO₂), let us suggest that polar compounds tend to interact strongly with the polar alumina surface through dipole-dipole interactions, hence template removal is incomplete. We suspected the failure with the acetate derivatives due to saponification of the ester link can tightly anchor the alumina membrane. Interestingly, most of the nanorods reported so far in the literature were obtained from hydrocarbon polymers or small molecules that generated nanomaterials with very smooth surfaces, in agreement with our experimental observations (Figure 4.38).¹²⁴

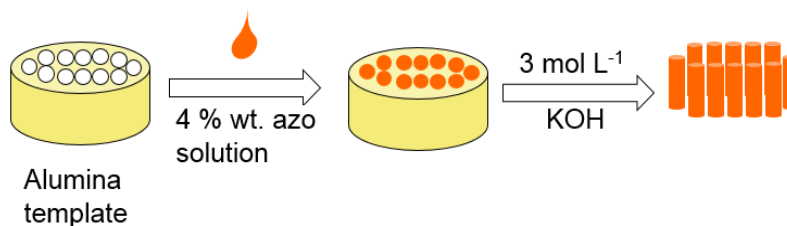


Figure 4.36. Fabrication of organic nanorods following a drop-casting method based on the filling of alumina membrane pores with a concentrated organic solution.

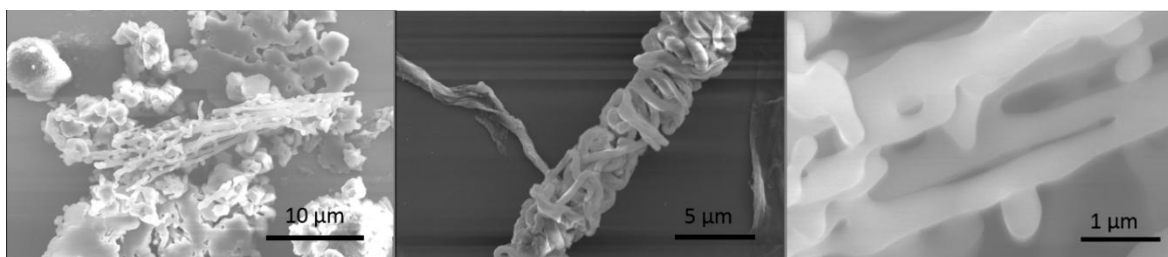


Figure 4.37. Dissolution of alumina template with 1 mol L⁻¹ H₃PO₄ solution leaving tBuNO₂ rods deformed.

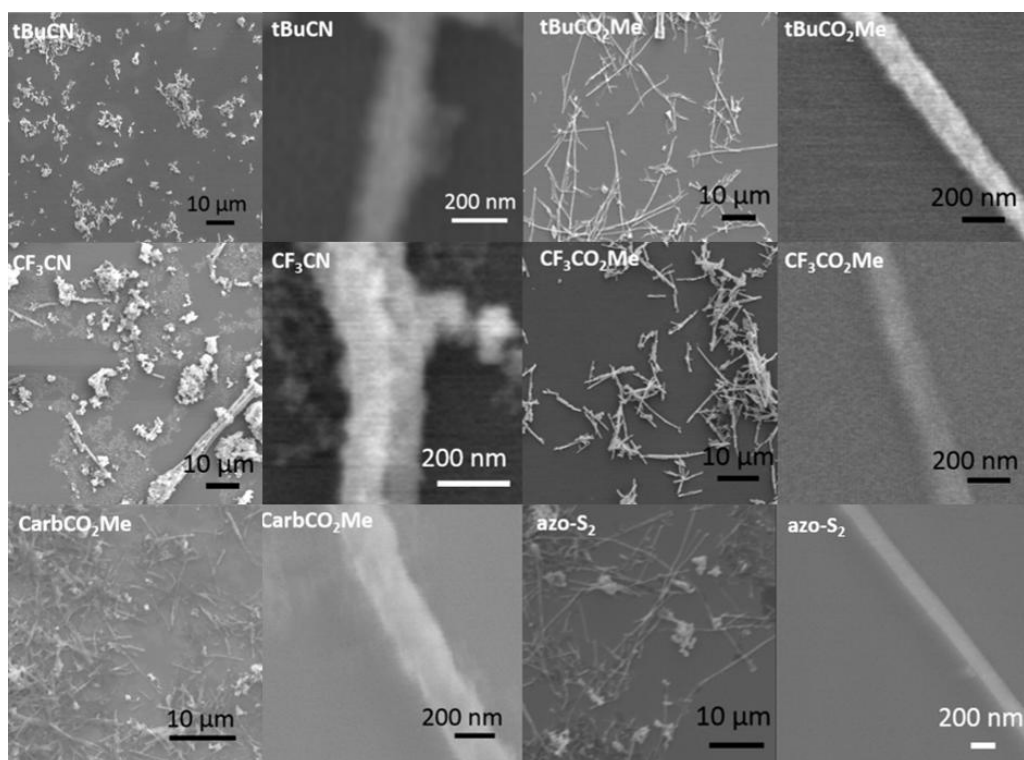


Figure 4.38. SEM images of organic nanorods deposited on silicon wafer.

4.4.2 Synthesis of hybrid nanorods chelated to AuNPs

Attempts to chelate AuNPs ($\phi = 20$ nm) around the azo-S₂ nanorods were performed, by stirring, using a vortex, a 4.2×10^{-5} mol L⁻¹ solution of azo-S₂ nanorods with a 0.2 wt % solution of citrate-stabilized AuNPs for 4 days (Figure 4.39). This way of stirring was used to prevent organics from sticking onto the Teflon stirring bar. After the AuNPs coordinated to the nanorods, the resulting nanoassemblies were cleaned of excess AuNPs by centrifugation. However, even when changing the spinning speed, the nanorods stuck to the surface of the centrifuge container. We then let the nanoassemblies smoothly decant. The azo-S₂ nanorods were then characterized using SEM and TEM (Figure 4.40).

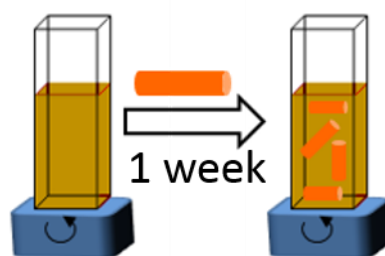


Figure 4.39. Scheme for coating azo nanorods with chelating AuNPs. A solution of azo nanorods were vortexed in a 0.2 wt % solution of citrate AuNPs ($\phi = 20$ nm) for 4 days yielding the azo@Au nanorod.

The images of hybrid photochromic nanorods show rods with a 200 nm diameter and inhomogeneous coating of AuNPs. The latter feature can be due to some traces of remaining template, thus restricting the ability of AuNPs to be bound by the nanorod surface. UV-vis spectroscopy was then used to gain insight into the nanorod photoisomerization.

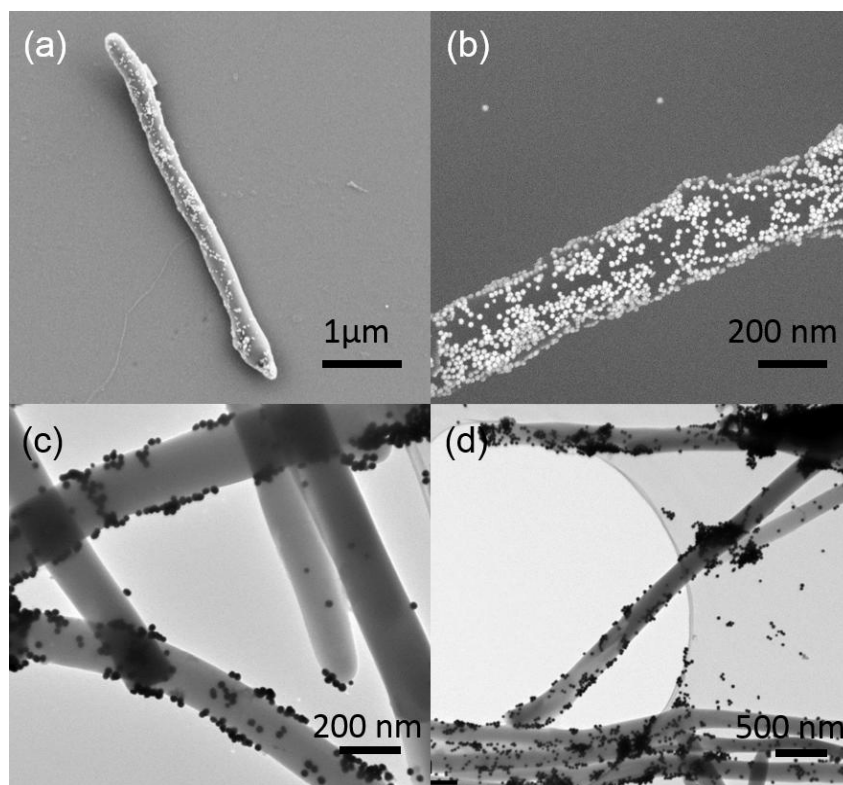


Figure 4.40. Characterizations of the azo-S₂ nanorods chelating AuNPs by using (a) and (b) SEM imaging, (c) and (d) TEM imaging.

4.4.3 Photochromic and optical properties of hybrid nanorods

First, absorption spectra of the azo-S₂ nanorods and hybrid azo-S₂ rods @ AuNPs were recorded and compared with those of the separated units (Figure 4.41). The absorption maximum of the azo-S₂ solution changes from 471 nm to 501 nm for the azo-S₂ rods. Such common bathochromic shifts encountered in the solid state can be either ascribed to J-aggregates or to more polar surroundings than those in toluene solution. Giving the structural similarity of azo-S₂ with the tBuX series, we can reasonably discard any close packing of the azo aromatic backbones due to the presence of *tert*-butylphenyl bulky groups. Upon forming the hybrid azo-S₂ rod @ AuNPs, the maximum absorption wavelength was more red shifted, ($\lambda_{\text{max}} = 538 \text{ nm}$) as a result of the contribution of the gold LSPR band. Also, it is noteworthy that the absorbance of both bands in the visible and UV ranges have drastically decreased. One can invoke two reasons. The first reason could be related to the optical coupling between the AuNPs and organic nanorods since both units absorb in the same region as already observed with the Au@azo nanospheres. The second explanation could stem from the quick decantation of the hybrid nanorods resulting in an inaccurate

absorption reading. Unfortunately, because of the latter process, the photoisomerization of the azo-S₂ rods coated with AuNPs could not be studied. Instead, the photoisomerization of the azo-S₂ rods without AuNPs was investigated using the usual procedure.

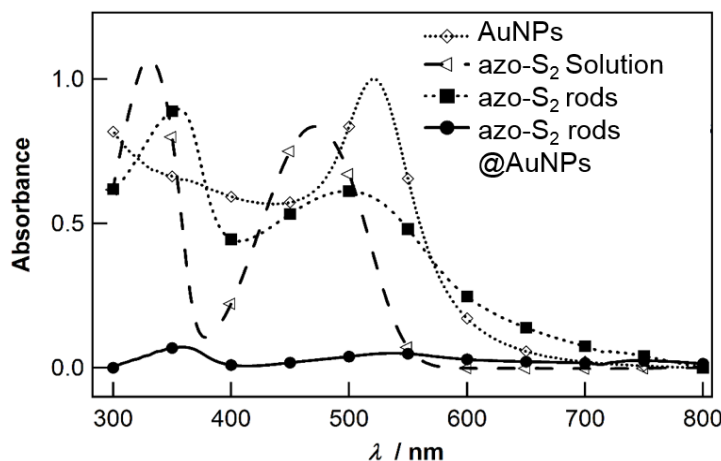


Figure 4.41. UV-vis absorption spectra of azo-S₂ toluene solution, the citrate-stabilized AuNPs, the azo-S₂ rods and the azo-S₂ rods@ AuNPs dispersed in water.

The photoisomerization reaction was performed on a solution of azo-S₂ nanorods whose concentration in azo units was valued to be $4.2 \times 10^{-5} \text{ mol L}^{-1}$, assuming the same molar absorption coefficient for the azo compounds in solution and shaped as nanorods. The solution (3 mL) was irradiated using a 488 nm light source operating at the power of 8 mW. cm^{-2} . During irradiation, the UV vis absorption spectra were recorded every 20 s until the photostationary state was reached (Figure 4.42). A minor blue shift of the absorption maximum wavelength was observed from 528 nm to 523 nm while the minimum photochemical conversion was determined to be only 0.5 %. The back thermal relaxation could not be calculated due to most of the rods precipitated out of the solution. We assumed here a change in the dipolar surface contribution due to the surface accumulation of the less polar Z photoisomers, giving rise to less interfacial solvation in water. SEM imaging of the precipitated material was realized to characterize any major geometry changes.

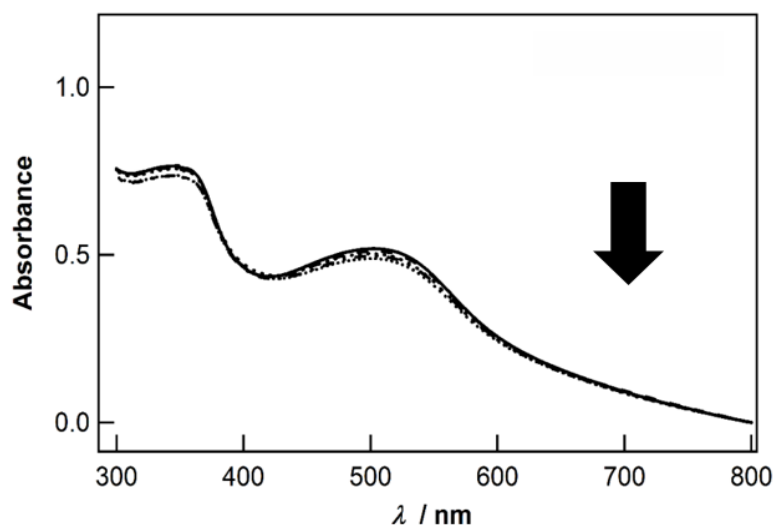


Figure 4.42. Evolution of the UV-vis absorption spectra for the azo-S₂ nanorods in solution upon irradiation at 488 nm, $P = 8 \text{ mW. cm}^{-2}$ at intervals of 10 s until the photostationary state was reached.

SEM imaging revealed nanorods with reduced or enlarged diameters along with curved nanorods and nanospheres (Figure 4.43). Images at higher magnification show that the nanorods are merged together causing irreversible aggregation, which can explain the formation of precipitated product. Optical transmission microscopy was then used to see what happens when the sample was irradiated.

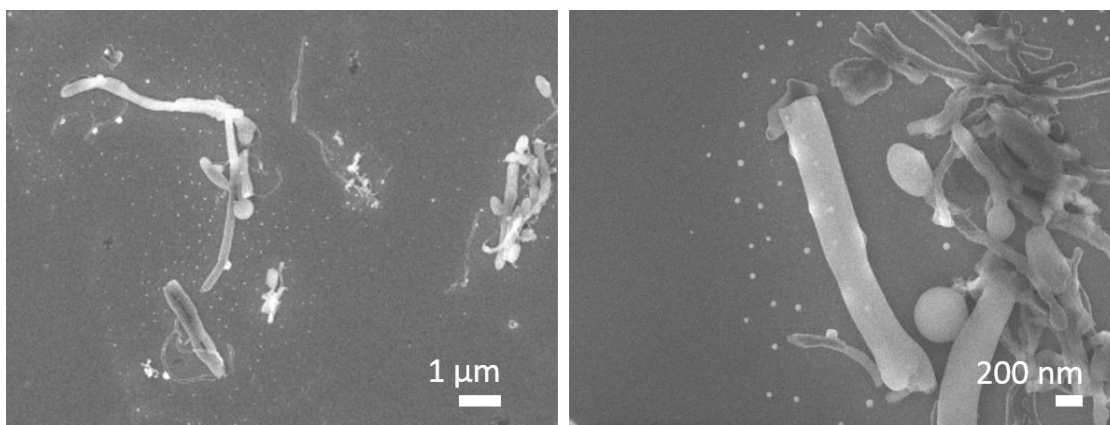


Figure 4.43. SEM images of the azo-S₂ nanorods irradiated at 488 nm at a power of 8 mW. cm^{-2} for 60 min and deposited on silicon wafer.

In order to monitor the geometrical deformation of the azo nanorods, we resorted to optical microscopy imaging using a Nikon microscope equipped with a 63× oil immersion objective and an excitation light source at $\lambda_{\text{exc}} = 482 \pm 18 \text{ nm}$ (Figure

4.44). A 50 μL droplet of the azo- S_2 nanorods solution was deposited onto the surface of a 0.17 mm thin glass coverslip. A video showed how the nanorods first coiled up until forming nanospheres. This deformation was a major one, while some other nanorods remained almost unchanged maybe due to some alumina template remaining on the surface. When water evaporated, leaving the nanorods almost dry, no structural changes could be observed. The same kind of experiment was performed with the hybrid azo- $\text{S}_2@\text{Au}$ nanorods. However very little to no change could be observed, despite the low number of AuNPs onto the azo nanorods, confirming again the strong coupling between the azo and the gold materials. We thus employed Raman microscopy again to try characterizing the tight connection between the AuNPs and the azo nanorods.

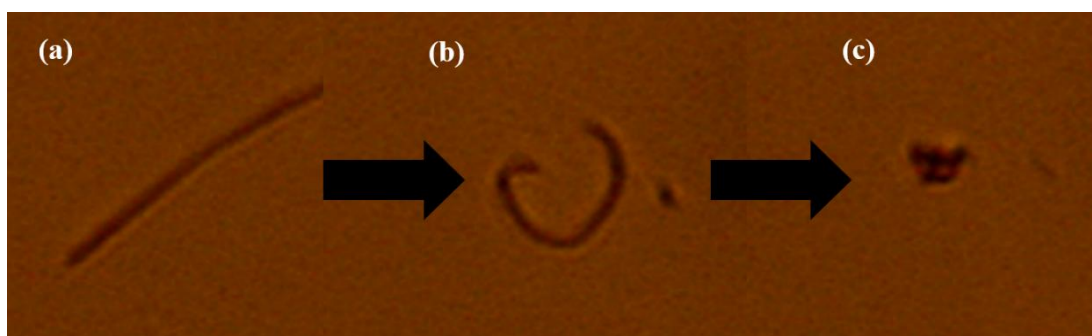


Figure 4.44. Images from a video at 0 s (a), 15 s (b), and 30 s(c) azo- S_2 nanorods irradiated at 482 nm, $P = 360 \text{ mW} \cdot \text{cm}^{-2}$.

4.4.4 Raman microscopy of nanorods

Raman spectra of the azo- S_2 nanorods and the hybrid azo- $\text{S}_2@\text{Au}$ nanorods were recorded (Figure 4.45), using a 785 nm laser, with an exposure time of 1 s, and 10 accumulations for each measurement. Such conditions were chosen to avoid undesirable degradation or melting effects on the sample. The Raman spectrum of a single azo nanorod showed very low signal with undefined stretches due to the low azo concentration addressed upon irradiation, due to the size of the nano object. By contrast, the Raman spectrum of hybrid azo- $\text{S}_2@\text{Au}$, collected under the same conditions, displayed distinct vibrational stretches whose intensities are globally enhanced by three orders of magnitude. Such signal enhancement is typical of a SERS effect that is to be related to closely lying AuNPs. We further investigated the structure on a nanometric scale using tip-enhanced Raman spectroscopy (TERS).

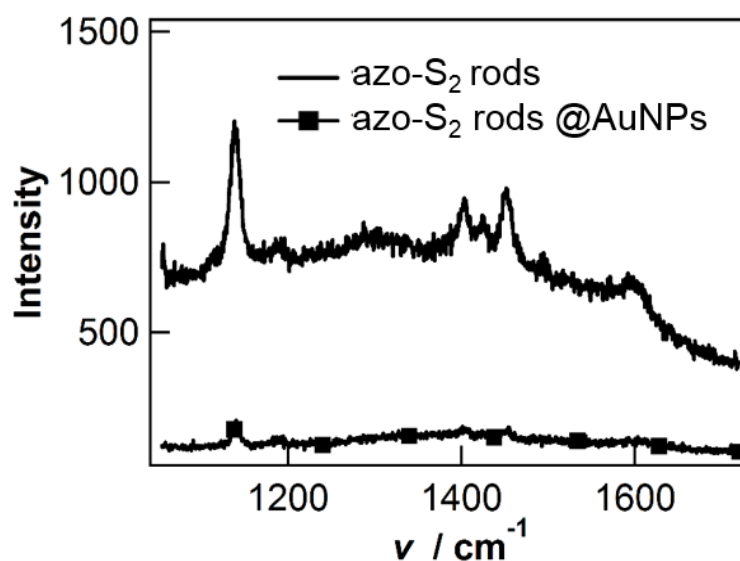


Figure 4.45. Raman spectra of azo-S₂ nanorods and azo-S₂ nanrods @ AuNPs in solid state recorded after laser excitation at 785 nm.

4.4.5 Tip-enhanced Raman spectroscopy of nanorods

TERS is a technique based on the Raman signal enhancement using metallic nanoparticles that display strong LSPR and are attached to the extremity of an AFM tip. When the AFM tip is in close proximity to the surface, the free electrons of the metallic nanoparticles start oscillating, forming a localized electric field that enhances the Raman signal of the sample. This technique can be used to map areas of nano/micro objects to provide better insight into the azo molecular organization within the rod. We first optimized the azo response with the tBuCO₂Me model nanorods, providing reproducible Raman spectra over time with an excitation wavelength of 785 nm. TERS was then performed on a tBuCO₂Me nanorod showing a 40 % enhancement of the Raman intensity when the tip was in the approach mode. Conversely, when the tip was retracted 200 nm away, the Raman signal decreased by 40 % of its initial value when the tip was approached (Figure 4.46). When Raman mapping of the hybrid azo-S₂@Au nanorods was attempted, these latter deformed while the Raman signal decreased with longer exposure time independently of the laser power. When doing TERS on hybrid azo-S₂@Au nanorods, numerous nanorods appeared aggregated together, as AuNP chelation by the nanorods, involving ligand exchange, required almost one week. To synthesize well-dispersed nanohybrids, two

parameters can be accounted for, either the time of the ligand exchange reaction or the repulsive interactions between nanoparticles to avoid deleterious aggregations.

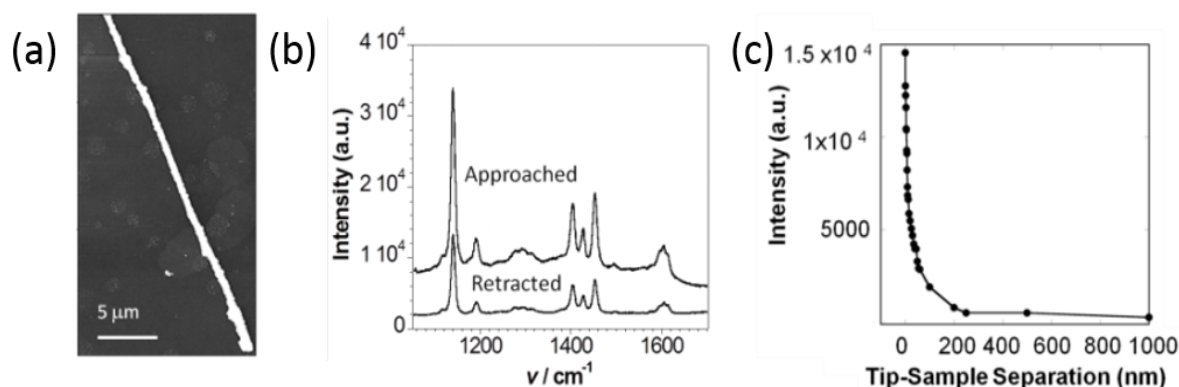


Figure 4.46. (a) AFM image of a single tBuCO_2Me nanorod. (b) Raman spectra of the nanorods with an gold AFM cantilever approached and retracted, (c) and the monitoring of the decrease of Raman intensity as the tip is retracted.

4.4.6 Polyelectrolyte stabilized nanorods

We decided to stabilize the nanorods using a cationic polyelectrolyte and entangling it around the nanorods that exhibit a negative surface potential (-40 mV), as measured by zetametry. Such stabilization was performed using polydiallyldimethyl ammonium chloride (PDPA) ($M_w = 100,000 - 200,000 \text{ g.mol}^{-1}$) that is insensitive to pH due to the nitrogen atom quaternarization. Optimization of the PDPA concentration (molar ratio of nanorods to PDPA: 1:1, 1:2, 1:8) with regard to the number of nanorods was previously performed to avoid any material excess that would lead to nanorod bridging. It turns out that a 1:1 molar ratio of PDPA: nanorod provided the best results. The polyelectrolyte (1 mg) was added to a 2 mL suspension of azo nanorods ($4.2 \times 10^{-5} \text{ mol L}^{-1}$), and further stirred using a vortex for 24 h. PDPA clearly acts as a stabilizing agent of the nanorods as these latter stay suspended in water without decanting in the course of time in contrast with PDPA-free nanorods (Figure 4.47). AFM characterizations were performed to image the surface of the nanorods and ascertain the absence of aggregated nanorods. Compared to SEM analyses implying an electron beam often too energetic for organic materials, AFM measurements represent no risk of damaging the sample unless the latter is scratched by the tip during scanning.

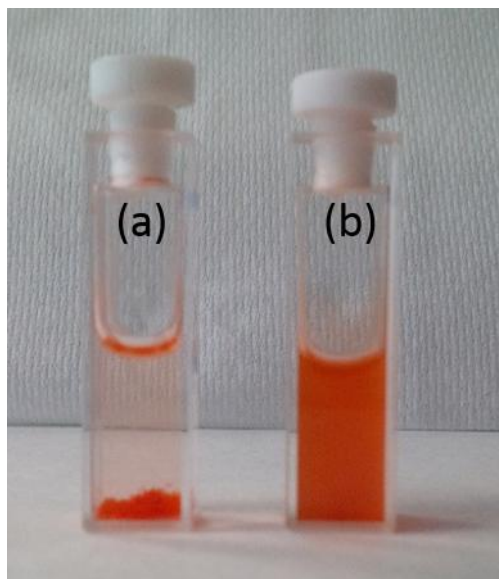


Figure 4.47. A solution of (a) free-PDDA azo-S₂ nanorods and (b) PDDA-coated azo-S₂ nanorods left alone in water for 12h.

The PDDA-free *azo*-S₂ nanorod presented a smooth surface and rounded tips whereas the surface of a PDDA-coated nanorod appeared to be rougher. Phase images (inlet) better evidence the distinct elastic responses of the nanorod depending on the absence or presence of an external coating. As noticed before, the presence of a polymer coating onto azo nanospheres severely reduced the azo photochromic ability. We thus wondered if the PDDA coating would also affect the photochromic properties of the azo nanorods (Figure 4.48).

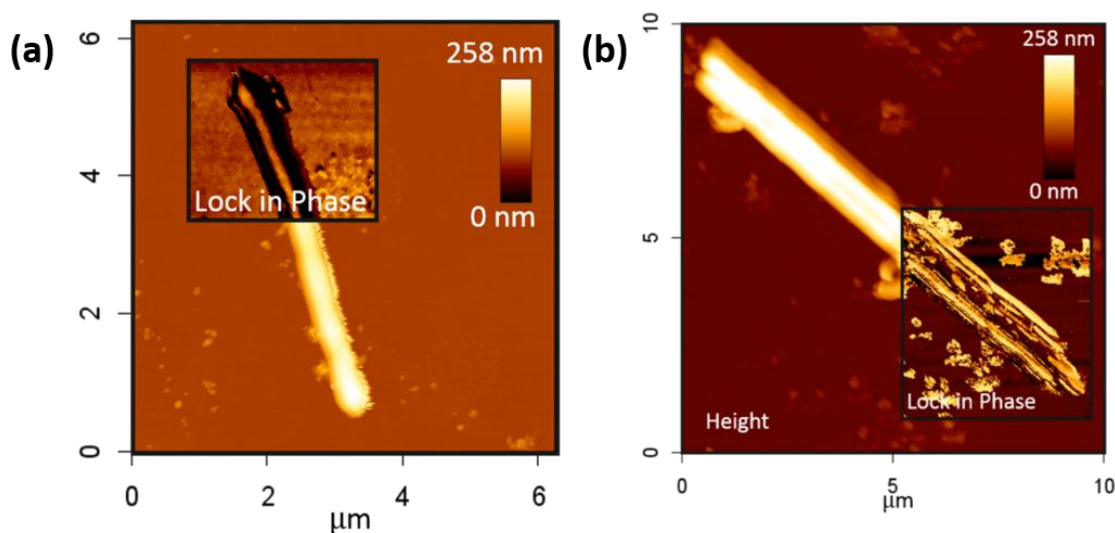


Figure 4.48. AFM image of the free-PDDA azo-S₂ nanorods (a) and PDDA-coated azo-S₂ (b)

The UV-vis absorption spectrum of PDDA-coated azo nanorods showed two bands at 332 nm and 510 nm as commonly observed for all the azo compounds reported in this manuscript (Figure 4.49). The absorption spectra evolved under irradiation at 488 nm using the usual conditions, and displayed a 5 nm hypsochromic shift of the azo-centered charge transfer band. The minimum photochemical conversion was calculated to be 7 %, which is higher than that obtained for free PDDA azo nanorods ($\rho = 0.5\%$). The back thermal relaxation was recorded in the dark over 16 h and showed fully reversible reaction $Z \rightarrow E$ to the initial state before illumination, demonstrating that photoisomerization is not fully impaired by the surrounding polyelectrolyte.

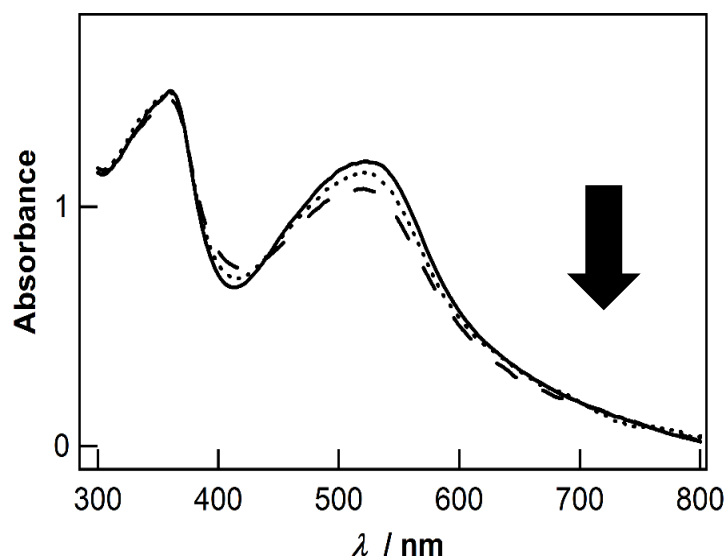


Figure 4.49. UV-vis absorption spectra for the PDDA-coated azo-S₂ nanorods suspended in water upon irradiation at 488 nm, $P = 8 \text{ mW} \cdot \text{cm}^{-2}$ at intervals of 10 s until the photostationary state was reached.

The dispersed PDDA-coated azo nanorods were then stirred with citrate-stabilized AuNPs ($\phi = 15 \pm 3 \text{ nm}$) to try to avoid the nanorods aggregating together and precipitating to the bottom of the vial. However, after two hours, the material started to sediment upon aggregation in solution (Figure 4.50). A TEM grid was loaded with a droplet of the resulting precipitate to gain insight into the structure of the materials.

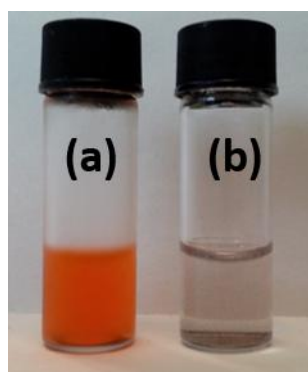


Figure 4.50. Pictures of solution of PDDA-coated azo-S₂ nanorods in the absence (a) and in the presence of AuNPs (b).

We can again observe that the nanorods were not homogeneously coated and their surface exhibited instead strongly aggregated gold nanoparticles. Although citrate-stabilized AuNPs and the positively charged PDDA polyelectrolyte can develop strong electrostatic interactions, non-uniform deposition of gold nanoparticles may

originate from possible polyelectrolyte rearrangement or partial nanorod coating with PDDA (Figure 4.51). At this stage, thermogravimetric studies could be useful to deduce the amount of polyelectrolyte wrapping the nanorods.

To go further in the grafting of gold nanoparticles and the stabilization of the resulting assemblies, the use of negatively charged gold seeds and the addition of an external positively charge polyelectrolyte could appear as an alternative method to generate nanoassembly suspensions with high colloidal stability.

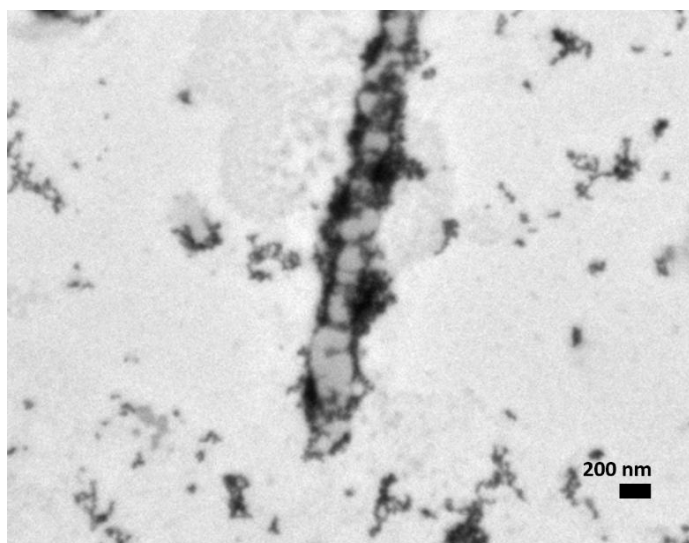


Figure 4.51. TEM image of the PDADMAC coated azo-S₂ nanorods @ AuNPs.

4.4.7 Conclusions

A variety of push-pull azo dyes has been used to form nanorods. Using an alumina template, we have established that the interfacial interactions developed between small molecules and alumina templates strongly depend on the polarity of the azo compounds, leading for more polar compounds to incompletely remove the alumina template. Disulfide-terminated azo compound azo-S₂ could be processed as nanorods that were stabilized by using a positively polyelectrolyte. The coating of Au NPs appeared to be very delicate as the citrate ions, used as stabilizing agents, were inefficient to bring enough repulsion after gold chelation by the nanorods (“naked” or PDDA-coated). The resulting nanoassemblies aggregated out of the solution, and can make spectroscopic and photochromic studies challenging. In order to go further with the tuning of AuNP location using photochromic nano objects, we must first impart the nanostructures with higher colloidal stability. This latter can be achieved by

modifying the way of grafting gold NPs as well as by using appropriate polyelectrolytes, known to stabilize large nanoassemblies better than small ligands. The second point to optimize actually relies on the optical coupling between the azo compounds and gold NPs that appear more deleterious than cooperative. Reducing the charge transfer magnitude within the azo compound would lead to azo absorption at higher energy, giving rise to less spectral overlap with the LSPR band and hopefully larger photoisomerization conversion.

4.5 Conclusions and perspectives

Different push-pull azo molecules have been synthesized and used to form various nano objects. These nano objects have been used to organize at their surface AuNPs, fabricated following three distinct procedures. The studies of the azo photochromic properties evidenced an optical coupling between the AuNPs and the azo nano objects. Further work being done in the group now involves iron oxide NPs, to see if the migration properties of the azo molecules can also be exploited to move and organize such non-plasmonic nanoparticles.

Chapter 5

Conclusions and perspectives

The synthesis and characterization of a series of push pull molecules in solution and solid states were examined. In solution, the photoisomerization of the dyes showed to be driven by the electron withdrawing group para to the azo group. However, the photoisomerization in the solid state was more driven by the free volume from the bulky substituents. PM-IRLD studies on these thin films suggested a correlation between the electron withdrawing group and the degree of relaxation of the molecular orientation. The birefringence of these azo thin films confirms first that the degree of birefringence was dependent of the bulkiness of the substituents, and second, the orientation of these small push pull molecules occurs at a significantly higher rate than a similar azo polymer.

The thin films of these push-pull azo derivatives were used to organize aqueous polystyrene nanoparticles in suspension. Such experiments were possible because of the compatibility of the azo thin films with the colloidal solution of polystyrene particles ruling out any surface deformation. A series of experiments were conducted, depositing the nanoparticles onto the thin films before or after interferential illumination. The results showed that the mass transport of the azo material can drag the nanoparticles and organize them within the grooves of the periodic surface relief gratings allowing for the azo thin films to be used as a template to organize the nanoparticles. When changing the nanoparticles to gold, the organization and mass transportation did not occur, highlighting the importance of the size and the density of the particles as well as their capacity to aggregate along with an optical coupling that presumably prevents the formation of surface relief gratings.

The gold nanoparticles were then attached onto the surface of different photochromic objects such as nanospheres and nanorods. The photochromic behaviour of the nanospheres showed a larger photochemical conversion than their corresponding thin film. This was explained by the large surface-to-volume ratio of the photochromic material on the surface of the nanospheres. Photodeformation of these nanospheres were reported and to more clearly observe this deformation, gold nanoparticles were chelated on the surface of the sphere. The azo nanospheres in the presence of gold

drastically reduce the photochromic properties of the azo material, likely due to an energy transfer. These photochromic nanospheres in absence of gold could be deposited onto a glass substrate to see if there are any enhanced features in comparison to the traditional thin films.

The azo-S₂ nanorods were synthesized, characterized, and chelated to citrate AuNPs. The photoisomerization of such hybrid species was unable to be studied due to the aggregation of the nanorods during the chelation to the particles. To try to overcome this issue the nanorods were coated with a polymer that was positively charged, allowing for the repulsion of the nanorods, and more efficient coordination of the citrate AuNPs via electrostatic interactions. Once the AuNPs assembled onto the PDDA azoS₂, the rods precipitated and the photochromic properties were challenging to study. Future perspective involve either synthesizing these hybrids with nanoparticles that do have a SPR band or it does not absorbing in the same region as the azo molecule.

Different photochromic materials were synthesized and used to organize nanoparticles. Due to an energy transfer between the gold nanoparticles and the photochromic materials, the photoisomerization of the materials in the presence of gold seems to be hindered. In the future, further work will be done using similar photochromic materials to organize different metallic nanoparticles.

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Appendices

Appendix A

A.1 Synthetic Protocols

A.1.1 General Experimental

All chemical reagents and solvents were purchased from commercial sources (Aldrich, Acros, SDS) and used as received. The polystyrene nanoparticles and PDDA were purchased from Polysciences. Inc and the PVP polymer was purchased from Aldrich. ^1H and ^{13}C NMR spectra were recorded on Burker 300 MHz spectrometer and chemical shift were reported in ppm relative to tetramethylsilane (TMS) or referenced to the residual solvent. High resolution mass spectra were obtained by MALDI-TOF (Voyager DE-STR, Applied Biosystems).

A.1.2 Synthetic procedure of organic compounds

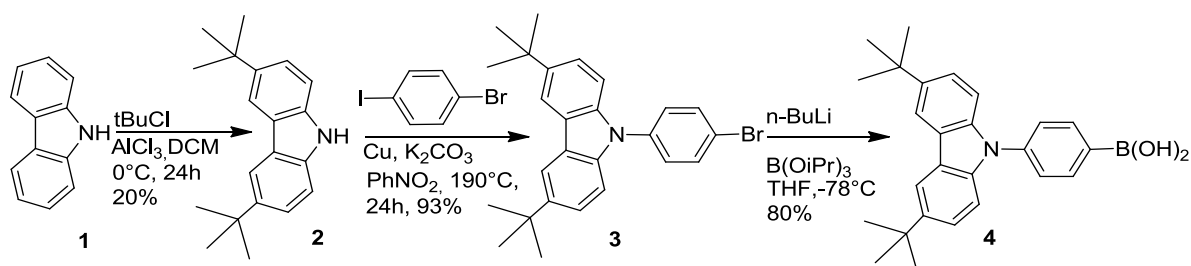


Figure A.1. Synthetic pathway for the synthesis of tBu carbazole boronic acid (4).

Synthesis of *tert*-butyl carbazole (2):

Carbazole (10 g, 60 mmol) and aluminium trichloride (8 g, 60 mmol) were dissolved in dry dichloromethane and cooled to 0 °C. *tert*-butyl chloride (11 g, 120 mmol) was added dropwise to the cooled solution and stirred for an additional 30min at 0 °C. The solution was then warmed up to room temperature and stirred for 24 h. The solution was neutralized with 2 mol L⁻¹ HCl and water (50 mL) was added. The compound was extracted with dichloromethane (3x 20 mL) and the solvent was removed under vacuum. The compound was then recrystallized using methanol and collected by filtration (33 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.08 (2H, s), 7.86 (1H,

broad), 7.47 (2H, d, $J = 8.4$ Hz), 7.33 (2H, d, $J = 8.4$ Hz) 1.45 (36H, s); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 142.4, 138.2, 123.6, 123.5, 116.3, 110.1, 34.8, 32.2; MALDI-MS: Calculated mass: $\text{C}_{20}\text{H}_{26}\text{N}$: 280.2059 m/z, Exact mass: $\text{C}_{20}\text{H}_{26}\text{N}$: 280.2049 m/z.

Synthesis of 4-bromophenyl-*tert*-butyl carbazole (3):

To a 100 mL Schlenk tube *tert*-butyl carbazole (4.5 g, 16 mmol), iodophenyl bromide (13.5 g, 48 mmol), copper powder (4.0 g, 64 mmol), potassium carbonate (8.8 g, 64 mmol), and 18-crown ether -6 (1.8g, 6.7 mmol) were added to nitrobenzene (50 mL). The solution was degassed under vacuum using argon and refluxed at 190 °C for 6.5 h. The solution was cooled to room temperature and passed through a celite filter to remove the copper powder and the filtrate was washed with dichloromethane (3 x 20 mL) and transferred to a 500 mL round bottom flask where azeotropic distillation of nitrobenzene was performed. The compound was then purified by flash column chromatography on silica gel (9:1 petroleum ether: CH_2Cl_2) to yield a white powder (93 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.13 (2H, s), 7.70 (2H, d, $J = 9$ Hz), 7.48 (2H, d, $J = 9$ Hz), 7.47 (2H, d, $J = 9$ Hz), 7.32 (2H, d, $J = 9$ Hz); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 143.3, 139.1, 137.5, 133.1, 128.4, 123.9, 123.6, 120.4, 116.5, 109.2, 34.9, 32.1; MALDI-MS: Calculated mass: $\text{C}_{26}\text{H}_{28}\text{BrN}$: 433.1400 m/z, Exact mass: $\text{C}_{46}\text{H}_{45}\text{N}_3\text{O}$: 433.1389 m/z.

Synthesis of 4-*tert*-butyl carbazole phenyl boronic acid (4):

Compound (3) (1 g, 2.3 mmol) was dissolved in dry THF (15 mL) and purged of oxygen using nitrogen. The solution was cooled to -78 °C using a liquid nitrogen and acetone bath. Butyl lithium (0.18 g, 2.8 mmol) was added dropwise to the solution over 15 min. The solution continued to react at -78 °C for 1 h, then isopropyl borate (2.6 g, 13 mmol) was added dropwise (15 min) and reacted for an additional hour at -78 °C. After the liquid nitrogen and acetone bath was removed, the solution heated up to room temperature (18 °C) and stirred for an additional 3 h. Here the solution changed from clear to white to a pale yellow. After the 3 h the solution was cooled to 0 °C and 1 mol L⁻¹ HCl was used to neutralized the solution. The compound was extracted using DCM and water. The organic layer was collected and dried using Na_2SO_4 and the solvent was evaporated. The compound was precipitated in the present of hexanes and the white powder solid was collected (80 %). ^1H NMR (300

MHz, CDCl₃): δ (ppm): 8.54 (2H, d, J = 8.1 Hz), 8.18 (2H, s), 7.79 (2H, d, J = 8.1 Hz), 7.51 (4H, broad), 1.49 (36H, s); ¹³C NMR: (75 MHz, CDCl₃): δ (ppm): 143.3, 142.6, 139.0, 137.4, 135.2, 126.0, 123.9, 123.8, 116.5, 109.4, 34.9, 32.1; ESI: Calculated mass: C₂₆H₃₁O₂NB: 400.24424 m/z, Exact mass: C₂₆H₃₁O₂NB: 400.24359 m/z.

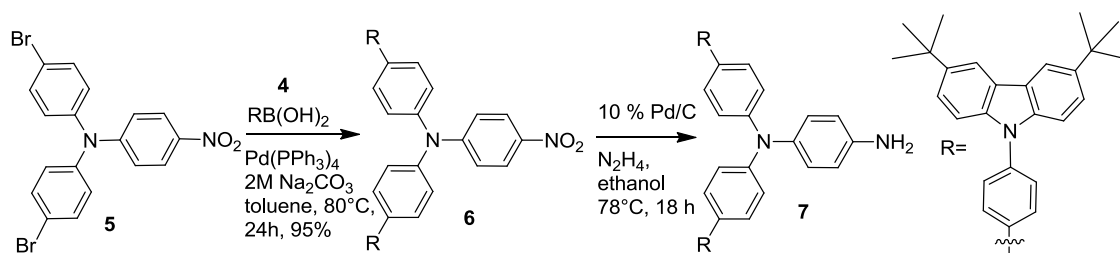


Figure A.2. Synthetic pathway to tBu carbazole phenyl amine (7).

Synthesis of 4'-((3,6-di-*tert*-butyl-9H-carbazol-9-yl)-N-(4'-((3,6-di-*tert*-butyl-9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-N-(4-nitrophenyl)-[1,1'-biphenyl]-4-amine (6):

In a schlenk tube 4-bromo-N-(4-bromophenyl)-N-(4-nitrophenyl) aniline (5) (0.45 g, 1 mmols) and tetrakis(triphenylphosphine) palladium(0) (58 mg, 0.05 mmol) were dissolved in toluene (20 mL). The flask was purged using argon and stirred at room temperature for 20 min. Afterwards, an aqueous solution of Na₂CO₃ (1 mL, 2 molL⁻¹) and 4-*tert*-butyl carbazole phenyl boronic acid (4) (0.89 g, 2.2 mmol) dissolved in methanol (1 mL) was added. The mixture was purged of oxygen and stirred at 90 °C under argon for 24 h. The compound was then washed with NaNH₄ aqueous solution (3 x 20 mL), extracted with toluene (3 x 20 mL), and dried with MgSO₄ to yield a brown oil. The compound was then purified by column chromatography with a solvent system of 1:1 dichloromethane to petroleum ether to yield a bright orange-yellow crystal in 95 % yield. ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.15 (4H, s), 7.81 (4H, d, J = 8.7 Hz), 7.72 (4H, d, J = 8.7 Hz), 7.66 (4H, d, J = 8.7 Hz), 7.49 (4H, d, J = 8.7 Hz), 7.41 (4H, d, J = 8.7 Hz), 7.36 (2H, d, J = 8.7 Hz), 7.13 (2H, d, J = 8.7 Hz).

Synthesis of N1,N1-bis(4'-((3,6-di-*tert*-butyl-9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)benzene-1,4-diamine (7):

Compound (**6**) (0.87 g, 0.87 mmol), 10 % Pd on charcoal (0.2 g) and ethanol (100 mL) was brought to a reflux. A 65 % solution of hydrazine monohydrate (0.87 g, 17 mmol) was added the solution dropwise and refluxed for 8 h, until a color change (from yellow to colorless) was observed indicating completion of the reaction. Many attempts to purify and isolate this compound was done with no success, a second method of synthesis was then employed.

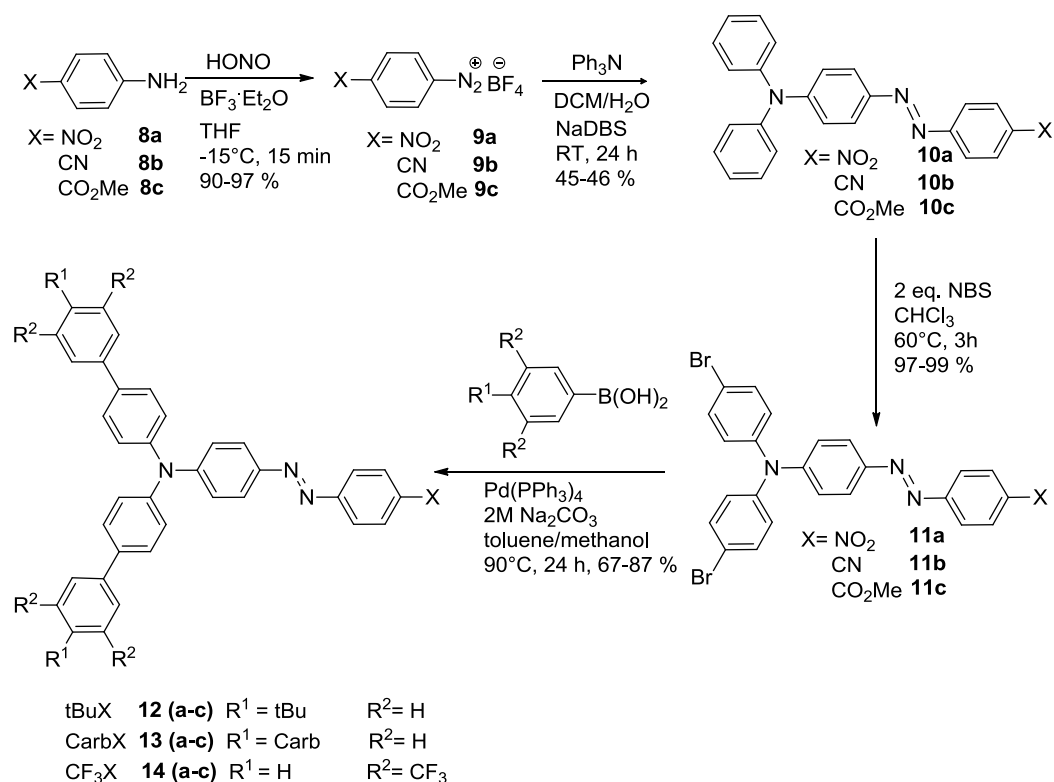


Figure A.3. Synthetic pathway for the formation of a series of push-pull azo dyes (12-14 a-c).

Synthesis of 4-nitrophenyldiazonium tetrafluoroborate salt (**9a**):

In a three neck 250 mL rounded bottom flask boron trifluoride diethyl etherate (9.3 g, 0.07 mol) was cooled to -5 °C. Nitroaniline (6.0 g, 0.04 mol) was dissolved in dry THF (20 mL) and added to the solution. The solution was stirred for an additional 10 minutes before isopentyl nitrite (6.7 g, 0.06 mol) was added dropwise. The mixture was stirred for 15 min before the solution was warmed up to room temperature and pentanes were added to the solution and the cream precipitate was filtered off (97 %). ¹H NMR (300 MHz, D₂O): δ (ppm): 8.89 (2H, d, J = 9.5 Hz), 8.73 (2H, d, J = 9.5 Hz).

Synthesis of 4-cyanophenyldiazonium tetrafluoroborate salt (9b):

Adapted procedure of (9a) to yield a pale yellow powder (95 %). ^1H NMR (300 MHz, D_2O): δ (ppm): 8.53 (2H, d, $J=9$ Hz), 7.90 (2H, d, $J=9$ Hz)

Synthesis of 4-methylesterphenyldiazonium tetrafluoroborate salt (9c):

Adapted procedure of (9a) to yield a pale yellow powder (90 %). ^1H NMR (300 MHz, D_2O): δ (ppm): 8.68 (2H, d, $J=9$ Hz), 8.46 (2H, d, $J=9$ Hz), 3.99 (3H, s).

Synthesis of 4-(N-phenylamino)-4'-nitroazobenzene (10a):

4-nitrophenyldiazonium tetrafluoroborate salt (6.33 g, 0.028 mol) was dissolved in water (100 mL) and stirred. Triphenylamine (6 g, 0.025 mol) and sodium dodecylbenzene sulfonate (1.27 g, 3.7 mmol) were dissolved in dichloromethane (100 mL) and added to the solution. The biphasic mixture was stirred for 24 h. The compound was worked up using brine solution and extracted using dichloromethane. The organic solution was dried over MgSO_4 and purified by column chromatography by eluting the compound with a solvent system of 1:9 dichloromethane to petroleum ether. The polarity of the solution was slowly increased to 4:6 dichloromethane to petroleum ether. Precipitation of the compound was performed with hexanes; and the precipitate was collected through filtration yielding 4.5 g (46 %) of a dark red crystal. ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.34 (2H, d, $J = 9$ Hz), 7.95 (2H, dt, $J = 9$ Hz), 7.83 (2H, dt, $J = 9$ Hz), 7.35 (2H, d, $J = 8.1$ Hz), 7.33 (2H, d, $J = 8.1$ Hz), 7.19 (d, 4H, $J = 7.3$ Hz), 7.16 (t, 2H, $J = 7.3$ Hz), 7.08 (2H, dt, $J = 9$ Hz); ^{13}C NMR: (75 MHz, CDCl_3): δ : (ppm): 156.5, 152.1, 148.2, 146.9, 146.6, 129.8, 126.2, 125.3, 124.8, 123.0, 120.0; MALDI-HRMS [M^+]: Calculated mass: 395.1503 m/z, Exact mass: $\text{C}_{24}\text{H}_{18}\text{N}_4\text{O}_2$: 395.1493 m/z.

Synthesis of 4-(N-phenylamino)-4'-cyanoazobenzene (10b):

Adapted procedure of (10a) yielded an orange powder (45 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 7.92 (2H, d, $J = 8.7$ Hz), 7.82 (2H, d, $J = 9$ Hz), 7.77 (2H, d, $J = 8.7$ Hz), 7.35 (2H, d, $J = 8.1$ Hz), 7.33 (2H, d, $J = 8.1$ Hz), 7.19 (4H, d, $J = 7.5$ Hz), 7.16

(2H, t, $J = 7.5$ Hz), 7.09 (2H, d, $J = 9$ Hz). ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 155.2, 151.9, 146.8, 146.6, 133.2, 129.8, 126.1, 125.1, 124.9, 123.1, 120.8, 118.9, 112.9. MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{25}\text{H}_{18}\text{N}_4$: 375.1604 m/z, Exact mass: $\text{C}_{25}\text{H}_{18}\text{N}_4$: 375.1613 m/z.

Synthesis of 4-(N-phenylamino)-4'-methylesterazobenzene (10c):

Adapted procedure of (10a) yielded an orange powder (45 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.15 (2H, d, $J = 8.4$ Hz), 7.88 (2H, d, $J = 8.4$ Hz), 7.82 (2H, d, $J = 9$ Hz), 7.34 (4H, t, $J = 7.8$), 7.31 (4H, t, $J = 7.8$), 7.18 (4H, d, $J = 7.8$ Hz), 7.13 (2H, t, $J = 7.8$ Hz) 7.10 (2H, d, $J = 9$ Hz), 3.94 (3H, s); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 166.7, 155.4, 151.6, 146.8, 146.6, 130.5, 129.6, 125.8, 124.8, 124.5, 122.2, 120.9, 118.9, 52.2; MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_2$: 408.1707 m/z, Exact mass: $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_2$: 408.1707 m/z.

Synthesis of 4-[N-di(4-bromo)phenylamino]-4'-nitroazobenzene (11a):

4-(N-phenylamino)-4'-nitroazobenzene (3.6 g, 7 mmol) and N-bromosuccinimide (2.6 g, 14 mmol) were dissolved in chloroform (100 mL) and refluxed for 4 hours. The solvent was evaporated and the solid was collected by filtration and rinse thoroughly with warm water to remove any excess N-bromosuccinimide. The compound was then dried yielding 4.8 g of a dark purple crystal (97 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.35 (2H, d, $J = 9$ Hz), 7.97 (2H, d, $J = 9$ Hz), 7.85 (2H, d, $J = 9$ Hz), 7.44 (4H, d, $J = 9$ Hz), 7.10 (2H, d, $J = 9$ Hz), 7.04 (4H, d, $J = 9$ Hz); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 156.3, 151.0, 148.4, 147.6, 145.4, 133.0, 127.2, 125.3, 124.9, 123.2, 121.7, 117.9; MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{24}\text{H}_{17}\text{Br}_2\text{N}_4\text{O}_2$: 550.97101 m/z, Exact mass: $\text{C}_{24}\text{H}_{17}\text{Br}_2\text{N}_4\text{O}_2$: 550.97128 m/z.

Synthesis of 4-[N-di(4-bromo)phenylamino]-4'-cyanoazobenzene (11b):

Adapted procedure of (11a) to yield a red powder (98 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 7.93 (2H, d, $J = 8.7$ Hz), 7.84 (2H, d, $J = 8.7$ Hz), 7.78 (2H, d, $J = 8.7$ Hz), 7.44 (4H, d, $J = 8.7$ Hz), 7.10 (2H, d, $J = 8.7$ Hz), 7.03 (4H, d, $J = 8.7$ Hz); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 155.0, 150.8, 147.5, 145.5, 133.3, 133.0, 127.1, 125.1, 123.2, 121.8, 118.7, 117.8, 113.3; MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{25}\text{H}_{17}\text{Br}_2\text{N}_4$: 530.98145 m/z, Exact mass: $\text{C}_{25}\text{H}_{17}\text{Br}_2\text{N}_4$: 530.98047 m/z.

Synthesis of 4-[N-di(4-bromo)phenylamino]-4'-methylesterazobenzene (11c):

Adapted procedure of (11a) to yield a red powder (99 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.15 (2H, d, $J = 8.1$ Hz), 7.89 (2H, d, $J = 8.1$ Hz), 7.83 (2H, d, $J = 8.1$ Hz), 7.42 (4H, d, $J = 8.1$ Hz), 7.09 (2H, d, $J = 8.1$ Hz), 7.02 (4H, d, $J = 8.1$ Hz), 3.94 (3H, s); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 166.7, 155.5, 150.3, 147.8, 145.6, 132.9, 131.3, 130.7, 126.9, 124.9, 122.5, 122.1, 117.4, 52.4; MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{26}\text{H}_{19}\text{Br}_2\text{N}_3\text{O}_2$: 563.9917 m/z, Exact mass: $\text{C}_{26}\text{H}_{19}\text{Br}_2\text{N}_3\text{O}_2$: 563.9917 m/z.

Synthesis of 4-[bis(4'-*tert*-butylbiphenyl-4-yl)amino]-4'-nitroazobenzene (12a):

Compound (11a) (200 mg, 0.35 mmol), tetrakis(triphenylphosphine) palladium(0) (20 mg, 0.02 mmol), and toluene (10 mL) were combined in a 100 mL Schlenk tube. The flask was purged using argon and stirred at room temperature for 20 min. Afterwards, an aqueous solution of Na_2CO_3 (1 mL, 2 mol.L $^{-1}$) and *tert*-butylphenylboronic acid (200 mg, 0.78 mmol) dissolved in methanol (1 mL) was added. Argon was used to purge the mixture as it stirred for 18 h at 90 °C. The compound was then washed with 2 mol L $^{-1}$ Na_2CO_3 aqueous solution (3 x 20 mL) and extracted with toluene. The organic layers were dried over the anhydrous Na_2SO_4 and concentrated under reduced pressure. The compound was then purified by flash column chromatography on silica gel (6:4 petroleum ether: CH_2Cl_2) and yielded a dark violet powder. The product was subsequently recrystallized from a CHCl_3 /acetonitrile mixture to give a 73 % yield. ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.36 (2H, d, $J = 9$ Hz), 8.00 (2H, d, $J = 9$ Hz), 7.92 (2H, d, $J = 9$ Hz), 7.58 (4H, d, $J = 8.4$ Hz), 7.55 (4H, d, $J = 8.4$ Hz), 7.48 (4H, d, $J = 8.4$), 7.29 (4H, d, $J = 8.4$ Hz), 7.20 (2H, d, $J = 9$ Hz), 1.37 (18H, s); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 156.5, 151.8, 148.2, 147.2, 145.7, 140.4, 137.8, 128.4, 127.4, 127.0, 126.2, 125.3, 124.9, 123.2, 121.3, 34.8, 31.7; $T_g = 118$ °C; UV-vis (toluene, *E*-isomer): λ_{max} (ϵ) = 499 (27077 mol $^{-1}$ Lcm $^{-1}$); MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{46}\text{H}_{45}\text{N}_3\text{O}$: 659.3381 m/z, Exact mass: $\text{C}_{46}\text{H}_{45}\text{N}_3\text{O}$: 659.3366 m/z.

Synthesis of 4-[bis(4'-*tert*-butylbiphenyl-4-yl)amino]-4'-cyanoazobenzene (12b):

Adapted procedure of **(12a)** to yield a red powder (76 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 7.94 (2H, d, $J = 8.7$ Hz), 7.87 (2H, d, $J = 8.7$ Hz), 7.79 (2H, d, $J = 8.4$ Hz), 7.58 (4H, d, $J = 8.1$ Hz), 7.55 (4H, d, $J = 8.4$ Hz), 7.48 (4H, d, $J = 8.4$ Hz), 7.28 (4H, d, $J = 8.1$ Hz), 7.21 (2H, d, $J = 8.4$ Hz), 1.37 (18H, s); ^{13}C NMR (75 MHz, CDCl_3), δ (ppm): 155.1, 151.5, 150.3, 147.0, 145.2, 137.4, 133.1, 128.1, 126.5, 126.0, 125.8, 125.1, 123.0, 121.1, 118.8, 112.9, 77.34, 34.6, 31.4; $T_g = 121$ °C; UV-vis (toluene, *E*-isomer): λ_{max} (ϵ) = 479 (27474 $\text{mol}^{-1}\text{Lcm}^{-1}$); MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{46}\text{H}_{45}\text{N}_3\text{O}$: 659.3381 m/z, Exact mass: $\text{C}_{46}\text{H}_{45}\text{N}_3\text{O}$: 659.3366 m/z.

Synthesis of 4-[bis(4'-*tert*-butylbiphenyl-4-yl)amino]-4'-methyl ester azobenzene (12c):

Adapted procedure of **(12a)** to yield a red powder (73 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.17 (2H, d, $J = 8.7$ Hz), 7.93 (2H, d, $J = 8.7$ Hz), 7.91 (2H, d, $J = 6.6$ Hz), 7.57 (4H, d, $J = 8.4$ Hz), 7.54 (4H, d, $J = 6.6$ Hz), 7.47 (4H, d, $J = 8.4$), 7.27 (4H, d, $J = 9$ Hz), 7.21 (2H, d, $J = 8.7$ Hz), 3.95 (3H, t), 1.37 (18H, s); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 166.7, 155.5, 150.6, 148.2, 145.8, 137.8, 137.6, 132.9, 131.3, 130.9, 128.4, 126.8, 126.2, 125.4, 124.9, 122.6, 121.8, 52.6, 34.8, 31.7; $T_g = 89$ °C; UV-vis (toluene, *E*-isomer): λ_{max} (ϵ) = 468 (27474 $\text{mol}^{-1}\text{Lcm}^{-1}$); MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{46}\text{H}_{45}\text{N}_3\text{O}$: 672.3585 m/z, Exact mass: $\text{C}_{46}\text{H}_{45}\text{N}_3\text{O}$: 672.3572 m/z.

Synthesis of 4-[bis(4'-*tert*-butyl carbazole biphenyl-4-yl)amino]-4'-nitro azobenzene (13a) :

Adapted procedure of **(12a)** yielding a dark red powder (67 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.37 (2H, d, $J = 8.7$ Hz), 8.16 (4H, s), 8.03 (2H, d, $J = 8.7$), 7.98 (2H, d, $J = 8.1$ Hz), 7.83 (4H, d, $J = 8.4$ Hz), 7.72 (4H, d, $J = 8.4$ Hz), 7.66 (4H, d, $J = 8.4$ Hz), 7.49 (4H, dd, $J = 8.7$ Hz), 7.42 (4H, d, $J = 9$ Hz), 7.39 (4H, d, $J = 8.7$ Hz), 1.48 (36H, s); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 156.4, 151.7, 148.3, 147.4, 146.0, 143.1, 139.3, 138.9, 137.6, 136.8, 128.4, 128.2, 127.1, 126.3, 125.4, 124.9, 123.8, 123.6, 123.2, 121.7, 116.4, 109.4, 34.9, 32.1; $T_g = 199$ °C; UV-vis (toluene, *E*-isomer): λ_{max} (ϵ) = 493 (30517 $\text{mol}^{-1}\text{Lcm}^{-1}$); MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{76}\text{H}_{72}\text{N}_6\text{O}_2$: 1101.5790 m/z, Exact mass: $\text{C}_{76}\text{H}_{72}\text{N}_6\text{O}_2$: 1101.5793 m/z.

Synthesis of 4-[bis(4'-*tert*-butyl carbazole biphenyl-4-yl)amino]-4'-cyano azobenzene (13b) :

Adapted procedure of (12a) yielding an orange powder (70 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.17 (4H, s), 7.96 (2H, d, $J = 12$ Hz), 7.93 (2H, d, $J = 12$ Hz), 7.83 (2H, d, $J = 9$ Hz), 7.80 (4H, d, $J = 6$ Hz), 7.71 (4H, d, $J = 9$ Hz), 7.66 (4H, d, $J = 9$ Hz), 7.50 (4H, dd, $J = 9$ Hz), 7.43 (4H, d, $J = 9$ Hz), 7.38 (4H, d, $J = 9$ Hz), 7.29 (2H, d, $J = 9$ Hz), 1.48 (36H, s); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 155.0, 151.4, 146.1, 143.2, 139.4, 139.0, 137.6, 136.8, 133.4, 128.5, 128.3, 127.2, 126.3, 125.3, 123.9, 123.7, 123.3, 121.9, 116.5, 109.5, 34.9, 31.1; $T_g = 201$ °C; UV-vis (toluene, *E*-isomer): λ_{max} (ϵ) = 473 (29388 $\text{mol}^{-1}\text{Lcm}^{-1}$); MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{77}\text{H}_{72}\text{N}_6$: 1081.5891 m/z, Exact mass: $\text{C}_{77}\text{H}_{72}\text{N}_6$: 1081.5931 m/z.

Synthesis of 4-[bis(4'-*tert*-butyl carbazole biphenyl-4-yl)amino]-4'-methyl ester azobenzene (13c):

Adapted procedure of (12a) yielding an orange powder (40 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.21 (2H, multiplet), 8.18 (4H, s), 7.94 (2H, d, $J = 8.4$ Hz), 7.94 (2H, d, $J = 9$ Hz), 7.83 (4H, d, $J = 8.4$ Hz), 7.70 (4H, d, $J = 8.7$ Hz), 7.65 (4H, d, $J = 8.4$ Hz), 7.50 (4H, dd, $J = 8.4$ Hz), 7.44 (4H, d, $J = 8.7$ Hz), 7.37 (4H, d, $J = 8.4$ Hz), 7.30 (2H, d, $J = 9\text{Hz}$); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 166.8, 155.7, 151.0, 147.6, 146.2, 143.1, 139.3, 138.9, 137.5, 136.4, 131.2, 130.8, 128.3, 128.2, 127.1, 126.0, 125.0, 123.8, 123.6, 122.5, 122.2, 116.4, 109.4, 52.4, 34.9, 31.1; $T_g = 187$ °C; UV-vis (toluene, *E*-isomer): λ_{max} (ϵ) = 461 (28447 $\text{mol}^{-1}\text{Lcm}^{-1}$); MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{78}\text{H}_{75}\text{N}_5\text{O}_2$: 1114.5994 m/z, Exact mass: $\text{C}_{78}\text{H}_{75}\text{N}_5\text{O}_2$: 1114.5973 m/z.

Synthesis of 4-[N-di(3',5'- bis(trifluoromethyl) biphenyl)amino]-4'-nitro azobenzene (14a):

Adapted procedure of (12a) yielding a red powder (85 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.38 (2H, d, $J = 9$ Hz), 8.02 (4H, s), 8.01 (2H, d, $J = 9$ Hz), 7.94 (2H, d, $J = 9\text{Hz}$), 7.86 (2H, s), 7.61 (4H, d, $J = 9$ Hz), 7.35 (4H, d, $J = 9$ Hz), 7.27 (2H, d, $J = 9$ Hz); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 150.8, 148.5, 148.2, 147.2, 142.5, 134.5, 132.6, 132.2, 128.8, 127.0, 126.1, 125.4, 124.9, 123.3, 122.67, 121.3, 121.0; T_g

= 70 °C; UV-vis (toluene, *E*-isomer): $\lambda_{\max} (\epsilon) = 466$ (243627 mol⁻¹Lcm⁻¹); MALDI-HRMS [M⁺]: Calculated mass: C₄₀H₂₂F₁₂N₄O₂: 819.1624 m/z, Exact mass: C₄₀H₂₂F₁₂N₄O₂: 819.1629 m/z.

Synthesis of 4-[N-di(3',5'- bis(trifluoromethyl)biphenyl)amino]-4'-cyanoazobenzene (14b):

Adapted procedure of (12a) yielding an orange powder (87 %). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.02 (4H, s), 7.96 (2H, d, J = 9 Hz), 7.92 (2H, d, J = 9 Hz), 7.86 (2H, s), 7.80 (2H, d, J = 9 Hz), 7.61 (4H, d, J = 9 Hz), 7.34 (4H, d, J = 9 Hz), 7.26 (2H, d, J = 9 Hz); ¹³C NMR: (75 MHz, CDCl₃): δ (ppm): 155.0, 150.7, 148.0, 147.2, 142.5, 134.4, 133.0, 132.6, 132.2, 128.7, 127.0, 126.0, 125.2, 123.3, 121.7, 121.0, 118.8, 113.5; *T_g* = 70 °C; UV-vis (toluene, *E*-isomer): $\lambda_{\max} (\epsilon) = 452$ (27053 mol⁻¹Lcm⁻¹); MALDI-HRMS [M⁺]: Calculated mass: C₄₁H₂₂F₁₂N₄: 799.1726 m/z, Exact mass: C₄₁H₂₂F₁₂N₄: 799.1749 m/z.

Synthesis of 4-[N-di(3',5'- bis(trifluoromethyl)biphenyl)amino]-4'-methyl ester azobenzene (14c):

Adapted procedure of (12a) yielding an orange powder (86 %). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.16 (2H, d, J = 8.7 Hz), 8.09 (4H, s), 7.91 (2H, d, J = 8.7 Hz), 7.90 (2H, d, J = 8.7 Hz), 7.83 (2H, s), 7.57 (4H, d, J = 8.7 Hz), 7.31 (4H, d, 8.7 Hz), 7.22 (2H, d, J = 8.7 Hz), 3.94 (3H, s); ¹³C NMR: (75 MHz, CDCl₃): δ (ppm): 166.8, 155.6, 150.3, 148.4, 147.5, 142.6, 134.2, 133.1, 132.7, 131.8, 128.8, 127.0, 125.6, 125.1, 123.3, 122.7, 121.8, 121.0, 52.5; *T_g* = 80 °C; UV-vis (toluene, *E*-isomer): $\lambda_{\max} (\epsilon) = 444$ (23900 mol⁻¹Lcm⁻¹); MALDI-HRMS [M⁺]: Calculated mass: C₄₂H₂₅F₁₂N₃O₂: 832.1828 m/z, Exact mass: C₄₂H₂₅F₁₂N₃O₂: 832.1794 m/z.

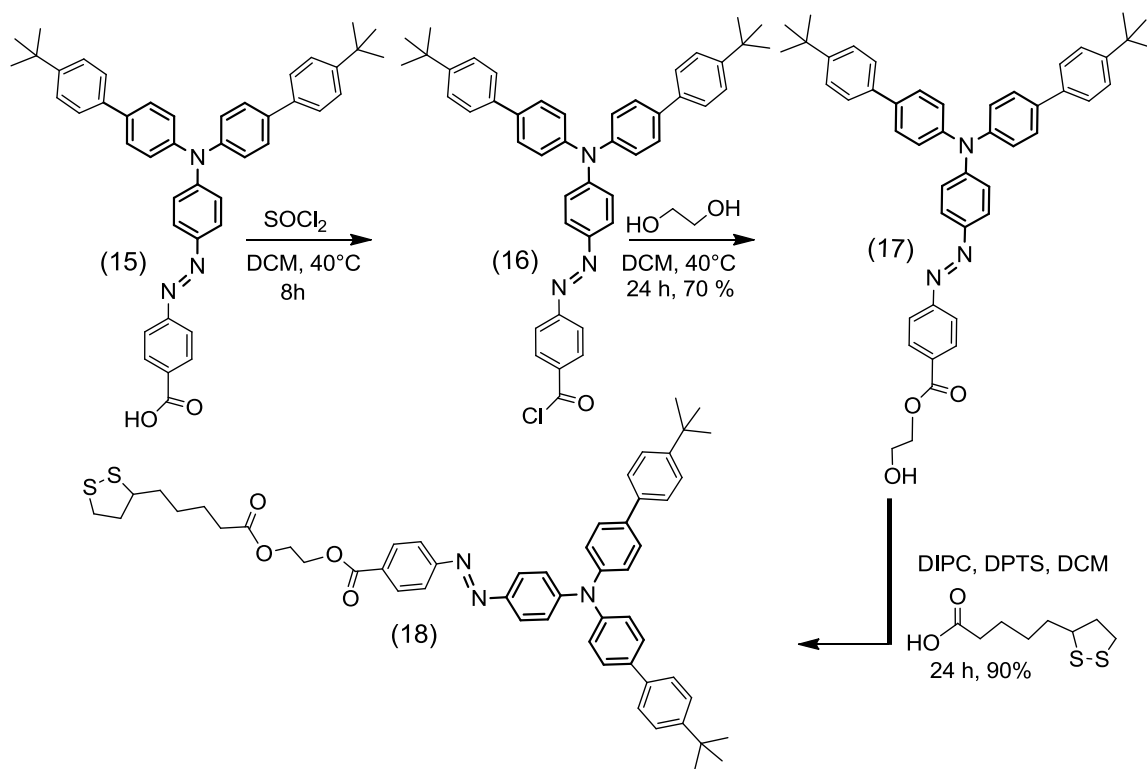


Figure A.4. Synthetic pathway to azo-S₂ (18).

Synthesis of 4-[bis(4'-*tert*-butylbiphenyl-4-yl)amino]-4'-carboxylic acid azobenzene (15):

Compound (12c) (0.5 g, 0.74 mmol) was dissolved in dry THF (20 mL) and stirred. To this solution 3M potassium hydroxide (10 mL) was added and the solution was refluxed overnight. 12 mol L⁻¹ HCl was then added dropwise until the pH of the solution was neutral. The solution was then extracted with ethyl acetate (3 x 30 mL) and the solvent was reduced under pressure. The product was rinsed with petroleum ether and the red crystals were collected by filtration (97 %). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.51 (2H, d, J = 9 Hz), 8.35 (2H, d, J = 9 Hz), 8.18 (2H, d, J = 8.7 Hz), 7.67 (4H, d, J = 8.4 Hz), 7.55 (4H, d, J = 8.7 Hz), 7.50 (4H, d, J = 8.7 Hz), 7.34 (4H, d, J = 8.4 Hz), 7.15 (2H, d, J = 8.7 Hz), 1.37 (18H, s); ¹³C NMR: (75 MHz, CDCl₃): δ (ppm): 170.2, 155.5, 150.6, 148.2, 145.7, 137.6, 137.3, 131.1, 128.2, 126.6, 125.9, 125.0, 122.5, 121.6, 34.68, 31.5; MS-ES: Calculated mass: C₄₇H₄₇N₃O₃: 656.3277 m/z, Exact mass: C₄₇H₄₇N₃O₃: 656.3270 m/z.

Synthesis of (*E*)-4-((4-(bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)amino)phenyl)diazenyl) benzoyl chloride (16**):**

The azo acid (**15**) (0.17 g, 0.3 mmol) was dissolved in dry dichloromethane (10 mL). The solution was purged with argon and thionyl chloride (4.9 mg, 0.5 mmol) was added dropwise, which immediately let the orange solution turn dark violet. After heating under reflux for 4 h, the excess thionyl chloride was removed under pressure, and compound (**16**) was used neat in the next reaction. ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.41 (2H, d, $J = 9$ Hz), 8.25 (4H, multiplet), 7.67 (4H, d, $J = 8.1$ Hz), 7.56 (4H, d, $J = 8.4$ Hz), 7.50 (4H, d, $J = 8.4$ Hz), 7.34 (4H, d, $J = 8.4$ Hz), 7.18 (2H, d, $J = 9$ Hz), 1.37 (18H, s).

Synthesis of (*E*)-2-hydroxyethyl-4-((4-(bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)amino)phenyl)diazenyl) benzoate (17**):**

A solution of compound (**16**) (0.3 g, 0.51 mmol) and ethylene glycol (10 g, 0.154 mol) in anhydrous CH_2Cl_2 (5 mL) was refluxed under argon for 18 h. After addition of water and extraction with CH_2Cl_2 , the organic layer was dried over anhydrous Na_2SO_4 . The solvent was removed under reduced pressure and the resulting solid was purified by flash column chromatography on silica gel using as an eluent the mixture petroleum ether: CH_2Cl_2 4:6. Compound (**17**) was obtained as a bright red powder (56 %). ^1H NMR (300 MHz, CDCl_3): δ (ppm): 8.19 (2H, d, $J = 8.7$ Hz), 7.94, (2H, d, $J = 8.4$ Hz), 7.91 (2H, d, $J = 8.7$ Hz), 7.56 (4H, d, $J = 8.1$ Hz), 7.53 (4H, d, $J = 8.1$ Hz), 7.48 (4H, d, $J = 8.4$ Hz), 7.28 (4H, d, $J = 7.5$ Hz), 7.21 (2H, d, $J = 8.7$ Hz), 4.51 (2H, t, $J = 4.5$ Hz), 3.99 (2H, t, $J = 4.2$ Hz), 1.37 (18H, s); ^{13}C NMR: (75 MHz, CDCl_3): δ (ppm): 166.7, 156.0, 151.3, 150.9, 150.4, 147.3, 145.7, 145.6, 137.6, 137.3, 130.9, 128.2, 127.2, 126.3, 124.9, 122.5, 121.6, 67.3, 61.8, 34.9, 31.4; MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{47}\text{H}_{47}\text{N}_3\text{O}_3$: 702.3690 m/z, Exact mass: $\text{C}_{47}\text{H}_{47}\text{N}_3\text{O}_3$: 702.3682 m/z.

Synthesis of (*E*)-2-((6-(1,2-dithiolan-3-yl)hexanoyl)oxy)ethyl-4-((4-(bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)amino)phenyl)diazenyl)benzoate (azoS₂) (18**):**

Compound (**17**) (0.2 g, 0.3 mmol), lipoic acid (0.07 g, 0.3 mmol), and dimethylaminopyridinium *p*-toluenesulfonate (DPTS) (0.04 g, 0.14 mmol) were

dissolved in anhydrous dichloromethane (25 mL), and the resulting solution cooled to 0 °C using an ice bath. Diisopropylcarboxydiimide (DIPC) (0.07 g, 0.56 mmol) was added dropwise and the solution color darkened. The solution was then slowly warmed up to room temperature, and stirred for an additional 2 days. After solvent removal under reduced pressure, the crude product was purified by flash column chromatography on silica gel using CH₂Cl₂ as an eluent. Compound (**18**) was obtained as a bright red powder (90 %). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.17 (2H, d, J = 8.7 Hz), 7.93 (2H, d, J = 8.7 Hz), 7.90 (2H, d, J = 8.7 Hz), 7.56 (4H, d, J = 8.1 Hz), 7.53 (4H, d, J = 8.1 Hz), 7.49 (4H, d, J = 8.7 Hz), 7.28 (4H, d, J = 8.4 Hz), 7.21 (2H, d, J = 8.7 Hz), 4.55 (2H, multiplet), 4.45 (2H, multiplet), 3.53 (1H, multiplet), 3.12 (2H, multiplet), 2.35 (3H, multiplet), 1.87 (1H, multiplet), 1.66 (4H, multiplet), 1.47 (2H, multiplet), 1.37 (18H, s). ¹³C NMR: (75 MHz, CDCl₃): δ (ppm): 173.4, 166.7, 156.0, 151.3, 150.4, 147.3, 145.7, 145.6, 137.6, 137.4, 130.9, 128.2, 126.6, 126.0, 125.0, 122.5, 121.6, 62.2, 61.7, 56.5, 40.9, 38.6, 34.7, 34.0, 31.5, 31.0, 28.9, 24.8; *T*_g = 63 °C; UV-vis (toluene, *E*-isomer): λ_{max} (ϵ) = 471 nm (27000 mol⁻¹ Lcm⁻¹); MALDI-HRMS [*M*⁺]: Calculated mass: C₅₆H₆₁N₃O₄S₂: 890.4020 m/z, Exact mass: C₅₆H₆₁N₃O₂S₂: 890.3980 m/z.

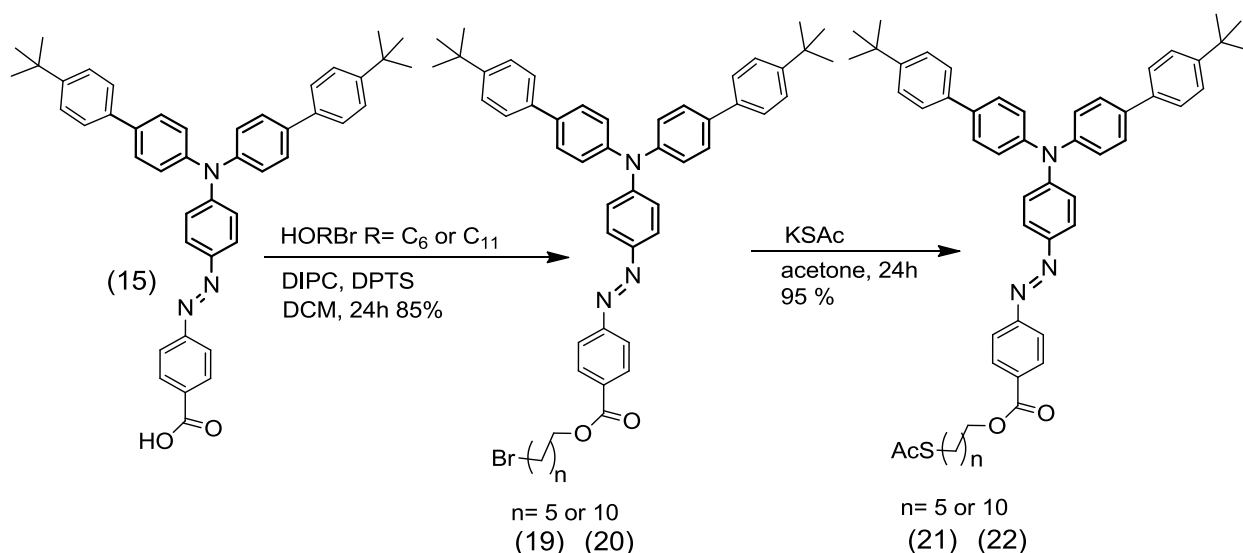


Figure A.5. Synthetic pathway toward azo6-SAc (**21**) and azo11-SAc (**22**).

Synthesis of (*E*)-6-bromohexyl 4-((4-(bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)amino) phenyl) diazenyl) benzoate (19):

Compound (15) (0.4 g, 0.6 mmol), 6-bromohexan-1-ol (0.13 g, 0.7 mmol), and dimethylaminopyridinium *p*-toluenesulfonate (0.08 g, 0.3 mmol) were dissolved in anhydrous dichloromethane (25 mL) and the resulting solution cooled at 0 °C using an ice bath. Diisopropylcarboxidiimide (0.15 g, 1.2 mmol) was added dropwise and the solution color darkened. The solution was then slowly warmed up to room temperature, and stirred for an additional 2 days. After solvent removal under reduced pressure, the crude product was purified by flash column chromatography on silica gel using CH₂Cl₂ as an eluent. Compound (19) was obtained as a bright red powder (85 %). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.17 (2H, d, *J* = 8.5 Hz), 7.91 (2H, d, *J* = 8.8 Hz), 7.88 (2H, d, *J* = 9.1 Hz), 7.57 (4H, d, *J* = 8.5 Hz), 7.54 (4H, d, *J* = 8.3 Hz), 7.48 (4H, d, *J* = 8.4 Hz), 7.27 (4H, d, *J* = 8.7 Hz), 7.22 (2H, d, *J* = 8.9 Hz), 4.35 (2H, t, *J* = 6.6 Hz), 3.43 (2H, t, *J* = 6.6 Hz), 1.93 (2H, tt, *J* = 6.5 Hz, *J* = 7.0 Hz), 1.84 (2H, tt, *J* = 6.5 Hz, *J* = 7.0 Hz), 1.47 (4H, multiplet), 1.37 (18H, s); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 166.4, 155.8, 151.2, 150.4, 147.3, 145.7, 137.6, 137.2, 131.5, 130.7, 128.2, 126.6, 125.9, 124.9, 122.4, 121.6, 61.3, 34.7, 33.8, 32.8, 31.5, 28.7, 28.0, 25.4; MALDI-HRMS [*M*⁺]: Calculated mass: C₅₁H₅₄BrN₃O₂ 820.3472 *m/z*, Exact mass: C₅₁H₅₄BrN₃O₂: 820.3492 *m/z*.

Synthesis of (*E*)-11-bromoundecyl 4-((4-(bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)amino) phenyl) diazenyl) benzoate (20):

Same procedure as that described for compound (19) except that compound (15) (0.22 g, 0.3 mmol), 11-bromoundecan-1-ol (0.12 g, 0.4 mmol), dimethylaminopyridinium *p*-toluenesulfonate (0.05 g, 0.2 mmol) and diisopropylcarboxidiimide (0.08 g, 0.6 mmol) were used. Compound (20) was obtained as a bright red powder (82 %). ¹H NMR (300 MHz, CDCl₃): δ (ppm): 8.17 (2H, d, *J* = 8.7 Hz), 7.91 (2H, d, *J* = 8.7 Hz), 7.87 (2H, d, *J* = 9.3 Hz), 7.57 (4H, d, *J* = 4.8), 7.54 (4H, d, *J* = 4.8 Hz), 7.47 (4H, d, *J* = 8.7 Hz), 7.27 (4H, d, *J* = 8.7 Hz), 7.22 (2H, d, *J* = 9.0 Hz), 4.35 (2H, t, *J* = 6.6 Hz), 3.41 (2H, t, *J* = 6.6 Hz), 1.86 (2H, tt, *J* = 7.5 Hz, *J* = 7.0 Hz), 1.81 (2H, tt, *J* = 7.5 Hz, *J* = 7.0 Hz), 1.63 (2H, multiplet), 1.42 (4H, multiplet), 1.38 (18H, s), 1.30 (8H, multiplet); ¹³C NMR (75 MHz, CDCl₃): δ (ppm): 166.5, 155.8, 151.3, 150.5, 147.5, 145.8, 137.7, 137.4, 131.6, 130.8, 128.3, 126.7, 126.1, 125.0, 122.6, 121.8, 65.6, 34.8,

34.3, 33.1, 31.6, 29.7, 29.6, 29.0, 28.9, 28.5, 26.3, 26.2; MALDI-HRMS [M^+]: Calculated mass: $C_{56}H_{64}BrN_3O_2$: 890.4255 m/z, Exact mass: $C_{56}H_{64}BrN_3O_2$: 890.4275 m/z.

Synthesis of (*E*)-6-(acetylthio)hexyl 4-((4-(bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)amino)phenyl)diazenyl) benzoate (azo6-SAc) (21):

A solution of compound (**19**) (0.1 g, 0.1 mmol) and potassium thioacetate (0.014 g, 0.12 mmol) in acetone (50 mL) was stirred at room temperature for 18 h. The precipitated potassium bromide salt was filtered off and the solution was evaporated under reduced pressure. Recrystallization from acetonitrile (25 mL) yielding compound (**21**) as a pure red powder (95 %). 1H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.17 (2H, d, J = 8.7 Hz), 7.91 (2H, d, J = 8.7 Hz), 7.88 (2H, d, J = 9 Hz), 7.57 (4H, d, J = 4.5 Hz), 7.55 (4H, d, J = 4.5 Hz), 7.48 (4H, d, J = 8.4 Hz), 7.27 (4H, d, J = 8.4 Hz), 7.22 (2H, d, J = 9 Hz), 4.34 (2H, t, J = 6.6 Hz), 2.90 (2H, t, J = 7.2 Hz), 2.33 (3H, s), 1.80 (2H, q, J = 6.6 Hz), 1.60 (4H, multiplet), 1.47 (2H, multiplet), 1.38 (18H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm): 196.0, 166.6, 155.9, 151.4, 150.5, 147.5, 145.9, 137.8, 137.4, 131.6, 130.9, 128.3, 126.7, 126.1, 125.1, 122.6, 121.8, 65.4, 34.8, 31.6, 31.0, 29.8, 29.3, 28.9, 28.8, 25.9; T_g = 59 °C; UV-vis (toluene, *E*-isomer): λ_{max} (ϵ) = 467 nm (26000 mol $^{-1}$ Lcm $^{-1}$); MALDI-HRMS: Calculated mass: $C_{53}H_{57}N_3O_3S$: 816.4193 m/z, Exact mass: $C_{53}H_{57}N_3O_3S$: 816.4170 m/z.

Synthesis of (*E*)-11-(acetylthio)undecyl 4-((4-(bis(4'-(*tert*-butyl)-[1,1'-biphenyl]-4-yl)amino) phenyl)diazenyl) benzoate (azo11-SAc) (22):

Same procedure as that described for compound (**21**) except that compound (**20**) (0.1 g, 0.1 mmol) and potassium thioacetate (0.014 g, 0.12 mmol) were used. The KBr salt was filtered and the solution was evaporated. Recrystallization from acetonitrile (20 mL) yielding compound (**22**) as a pure red powder (90 %). 1H NMR (300 MHz, $CDCl_3$): δ (ppm): 8.16 (2H, d, J = 8.4 Hz), 7.92 (2H, d, J = 8.6 Hz), 7.88 (2H, d, J = 8.8 Hz), 7.64 (4H, d, J = 8.5 Hz), 7.57 (4H, d, J = 8.6 Hz), 7.54 (4H, d, J = 8.1 Hz), 7.46 (4H, d, J = 8.6 Hz), 7.27 (4H, d, J = 8.6 Hz), 7.21 (2H, d, J = 9 Hz), 4.34 (2H, t, J = 6.7 Hz), 2.86 (2H, t, J = 7.3 Hz), 2.31 (3H, s), 1.79 (2H, multiplet), 1.56 (6H, multiplet), 1.38 (18H, s), 1.28 (10H, multiplet); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm):

196.4, 166.6, 155.9, 151.4, 150.5, 147.5, 145.9, 137.8, 137.4, 131.7, 130.9, 128.3, 126.8, 126.1, 125.1, 122.6, 121.8, 65.7, 34.9, 31.7, 30.9, 29.8, 29.8, 29.6, 29.5, 29.4, 29.1, 29.0, 26.4; $T_g = 40\text{ }^{\circ}\text{C}$; UV-vis (toluene, *E*-isomer): $\lambda_{\text{max}} (\epsilon) = 467$ ($28000\text{ mol}^{-1}\text{Lcm}^{-1}$); MALDI-HRMS [M^+]: Calculated mass: $\text{C}_{58}\text{H}_{67}\text{N}_3\text{O}_3\text{S}$: 816.4193 m/z, Exact mass: $\text{C}_{58}\text{H}_{67}\text{N}_3\text{O}_3\text{S}$: 816.4170 m/z.

A.1.3 Fabrication of nanomaterial

Synthesis of citrate stabilized gold nanoparticles:

All glassware was first thoroughly clean with aqua regia solution ($\text{HCl} : \text{HNO}_3$ 3:1) and rinsed three times with Millipore water. A solution of sodium citrate (0.068 g, 0.27 mmol) in Millipore water (30 mL) was heated to reflux, and cooled to $90\text{ }^{\circ}\text{C}$. Then, a solution of chloroauric acid HAuCl_4 (0.033 g, 0.1 mmol) dissolved in Millipore water (0.2 mL) was quickly added. The mixture was vigorously stirred at 90°C where a color change occurred from yellow to colorless, and finally purple. After stirring for 10 min, the reaction mixture was cooled to room temperature and any excess citrate was removed using dialysis for 12 h against Millipore water (membrane MCWO: 6-8 kDa). The gold nanoparticles stored at $4\text{ }^{\circ}\text{C}$. TEM analyses provided a mean diameter of $15 \pm 3\text{ nm}$ while UV-vis absorption measurements indicate a LSPR band, peaking at 528 nm.

Synthesis of TOAB gold nanoparticles:

A solution of chloroauric acid (8 mg, 0.023 mmol) in Millipore water (2 mL) was added to a 50 mL rounded bottom flask. A solution of tetraoctylammonium bromide (81 mg, 0.15 mmol) in toluene (5 mL) was added to the aqueous solution and stirred for 20 min until all the gold salt was transferred to the organic phase. The solution was vigorously stirred at 0°C when a freshly prepared solution of sodium borohydride (8 mg, 0.2 mmol) in Millipore water (1 mL) was added quickly. From here the organic phase was washed with water (3 x 30 mL) and the $4.3 \pm 2\text{ nm}$ gold nanoparticles were characterized by UV-vis spectroscopy showing a SPR band at 538 nm.

Synthesis of azo monolayer protected gold nanoparticles (direct Brust Schiffrin):

After cleaning the glassware with aqua regia solution and then rinsing the glassware three times with Millipore water, solution of chloroauric acid (8 mg, 0.023 mmol) in Millipore water (2 mL) was added to a 50 mL rounded bottom flask. A solution of tetraoctylammonium bromide (81 mg, 0.15 mmol) in toluene (5 mL) was added to the aqueous solution and stirred for 20 min. until all the gold salt was transferred to the organic phase. The organic phase was collected and cooled to 0 °C. Dodecanethiol (10 mg, 0.05 mmol) was then added and the orange solution was stirred until it appeared colorless. The azo ligand (azoS₂/ azo6-SAc/ azo11-SAc) (10 mg, 0.01mol) was dissolved in toluene (5 mL) and eventually added to the colorless solution. The solution was vigorously stirred at 0 °C and a freshly prepared solution of sodium borohydride (8 mg, 0.2 mmol) in Millipore water (1 mL) was quickly added. The organic layer underwent a color change from red to black indicating the formation of gold nanoparticles with the size of 1.9 ± 0.4 nm. The biphasic mixture was stirred for an extra hour, before ethanol (30 mL) was added, and subsequently stored in the fridge overnight. After 12 h, the gold particles precipitated out of the mixture. The ethanol solution and free ligands were decanted and the particles were re-dissolved in toluene. Toluene was removed under vacuum pressure such that the functionalized gold nanoparticles formed a black film on the flask. Ethanol (20 mL) was again added to the black film and swirled, and the solution was removed to eliminate any additional free ligand. This process of dissolving the nanoparticles in toluene, evaporating toluene, and rinsing them with ethanol was continued until the nanoparticles were redeemed pure via NMR spectroscopy.

Synthesis of Organic Nanorods

Melt method:

10 mg of azo compound were placed onto a glass slide and heated to 80 °C. When the compound was melted, the alumina template ($\varnothing = 200$ nm) was placed on top of the compound and absorbed it through capillary forces. The template was cooled and diamond paper was used to buff away any excess compound on the surface of the template. The template was then placed in 3 mol L⁻¹ KOH (aq) (2 mL) and allowed to stir for 45 min. The template did not seem to dissolve, so it was left overnight (18 h).

The next day the template appeared to be less stiff but still remained intact, thus leaving a new method of synthesis to be desired.

Drop cast method of nanorods:

Acidic dissolution:

A 5 % wt. solution of azo compound dissolved in anisole was dropcast (2 drops) onto an alumina template ($\phi = 200$ nm). The template dried overnight and the excess compound on the surface of the template was buffed away using a cotton swab. The organic nanorods were then released from the template by placing the template in a $1 \text{ mol L}^{-1} \text{ H}_3\text{PO}_4$ solution (2 mL per template) and stirred with glass stirring rods for 24-48 hours. The solution was then diluted by adding ultrapure water (2 mL) and transferred to a dialysis bag (MWCO 6-8,000) and the water was changed every hour for 18 h. The nanorods were characterized using SEM and showed to be deformed upon acid washing.

Alkaline dissolution:

A 5 % wt. solution of azo compound dissolved in anisole was dropped casted (2 drops) onto an alumina template. The template was covered with a beaker and allowed to slowly dry overnight. Any excess compound on the surface of the template was buffed away using a cotton swab. The organic nanorods were released from the template by placing the template in a $3 \text{ mol L}^{-1} \text{ KOH}$ solution (2mL per template) and stirred with glass stirring rods for 24-48 hours. The solution was diluted by adding ultrapure water (2 mL) and dialyzed against water using a dialysis bag (MWCO 6-8,000). The solution was changed every hour for 18 hours. Here a drop of the solution was dispersed onto a silicon wafer and organic nanorods were characterized. The organic nanorods appeared to have a diameter of 200 nm and a length of 10 μm ranging up to 40 μm .

A.2 Thermal and Photophysical Characterizations

The glass transition temperatures were obtained using differential scanning calorimetry (DSC) (Maia 205 C – Netzsch) in alumina caps under a nitrogen flow at a

scan rate of $20\text{ }^{\circ}\text{C min}^{-1}$ over the temperature range $25\text{--}250\text{ }^{\circ}\text{C}$. The photophysical and photochromic studies of all dyes in solution or processed as thin films and nano-objects were performed using spectroscopic grade solvents. The UV-vis absorption spectra were recorded using a Varian Model Cary 5000 spectrophotometer. The photochromic studies were performed by irradiating a $3 - 5 \times 10^{-5}\text{ mol L}^{-1}$ solution in toluene, thin films or solutions of azo nanoparticles directly using a Hamamatsu UV Light Source Xe-Hg lamp equipped with a 488 nm interferential filter ($\sim 8\text{ mW. cm}^{-2}$)

A.3 Thin Film Preparation

The glass plates were cleaned by sonication in a 2 % alkaline solution for 30 min, and rinsed with Millipore water and ethanol before drying with argon. The organic materials were spin-coated on to the glass substrate using a concentrated solution of the compound in chloroform (4 % wt.) at a spin acceleration of 500 rpm.min^{-1} and a speed of 1000 rpm for 2 minutes. The thin films were allowed to dry in the atmosphere for 24 hours.

A.4 Surface Relief Grating Setup

Surface relief gratings (SRGs) were formed on the spin-coated thin films with a two-arm interferometer that generates an interferometer pattern. The argon-ion laser ($\lambda = 488\text{ nm}$) was polarized using a $\lambda/2$ wave plate and then passed through a polarizer, before it was expanded to a spot diameter of 1.1 mm and collimated with a spatial filter consisted of two convergent lenses (f50 and f150). The beam was split with a cube beamsplitter (20x20x20) into two quasi-isoenergetic beams (160 mW. cm^{-2}) and recombine onto the sample using two mirrors. The first-order diffraction efficiencies were monitored using a photodiode (Ophir PD300 and PD300 UV head) in situ while the SRG were formed by means of a low-energy helium-neon laser beam working at 633 nm. Topographic images of the SRGs were recorded using a JPK atomic force microscope working in a tapping mode. SEM images obtained by using a JEOL- F scanning electron microscopy operated at an accelerating voltage of 6400 – 7600 V. TEM images were obtained using a Hitachi HF2000-FEG transmission electron microscopy where the samples were loaded onto holey carbon-coated copper grids (300 mesh).

Appendix B

B.1 PM-IRLD and Birefringence studies

Below is shown the PM-IRLD for all 9 push-pull are shown.

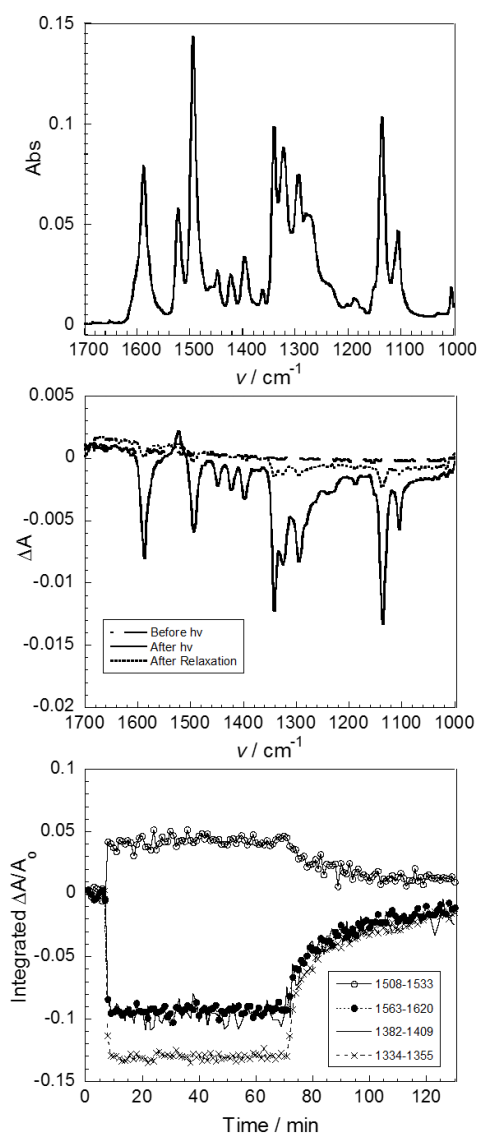


Figure B.1. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 1350 cm^{-1} , and the dynamic curves of selected vibration for 4-[bis(4'-tert-butylbiphenyl-4-yl)amino]-4'-nitroazobenzene (tBuNO_2) (12a) thin films with a thickness of 450 nm.

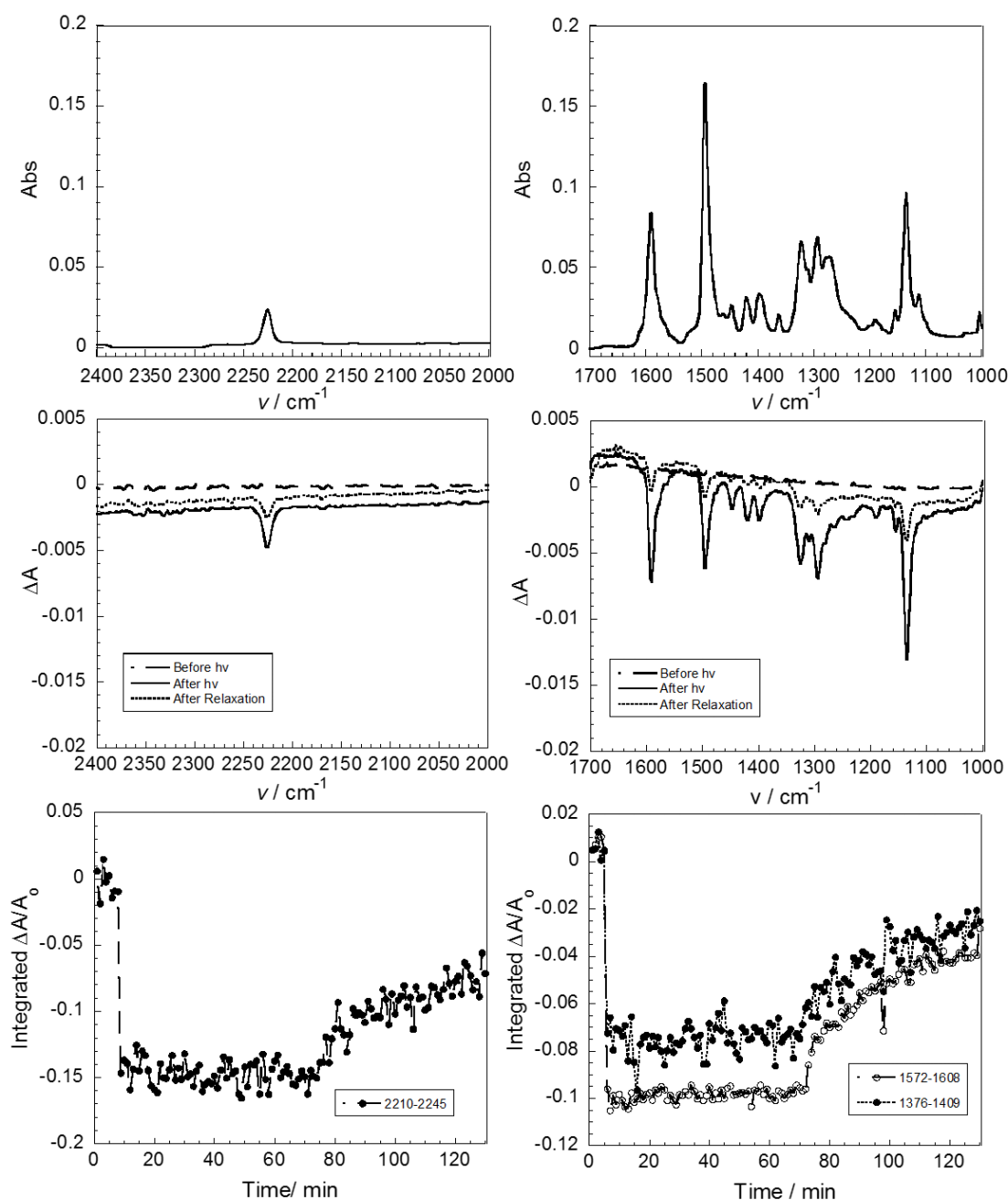


Figure B.2. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 2400 (left) and 1350 cm^{-1} (right), and the dynamic curves of selected vibration for 4[bis(4'-tert-butylbiphenyl-4-yl)amino]-4'-cyanoazobenzene (tBuCN) (12b) thin films with a thickness of 580 nm.

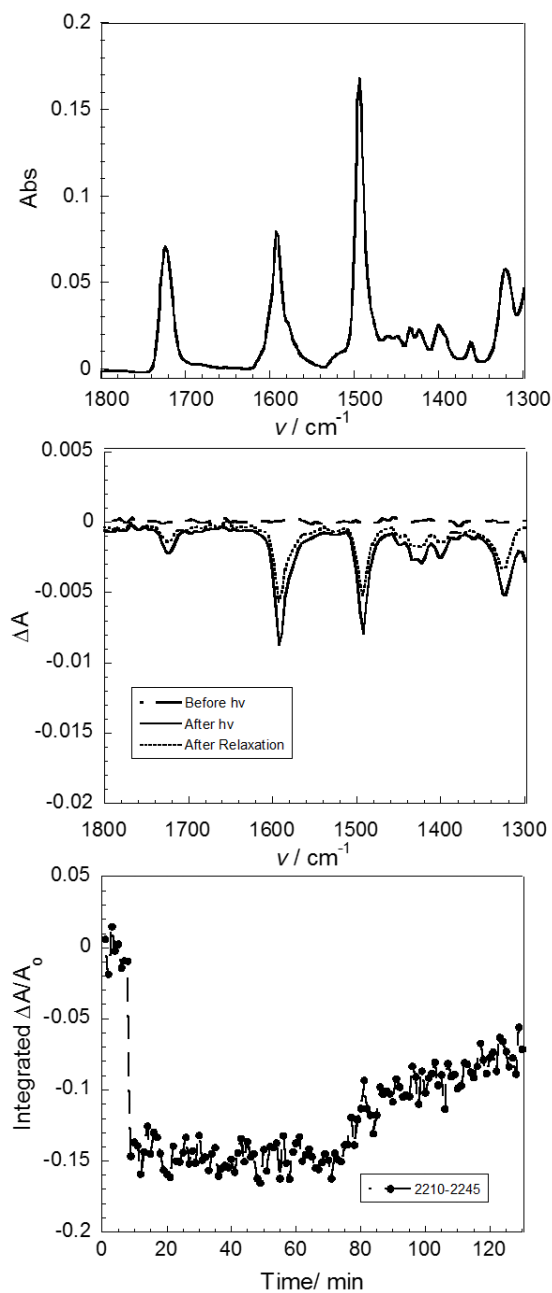


Figure B.3. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 1700 cm^{-1} , and the dynamic curves of selected vibration for 4-[bis(4'-tert-butylbiphenyl-4-yl)amino]-4'-methylesterazobenzene (tBuCO₂Me) (12c) thin films with a thickness of 520 nm.

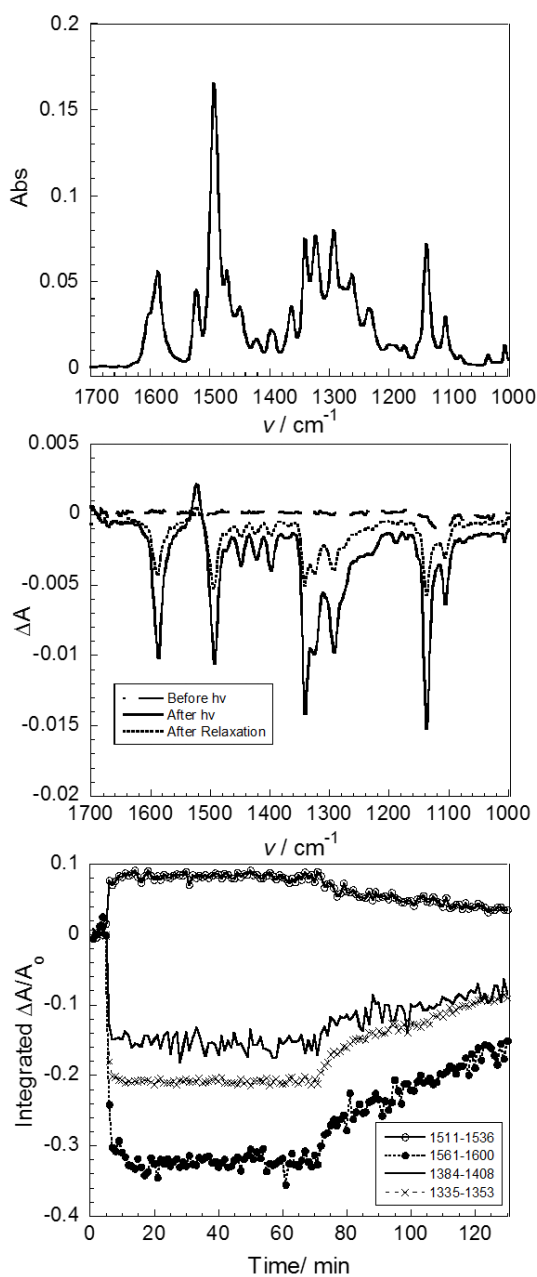


Figure B.4. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 1350 cm^{-1} , and the dynamic curves of selected vibration for 4-[bis(4'-tert-butyl carbazolebiphenyl-4-yl)amino]-4'-nitroazobenzene (CarbNO₂) (13a) thin films with a thickness of 480 nm.

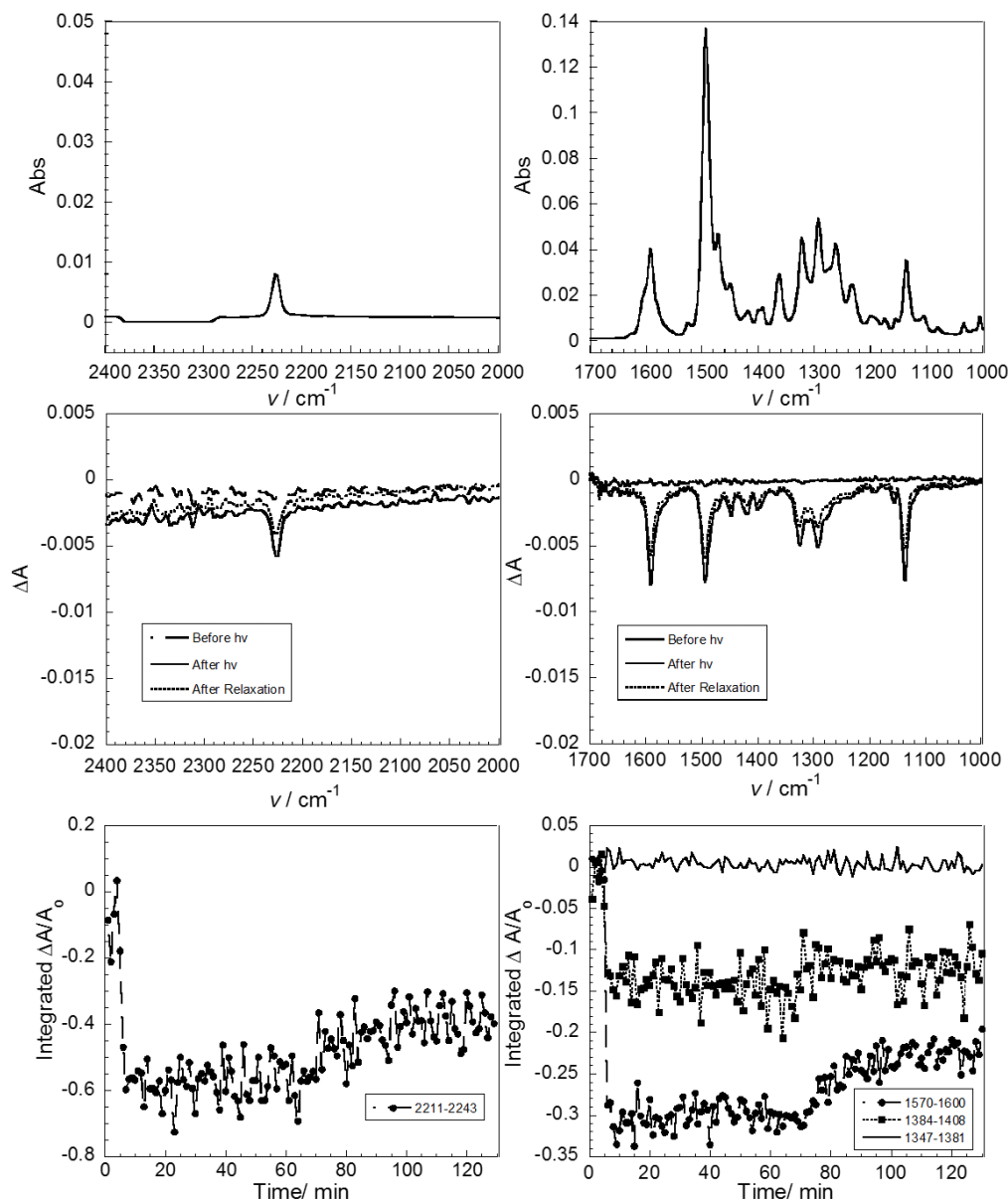


Figure B.5. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 2400 (left) and 1350 cm^{-1} (right), and the dynamic curves of selected vibration for 4-[bis(4'-tert-butyl carbazolebiphenyl-4-yl)amino]-4'-cyanoazobenzene (CarbCN) (13b) thin films with a thickness of 375 nm.

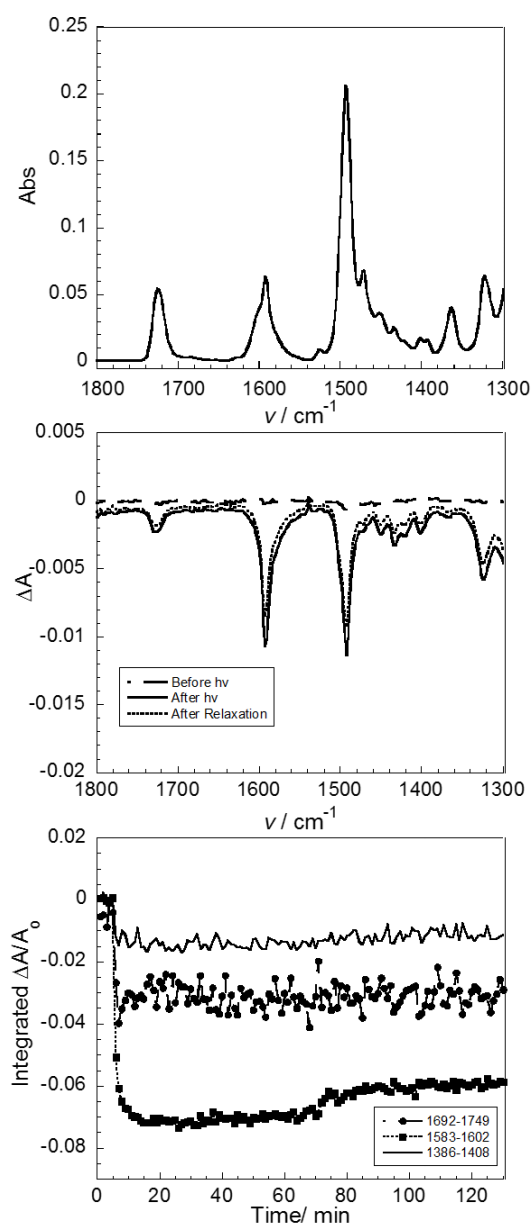


Figure B.6. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 1700 cm^{-1} , and the dynamic curves of selected vibration for 4-[bis(4'-tert-butyl carbazolebiphenyl-4-yl)amino]-4'-methylesterazobenzene (CarbCO₂Me) (13c) thin films with a thickness of 550 nm.

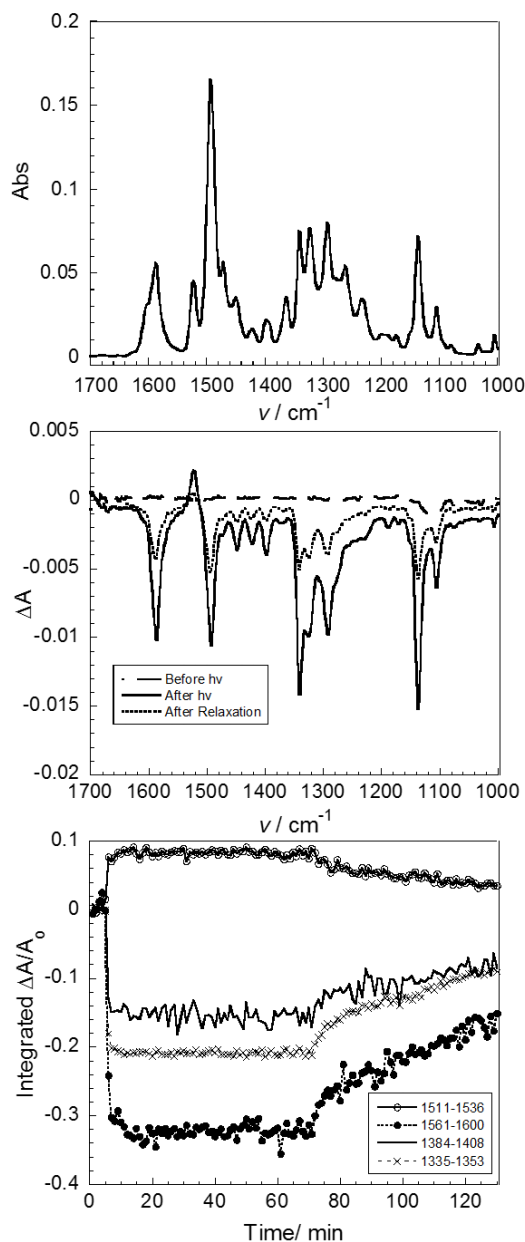


Figure B.7. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 1350 cm^{-1} , and the dynamic curves of selected vibration for 4-[N-di(3',5'-bis(trifluoromethyl) biphenyl)amino]-4'-nitro azobenzene (CF_3NO_2) (14a) thin films with a thickness of 300 nm.

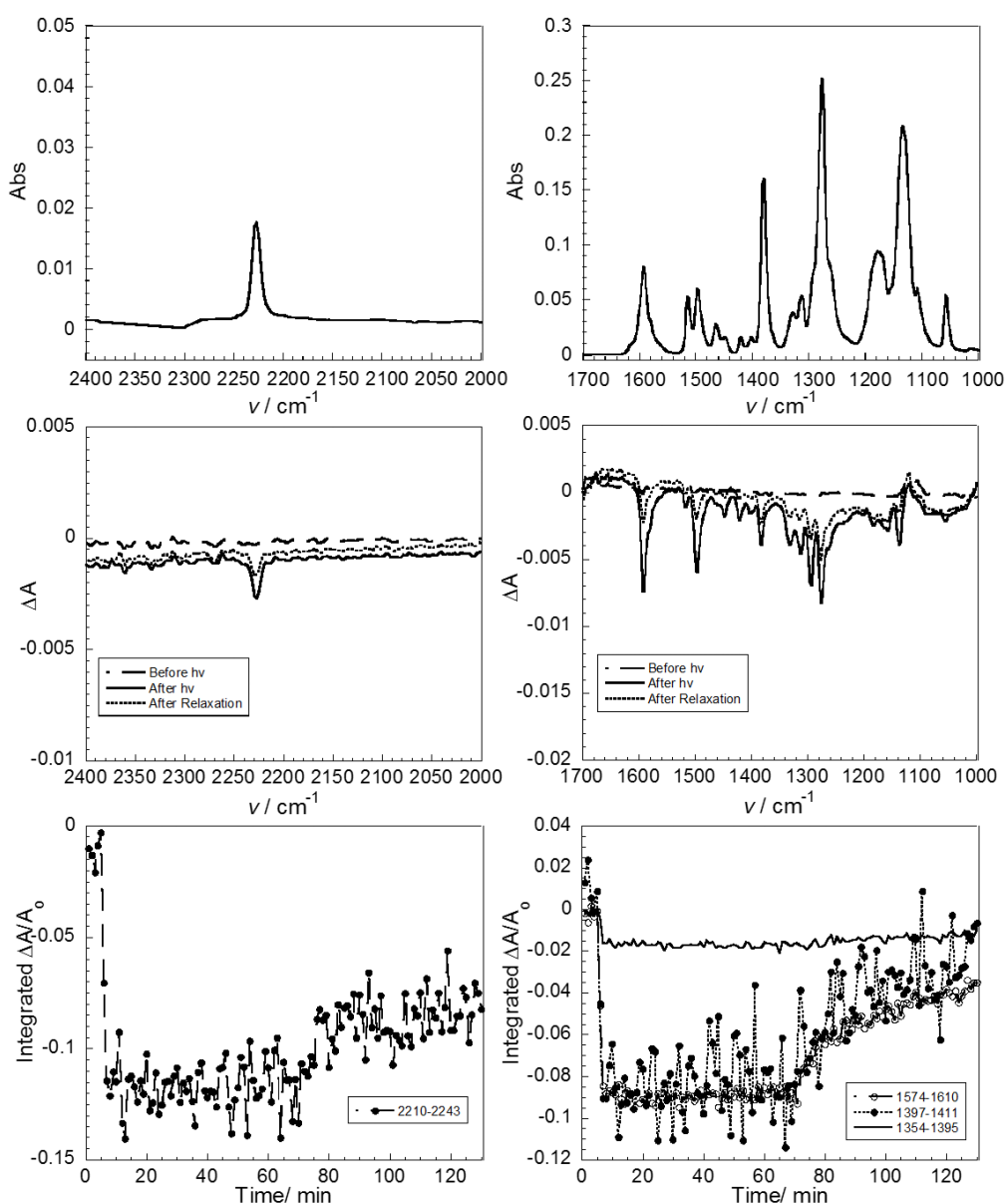


Figure B.8. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 2400 (left) and 1350 cm^{-1} (right), and the dynamic curves of selected vibration for 4-[N-di(3',5'- bis(trifluoromethyl)biphenyl)amino]-4'-cyanoazobenzene (CF_3CN) (14b) thin films with a thickness of 450 nm.

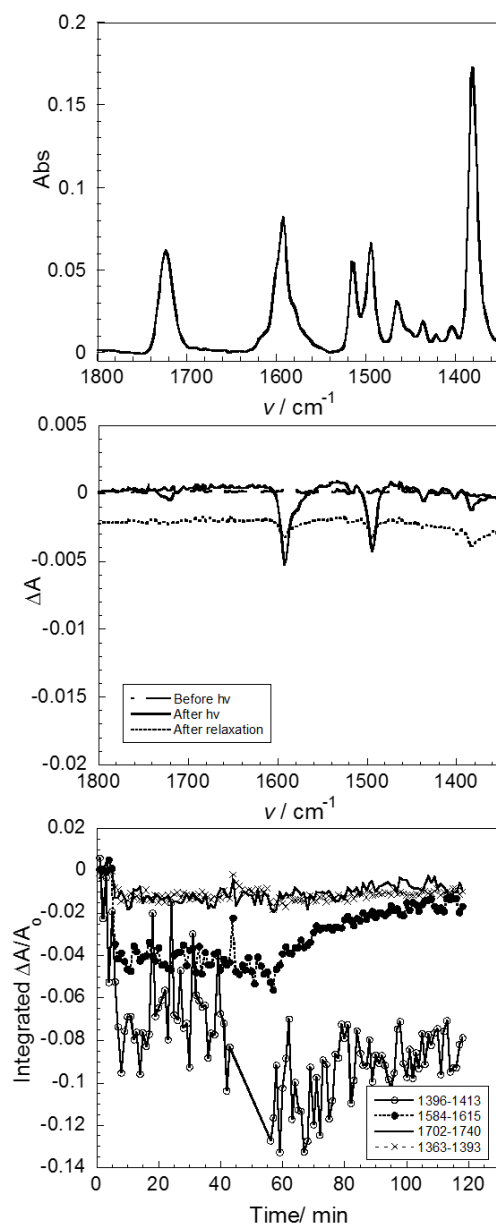


Figure B.9. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 1700 cm^{-1} , and the dynamic curves of selected vibration for 4-[N-di(3',5'-bis(trifluoromethyl) biphenyl)amino]-4'-methylesterazobenzene ($\text{CF}_3\text{CO}_2\text{Me}$) (14c) thin films with a thickness of 350 nm.

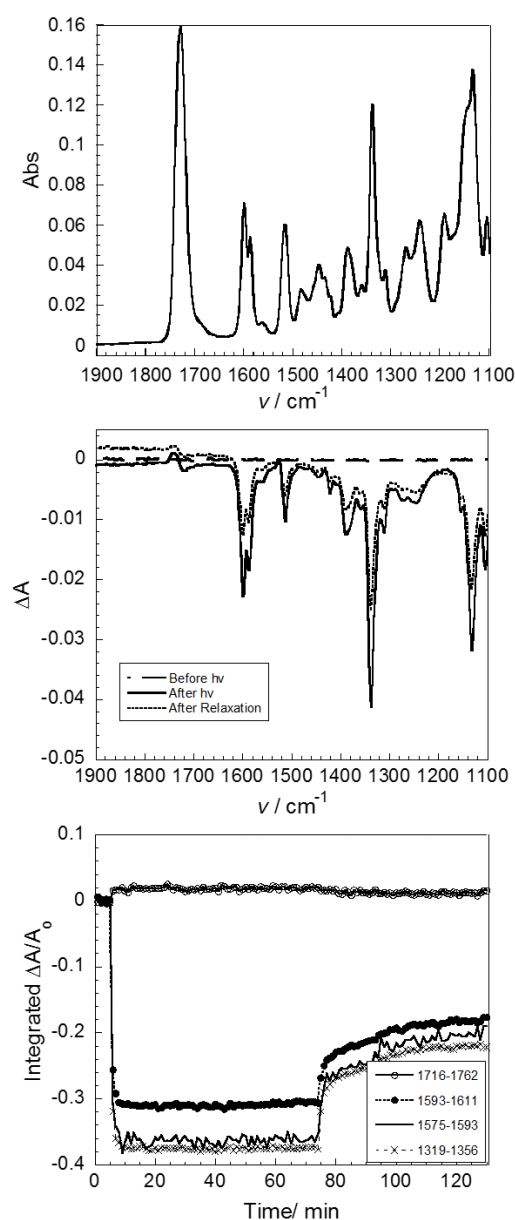


Figure B.10. The FTIR spectrum (top), the ΔA spectra before irradiation, after 60 min of irradiation and then after 60 min of relaxation (middle) modulated at 1400 cm^{-1} , and the dynamic curves of selected vibration for poly[4-nitrophenyl-4'-[[2-(methacryloyloxy) ethyl]ethyl-aminophenyldiazene] (pDR₁M) thin films with a thickness of 470 nm.

Compound	ν (cm ⁻¹)	$\int \Delta A / A_0$				
		A ₀	t=0 min	t=60 min	t=125 min	% Relaxation
tBuNO ₂	1342	0.470	0.000	-0.130	-0.017	86.923
tBuCN	2225	0.240	0.000	-0.150	-0.073	51.333
tBuCO ₂ Me	1724	1.230	0.000	-0.025	-0.017	32.000
CF ₃ NO ₂	1342	0.430	0.000	-0.130	-0.079	39.231
CF ₃ CN	2227	0.170	-0.010	-0.120	-0.080	36.364
CF ₃ CO ₂ Me	1724	0.984	0.000	-0.013	-0.009	28.184
CarbNO ₂	1342	0.350	0.000	-0.210	-0.096	54.286
CarbCN	2225	0.080	-0.050	-0.560	-0.380	35.294
CarbCO ₂ Me	1724	0.950	0.000	-0.031	-0.031	0.000

Table B.1. Summary of the results for all the compounds $\int \frac{\Delta A}{A_0}$ and % relaxation for the- C=C- bond.

Compound	ν (cm ⁻¹)	$\int \Delta A / A_0$				
		A ₀	t=0 min	t=60 min	t=125 min	% Relaxation
tBuNO ₂	1588	1.427	0.000	-0.093	-0.015	84.210
tBuCN	1591	1.016	0.000	-0.098	-0.040	59.036
tBuCO ₂ Me	1593	0.643	0.000	-0.117	-0.077	34.552
CF ₃ NO ₂	1591	0.917	0.000	-0.095	-0.052	44.628
CF ₃ CN	1593	1.024	0.000	-0.089	-0.041	53.608
CF ₃ CO ₂ Me	1593	0.759	0.000	-0.046	-0.018	59.922
CarbNO ₂	1586	0.427	0.000	-0.321	-0.169	47.449
CarbCN	1593	0.230	0.000	-0.305	-0.228	25.344
CarbCO ₂ Me	1593	0.343	0.000	-0.071	-0.060	15.278

Table B.2. Summary of the results for all the compounds $\int \frac{\Delta A}{A_0}$ and % relaxation for the- X bond.

“Matériaux moléculaires photochromiques pour l’organisation contrôlée de nanoparticules”

Les (nano)matériaux hybrides suscitent un intérêt considérable au sein de la communauté scientifique des matériaux en raison de la valeur ajoutée apportée par la combinaison d’entités organiques et inorganiques en termes de multifonctionnalité et d’interactions mutuelles pour des applications en bio-reconnaissance, en catalyse, et en photonique. De nombreux assemblages hybrides impliquent des plateformes inorganiques (surfaces de silice ou métalliques, architectures périodiques telles que les zéolithes, les argiles cationiques, les solides mésoporeux, et les nanotubes de carbone) dans/sur lesquelles des molécules organiques fonctionnelles individuelles sont incorporées/greffées. Rares en revanche sont les nanoparticules organiques fonctionnelles, considérées comme plateformes centrales de systèmes hybrides comportant des entités inorganiques. Pourtant, la densité élevée en composés actifs constituant les matériaux organiques non-dopés permet une détection aisée des signaux et réduit les risques de photoblanchiment, très problématiques pour des applications en photonique.

Dans ce contexte, nous nous sommes intéressés à la conception de systèmes photochromes de type azoïque, connus pour le changement réversible de leurs spectres d’absorption sous excitation lumineuse, et aptes à transformer l’énergie lumineuse en un travail mécanique. C’est ainsi que des déformations macroscopiques de surface, dues à une migration physique ou à une réorientation de dérivés azoïques, ont pu être effectuées tandis que l’action est réalisée par des molécules individuelles. Dans ce travail de thèse, il s’agissait plus particulièrement de montrer qu’une telle photoactivation de la matière pouvait être exploitée à l’échelle nanométrique pour déplacer et organiser des nano-objets grâce à la lumière. La lumière est en effet un stimulus de choix de par sa polarisation, son énergie et son intensité qui peuvent être aisément modifiées en fonction des propriétés électroniques du système photochromique et des nanoparticules associées. L’utilisation d’un champ lumineux polarisé, jouant le rôle de véritable force motrice pour déplacer et contrôler le positionnement précis de nanoparticules à la surface du film mince, est apparue comme une approche séduisante, n’introduisant aucun contaminant, tout en étant dotée d’une grande adaptabilité. L’amplitude du transport de matière peut être

finement contrôlée en jouant sur la structure du composé azoïque et la nature chimique de la coordination des nanoparticules impliquées. Par conséquent, la maîtrise et la compréhension des interactions covalentes ou non-covalentes développées entre la nanoparticule cible et le composé azoïque photoactivable deviennent indispensables.

Au cours de ces travaux de thèse, nous avons synthétisé et étudié une série de matériaux photochromiques azoïques (Chapitre 2) dans le but d'organiser par voie optique des nanoparticules à la surface de films minces. Les structures retenues ont été dictées par la nécessité d'une photoisomérisation à l'état solide, d'une photomigration efficace et d'un greffage ultérieur de nanoparticules inorganiques. Afin de maximiser les propriétés de migration de ces composés azoïques, une structure de type *push-pull* (ou encore dite à transfert de charge) a été privilégiée en substituant les positions de part et d'autre d'une entité azobenzène par différents groupes électro-attracteurs ($X = \text{CN}, \text{NO}_2, \text{CO}_2\text{Me}$) et électro-donneurs (triphenylamino) (Figure 1). Afin de conférer des propriétés amorphes aux matériaux résultants, des substituants encombrants ($\text{Ar} = 4\text{-tert-butylphényl}$, $4\text{-bis}(4\text{-tert-butyl})\text{carbazolylphényl}$ and $3,5\text{-bis}(\text{trifluorométhyl})\text{phényl}$) ont également été incorporés dans la structure moléculaire. Ces substituants limitent les phénomènes d'agrégation intermoléculaire par empilement des squelettes aromatiques, à l'origine de la formation de microcristaux et d'une diminution des performances par diffusion de la lumière incidente (Figure 1).

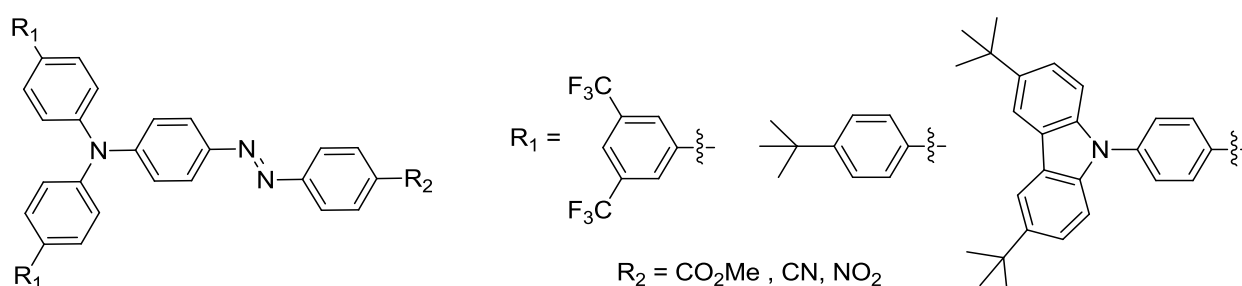


Figure 1. Structures de petites molécules azoïques à transfert de charge.

Les propriétés photochromiques d'une série de neuf molécules azoïques ont tout d'abord été caractérisées en solution. Les résultats obtenus soulignent que les composés les plus polaires présentent les cinétiques de retour thermique à l'état initial les plus rapides. Nous pouvons citer à titre d'exemple pour les deux composés aux extrémités de l'échelle de polarité ($\text{tBuNO}_2 : \mu = 10,49 \text{ D}$ et $\text{CF}_3\text{CO}_2\text{Me} : \mu = 2,01 \text{ D}$)

des constantes de vitesse k_{ZE} , variant de $2,9 \times 10^{-5} \text{ s}^{-1}$ à $70,8 \times 10^{-5} \text{ s}^{-1}$, soit une différence d'un facteur 30. Ce retour thermique très rapide explique le taux de photoisomérisation moindre pour les composés les plus polaires dont la forme *Z* relaxe plus rapidement vers son isomère *E* initial. Cependant, à l'état solide et plus spécifiquement sous forme de films minces, les composés azoïques voient leurs propriétés photochromiques influencées plus fortement par l'encombrement stérique des substituants que par la polarité seule des structures. En raison du volume libre conséquent créé lors des réactions de photoisomérisation impliquant des mouvements de rotation et de torsion importantes, la série Carb, comportant les substituants les plus encombrants, est apparue la plus efficace pour assurer des processus de photomigration de la matière. Des études de dichroïsme linéaire infrarouge modulé en polarisation nous ont permis de mettre en évidence une dynamique plus rapide de l'orientation sous faisceau polarisé de molécules azoïques par rapport à celles de systèmes polymères analogues. L'absence d'interactions entre les petites molécules donne lieu des mouvements à l'état solide bien moins contraints que ceux présents au sein d'un polymère, d'où des constantes de vitesse de relaxation thermique comparables à celles obtenues en solution pour certains composés.

Les travaux se sont poursuivis au travers de la formation de réseaux de surface à partir de films minces azoïques dans la perspective d'utiliser la photodéformation de surface pour organiser des nanoparticules, préalablement déposées (Chapitre 3). Les surfaces azoïques hydrophobes se sont révélées mécaniquement instables vis-à-vis du dépôt de suspensions aqueuses de nanoparticules. Cette déformation conduisant à des reliefs micrométriques a été attribuée à des tensions de surface entre le film azoïque hydrophobe déposé sur une surface hydrophile de verre et les molécules d'eau de la suspension. L'utilisation de l'un des composés les plus polaires CarbNO₂, nous a permis de nous affranchir de ces instabilités structurales, si bien que ce composé a été sélectionné comme candidat pour organiser des nanoparticules de polystyrène.

Nous avons donc exploité les propriétés de structuration photoinduite de films azoïques sous forme de réseaux de surface pour organiser des nanoparticules. Deux approches ont été suivies. La première approche consistait à déposer les nanoparticules à la surface de films minces avant de former le réseau de surface par illumination interférentielle à 488 nm. La seconde méthode impliquait le dépôt de

nanoparticules sur un réseau de diffraction préalablement inscrit. Les clichés de microscopie électronique à balayage (MEB) indiqués en Figure 2 résument les résultats issus des deux méthodes suivies pour aligner des nanoparticules de polystyrène ($\varnothing = 200$ nm) par un réseau de surface. Selon la méthode de fabrication adoptée, les particules sont soit incorporées dans la matrice azoïque lors de la photomigration des molécules pour former le réseau (méthode 1, Figure 2a), soit alignées lors du dépôt sur le réseau préalablement inscrit (méthode 2, Figure 2b).

L'incorporation des nanoparticules a également été démontrée en utilisant des nanoparticules fluorescentes dont les bandes d'émission se recouvraient avec la bande d'absorption des composés azoïques CarbNO₂. Le signal de fluorescence émis par des nanoparticules fluorescentes de polystyrène déposées sur un film azoïque diminuait fortement après leur enfouissement dans la matrice azoïque, alors photodéformée sous forme de réseaux de surface. Lorsque les nanoparticules fluorescentes étaient déposées sur un réseau de surface pré-formé, des lignes fluorescentes ont pu être observées par microscopie optique de fluorescence.

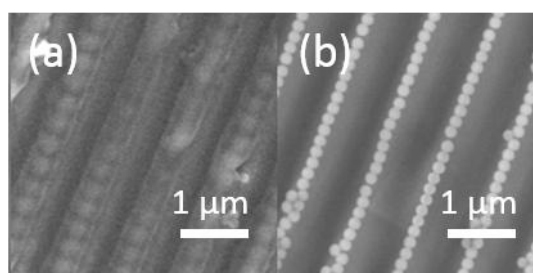


Figure 2. Images MEB de particules de polystyrène incorporées au sein d'un réseau de surface photoinscrit sur un film mince azoïque (a) et alignées dans les creux d'un réseau de surface préalablement photoinscrit.

Afin de tester la réversibilité de l'organisation des nanoparticules, les films azoïques ont été éclairés de manière homogène dans le visible (plus exactement à 482 nm avec une irradiance de 360 mW. cm⁻²). Pour les films azoïques incorporant les nanoparticules, des agglomérats se sont formés à l'intérieur desquels résidaient des nanoparticules ayant conservé leur alignement préalable. En revanche, pour des échantillons où les nanoparticules remplissaient les creux d'un réseau préalablement inscrit, le film azoïque perdait pratiquement toute sa structure initiale, laissant les nanoparticules encore alignées. Si la photo-organisation de nanoparticules n'apparaît pas vraiment réversible, elle permet en revanche d'aboutir à des surfaces

périodiquement structurées de manière simple et sans contact, c'est-à-dire sans risque de contamination directe.

Cette méthode de structuration a été exploitée pour aligner des nanoparticules d'or afin de créer des lignes métalliques conductrices. Malgré la faible taille des nanoparticules fabriquées au laboratoire (15 nm), il nous est apparu impossible de former des réseaux de surface. Nous avons attribué cette extinction des réactions de photoisomérisation, responsables de la formation de réseaux de surface, à des phénomènes de couplage optique entre les nanoparticules d'or et les composés azoïques absorbant tous deux dans la même plage de longueurs d'onde. Les matériaux photochromiques synthétisés ont démontré une réelle efficacité pour aligner des nanoparticules de polystyrène. En réalité, leurs réponses dépendent de nombreuses propriétés tant structurales (nature et densité du matériau, nature du solvant) que physiques (pas du réseau, diamètre des particules), essentielles à l'induction d'une orientation bien spécifique de nano-objets grâce à une structuration en surface du support.

Ces matériaux photochromiques ont été ensuite utilisés pour fabriquer différents nano-objets hybrides sous la forme de nanosphères et de nanobâtonnets (Chapitre 4). Ces nano-objets ont été exploités pour chélater des nanoparticules d'or afin i- d'estimer leur aptitude à servir de plateformes pour des matériaux plus complexes et d'éléments organisateurs centraux, et ii- d'évaluer la capacité de déplacement des nanoparticules alors greffées à la surface du coeur photochromique. Trois nouveaux composés, possédant des fonctions soufrées terminales connues pour leur affinité élevée pour les nanoparticules d'or, ont été synthétisés et façonnés sous forme de nano-objets (Figure 3a) Des nanoparticules organiques ont été fabriquées par reprecipitation dans l'eau du composé azoïque correspondant, préalablement dissous dans un solvant miscible avec l'eau. Les nanosphères obtenues présentaient un diamètre d'une centaine de nanomètres variant avec la concentration de la solution mère ajoutée (Figure 3b). Quant à l'obtention de nano-objets anisotropes, en l'occurrence des nanobâtonnets, des membranes d'alumine ont été utilisées en guise de moules. Après remplissage des pores par une solution concentrée en composés azoïques, la matrice d'alumine a été dissoute par traitement alcalin ($\text{KOH } 3 \text{ mol.L}^{-1}$),

conduisant à la libération de nanobâtonnets présentant une distribution très étroite en termes de diamètre (Figure 3c).

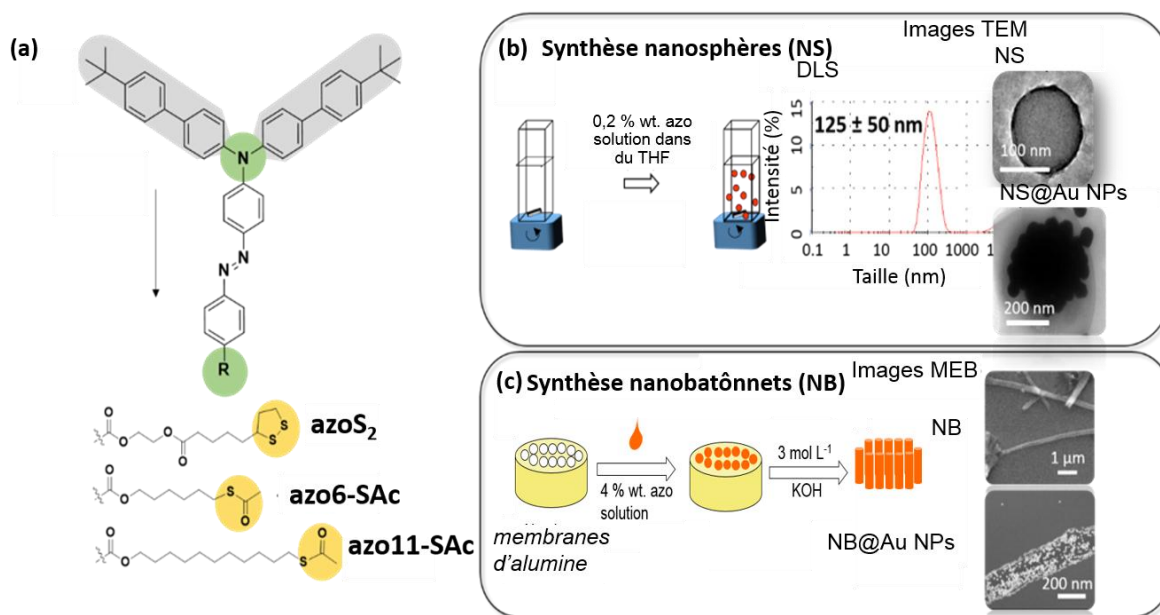


Figure 3. (a) Molécules azoïques comportant des groupes soufrés terminaux permettant la chélation de particules dor. Protocoles de synthèse(b) de nanosphères azoïques par nanoreprécipitation dans l'eau, (c) de nanobâtonnets à l'aide de membranes d'alumine.

Les propriétés photochromiques des objets ont également été étudiées et comparées avec celles des films minces correspondants. Dans le cas de nanosphères organiques, la réaction de photoisomérisation présentait un rendement de conversion minimal de l'ordre de 21 %, systématiquement plus élevé que ceux des films minces (14 %) malgré des propriétés d'absorption quasi-identiques. Les constantes de vitesse de relaxation thermique des nanosphères organiques une fois irradiées ($k_{ZE} \sim 10 \times 10^{-5} \text{ s}^{-1}$) ont été trouvées indépendantes de la nature des substituants du dérivé azoïque. Leurs valeurs font écho à celles mesurées en solution dans le toluène ($k_{ZE} \sim 7 \times 10^{-5} \text{ s}^{-1}$). Les nanosphères azoïques coordonnant en surface des nanoparticules d'or stabilisées ($\varnothing = 15 \text{ nm}$) présentaient une conversion photochimique amoindrie ($\sim 10 \%$), comparativement à celles des nanosphères azoïques ($\sim 21 \%$). De manière intéressante, l'allongement de l'espaceur entre la fonction azoïque et la fonction soufrée chélatante conduit à une légère augmentation de la conversion photochimique. Cette augmentation a été attribuée à une diminution du couplage optique entre le photochrome et les nanoparticules d'or (et des transferts d'énergie), connu pour être

très sensible à la distance entre les deux entités. La proximité des nanoparticules d'or vis-à-vis du cœur organique a été révélée par microscopie Raman. Une exaltation des transitions vibrationnelles des nano-objets azoïques recouverts de nanoparticules d'or a été clairement mise en évidence. Des signaux de près de trois ordres de grandeur plus intenses que ceux obtenus sur des nano-objets azoïques seuls ont pu être mesurés.

Dans le cas des nanobâtonnets azoïques, leur irradiation conduit à leur agrégation et à leur précipitation au sein de la solution aqueuse. Vu le potentiel de surface négatif des nanobâtonnets mesuré par zétamétrie, leur stabilisation colloïdale a été assurée par un polyélectrolyte cationique (poly(chlorure de diallyldiméthylammonium)). La suspension de nanoparticules recouvertes de polyélectrolyte s'est révélée stable au cours de l'irradiation. Une conversion photochimique minimale de 8 % a été mesurée pour ces nouveaux systèmes stabilisés, soit nettement inférieure à celle obtenue pour les nanoparticules ou les films minces. Nous avons attribué cette différence significative aux interactions développées entre le polyélectrolyte et la surface azoïque, jouant un rôle majeur dans l'amorçage de la photoisomérisation à l'état solide.

En conclusion, une série de matériaux photochromes a été synthétisée et caractérisée grâce à un arsenal de mesures optiques et spectroscopiques. En combinant différentes stratégies, nous avons été en mesure d'organiser des nanoparticules à la surface de films minces, de fabriquer des nanosphères et des nanobâtonnets azoïques, et enfin de fonctionnaliser la surface de ces nano-objets par des nanoparticules d'or. Ces nouvelles structures ouvrent la voie vers des études fondamentales et appliquées pour expliquer les effets d'extinction de la photoréaction des photochromes par des nanoparticules d'or en dépit d'une densité en nanoparticules d'or très réduite. La réaction de photoisomérisation étant la clé de voûte de ces études, une meilleure compréhension des interactions entre matériaux azoïques avec des nanoparticules métalliques représente donc une étape préliminaire-clé qui permettra à termes de valoriser ces matériaux dans des applications en optique et notamment de stockage optique.

RESUMÉ et MOTS CLÉS

Titre français : Matériaux moléculaires photochromiques pour l'organisation contrôlée de nanoparticules

Mots-clés: matériaux photochromiques, molécules azoïques, spectroscopie Raman, réseaux de surface, nanoparticules organiques, nanoparticules d'or, nanomatériaux hybrides.

Résumé:

Les travaux effectués portent sur la synthèse et les études de petites molécules azoïques aptes à former des matériaux auto-assemblés stables pour organiser des nanoparticules de manière photomécanique ou chimique. Tout d'abord, une famille de molécules azoïques de type donneur-accepteur différant par leur polarité, leur hydrophobicité et leur encombrement a été synthétisée et caractérisée. Des études de dichroïsme linéaire infrarouge modulé en polarisation et des mesures de biréfringence ont mis en exergue une orientation des composés azoïques moléculaires façonnés sous forme de films minces, dix fois plus rapide que celle observée pour des polymères fonctionnalisés par des entités azoïques. L'aptitude des films minces photochromes à réaliser des transports de matière sous illumination interférentielle a été exploitée pour aligner des nanoparticules sur les sommets et dans les creux des reliefs photoinscrits. Par ailleurs, des nanosphères ont été fabriquées par nanoprécipitation des molécules synthétisées. De manière intéressante, elles présentent des rendements de conversion intermédiaires entre ceux en solution et en film mince. Des structures hybrides cœur-coquille ont été générées en recouvrant de nanoparticules d'or les nanosphères azoïques comportant des fonctions soufrées terminales. Des études par microscopie Raman ont prouvé la grande cohésion entre le matériau azoïque et les nanoparticules azoïques grâce à l'apparition d'effets SERS. De tels assemblages, obtenus selon une approche inversée, représentent le premier exemple de nanoparticules hybrides photochromes comportant une densité élevée en unités photoactives.

Titre anglais : Photochromic molecular materials for the controlled organization of nanoparticles

Keywords: Photochromic materials, azo molecules, Raman spectroscopy, surface relief gratings, photoorganization, organic nanoparticles, hybrid nanomaterials, gold nanoparticles.

Abstract:

The reported work deals with the synthesis and the studies of small azo molecules amenable to form stable self-assembled materials and organize nanoparticles photomechanically or chemically. Firstly, a series of push-pull azo molecules with distinct polarity, hydrophobicity and steric crowding has been synthesized and characterized. Polarisation modulation infrared linear dichroism spectroscopy and birefringence measurements have evidenced that the molecular azo dyes processed as thin films orientated ten times quicker than similarly reported azo functionalized polymer. The ability of the resulting photochromic thin films to undergo periodic bulk mass transfer under interferential illumination was exploited to align polystyrene nanoparticles in the crests or in the troughs of the photowritten reliefs. Secondly, nanospheres have been obtained out of the synthesized molecules using the nanoreprecipitation method. Interestingly, they exhibit photoconversion yields intermediate between those in free-constraint solutions and in thin films. Core-shell hybrid structures have been generated by coating sulfur-terminated azo nanospheres with gold nanoparticles. Stiff cohesion between the azo material and gold nanoparticles was proved by Raman microscopy showing SERS effects. Such assemblies, following a reverse architecture, represent the first example of photochromic hybrid nanoparticles with a high payload of photoactive units.