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A Cyclic Azobenzenophane-Based Smart Polymer for Chiroptical Switches

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Jinjie Lu,[a] Ganquan Jiang,[a] Zhengbiao Zhang,[a] Wei Zhang,[a] Yonggang Yang,[a] Yong Wang,*[b] Nianchen Zhou,*[a] Xiulin Zhu*[a]

The photoresponsive smart polymer with asymmetric cyclic azobenzenophanes as pendant groups is synthesized for the first time. In the beginning, we pre-surveyed the chiroptical properties of planar chiral azobenzenes (9a, 9b and 9c) with different methylene spacers (n = 2, 6, 11) *via* experimentaland theoretical approaches, finding that the cyclic configuration with six-methylene spacers showsinteresting chiroptical behavior for oscillating “Zero-negative-Zero” CD signal changes at theabsorption region of azobenzene segments during the photoisomerization process. And these experimental data were strongly supported by theoreticalcalculation. Moreover, three functional polymers with different cyclic azobenzenophanes as pendants were prepared and their chiroptical properties were also studied detailedly. We found, unlike the other two polymers derived from 9a or 9c, the unique properties of the cyclic pendants 9b can effectively transfer to the corresponding polymer (PCM) through the reflection of the specific optical rotation measurement under alternating UV/Vis lights irradiation and signify no fatigue. It means the obtained polymeric materials PCM is a good candidate for a chiroptical switch based on *zero*-rotation/*levo*-rotation.

Introduction

In recent years, smart responsive materials have captured increasing interests due to their sensitivities to external stimuli such as pH, temperature, light, enzyme, electric field and so on.[1-5] Especially, azobenzene-containing compoundsare promising smart materialsas logical gates, molecular switches and drug carriers[6-9]owing to the reversible *trans-cis* photoisomerization of azobenzene units.[10] On the other hand, binaphthyl segments have stable chiral configuration, and the dihedral angle between the two naphthalene rings may twist at various external fields. Accordingly molecules with 2, 2’-disubstituted binaphthyl segments have been widely utilized as asymmetric catalysts, organic light-emitting diodes and chiral recognition agents.[11-13]As expected, the combination of photoregulated azobenzene and chiral binaphthyl moieties have provided an opportunity for the rational design and facile synthesis of “smart” materials systems. In the past few decades, diverse linear azobenzenophanes (molecules composed of azobenzene and binaphthyl segments) have been reported and impressively used as chiral dopants of liquid crystals.[14-18]Since the first kind of cyclic azobenzenophane was synthesized by Rajakumar[19] in 2006, various of its derivatives have been emerged as promising alternative structures. Li and Takaishi found that the topological constraint imposed by ring backbones on molecules offers superior properties and additional skills (especially in the chiroptical field) contrasting to linear analogues.[20-30]As we all know, novel and reversible chiroptical switches, such as *levo*- (On)/*zero*- (Off) switches, whose chiral output can be adjusted by specific lights, have been poised to play expanded roles in many applications including chiral catalysis, electro-optical displays and telecommunications.[31-34] So, cyclic azobenzenophanes may be a potential candidate for it.

In general, polymer materials show better designability, machinability compared to small molecules. Meanwhile chirality in covalent or supramolecular polymers has attracted considerable interests due to their promising applications thereof.[35-37]Consequently, extensive efforts have been devoted to incorporate azobenzenophanes segments into macromolecular scaffolds. So far, embedding photochromic molecular geometries and chiralbinaphthylene segments into the polymeric main chain have been studied by Jaycox’s group.[38-41] Inspired by the works of Takaishi and Jaycox’s research groups, we have always been striving to develop some excellent polymeric chiroptical switches that can be benefited from cyclic azobenzenophanes in recent years. And to the best of our knowledge, few studies on the cyclic azobenzenophanes-based polymers have been reported so far.

Herein, we report our latest research on the preparation of macromolecules based on cyclic azobenzenophanes. Firstly, we designed and obtained three kinds of linear α-azide-ω-alkyne azobenzenophanes with different methylene spacers (n = 2, 6, 11).

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[a] *Jiangsu Key Laboratory of Advanced Functional Polymer Design and Application College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou, 215123, P. R. China. E-mail: xlzhu@suda.edu.cn.; nczhou@suda.edu.cn.*

[b] *Key Laboratory of Organic Synthesis of Jiangsu Province College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China. E-mail: yowang@suda.edu.cn.*

Electronic Supplementary Information (ESI) available: Experimental details for synthesis of 9a-c and PCM, polymerizations, structural characterization of obtained compounds and computational results. See DOI: 10.1039/x0xx00000x

Following, their cyclic enantiomers were prepared with relatively high yields (> 80%) *via* CuAAC[42] (Cu-Catalyzed Azide-Alkyne Cycloaddition) method. The synthetic routes of cyclic azobenzenophanes are shown in Scheme S1. And all structures have been confirmed by ^{1}H NMR (Figures S1-S3), high-resolution mass spectroscopy (HR-MS) and elemental analysis (EA) before further studies (See Supporting Information). Differed from the symmetric structures reported before,[21] the current cyclic constructions are asymmetry, in which azobenzene unit and binaphthyl segment are connected by two different linkers. We considered that such an asymmetric configuration will inevitably endow the compounds novel chiroptical properties. Thus it is worthy to investigate and compare the photoisomerization behavior and optical property of three cyclic compounds with diverse linker lengths *via* experimental and theoretical methods. As was expected, the obtained cyclic azobenzenophanes demonstrated unique properties, and cyclic construction with six-methylene spacers (9b) showed interesting chiroptical behavior *via* the confirmation of experimental and theoretical data. As mentioned above, the introduction of small rings into polymers can retain the both advantages of the cyclic molecules and polymers. Thereupon we elaborately designed and synthesized a serial of vinyl monomers derived from 9a, 9b and 9c by Suzuki coupling reactions, and then obtained the homo polymer bearing them as pendent groups by free radical polymerization, as shown in Scheme 1. Similarly, the optical activities of the polymers have also been investigated in details.

Experimental

All experimental section was detailed in the Supporting Information.

Results and discussion

Figure 1 shows the changes in UV/Vis spectra of 9a, 9b and 9c in chloroform by irradiating with 365 nm UV light and 436 nm visible light, respectively. It is seen that they exhibit similar photoisomerization behavior when measured at the same conditions. As reported previously, the absorption of the binaphthyl groups was less than 350 nm. So the typical peaks at 241, 296 and 323 nm can be assigned as the ^{1}Bb, ^{1}La and ^{1}Lb transitions of the binaphthyl group. The ^{1}Bb and ^{1}Lb bands correspond to the long axis of the naphthyl group, while the ^{1}La band corresponds to the short axis.[22] Then, the absorption at 367 nm is the characteristic intense π → π* transition of *trans* azobenzene moiety. Moreover, the rates constants of *trans* → *cis* (k_e) and *cis* → *trans* (k_h) photoisomerization of three cyclic structures have been calculated *via* their corresponding first-order kinetic curves as plotted in Figure S7, which are listed in Table 1. It shows that the cyclic azobenzenophane 9a has both slower photoisomerization rates of *trans* → *cis* and *cis* → *trans* than those of its similar counterparts 9b and 9c, because the shorter linkers increase the rigidity of smaller ring 9a, making isomerization of azobenzene segments relatively harder.

The CD spectra of cyclic azobenzenophanes at initial states, photostationary states (PSS$_{uv}$ and PSS$_{vis}$) are shown in Figure 1. The distinguishing differences among three cyclic analogues were reflected. Just like previous research,[43] the region we studied mainly is from 380 nm to 500 nm for only n → π* transition of azobenzene segment presented on this optical wavelength range. As expected, linker length has a great impact on the CD signals. The cyclic construction 9a with shortest linkers shows distinct Cotton effect for the planar chirality induced by chiral transfer from binaphthyl than the other two. However it's an interesting phenomenon that after irradiating by 365 nm light, the molecular 9b with six-methylene spacers exhibited larger change of the exciton couplet signals at 400-500 nm than 9a with two-methylene spacers, which is different from the variation characterizations of symmetric cyclic azobenzenophanes described by Takaishi.[26] Conversely, the CD spectra reversed fast to the initial states upon 436 nm light irradiation. Due to the long linkers that may thwart the chirality transfer, compound 9c almost shows no chiroptical response in the research region. Meanwhile, it's noteworthy that for 9b, a "Zero-negative-Zero" CD signal change was observed during photoisomerization process, which can endow 9b a potential application as novel *levo/zero* switches.

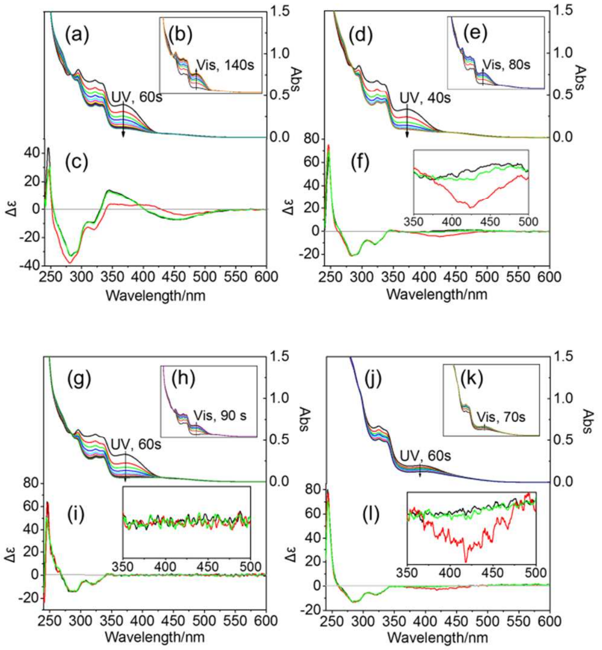


Figure 1 (a), (d), (g) and (j) changes in the absorption spectra of 9a-c and PCM after 365 nm light irradiation. (b), (e), (h) and (k) changes in the absorption spectra of 9a-c and PCM after 436 nm light irradiation. (c), (f), (i) and (l) CD spectra of 9a-c and PCM at the initial states (black line) and the photostationary states resulting from irradiation at 365 nm light (red line) and 436 nm light (green line) in chloroform. Conditions: 0.033 mg/mL, 25 °C, irradiation wavelengths = 365 nm (10 mW/cm^2) and 436 nm (3.6 mW/cm^2).

Furthermore, calculation of the electronic circular dichroism (ECD) spectra of cyclic azobenzenophanes was carried out using the TD-DFT-M06-2x/6-31G(d) level with Gaussian 09.[44] In order to cover the 200–600 nm range, 30 transitions were calculated. Seen from Figure 2, the simulated spectra of 9a-c appeared different positive/negative signals, which agreed well with the experimental results (as shown in Figure 1). As expected, the lowest energy band experimentally found for complex 9a-*trans* around 489 nm mainly originates from HOMO-8 → LUMO transition, which can be assigned to $\pi_{azo} \rightarrow \pi^*_{azo}$ due to their orbital characters of the corresponding starting and arriving states (See Figures S11-S12 and Tables S2-S3). Accordingly, the lowest energy band experimentally found for complex 9a-*cis* around 458 nm mainly originates from HOMO-2 → LUMO and HOMO-3 → LUMO transition, which can be assigned to $\pi_{bin} \rightarrow \pi^*_{azo}$, $\pi_{azo} \rightarrow \pi^*_{azo}$, and $\pi_{N3} \rightarrow \pi^*_{azo}$, respectively, contributing to the cyclic azobenzenophane 9a geometry transfer from *trans*- to *cis*- isomer. Not surprisingly, similar $\pi \rightarrow \pi^*$ transitions could also be located for other cyclic azobenzenophane 9b and 9c, as shown in Figures S13-S16 and Tables S4-S7.

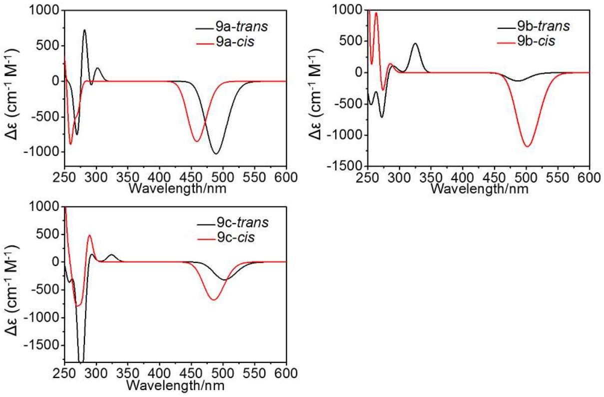


Figure 2 Calculated CD curves of cyclic azobenzenophanes 9a-c at the level of TD-M06-2x/6-31G(d).

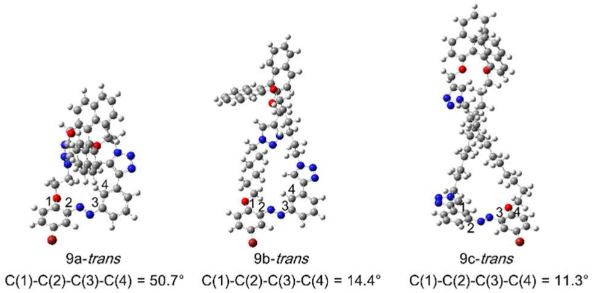


Figure 3 M06-2x/6-31G(d)-optimized structures of 9a-c at *trans*- states.

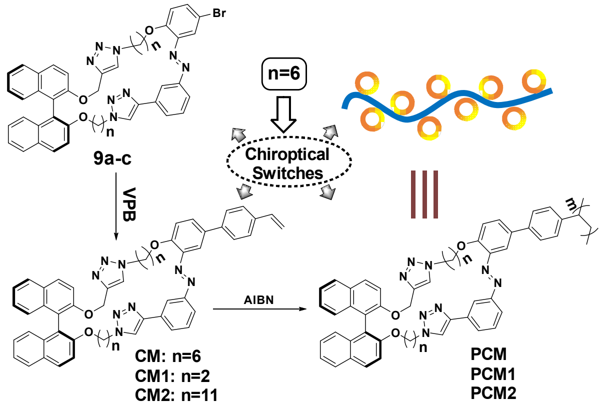
Simultaneously, the optimized geometries of 9a-c *trans*-isomers obtained by DFT calculation at the M06-2x/6-31G(d) level are shown in Figure 3. Generally, the twist of the azobenzene moieties can reflect indirectly the CD intensity and the Cotton-effect pattern at its absorption region. So, the torsion angles of C(1)-C(2)-C(3)-C(4) between the two benzene rings of azobenzene in compounds 9a-*trans*, 9b-*trans* and 9c-*trans* have been calculated as 50.7°, 14.4° and 11.3° respectively. These results illustrate that the azobenzene moieties are not fully planar and 9a has a most distorted configuration than the other two structures. It means that 9a-*trans* should theoretically exhibit most intensive response in the CD spectra at longer wavelengths, which is also well agreement with the experimental results.

On the other hand, because of chirality induced by the nature of nonplanar configurations, these compounds can undergo photo induced oscillations in optical rotatory power when they suffer UV-light/visible-light illumination that drive *trans* → *cis* isomerization of azobenzene segments. In all cases, rotational data were collected at the sodium D-line (589 nm) to avoid degradation arising from the shorter wavelength $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ azobenzene transitions. The specific optical rotations measurements were carried out in chloroform. The $[\alpha]_D$ values at initial state, PSS_{uv} and PSS_{vis} states are listed in Table 1. In accordance with the CD results, though 9a with the shortest linkers has largest $[\alpha]_D$ value before UV light irradiation, its optical rotation varies little as well as the molecule 9c after photoirradiation. Unexpectedly, the $[\alpha]_D$ value of 9b demonstrated a dramatic increasing after the illumination of UV light. For instance, the $[\alpha]_D$ value of 9b in the initial state was -8° that nearly means no chirality, whereas this value was actually turned to a distinct levorotatory rotation about -225° in the PSS_{UV} state, exhibiting a big difference of 217° that about 2713 % is changed in $[\alpha]_D$ value. And then reversed to the initial state basically. In other words, the planar chirality induced by the azobenzene moiety along with the chiral axis of binaphthyl in 9b can be turned into "Off" or "On" reversibly during the *trans* → *cis* and *cis* → *trans* isomerization process.

Table 1 $[\alpha]_D$ of 9a-c and PCM before and after photoirradiation[a]

Comp.	k_e/s^{-1}	k_h/s^{-1}	Ini.	365 nm	436 nm	$\Delta[\alpha]_D/[\alpha]_D$ [b] （%）
9a	0.071	0.032	-261	-263	-255	0.8
9b	0.131	0.053	-8	-225	-19	2713
9c	0.107	0.042	-36	-43	-40	19
PCM	0.070	0.051	-28	-212	-32	704

[a] Conditions: c = 0.10 g/dL, 20 °C, in chloroform. Light path length = 10 cm, irradiation wavelength = 365 nm (10 mW/cm^2, 600 s) and 436 nm (3.6 mW/cm^2, 600 s). [b] Percent change in $[\alpha]_D$ observed in going from the initial state to PSS_{uv}.



Scheme 1 Synthetic route of the homopolymers (PCM, PCM1, PCM2) bearing cyclic azobenzenophanes at side chains.

Encouraged by the special chiroptical properties of cyclic azobenzenophanes, we further tried to introduce them into the polymer skeletons to fabricate some novel optically active polymers that may show potential applications as polymeric chiroptical switches. Herein, a serial of novel vinyl monomers (CM, CM1 and CM2), are firstly synthesized *via* the Suzuki coupling reaction between the corresponding cyclic azobenzenophanes and 4-vinylphenylbronic acid (VPB), and their structures were characterized by ^{1}H NMR, and ^{13}C NMR spectra, HR-MS, EA and melting points (T_m) measurement (see supporting information, Figure S4-S6). Subsequently, three topological homopolymers (PCM, PCM1 and PCM2) with different cyclic azobenzenophanes as side chains were successfully obtained by free radical polymerization using AIBN as initiator (shown in Scheme 1). The

GPC elution curves of the polymers and their molecular weights are given in Figure S8-S10. In order to rise the research efficiency, we have firstly measured the $[\alpha]_D$ values of the three polymers in DMF or chloroform at initial state, PSS_{uv} and PSS_{vis} states (PCM1 can be only dissolved in DMF), the results were listed in Table 1 and Table S1, respectively. The similar optical rotation changes like 9b can also be observed in PCM (starting with a preirradiated near-zero specific rotation of -28^{o} and then reached to -212^{o} after the illumination of 365 nm light). However, it seems hardly no optical rotation changes for PCM1 or PCM2 after irradiating by UV light. So, naturally, we investigated the chiroptical behavior of PCM in detail below because neither of the other two polymers shows better chiroptical properties than PCM. As shown in Figure1, the photoisomerization behavior of PCM was studied firstly. The first-order kinetics curves are plotted in Figure S7, meanwhile the both values of k_e and k_h are listed in Table 1. In contrast with the cyclic molecule 9b, PCM shows a much smaller k_e value, indicating that PCM possesses an extremely slow UV driven *trans* → *cis* isomerization, which may be due to the large steric effect between adjacent cyclic pendants resulted from polymeric random coil.[45] Inevitably, the CD spectrum of the homopolymer PCM was also measured in chloroform, as shown in Figure 1(l). Predictably, it shows the similar result as 9b, but the CD signal changes were slightly less than that of the 9b under the same conditions, because PCM has a lower *trans* → *cis* photoconversion ratio than 9b under the UV light irradiation as presented in Figure 1(d) and 1(j). We suppose that the azobenzene segments are all in *trans* states before irradiating by UV light, so the *trans* → *cis* photoconversion ratios of 9b and PCM were estimated as 69% and 48 % by calculated the Abs changes of *trans* azobenzene at 367 nm, respectively.

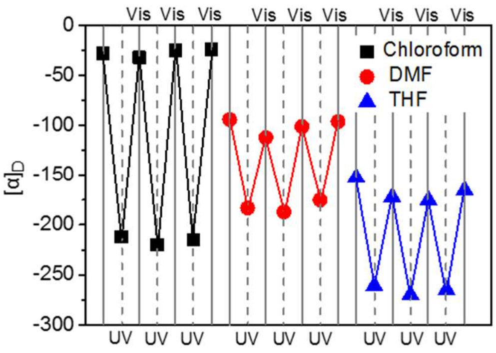


Figure 4 UV/Vis light induced oscillations in D-line specific rotations for PCM in chloroform, DMF and THF.

Simultaneously, it's well known that an ideal chiroptical switch should possess high sensitivity and fatigue resistance under the external stimuli, since non-destructive readout is required for storing information permanently when used as memory devices.[24] Therefore the photoregulated oscillatory responses of polymer were examined as indicated in Figure 4, showing that it can be periodically repeated at least four times by alternative UV-/Vis- light illumination in different solvents, such as chloroform, DMF and THF. The different response ranges of optical rotation were observed when tested in these solvents. As is readily apparent, PCM exhibited near-zero D-line optical rotation in chloroform, whereas the values in THF and DMF were noticeably increased. Furthermore, as can be seen in Figure 4, PCM showed largest light-driven oscillations in optical rotatory power in chloroform in comparison with the other two solvents. So, undoubtedly, chloroform is the best medium for the resultant polymer material to be used as *zero*/*levo* switches. Many researches on the solvent effect on chiroptical switches have been reported.[36,46,47] We guess the interesting solvent-depending properties can be attributed to the polarity effect. As discussed earlier, the photoisomerization behavior of azobenzene unit and the dihedral angle of 2,2'-disubstituted binaphthyl group can be influenced by solvent polarities,[11,48] which lead to the change of three-dimensional geometries of each chiral macromolecule.

Conclusions

In summary, three kinds of asymmetric cyclic azobenzenophanes with different linker length (n = 2, 6, 11) have been obtained *via* CuAAC cyclization with high yields, and their chiroptical activities were investigated by the combination of experiments with time-dependent density functional theory (TD-DFT) calculations. Unexpectedly, a "Zero-negative-Zero" CD signal change was observed in 9b during the photoisomerization process. Furthermore, we also have investigated the chiroptical behavior of three functional polymers with different cyclic azobenzenophanes (9a, 9b and 9c) as pendants and found that the polymers still can keep the similar optical properties as the corresponding cyclic units. Especially, the polymer PCM can also exhibit reversible "Off" or "On" optical rotation power changes in chloroform. We think this work not only facilitates better understanding for structure-property relationship in various cyclic architectures containing azobenzenophanes moiety, but also provides a novel smart polymeric chiroptical switch and memory device.

Acknowledgements

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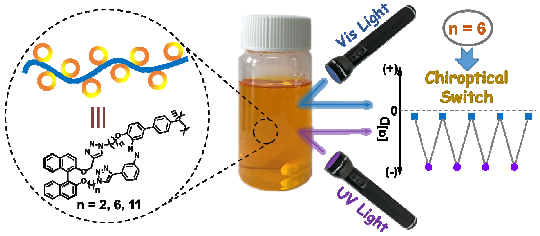

A Cyclic Azobenzenophane-Based Smart Polymer for Chiroptical Switches

Jinjie Lu, Ganquan Jiang, Zhengbiao Zhang, Wei Zhang, Yonggang Yang, Yong Wang,* Nianchen Zhou,* Xiulin Zhu*

Polymers based on cyclic azobenzenophanes as pendants with different methylene spacers (n = 2, 6, 11) have been synthesized. And the one with six-methylene spacer is a good candidate for chiroptical switches.