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Light-induced contraction/expansion of one-dimensional photo-switchable metallopolymer monitored at the solid-liquid interface

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ABSTRACT

The use of a bottom-up approach to the fabrication of nano-patterned functional surfaces, which are capable to respond to external stimuli, is of great current interest. Herein, we describe the preparation of light-responsive, linear supramolecular metallopolymers constituted by the ideally infinite repetition of a ditopic ligand bearing an azoaryl moiety and Co(II) coordination nodes. The supramolecular polymerization process is followed by optical spectroscopy in DMF solution. Noteworthy, a sub-molecularly resolved scanning tunnelling microscopy (STM) study of the *in situ* reversible *trans*-to-*cis* photo-isomerization of a photo-switchable metallopolymer that self-assembles into two-dimensional (2D) crystalline patterns onto a highly oriented pyrolytic graphite (HOPG) surface is achieved for the first time. The STM analysis of the nano-patterned surfaces is corroborated by modelling the physisorbed species onto a graphene slab before and after irradiation by means of density functional theory (DFT) calculation. Significantly, switching of the monolayers consisting of supramolecular Co(II) metallopolymer bearing *trans*-azoaryl units to a novel pattern based on *cis* isomers can be triggered by UV light and reversed back to the *trans* conformer by using visible light, thereby restoring the *trans*-based supramolecular 2D packing. These findings represent a step forward towards the design and preparation of photo-responsive “smart” surfaces organized with an atomic precision.

1. Introduction

The synthesis of sophisticated building blocks designed to interact through non-covalent forces is widely explored as it allows construction of various self-assembled systems and materials with a sub-nanometer precision.^[1] In particular, supramolecular chemistry offers numerous straightforward solutions towards the *bottom-up* functionalization of surfaces and interfaces with *ad-hoc* molecules. Such strategy makes possible to generate functional nanostructures for various application in materials science. By judicious molecular design, a range of different functionalities can be chemically encoded at the molecular level thus yielding organized nanostructures that are capable to respond to external inputs such as thermal,^[2] electrical,^[3] chemical^[4] and optical^[5] stimuli. The latter is of major interest because light-induced excitation allows remote and spatiotemporal control of the applied stimulus. In addition, introduction of photo-responsive moieties might allow orthogonal selection of both excitation wavelength and output response, such as luminescence, energy and/or electron transfer processes, reactivity and catalytic properties, to cite some.

Nowadays, a number of photo-induced reactions and processes are known and amongst those, *trans-to-cis* isomerization in a series of derivatives such as stilbenes,^[6] azobenzenes,^[7] as well as opening/closing processes in diarylethenes^[5e, 8] have been extensively studied both from fundamental and application points of view. Amongst photo-switches, systems based on azobenzene scaffolds hold a leading position due to their peculiar characteristics including relatively straightforward synthetic procedures, thermal and photochemical reversibility, selection of the excitation wavelength that can be modulated by electronic and steric effects upon variation of the substituents,^[9] as well as large geometrical and dipole reorganization that accompany the photo-induced isomerization. In this respect, some of us have recently reported on a novel photo-responsive class of supramolecular metallopolymer bearing diazoaryl moieties that are suitable for the preparation of self-healable and photo-responsive gels.^[10]

Scanning tunneling microscopy (STM) is an established tool to investigate structures and numerous physical and chemical properties of molecules at surfaces with a sub-nanometer spatial resolution.^[11] Its use to explore molecular physisorption at interfaces is particularly appealing, as it makes possible to explore dynamic processes *in situ* and in real-time, including switching processes and chemical reactions.^[4b, 4c, 7e]

Seeking for the possibility to monitor photo-switching processes and construct photo-responsive surfaces, we herein report on the preparation of a linear metallopolymer based on a photo-switchable *bis*-terpyridine ditopic ligand and containing Co(II) coordination nodes, namely [**Azo-*bistpy*-Co**]_n.

Noteworthy, some of us studied in the past the self-assembly of three-component metallopolymer, in which **Azo-*bistpy*** was used as one out of the two organic ligands.^[10] However, such systems are not suitable for studying the photo-switching processes of the self-assembled structures, as the two organic components have very different adsorption energies. Therefore, phase segregation or self-assembly of only one component with higher affinity towards the solid substrate is expected under thermodynamic equilibrium.^[12]

Upon titration, the formation of the supramolecular polyelectrolyte was followed in solution by means of UV-visible absorption spectroscopy. Noteworthy, when the metallopolymer was prepared *in situ* at 1-phenyloctane/HOPG interface the formation of a 2D pattern of self-assembled arrays could be monitored by STM that showed azoaryl moieties in their *trans* form. A photonic stimulus was used to reversibly switch azobenzene between *trans* and *cis* conformers by using UV and visible light, respectively, resulting in a neat variation of the surface pattern as also supported by theoretical modeling at density functional theory (DFT) level on HOPG surface. In this manner, nano-patterned photo-responsive surfaces could be fabricated.

2. Results and discussion

2.1. Synthesis and characterization

The chemical structure of the ditopic ligand containing a photoswitchable azoaryl moiety, namely **Azo-*bistpy***, is depicted in **Scheme 1** along with the corresponding cobalt(II) metallopolymer, namely **[Azo-*bistpy*-Co]_n**. The ligand **Azo-*bistpy*** has been synthesized in its thermodynamically stable *trans* configuration, namely *trans*-**Azo-*bistpy***, by reaction of 4'-(4-aminophenyl)-2,2':6,2''-terpyridine with ^tBuOK in DMSO/^tBuOH solvent mixture. The experimental details of the synthetic procedures are reported elsewhere.^[13] In a first attempt, synthesis of the metallopolymers containing Co(II) coordination nodes was carried out as bulk reaction by using a cobalt salt and **Azo-*bistpy*** in CHCl₃. Although **Azo-*bistpy*** can form metallopolymers with various metal ions such as Fe(II) or Zn(II)^[10], Co(II) has been chosen in this studies as a coordination node because it offers low kinetic lability, which allows *in situ* generation of elongated 1D mettalopolymers at the solid/liquid interface. Moreover, Co(II)/***bistpy*** mattalopolymers and complexes are in general thermodynamically more stable than Zn(II) annalougs.

It is important to note, that the nature of the solvent, ligand:cobalt ratio and the nature of the Co counter-anion are crucial points for determining the final outcome in a reaction between *bis*-terpyridine type of ligands and a cobalt(II) salt.^[14] Thus, we have chosen to perform the reaction using CoCl₂ as the cobalt source and in a 1:1 ratio **Azo-*bistpy***:Co²⁺ since quantitative coordination of the N-based ligand onto metal ion is expected to occur under our reaction condition, giving the target metallopolymer **[Azo-*bistpy*-Co]_n**. Unfortunately, this synthetic procedure afforded an insoluble solid, thus hampering any deeper chemical characterization of the obtained product. Such finding is in agreement with related reactions carried out under similar condition and reported previously.^[14]

Scheme 1. Chemical structure of the ditopic ligand **Azo-bistpy** in its *trans*- conformation and the corresponding linear Co(II)-based metallopolymer **[Azo-bistpy-Co]_n** prepared at 1:1 ligand:CoCl₂ ratio.

Thus, we decided to carry out an *in situ* complexation between the ditopic *trans*-**Azo-bistpy** ligand and the CoCl₂ and follow the polymerization process by UV-visible spectrophotometry in dilute DMF solution. A sample of **Azo-bistpy** ligand at concentration of 2.0×10^{-5} mol was titrated with 20 μL aliquots of a solution of CoCl₂ at concentration of 2.5×10^{-4} mol. Formation of Co(II) coordination polymer was monitored by UV-vis upon stepwise addition of metal cation. The UV-vis titration curves and the corresponding plot displaying the variation of the absorbance recorded at 335 nm upon different addition of CoCl₂ aliquots are depicted in **Figure 1**.

Figure 1. (a,b) UV-Visible spectra and (c) plot of the variation of the absorbance monitored at 335 nm vs. Co²⁺:**Azo-bistpy** ligand ratio recorded in DMF ([**Azo-bistpy**] = 2.0×10^{-5} mol). Black arrows indicated the variation of the absorbance upon addition of CoCl₂ aliquots in the range 0–1 and 1.1–2.4 equiv. for panel (a) and (b), respectively. In (c), dotted gray lines are only intended to guide the eye.

In **Figure 1c** two steep changes in the absorbance trend at around one and two equivalents of CoCl_2 can be clearly identified corresponding to three different regimes. The first regime (between 0 and 1 equiv. of CoCl_2) is indicative of a polymerization process between molecules of *trans*-**Azo-bistpy** ligands and metal center, which yields the metallopolymeric species $[\textit{trans}\text{-Azo-bistpy-Co}]_n$. The second regime corresponds to a *trans*-**Azo-bistpy**: Co^{2+} 1:1 to 1:2 ratio and it is ascribed to the subsequent depolymerization process of $[\textit{trans}\text{-Azo-bistpy-Co}]_n$ into the dimetallic species with *trans*-**Azo-bistpy**: Co^{2+} 1:2 stoichiometry. Subsequently, above two equivalents of CoCl_2 , no substantial change in the absorbance is observed, indicating that complete depolymerization has occurred. Although supramolecular polymerization processes of ditopic ligands of terpyridine and other types of N-based ligands have been already shown to afford a mixture of metallo-macrocyclic species and linear polymeric counterparts at variable ratio depending on counterion, solvent and even more importantly concentration, we confidentially assume that $[\textit{trans}\text{-Azo-bistpy-Co}]_n$ metallopolymer possesses a linear arrangement on the basis of the rigid and rod-like nature of the divergent ditopic ligand *trans*-**Azo-bistpy**.^[15] Such linear and ideally infinite arrangement of the $[\textit{trans}\text{-Azo-bistpy-Co}]_n$ is further corroborated by direct visualization *via* scanning probe technique at the solid/liquid interface (*vide infra*).

Our molecular design was made in such a way to introduce a unit responsive to light input, *i.e.* a diazoaryl moiety, capable to undergo *trans-cis* photoisomerization, while keeping a certain extent of molecular rigidity of the 1D linear architecture. To investigate the photo-responsiveness of the cobalt-containing metallopolymer, a DMF solution of $[\textit{trans}\text{-Azo-bistpy-Co}]_n$ at concentration of 1.0×10^{-5} mol was irradiated with a continuous-wave LED light source at 365 nm under an irradiance of 21 mW cm^{-1} and the process monitored by UV-vis spectroscopy. As displayed in Figure 2, upon UV photo-irradiation, absorption spectra show a sizeable decrease of the symmetry-allowed $\pi\text{-}\pi^*$ transition centered at 357 nm over

irradiation-time and an isosbestic point at $\lambda_{\text{abs}} = 322$ nm. This finding is indicative of a *trans*→*cis* photo-isomerization process involving the diazoaryl moiety and the photo-stationary state (PSS) is reached within 60 s of irradiation.^[9a] However, the parallel increase of the *n*- π^* absorption band, which becomes less symmetry-forbidden in the *cis* conformation, is not clearly visible. Nonetheless, this is most likely due to the large spectral overlap with the much more intense metal to ligand charge transfer (MLCT) band between 450 and 550 nm corresponding to the $[(\text{tpy})_2\text{Co}]^{2+}$ fragment.^[16] Noteworthy, the isomerization process can be readily reversed, thus yielding back the thermodynamically stable *trans* conformer upon irradiation into the diazoaryl *n*- π^* absorption band with a 455 nm LED (irradiance 31 mW cm^{-1}).

Figure 2. Kinetic studies of the photo-isomerization process for $[\text{trans-Azo-bistpy-Co}]_n$ in DMF (1×10^{-5} mol) carried out by UV-vis spectrophotometry. (a) *Trans*-to-*cis* photo-isomerization upon irradiation at 365 nm. Spectra were recorded between 0 (black trace) and 180 seconds (red trace) light exposure. (b) *Cis*-to-*trans* back isomerization obtained upon irradiation with a LED at 455 nm. UV-visible spectra were recorded between 0 (red trace) and 180 seconds (black trace) light exposure. Black arrows indicate the variation of absorbance over photo-irradiation time.

2.2. Density Functional Theory studies

To gain deeper insights into the structural and electronic properties of the **Azo-bistpy** and its Co(II)-metallopolymer, theoretical investigations were performed at their electronic ground state geometry using density functional theory (DFT) as implemented in the CP2K software package.^[17] The geometry optimization of **Azo-bistpy** and its complexes, namely *trans-Azo-bistpy-Co*, *cis-Azo-bistpy-Co*, were performed in gas phase and on a graphene surface. All

the structures are displayed in Figure S1–S5 of the Electronic Supplementary Information (ESI).

Figure S2 of the ESI displays the frontier molecular orbitals (MO) as the highest occupied and lowest unoccupied MOs, namely HOMO and LUMO, respectively, computed for **Azo-bistpy** at its electronic ground state. As far as the *trans*-**Azo-bistpy** conformer is concerned, the HOMO is localized on the azoaryl group whereas the LUMO is delocalized on the azobenzene and on the two central pyridyl moieties of the terpyridil groups. For *cis*-**Azo-bistpy**, while HOMO is delocalized on the azobenzene and the two central pyridyl groups, the LUMO is delocalized on the entire molecule. Such orbitals are computed at –4.96 and –3.24 eV, for *trans*-**Azo-bistpy**, and –5.09 eV and –3.03 eV for *cis*-**Azo-bistpy**, respectively.

According to our previous investigations,^[18] the combination of the CoCl₂ and the pyridyl/terpyridyl moieties should generate a coordinated one-dimensional polymeric structure (see Scheme 2). In the gas phase and as displayed in Figure S4a–S5a of the ESI for *trans*-**Azo-bistpy-Co** and *cis*-**Azo-bistpy-Co**, respectively, both conformers show an idealized octahedral geometry around the metal center (tpy-Co-tpy), *i.e.* the two terpyridines coordinated to Co(II) adopt an angle of 90°±7. However, such geometrical arrangement becomes sizably distorted upon adsorption of the tpy-Co-tpy moiety onto the graphite surface, where the angle of tpy-Co-tpy moiety become (90±15)° as observed and (90±10)° for *trans*-**Azo-bistpy-Co** and *cis*-**Azo-bistpy-Co**, respectively, as shown in Figure S4b–S5b. In **Table S1** of the ESI are summarized the computed adsorption energies (E_d) for all the investigated structures optimized on a graphene slab. The E_d computed for [*trans*-**Azo-bistpy-Co**]_n assembly onto a graphene surface (–4.2 eV) was found lower than for the *cis*- counterpart (–3.81 eV), supporting the higher stability of *trans* assemblies on graphite when compared to its *cis* conformer.

2.3. Scanning Tunneling Microscopy analysis

Azo-bistpy ligand offers peripheral and divergent coordination points based on two terdentate terpyridyl moieties. The combination of such ditopic ligand in a two-fold symmetry with an octahedral metallic center is thus expected to lead to the formation of a 1D extended periodic molecular architecture. The formation of the coordinated complexes was achieved at the 1-phenyloctane/graphite interface. The azoaryl group offers the possibility to switch between *trans* and *cis* conformer under UV-vis irradiation. Interestingly, this process can be now exploited to create dynamic changes of the molecular packing of **Azo-bistpy** on graphite surface in an unprecedented manner.

With this goal in mind, scanning tunnelling microscopy (STM) was used to probe *in situ* the self-assembly behavior of the neat **Azo-bistpy** molecule at the HOPG/liquid interface. The process was carried out by drop-casting 4 μL solution of **Azo-bistpy** in 1-phenyloctane at concentration of 0.1 mmol onto the HOPG surface. Figure 3a displays a survey STM image of the obtained molecular monolayer providing evidence for the formation of a 2D crystalline structure extended over a scale of several hundreds of nm^2 .

Figure 3. STM images of the *trans*-Azo-*bistpy* networks formed at the 1-phenyloctane solution/HOPG interface. (a) Survey image, average tunneling current (I_t) = 25 pA, tip bias (V_t) = 550 mV. (b) Height STM image, zoom-in, I_t = 25 pA, V_t = 800 mV. (c) Proposed molecular model. (d) DFT simulated model on graphene surface.

For all crystalline patterns the unit cell parameters, *i.e.* the length of the vectors (*a*) and (*b*), the angle between the vectors (α), the unit cell area (*A*), the number of molecules in the unit cell (N_{mol}) and the area occupied by a single molecule in the unit cell (A_{mol} , with $A_{mol}=A/N_{mol}$) are reported in the Table 1.

Table 1. Experimental and theoretical unit cell parameters of the structure Azo-*bistpy* and [Azo-*bistpy*-Co]_n.

Structure	Azo- <i>bistpy</i>				[Azo- <i>bistpy</i> -Co] _n			
	Experimental		Computed		Experimental		Computed	
	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>	<i>trans</i>	<i>cis</i>
<i>a</i> [nm]	2.6 ± 0.1	NA	2.7	NA	2.1 ± 0.1	2.2 ± 0.1	2.2	2.2
<i>b</i> [nm]	1.6 ± 0.1	NA	1.6	NA	1.4 ± 0.1	1.7 ± 0.1	1.3	1.7
α [°]	43 ± 2	NA	42	NA	51 ± 2	90 ± 2	53	90
<i>A</i> [nm ²]	2.8 ± 0.2	NA	2.89	NA	2.3 ± 0.2	3.7 ± 0.2	2.3	3.7
N_{mol}	1	NA	1	NA	1	1	1	1

$A_{mol} [nm^2]$	2.8 ± 0.2	NA	2.89	NA	2.3 ± 0.2	3.7 ± 0.2	2.3	3.7

The STM images were acquired by applying a positive sample bias. Therefore, bright protrusions observed in Figure 3b can be assigned to the LUMO of the molecules adsorbed on the HOPG surface. Since the LUMO of *trans-Azo-bistpy* displays a rectangular shape (see Figure S2 in ESI), we assign each bright feature visible on STM images to a single *trans-Azo-bistpy* molecule. Also, such LUMO orbital is delocalized along the core of the molecule, which corroborates the fact that the two external pyridyl rings of terpyridyl groups cannot be seen in the STM images. The analysis of the unit cell parameters and the contrast of the STM images suggest that all *trans-Azo-bistpy* molecules are oriented along the same direction. The formations of such self-assembled structure can be expected to be thermodynamically favored since it can be stabilized by the minimization of dipolar interactions.^[18a, 18b] A proposed molecular model is presented in the Figure 3c. The molecular structure was also computed by means of DFT computations and the result is presented in the Figure 3d. A good agreement is found between the experimental and theoretical data as evidenced by experimental and computed dimension of the unit cell (see Table 1).

The monolayer structure of *trans-Azo-bistpy* on HOPG was then exposed to UV light irradiation ($\lambda_{exc} = 365$ nm) for 10 minutes. As a result, desorption of *Azo-bistpy* molecules from the surface and formation of disordered aggregates was observed. Interestingly, by exposing the same sample to visible light ($\lambda_{exc} = 455$ nm) for an irradiation time as short as 5 minutes, the initial molecular packing of *trans-Azo-bistpy* was restored on graphite surface owing to the back *cis-to-trans* photo-isomerization process. At this stage, it is worth to point out that although supramolecular assemblies containing azoaryl moieties as *trans* conformation can often be visualized by the means of STM, monolayers composed entirely of *cis*-isomers are rarely observed.^[7e, 19] Indeed, upon irradiation with UV light and consequent *trans-to-cis* photo-isomerization, desorption of molecules typically occurs due to the inability

of the resulting non-planar *cis*- conformation to pack efficiently onto a surface.^[20] As discussed in the computational section (*vide infra*), this behaviour is further supported by the much lower E_d computed for *cis*-**Azo-bistpy** with respect to its *trans*- counterpart.

To shed light onto the ability of this class of photo-responsive metallopolymers to physisorb at surfaces into ordered assemblies and monitor their photoswitching behaviour, STM investigation at the solid-liquid interface has been performed both on the linear supramolecular polymers [**Azo-bistpy-Co**]_n using CoCl₂ as the octahedral coordination node, formed *in situ* and *ex situ*. *In situ* formation of [**Azo-bistpy-Co**]_n has been achieved by the addition of one equivalent of CoCl₂ × 2H₂O (*i.e.* 4 μL drop of 0.1 mM solution of isopropanol:1-phenyloctane 1:99 ^{v/v}) on the top of a pre-existing monolayer of *trans*-**Azo-bistpy** molecule. STM images of the assembled crystalline patterns are shown in the Figure 4a. It is worth to notice that combination of **Azo-bistpy** and Co(II) resulted in the formation of linear arrays physisorbed on the graphite surface. Within those linear architectures that appear periodically distributed, bright features can be seen with their interchain distance corresponding to the length of a single *trans*-**Azo-bistpy** molecule (see Table 1). According to the simulated LUMO of [*trans*-**Azo-bistpy-Co**]_n structures, those bright protrusions can be attributed to a Co(II) node and two terpyridyl moieties of two consecutive *trans*-**Azo-bistpy** molecules (see Figure 4c and Figure S7b of the ESI). Moreover, the simulated unit cell parameters match perfectly those determined experimentally (Table 1).

Figure 4. STM images of $[trans\text{-Azo-bistpy-Co}]_n$ networks formed at 1-phenyloctane solution/HOPG interface. (a) Survey image, $I_t = 25$ pA, $V_t = 550$ mV. (b) Height STM image, zoom-in, $I_t = 30$ pA, $V_t = 500$ mV. (c) Proposed molecular model. (d) DFT simulated model on graphene.

Surprisingly, exposure of the existing 2D molecular layer of $[trans\text{-Azo-bistpy-Co}]_n$ to UV light ($\lambda_{exc} = 365$ nm) for an irradiation period of 15 minutes resulted in clean re-arrangement of $[Azo-bistpy-Co]_n$ metallopolymers and formation of a new pattern onto the HOPG surface. The STM image of the interface after *in situ* irradiation is displayed in Figure 5a. The crystalline pattern features a different structural motif if compared to that before irradiation (see Figure 4). Similarly to the $[trans\text{-Azo-bistpy-Co}]_n$ monolayers, the 2D crystalline structure shown at in Figures 5a and 5b consist of linear arrays composed by bright protrusions, yet, differentl to the case of $[trans\text{-Azo-bistpy-Co}]_n$. The interspacing between them was measured as (1.7 ± 0.1) nm, which is 0.3 nm larger than that found in *trans*-based monolayers (1.4 ± 0.1) nm.

Figure 5. STM images of $[cis\text{-Azo-bistpy-Co}]_n$ formed at 1-phenyloctane solution/HOPG interface after UV irradiation using a wavelength of 365 nm. (a) Survey image, $I_t = 25$ pA, $V_t = 600$ mV. (b) Current STM image, zoom-in, $I_t = 25$ pA, $V_t = 600$ mV. (c) Proposed molecular model. (d) DFT simulated model on graphene.

Such large variation of the unit cell parameters upon UV irradiation is being associated to the *trans*-to-*cis* isomerization of azoaryl moieties, which undergo large conformational changes upon photo-induced isomerization. As a result, the area of the unit cell of *cis*-metallopolymer is 1.3 nm larger than the *trans* (Table 1). Although we cannot provide detailed and unambiguous insight into the geometry adopted by the *cis*-Azo units within the supramolecular polymers, the molecular model simulated with DFT (Figure 5d and S7d), and in particular the unit cell parameters, fits very well with the experimental results. Based on these findings, these linear supramolecular architectures can be ascribed to metallopolymers of $[cis\text{-Azo-bistpy-Co}]_n$.

Interestingly, upon irradiation of monolayer sample of [*cis*-**Azo-bistpy**-Co]_n with a visible light (white light bulb), the 2D pattern corresponding to the metallopolymer [*trans*-**Azo-bistpy**-Co]_n is completely restored. Indeed, an illumination period as short as 1 minute leads to immediate desorption of the molecules, followed by re-adsorption onto the HOPG surface of the *trans*-conformer of the supramolecular polymer assembly within about 15 min, confirming the reversible nature of the light-induced processes at play and formation of the photo-responsive surface.

3. Conclusion

In summary, *in situ* preparation of supramolecular metallopolymers bearing an azoaryl units on the backbone and Co(II) coordination nodes was achieved and its photo-switching ability in solution has been investigated in DMF solution by optical spectroscopy. In addition, 1D directional metallopolymer networks resulting from interconnection of such photofunctional molecules bearing two terpyridyl coordinating poles with CoCl₂ were generated on a HOPG surface by combining the supramolecular approach at the solid/liquid interface with *in situ* STM nanoscale-resolved imaging. The photo-isomerization of the monolayers consisting of *trans*-conformer of the bare ditopic ligand to the corresponding assemblies based on *cis* isomers has been triggered by UV light. In the case of the **Azo-bistpy** assemblies, the conformational changes accompanying the *trans*-to-*cis* transition as well as the computed low interaction energy of *cis*-**Azo-bistpy** with graphite resulted in formation of disordered supramolecular structures. However, the embedment of **Azo-bistpy** in metallopolymeric chain [**Azo-bistpy**-Co]_n limits the degree of molecular freedom and prevents the **Azo-bistpy** from fast desorption. Therefore, **Azo-bistpy** moieties could be reversibly isomerized within the metallopolymeric patterns, leading to a significant structural change of the in-plane self-assembly as a result of the contraction/expansion process of the supramolecular metallopolymeric structure associated with the *trans*-*cis* photo-isomerization processes. To

the best of our knowledge, these results provide the first examples of sub-molecularly resolved switchable metallopolymers in physisorbed monolayers and offer the possibility to prepare photo-responsive nanopatterned surfaces by controlling the switching of azobenzenes in supramolecular linear arrays.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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