



Photochromic Torsional Switch (PTS): a light-driven actuator for the dynamic tuning of π -conjugation extension†

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Here we present a molecular architecture that can reversibly change the geometric conformation of its π -system backbone via irradiation with two different wavelengths. The proposed 'molecular actuator' consists of a photoswitchable azobenzene orthogonally connected to a π -conjugated bithiophene by both direct and aliphatic linker-assisted bonding. Upon exposure to 350 nm light, the *trans* azobenzene moiety isomerizes to its *cis* form, causing the bithiophene to assume a semiplanar anti conformation (extended π -conjugation). Exposure to 254 nm light promotes the isomerization of the azobenzene unit back to its initial extended *trans* conformation, thus forcing the bithiophene fragment to twist out of coplanarity (restricted π -conjugation). The molecular conformation of the bithiophene was characterized using steady-state UV-vis and nuclear magnetic resonance spectroscopy, as well as *ab initio* computations. The proposed molecular design could be envisaged as a π -conjugation modulator, which has potential to be incorporated into extended linear π -systems, *i.e.* via the terminal α -thiophene positions, and used to tune their optical and electronic properties.

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Introduction

The ability to control mechanical motion at the molecular level is pivotal for the development of novel responsive materials able to translate external stimuli into work. In the last 20 years, a large variety of 'molecular actuators' able to convert thermal, chemical, and photochemical energy into operating motion have been successfully employed to perform tasks at the meso- and macroscopic levels.^{1–12} The restrained mechanistic action of these molecular actuators is commonly correlated with thoughtful design of their dynamic molecular structure. In order to provide different functions, various molecular architectures have been proposed, *e.g.* shuttles,^{13,14} rotors,^{15–19}

scissors,^{20,21} cars,^{22,23} chemical valves,^{24,25} and artificial molecular-based muscles.^{26–29} Despite the large variety of synthetic responsive architectures reported in the literature, examples of designs conceived to exploit the light-mediated molecular motion as a means to tune the conjugation length of linear π -systems are few. Molecular actuators proposed for such a scope commonly rely on their ability to mechanically modulate the π -bond geometry of a conjugated structure either by the cleavage-formation of π -bonds,^{30–33} or by the torsion-planarization of π -orbitals.^{34–36} In the first case, molecular actuators, *e.g.* diarylethenes, are usually incorporated as monomeric unit into the π -conjugated backbone of oligomers and polymers, however their operation reversibility efficiency decreases inversely with the enhancement of the π -system. In contrast, the second class of actuators are usually incorporated as pendant functionality along π -conjugated structures, thus their operation is not directly affected by the extension of π -system. The function of the latter type of actuators, however, is usually limited by the possibility to switch the orientation of their constituents between only two semiplanar conformations (*e.g.* *syn* and *anti*)^{34–36} that do not differ significantly in their electronic structure. The restricted operation of these molecular architectures does not offer the possibility to obtain highly twisted π -orbital geometries, which if achieved would allow for the full exploitation of the physical properties of π -conjugated systems.^{37–43} Molecular actuators able to modulate the π -bond geometry beyond the usual semiplanar conformation are thus

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extremely desirable as they can allow for preparation of novel responsive semiconductor materials, *e.g.* π -conjugated oligomers and polymers, that may allow for the fabrication of optical and electronic devices with unprecedented properties and tunability. Herein we report on a novel molecular design, referred to as a 'Photochromic Torsional Switch' (PTS), able to reversibly change the conformation of its π -conjugated backbone from twisted to planar in response to light. The proposed PTS actuator can be envisaged as a chemical motif that can be potentially incorporated into the backbone of linear π -systems to reversibly modulate their conjugation length.

Results and discussion

The design of PTS **1** is illustrated in Scheme 1. The PTS actuator consists of an azobenzene-switch laterally connected to a bithiophene unit by both direct and aliphatic linker-assisted bonding. Two methyl units in the *meta* position of the azobenzene guarantees its orientation in an orthogonal arrangement to the bithiophene fragment, thus reducing the communication between the π -orbitals of the two constituents. A ten-carbon alkene chain connected with an alkoxy benzene unit mechanically transfers the isomerization motion of the azobenzene to the bithiophene backbone. PTS actuator **1** was synthesized *via* a convergent route involving the attachment of the azobenzene and the resorcinol monomethyl ether groups to bithiophenic unit, followed by the introduction of terminal olefin side chains for the final macrocyclization. The desired PTS compound **1** was obtained as the pure *trans* conformer by intra-molecular cross metathesis of the two terminal alkenes of its open precursor (for details about the synthesis, see ESI[†]). The geometrical conformations of both **1.trans** and **1.cis**, were determined by replica-exchange molecular dynamic (REMD) computations performed at the density functional tight binding (DFTB) level (REMD@DFTB).⁴⁴ Several minima were identified and optimized statically at the density functional theory level (see ESI for details[†]). The lowest-lying structures revealed that when the azobenzene is in its extended *trans* conformation (**1.trans**), the bithiophene unit is forced to twist out of coplanarity with a dihedral angle (θ) of 55° (Fig. 1). Contrarily, when the azobenzene assumes its *cis* form (**1.cis**) the bithiophene assumes a more planar and π -conjugated conformation with

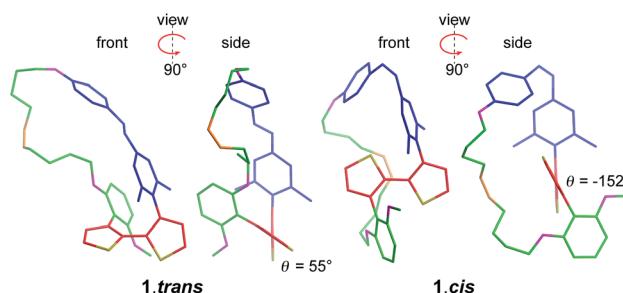
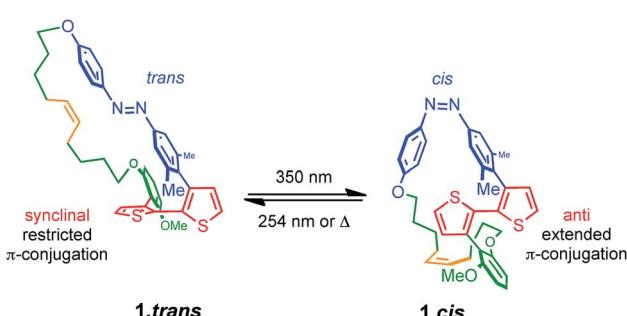


Fig. 1 Optimized geometries of **1.trans** (left) and **1.cis** (right) identified from REMD computation.

$\theta = -152^\circ$. The latter dihedral angle is in good agreement with the literature values reported for unsubstituted bithiophenes in their anti-conformation ($\theta = 146\text{--}152^\circ$).^{45,46} On the other hand, the bithiophene configuration in **1.trans** has a dihedral angle that significantly differs from the values commonly observed for either the *syn* or the *anti* conformers ($\theta = 35\text{--}37^\circ$).^{45,46} The synclinal arrangement assumed by the thiophenes in **1.trans** is the result of a suppressed rotation along the thiophene–thiophene bond derived by the stretching of the aryloxy alkene linker. Thus, the bithiophene is mechanically arrested in a conformation that would be energetically unfavourable for the corresponding unmodified counterparts. In order to probe any structural variations of the bithiophenes following azobenzene isomerization, we used UV-vis and nuclear magnetic resonance spectroscopy, and electronic structure computations. The absorption spectra of the **1.trans** and **1.cis** are the superposition of individual constituting components, namely the azobenzene, in its *trans* and *cis* form, and the phenylene–bithiophene segment (see ESI[†]). The absorption spectrum of **1.trans** displays four distinguishable peaks: 454 nm, 363 nm, 284 nm and 245 nm (Fig. 2a). According to TDDFT computation performed on top of the lowest-energy structures as extracted by REMD@DFTB, the first two bands correspond to the typical $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitations represented respectively by the $n\text{--}\pi^*$ and $\pi\text{--}\pi^*$ transitions localized on the azobenzene. The peak centred at 284 nm is mainly the result of the $S_0 \rightarrow S_4$ excitation of the phenyl-functionalized bithiophene. In the framework of the molecular orbitals, this excitation can be described as a $\text{HOMO} \rightarrow \text{LUMO}+1$ single particle transition involving the π and π^* orbitals prevalently localized on the bithiophene with partial delocalization on the phenylene segment and azobenzene unit (see ESI for details[†]). Notably, this peak is not observed for the open precursor of **1**, which exhibits a broader band centred at 363 nm with a shoulder at 270 nm (see ESI[†]). The resulting spectral broadening of the PTS-open precursor can be ascribed to the retention of full rotational freedom along the thiophene–thiophene bond. The last blue-shifted band of **1** at 245 nm is the result of a high-energy electronic transition involving the $\pi\text{--}\pi^*$ orbitals localized on the phenyl rings of the azobenzene. Upon irradiation at 350 nm approximately 86% of the *trans* isomer of azobenzene is converted to the *cis* form (Fig. 2a). The resulting absorption spectrum, **1.cis**, exhibits the typical signature of the azobenzene in its *cis* conformation, with



Scheme 1 Structures of the studied Photochromic Torsional Switch (PTS) unit.



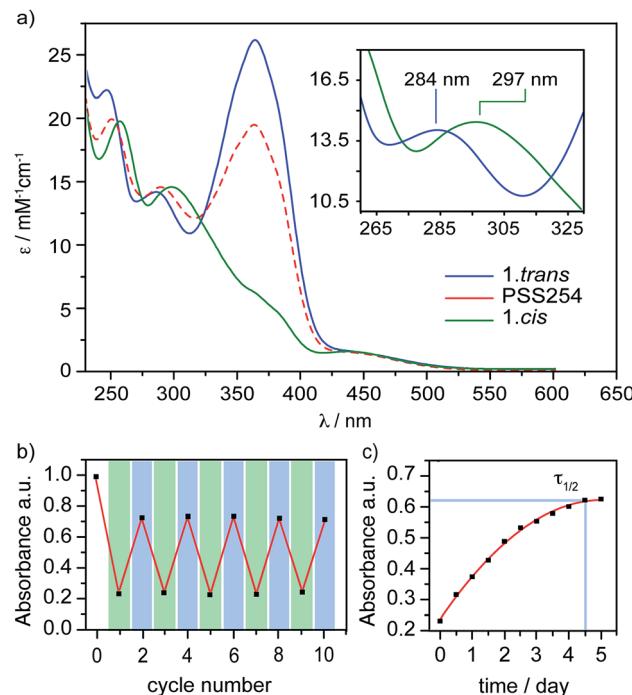


Fig. 2 (a) Absorption spectrum of **1.trans** (blue), **1.cis** (green), and the photostationary state PSS254 (red) in tetrahydrofuran (THF) solution. The inset shows the $S_0 \rightarrow S_4$ band of the phenylene–bithiophene segment on an enlarged scale. (b) Measured absorbance at $\lambda = 363$ nm of **1** in THF solution alternating irradiation at $\lambda = 350$ nm (green) and $\lambda = 254$ nm (blue) in repeated switching cycles. (c) Measured absorbance at $\lambda = 363$ nm of **1.cis** in THF solution during thermal relaxation.

a reduction in the oscillation strength for the $\pi-\pi^*$ transition ($\sim 23\%$ absorption intensity at 363 nm). However, no significant changes in the absorption profile were observed for the $S_0 \rightarrow S_1$ ($n-\pi^*$) transition. Conversely, bands at 284 nm and 245 nm exhibit a bathochromic shift of 13 nm and 11 nm, respectively (Fig. 2a). Since the π -conjugation extension of the bithiophene is directly correlated with the peak at 284 nm, any conformational change in its π -bonds geometry will result in a spectral shift of this band. According to the spectral changes and TDDFT assignments, the red-shift observed for this band is ascribable to the planarization of the bithiophenic segment which results in a more effective delocalization of its molecular orbitals along the two thiophene units. After the *trans*-to-*cis* isomerization of **1**, it is possible to recover about $\sim 55\%$ of the initial *trans* isomer by irradiating at 254 nm (photostationary state, Fig. 2a).⁴⁷ The latter wavelength was selected as an alternative excitation to the usual 430 nm due to the similar oscillator strengths of the $n-\pi^*$ band for the two conformers. Monitoring the UV-vis absorptions of **1** after many repeated alternating irradiation cycles at $\lambda = 350$ nm and at $\lambda = 254$ nm, respectively, did not result in any noticeable degradation of the compound, highlighting the robustness of the PTS architecture (Fig. 2b). The recovery of the initial **1.trans** conformer can also be obtained by thermal relaxation of the azobenzene moiety with a half-life ($\tau_{1/2}$) of ca. 4.5 days at 25°C (Fig. 2c). It is noteworthy that, such long thermal stability of the *cis* isomer is not observed for the non-

PTS alkoxy-azobenzene analogue (see ESI†). Slow thermal relaxation has been usually reported for azobenzenes that are functionalized in the *ortho* position with electron donating⁴⁸ and withdrawing⁴⁹ groups. The lack of electron directing functionality on the PTS azobenzene, along with the faster thermal relaxation of its open precursor and non-PTS azobenzene analogue suggest that the slow thermal relaxation of **1.cis** can be associated to a reduced degree of freedom in the isomerization motion (see ESI†).

Finally, ¹H-NMR spectroscopy was conducted to investigate the rotation along the thiophene-thiophene bond upon the isomerization of the azobenzene moiety. After the *trans*-to-*cis* isomerization of **1**, the aromatic protons of thiophene H_a (δ 7.47 ppm) and H_b (δ 6.81 ppm) showed a significant up-field shifts of 0.36 and 0.11 ppm, respectively (Fig. 3). On the other hand, the aromatic signals of the linker's phenylene, H_i, H_h and H_l, observed respectively at 7.10, 6.36, and 6.28 ppm for **1.trans**, showed downfield shifts of 0.17, 0.33, and 0.30 ppm, respectively. These spectral changes are reasonable given the different molecular geometry assumed by the two PTS conformers. In **1.trans**, the thiophene units assume a synclinal arrangement, orienting the two phenyl fragments of the linker and the azobenzene in a parallel-displaced conformation. Such arrangement leads to the lowering of the magnetic shielding effect in the thiophenes (downfield shift) while increasing that of the phenylenes due to $\pi-\pi$ stack interactions (upfield shift). When the azobenzene isomerizes to its *cis* form, the thiophenes assume a more planar conformation with concomitant edge-to-face arrangement with the corresponding pseudo-orthogonal phenyl rings of the linker and azobenzene. This conformation results in an increase in the magnetic shielding of the thiophene protons (upfield shift), and a decrease in the shielding of the phenylene counterpart (downfield shift). The resulting ¹H-NMR spectral profile of **1.cis** is in good agreement with bithiophene signature of the open analogue as well as with 'planarly constrained' bithiophenes reported by Sugiyasu *et al.*⁵⁰ Hence, it can be concluded that compound **1** undergoes a rotation-like (twisted-planar) motion along the thiophene-thiophene bond upon *trans*-*cis* isomerization of the azobenzene switch.

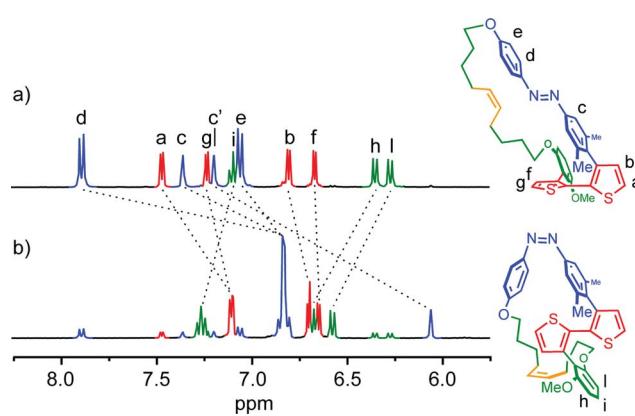


Fig. 3 Aromatic region of the ¹H-NMR spectrum of compound **1** in tetrahydrofuran-d8. Before (a) and after 1 h of irradiation at 350 nm (b).

Conclusions

In conclusion, a novel molecular actuator capable of modulating the extension of its π -conjugated backbone in response to light has been designed. The mechanical motion associated with the *trans-cis* isomerization of an azobenzene has been translated to a change in the planarity of the connected bithiophene, thus allowing for the dynamic tuning of its π -conjugation. This work provides a basis for the development of novel light-driven molecular actuators that can be used to tune the physical properties of extended π -conjugated system. The possibility to integrate the proposed PTS structure into conjugated oligomers and polymers, *i.e.* *via* the terminal α -thiophene positions, can potentially lead to the next-generation of photochromic molecular materials with both photochromic and photoconductive behaviour, and allow for the fabrication of novel light responsive optoelectronic devices.

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47 Note: ~55% of azobenzene *trans* isomer corresponds to ~72% absorption intensity at 363 nm. Irradiation at 254 nm does not result in any isomerization of olefin double bond (see ESI†).

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