

Light-Induced Contraction/Expansion of 1D Photoswitchable Metallopolymer Monitored at the Solid–Liquid Interface

Mohamed El Garah, Etienne Borré, Artur Ciesielski, Arezoo Dianat, Rafael Gutierrez, Gianaurelio Cuniberti, Stéphane Bellemin-Laponnaz,* Matteo Mauro,* and Paolo Samorì*

 \boldsymbol{T} he use of a bottom-up approach to the fabrication of nanopatterned functional surfaces. which are capable to respond to external stimuli, is of great current interest. Herein, 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 is described. The supramolecular polymerization process is followed by optical spectroscopy in dimethylformamide solution. Noteworthy, a submolecularly resolved scanning tunneling microscopy (STM) study of the in situ reversible trans-to-cis photoisomerization of a photoswitchable metallopolymer that self-assembles into 2D crystalline patterns onto a highly oriented pyrolytic graphite surface is achieved for the first time. The STM analysis of the nanopatterned surfaces is corroborated by modeling the physisorbed species onto a graphene slab before and after irradiation by means of density functional theory 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 toward the design and preparation of photoresponsive "smart" surfaces organized with an atomic precision.



full papers

1. Introduction

The synthesis of sophisticated building blocks designed to interact through noncovalent 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 toward 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 photoresponsive 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 photoinduced reactions and processes are known and among 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. Among photoswitches, 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 photoinduced isomerization. In this respect, some of us have recently reported on a novel photoresponsive class of supramolecular metallopolymers bearing diazoaryl moieties that are suitable for the preparation of self-healable and photoresponsive 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 subnanometer 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,c,7e]

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

Noteworthy, some of us studied in the past the selfassembly of three-component metallopolymers, in which **Azo-bistpy** was used as one out of the two organic ligands.^[10] However, such systems are not suitable for studying the photoswitching 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 toward 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/ highly oriented pyrolytic graphite (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, nanopatterned photoresponsive 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-bistov 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 potassium tert-butoxide ('BuOK) in dimethyl sulfoxide/tertbutanol (DMSO/t BuOH) 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 study as a coordination node because it offers low kinetic lability, which allows in situ generation of elongated 1D metallopolymers at the solid/liquid interface. Moreover, Co(II)/bistpy metallopolymers and complexes are in general thermodynamically more stable than Zn(II) analogs.

It is important to note, that the nature of the solvent, ligand:cobalt ratio, and the nature of the Co counteranion 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 $CoCl_2$ as the cobalt source and in a 1:1 ratio **Azo-***bis***tpy**: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-***bis***tpy-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]

Thus, we decided to carry out an in situ complexation between the ditopic *trans*-**Azo-***bist***py** ligand and the

www.small-journal.com





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.

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**.

In Figure 1c, two steep changes in the absorbance trend at around 1 and 2 equiv. 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 [*trans*-**Azo-bistpy**-**Co**]_n. The second regime corresponds to a *trans*-**Azo-bistpy**:Co²⁺ 1:1 to 1:2 ratio and it is ascribed to the subsequent depolymerization process of [trans-Azo-bistpy-Co]_n into the dimetallic species with trans-Azo-bistpy:Co²⁺ 1:2 stoichiometry. Subsequently, in the above 2 equiv. of CoCl₂, 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 the counterion, solvent, and even more importantly concentration, we confidentially assume that [trans-Azo-bistpy-Co], metallopolymer possesses a linear arrangement on the basis of the rigid and rod-like nature of the divergent ditopic ligand trans-Azobistpy.^[15] Such linear and ideally infinite arrangement of the [trans-Azo-bistpy-Co]_n is further corroborated by direct visualization via scanning probe technique at the solid/liquid interface (vide infra).



Figure 1. a,b) UV–visible spectra and c) plot of the variation of the absorbance monitored at 335 nm versus Co^{2+} :**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 $CoCl_2$ aliquots in the range 0–1 and 1.1-2.4 equiv. for panels (a) and (b), respectively. In (c), dotted gray lines are only intended to guide the eye.





Figure 2. Kinetic studies of the photoisomerization process for [*trans*-**Azo-***bistpy-Co***]_{***n***} in DMF** (1×10^{-5} mol) carried out by UV–vis spectrophotometry. a) *Trans*-to-*cis* photoisomerization upon irradiation at 365 nm. Spectra were recorded between 0 (black trace) and 180 s (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 s (black trace) light exposure. Black arrows indicate the variation of absorbance over photoirradiation time.

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 photoresponsiveness of the cobalt-containing metallopolymer, a DMF solution of [trans-Azo-bistpy-Co], at concentration of 1.0×10^{-5} mol was irradiated with a continuous-wave lightemitting diode (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 photoirradiation, absorption spectra show a sizeable decrease of the symmetry-allowed π - π * transition centered at 357 nm over irradiation-time and an isosbestic point at $\lambda_{abs} = 322$ nm. This finding is indicative of a *trans* \rightarrow *cis* photoisomerization process involving the diazoarvl moiety and the photostationary state is reached within 60 s of irradiation.^[9a] However, the parallel increase of the $n-\pi^*$ 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 band between 450 and 550 nm corresponding to the [(tpy)₂Co]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).

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 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 Figures S1–S5 (Supporting Information).

Figure S2 (Supporting Information) 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 terpyridyl 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 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 1D polymeric structure (see Scheme 1). In the gas phase and as displayed in Figures S4a and S5a (Supporting Information) for trans-Azobistpy-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 $(90 \pm 15)^{\circ}$ and $(90 \pm 10)^{\circ}$ for *trans*-Azo-*bist*py-Co and cis-Azo-bistpy-Co, respectively, as shown in Figures S4b and S5b (Supporting Information). In Table S1 (Supporting Information) 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 twofold 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, 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 μ L solution of **Azo-bistpy** in 1-phenyloctane at concentration of 0.1 mmol onto the HOPG surface. **Figure 3**a 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 nm².

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 ($N_{\rm mol}$), and the area occupied by a single molecule in the unit cell ($A_{\rm mol}$, with $A_{\rm mol} = A/N_{\rm mol}$) are reported in **Table 1**.



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 the Supporting Information), 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,b] A proposed molecular model is presented in Figure 3c. The molecular structure was also computed by means of DFT computations and the result is presented in 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).



Figure 3. STM images of the *trans*-**Azo-***bistpy* networks formed at the 1-phenyloctane solution/HOPG interface. a) Survey image, average tunneling current (l_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.

full papers



Structure	Azo-bistpy				[Azo- <i>bis</i> tpy-Co] _n			
	Experimental		Computed		Experimental		Computed	
	trans	cis	trans	cis	trans	cis	trans	cis
<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
A [nm ²]	$\textbf{2.8}\pm\textbf{0.2}$	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

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

The monolayer structure of *trans*-**Azo**-*bist***py** on HOPG was then exposed to UV light irradiation ($\lambda_{exc} = 365$ nm) for 10 min. As a result, desorption of **Azo**-*bist***py** molecules from the surface and formation of disordered aggregates were observed. Interestingly, by exposing the same sample to visible light ($\lambda_{exc} = 455$ nm) for an irradiation time as short as 5 min, the initial molecular packing of *trans*-**Azo**-*bist***py** was restored on graphite surface owing to the back *cis*-to-*trans* photoisomerization 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* photoisomerization, desorption of molecules typically occurs due to the inability of the resulting nonplanar *cis* conformation to pack efficiently onto a surface.^[20] As discussed in the computational section (vide infra), this behavior is further supported by the much lower E_d computed for *cis*-**Azo-bistpy** with respect to its *trans* counterpart.



Figure 4. STM images of [*trans*-**Azo**-*bis*tpy-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.



To shed light onto the ability of this class of photoresponsive metallopolymers to physisorb at surfaces into ordered assemblies and monitor their photoswitching behavior, 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 1 equiv. of $CoCl_2 \times 2H_2O$ (i.e., 4 µL drop of 0.1×10^{-3} M 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 in the Supporting Information). Moreover,

the simulated unit cell parameters match perfectly those determined experimentally (Table 1).

Surprisingly, exposure of the existing 2D molecular layer of [*trans*-**Azo**-*bist***py**-**Co**]_n to UV light ($\lambda_{exc} = 365$ nm) for an irradiation period of 15 min resulted in clean rearrangement of [**Azo**-*bist***py**-**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). Similar to the [*trans*-**Azo**-*bist***py**-**Co**]_n monolayers, the 2D crystalline structure shown at in Figure 5a,b consists of linear arrays composed by bright protrusions, yet, different to the case of [*trans*-**Azo**-*bist***py**-**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.

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 photoinduced 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



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

full papers



cis-Azo units within the supramolecular polymers, the molecular model simulated with DFT (Figure 5d and Figure S7d (Supporting Information)), 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*-Azo-*bis*tpy-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 min leads to immediate desorption of the molecules, followed by readsorption 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 photoresponsive 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 photoswitching 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 photoisomerization 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], 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 photoisomerization processes. To the best of our knowledge, these results provide the first examples of submolecularly resolved switchable metallopolymers in physisorbed monolayers and offer the possibility to prepare photoresponsive 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.

Acknowledgements

E.B., S.B.-L., and M.M. gratefully acknowledge the University of Strasbourg Institute for Advanced Study (USIAS) for funding this work with an USIAS Fellowship. The authors gratefully acknowledge financial support from the European Commission through the Marie Sklodowska-Curie project ITN project iSwitch (GA-642196), the Agence Nationale de la Recherche through the Labex projects CSC (ANR-10-LABX-0026 CSC) within the Investissement d'Avenir program (ANR-10-120 IDEX-0002-02), and the International Center for Frontier Research in Chemistry (icFRC). Computational resources were provided by the Center for Information Services and High Performance Computing (ZIH) of the Technische Universität Dresden.

Conflict of Interest

The authors declare no conflict of interest.

- a) J. H. van Esch, B. L. Feringa, Angew. Chem. Int. Ed. 2000, 39, 2263; b) J. A. A. W. Elemans, A. E. Rowan, R. J. M. Nolte, J. Mater. Chem. 2003, 13, 2661; c) Q. W. Li, W. Y. Zhang, O. S. Miljanic, C. H. Sue, Y. L. Zhao, L. H. Liu, C. B. Knobler, J. F. Stoddart, O. M. Yaghi, Science 2009, 325, 855.
- [2] a) M. Matena, A. Llanes-Pallas, M. Enache, T. Jung, J. Wouters, B. Champagne, M. Stöhr, D. Bonifazi, *Chem. Commun.* 2009, 0, 3525; b) R. Gutzler, T. Sirtl, J. F. Dienstmaier, K. Mahata, W. M. Heckl, M. Schmittel, M. Lackinger, *J. Am. Chem. Soc.* 2010, 132, 5084.
- [3] a) R. A. Bissell, E. Cordova, A. E. Kaifer, J. F. Stoddart, *Nature* 1994, *369*, 133; b) K. Itaya, *Prog. Surf. Sci.* 1998, *58*, 121; c) A. S. Klymchenko, S. Furukawa, K. Müllen, M. Van der Auweraer, S. De Feyter, *Nano Lett.* 2007, *7*, 791.
- [4] a) S. De Feyter, M. M. S. Abdel-Mottaleb, N. Schuurmans, B. J. V. Verkuijl, J. H. van Esch, B. L. Feringa, F. C. De Schryver, *Chem. Eur. J.* 2004, 10, 1124; b) A. Ciesielski, S. Lena, S. Masiero, G. P. Spada, P. Samorì, *Angew. Chem. Int. Ed.* 2010, 49, 1963; c) A. Ciesielski, M. El Garah, S. Haar, P. Kovaricek, J. M. Lehn, P. Samorì, *Nat. Chem.* 2014, 6, 1017.
- [5] a) P. Vanoppen, P. C. M. Grim, M. Rucker, S. DeFeyter, G. Moessner, S. Valiyaveettil, K. Mullen, F. C. DeSchryver, J. Phys. Chem. 1996, 100, 19636; b) M. Irie, Chem. Rev. 2000, 100, 1683; c) L. P. Xu, L. J. Wan, J. Phys. Chem. B 2006, 110, 3185; d) M. M. Russew, S. Hecht, Adv. Mater. 2010, 22, 3348; e) S. Bonacchi, M. El Garah, A. Ciesielski, M. Herder, S. Conti, M. Cecchini, S. Hecht, P. Samori, Angew. Chem. Int. Ed. 2015, 54, 4865.
- [6] a) W. Fuß, C. Kosmidis, W. E. Schmid, S. A. Trushin, Angew. Chem. Int. Ed. 2004, 43, 4178; b) C.-S. Tsai, J.-K. Wang, R. T. Skodje, J.-C. Lin, J. Am. Chem. Soc. 2005, 127, 10788; c) D. Riedel, M. Cranney, M. Martin, R. Guillory, G. Dujardin, M. Dubois, P. Sonnet, J. Am. Chem. Soc. 2009, 131, 5414.
- [7] a) M. Alemani, M. V. Peters, S. Hecht, K.-H. Rieder, F. Moresco, L. Grill, J. Am. Chem. Soc. 2006, 128, 14446; b) G. Pace, V. Ferri, C. Grave, M. Elbing, C. von Hänisch, M. Zharnikov, M. Mayor, M. A. Rampi, P. Samorì, Proc. Natl. Acad. Sci. USA 2007, 104, 9937; c) A. S. Kumar, T. Ye, T. Takami, B.-C. Yu, A. K. Flatt, J. M. Tour, P. S. Weiss, Nano Lett. 2008, 8, 1644; d) A. Safiei, J. Henzl, K. Morgenstern, Phys. Rev. Lett. 2010, 104, 216102; e) D. Bleger, A. Ciesielski, P. Samorì, S. Hecht, Chem. - Eur. J. 2010, 16, 14256.
- [8] a) S. J. van der Molen, H. van der Vegte, T. Kudernac, I. Amin,
 B. L. Feringa, B. J. van Wees, *Nanotechnology* 2006, 17, 310;

ADVANCED SCIENCE NEWS

b) R. Arai, S. Uemura, M. Irie, K. Matsuda, *J. Am. Chem. Soc.* 2008, *130*, 9371; c) Arramel, T. C. Pijper, T. Kudernac, N. Katsonis, M. van der Maas, B. L. Feringa, B. J. van Wees, *Nanoscale* 2013, *5*, 9277; d) T. Sakano, Y. Imaizumi, T. Hirose, K. Matsuda, *Chem. Lett.* 2013, *42*, 1537.

- [9] a) H. M. D. Bandara, S. C. Burdette, *Chem. Soc. Rev.* 2012, *41*, 1809; b) C. Knie, M. Utecht, F. L. Zhao, H. Kulla, S. Kovalenko, A. M. Brouwer, P. Saalfrank, S. Hecht, D. Bleger, *Chem. Eur. J.* 2014, *20*, 16492; c) D. Bléger, S. Hecht, *Angew. Chem. Int. Ed.* 2015, *54*, 11338.
- [10] a) E. Borré, J. F. Stumbé, S. Bellemin-Laponnaz, M. Mauro, *Angew. Chem. Int. Ed.* 2016, *55*, 1313; b) E. Borré, S. Bellemin-Laponnaz, M. Mauro, *Chem. - Eur. J.* 2016, *22*, 18718.
- [11] a) S. De Feyter, F. C. De Schryver, *Chem. Soc. Rev.* 2003, *32*, 139; b) F. Rosei, M. Schunack, Y. Naitoh, P. Jiang, A. Gourdon, E. Laegsgaard, I. Stensgaard, C. Joachim, F. Besenbacher, *Prog. Surf. Sci.* 2003, *71*, 95; c) J. V. Barth, G. Costantini, K. Kern, *Nature* 2005, *437*, 671; d) A. Ciesielski, C.-A. Palma, M. Bonini, P. Samorì, *Adv. Mater.* 2010, *22*, 3506.
- [12] a) S. De Feyter, M. Larsson, N. Schuurmans, B. Verkuijl, G. Zoriniants, A. Gesquière, M. M. Abdel-Mottaleb, J. van Esch, B. L. Feringa, J. van Stam, F. De Schryver, *Chem. Eur. J.* 2003, *9*, 1198; b) R. T. Baker, J. D. Mougous, A. Brackley, D. L. Patrick, *Langmuir* 1999, *15*, 4884.
- [13] T. Yutaka, M. Kurihara, H. Nishihara, *Mol. Cryst. Liq. Cryst.* 2000, *343*, 193.

- [14] E. C. Constable, K. Harris, C. E. Housecroft, M. Neuburger, J. A. Zampese, *Dalton Trans.* 2011, 40, 11441.
- [15] a) E. C. Constable, K. Harris, C. E. Housecroft, M. Neuburger, *Dalton Trans.* 2011, 40, 1524; b) E. C. Constable, C. E. Housecroft, M. Neuburger, S. Schaffner, C. B. Smith, *Dalton Trans.* 2005, 0, 2259.
- [16] a) C. Enachescu, I. Krivokapic, M. Zerara, J. A. Real, N. Amstutz,
 A. Hauser, *Inorg. Chim. Acta* 2007, *360*, 3945; b) S. Kremer,
 W. Henke, D. Reinen, *Inorg. Chem.* 1982, *21*, 3013.
- [17] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, *Comput. Phys. Commun.* 2005, *167*, 103.
- [18] a) A. Ciesielski, L. Piot, P. Samorì, A. Jouaiti, M. W. Hosseini, Adv. Mater. 2009, 21, 1131; b) M. El Garah, N. Marets, M. Mauro, A. Aliprandi, S. Bonacchi, L. De Cola, A. Ciesielski, V. Bulach, M. W. Hosseini, P. Samorì, J. Am. Chem. Soc. 2015, 137, 8450; c) M. Surin, P. Samorì, A. Jouaiti, N. Kyritsakas, M. W. Hosseini, Angew. Chem. Int. Ed. 2007, 46, 245.
- [19] C. L. Feng, Y. J. Zhang, J. Jin, Y. L. Song, L. Y. Xie, G. R. Qu, L. Jiang, D. B. Zhu, *Surf. Sci.* 2002, *513*, 111.
- [20] J. Zeitouny, C. Aurisicchio, D. Bonifazi, R. De Zorzi, S. Geremia, M. Bonini, C.-A. Palma, P. Samorì, A. Listorti, A. Belbakra, N. Armaroli, *J. Mater. Chem.* **2009**, *19*, 4715.

Received: May 29, 2017 Revised: July 19, 2017 Published online: