Non-destructive erasable molecular switches and memory using light-driven twisting motions†

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Novel types of chiroptical switches and memory with non-destructive readout that are entirely optically controlled for molecular devices in solution and neat films.

Artificial molecular machines are currently of interest because of their response to external stimuli such as electric field, temperature, pH, ionic strength, and light, which leads to changes in their molecular motions.[1] Photoresponsive molecular machines have received a great deal of attention in the past decade; their high sensitivity and fast response are of great interest for molecular devices. These compounds are expected to find application in the fields of molecular switches, memory, and logic gates.[2]

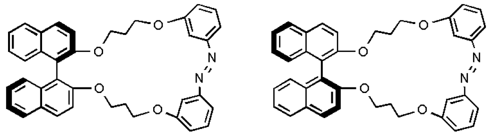
Chiroptical switches for light-driven molecular devices are one of the most promising strategies for optical data storage and processing.[3] An ideal chiroptical compound should simultaneously possess the properties of photobistability and fatigue resistance as well as high sensitivity and spatial resolution. Non-destructive readout is desirable for high-performance molecular switches and memory, because this method does not erase stored information.[4]

Azobenzene is a typical photochromic compound that changes its shape upon photoirradiation. It exhibits a large change in length upon photoisomerization, with the distance between the 4- and 4′-carbons decreasing from 9.0 Å (*trans* form) to 5.5 Å (*cis* form).[5] Several groups have demonstrated optical switching of azobenzene derivatives upon *trans–cis* photoisomerization.[6] Unfortunately, *cis–trans* thermal back isomerization of azobenzenes takes place even at room temperature, resulting in deterioration of the stored information. Azobenzene derivatives have lifetimes for *cis–trans* thermal back isomerization at room temperature ranging from seconds to days.[5] There has been an ever-growing effort to find effective compounds for inducing the *cis*-azobenzene with high thermal stability. However, the strategy for the thermally stable azobenzenes is still unclear at the present stage.

We previously reported novel light-driven chiral compounds containing a photoresponsive azobenzene moiety and a chiral binaphthyl moiety in a single species.[7] It was found that the compounds exhibit photomodulation of liquid-crystalline helical structures[7a] and photoinduced chirality by elliptically polarized light[7b] using *trans–cis* isomerization of the azobenzene moiety. If azobenzene derivatives are completely fixed in the *cis* conformation in the dark, they can be characterized as thermally irreversible and fatigue-resistant azobenzenes. Herein we report chiroptical switches and memory with non-destructive readout that are entirely optically controlled for molecular devices in solution and neat films. The switching behaviour exhibits high fatigue resistance and stored information remained stable over 1.7 months.

Fig. 1 shows the chemical structures of **R3A**, **S3A**, and **R2A** used in this study. The thermal behaviour of the compounds was investigated by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1}. On the first heating cycle, an endothermic peak (change in enthalpy (ΔH) = 30 kJ mol^{-1}) caused by melting was observed at 205 °C. Upon cooling to room temperature, the compound formed a transparent glass *via* a supercooled liquid state. We detected an endothermic event corresponding to the glass transition temperature at 112 °C on the second heating cycle. The formation of the glassy state was also evident in the X-ray diffraction patterns of the samples. Before thermal treatment, the sample exhibited sharp diffraction peaks because of its crystalline nature. After thermal treatment above the melting point, the diffraction pattern of the sample showed only a broad halo. Neat films with a thickness of 120 nm were prepared by spin coating a solution of **R3A** and **S3A** in chloroform onto a fused silica substrate. The samples exhibited isotropic properties because they lacked grain boundaries under a polarizing microscope.

The maximum absorption wavelengths (λ_{max}/nm) of **R3A** and **S3A** in 1,4-dioxane were 231 (ε/M^{-1} cm^{-1} 171 800), 295 (23 800), 331 (26 400), 365 sh (14 400) and 436 nm (850). Some of these can be assigned as the ^1B_b (231 nm), ^1L_a (293 nm), and ^1L_b (331 nm) transitions of the binaphthyl group. The ^1B_b and ^1L_b bands correspond to the long axis of the naphthyl group, while the ^1L_a band corresponds to the short axis.[8] The *trans* form of the azobenzene moiety in the compounds exhibited


R3A **S3A**

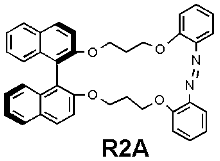

R2A

Fig. 1 Chemical structures of the photoresponsive chiral compounds **R3A**, **S3A**, and **R2A**, respectively.

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absorption maxima at 365 nm due to a π–π* transition and 436 nm from a n–π* transition. Circular dichroism (CD) spectra of **R3A** and **S3A** in 1,4-dioxane exhibited features that mirrored one another. Exciton couplets at *ca.* 240 and 440 nm were derived from ^1B_b transitions of the two naphthyl moieties and n–π* transitions of the azobenzene moieties, respectively.[8] The superimposed CD spectra of the films of **R3A** and **S3A** also formed a symmetrical image, providing evidence for the opposite chirality of the binaphthyl moieties, with the ^1B_b transitions appearing at 244 nm and a weak exciton couplet occurring between 400 and 600 nm.

Irradiation of **R3A** and **S3A** in 1,4-dioxane at 365 nm induced *trans–cis* isomerization of the azobenzene moiety. The ratio of the *trans* : *cis* isomers in the photostationary state was determined to be 15 : 85 using ^{1}H NMR spectroscopy.[9] On the other hand, the ratio after irradiation at 436 nm for the *cis–trans* photoisomerization process was 99 : 1, indicating that recovery of the initial state could be achieved. First-order rate constants (k) and thermodynamic parameters such as enthalpy of activation ($\Delta H^{\neq}$) and entropy of activation ($\Delta S^{\neq}$) for thermal *cis–trans* isomerization were determined in 1,4-dioxane according to the Eyring equations[10] (k at 298 K: 2.2×10^{-7} s^{-1}; $\Delta H^{\neq}$: 25 kcal mol^{-1}; $\Delta S^{\neq}$: −5.1 cal mol^{-1} K^{-1}). The lifetime (τ: $1/k$) of **R3A** at 298 K is 1263 h (52.6 days) (Fig. 2a), which is extremely long compared with those of azobenzene derivatives previously reported. The value of τ of the corresponding 2,2′-disubstituted model compound, **R2A**, is 122 h at 298 K, even though these compounds have the same molecular weight. The specific difference is interpreted in terms of the molecular shape of the structures. $\Delta S^{\neq}$ reflects the difference in the degree of freedom between the ground and transition states. The value of $\Delta S^{\neq}$ is derived from the cyclic structure by assuming that **R3A** shows limited formation compared with **R2A** ($\Delta S^{\neq}$: −1.3 cal mol^{-1} K^{-1}). In fact, a crystal structure of *trans*-**R3A** exhibited a strained structure in comparison to that of *trans*-**R2A** (Fig. 2b and c). Because the distance between the 3- and 3′-carbon atoms in the azobenzene moiety is longer than that of the 2- and 2′-carbon atoms, the cyclic linkage of **R3A** provides strong communication between the terminal groups of the azobenzene moiety attached to the binaphthyl moiety. In contrast, *cis*-**R3A** has greater steric hindrance and a distorted conformation compared to *cis*-**R2A** according to the results of density functional theory (DFT) calculations at the B3LYP/6-31(d) level. This difference in molecular shape significantly alters the stabilization of these compounds upon *cis–trans* isomerization.

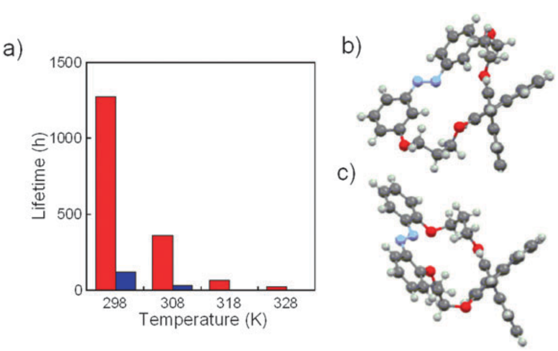

Fig. 2 (a) Lifetimes of *cis–trans* thermal back isomerization of **R3A** (red) and **R2A** (blue) in 1,4-dioxane at various temperatures. Crystal structures of (b) *trans*-**R3A** and (c) *trans*-**R2A**.

The change in the molar circular dichroism ($\Delta\varepsilon$) of a binaphthyl-based transition is dependent on the dihedral angle between the two naphthyl moieties. The change in the value of $|\Delta\varepsilon_{\mathrm{after}} - \Delta\varepsilon_{\mathrm{before}}|$ at 238 nm was 210 M^{-1} cm^{-1}. Rosini *et al.* calculated the relationship between the value of $\Delta\varepsilon$ and the dihedral angle.[11] From the results of the calculation, the change in the dihedral angle of the compound is estimated to be about 30° after photoirradiation. DFT calculations revealed that the dihedral angles of *trans*-**R3A** and *cis*-**R3A** are 103° and 75°, respectively, which is a change of approximately 30°.[12]

R3A and **S3A** exhibited specific suppression of *cis–trans* thermal back isomerization of the azobenzene moiety. Because of these desirable characteristics, the non-destructive molecular switches and memory of the compounds were investigated. When the chiral cyclic compounds are irradiated at 365 and 436 nm, the molecular twisting motion can be induced by *trans–cis* and *cis–trans* photoisomerization of the azobenzene moiety, respectively. In contrast, optical rotation ($[\alpha]_D$) can be monitored by irradiation at 589 nm without any substantial changes, because the chiral compounds are inactive toward photoisomerization at this wavelength. It is confirmed that the change in the value of the molar optical rotation ($[\Phi]_D^{20}$, c = 0.1 in chloroform) of **R3A** before and after irradiation at 365 nm in a photostationary state, $[\Phi]_D^{20}{}_{\mathrm{before}} - [\Phi]_D^{20}{}_{\mathrm{after}}$, was 1540°.[13] A specific large change in the $[\Phi]_D^{20}$ of **R2A** can be obtained by means of photoinduced molecular twisting motions. The magnitude of modulations of $[\Phi]_D^{20}$ after photoirradiation at 365 nm was approximately 9700°. These results indicate that the chiral cyclic compounds possess both a large change in the value of $[\Phi]_D^{20}$ upon irradiation and efficient reversibility. Because of these favorable properties, the compounds are regarded as promising for chiral switching applications.

Optically controllable neat films of the chiral compounds (thickness: 500 nm), which are driven by photon-mode processes with a non-destructive readout, were achieved by exploiting the dynamic twisting motion of the molecules. Photoinduced changes in the optical rotations, $|\alpha_{\mathrm{before}} - \alpha_{\mathrm{after}}|$, were about 100° cm^{-1} and these values can be switched by

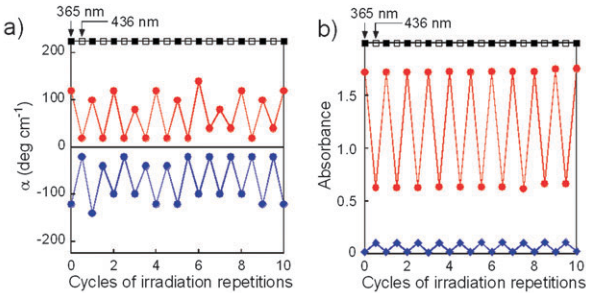

Fig. 3 (a) Chiroptical switching with non-destructive readout of the values of α of neat films of **R3A** (red) and **S3A** (blue) (monitoring wavelength: 589 nm) at 298 K. (b) Photoswitching of the absorbance of a neat film of **R3A** (monitoring wavelengths: 365 nm (circles) and 436 nm (diamonds)) at 298 K. Irradiation wavelengths: 365 nm (10 mW cm^{-2}, 600 s) and 436 nm (10 mW cm^{-2}, 600 s), film thickness: 500 nm.

alternating irradiation between 365 and 436 nm (Fig. 3a). Although the photoinduced changes in the values are not equal, the recovery of the initial state could be achieved by irradiation with visible light to cause *cis–trans* photoisomerization of the azobenzenes (Fig. 3b). The value of τ of the chiral cyclic compound in a neat film with respect to *cis–trans* thermal back isomerization of the azobenzene moiety at 298 K is 620 h (25.8 days). This means that neat films of **R3A** and **S3A** exhibit good fatigue resistance at the irradiated site. These results indicate that the chiral cyclic compounds can be used as optical switches as well as for optical data storage in the solid state.

In this work, molecular structures and device parameters such as the film thickness were not optimized. According to the absorption spectra, incident light at 365 and 436 nm is absorbed by the bulk of the neat film and photoisomerization of the compounds takes place over almost the whole area (Fig. 3b). As mentioned above, **R3A** and **S3A** formed smooth, uniform thin films that do not scatter light at 589 nm. The net population of the excited molecules formed by the absorption of photons could be controlled by choosing a suitable film thickness. Irie reported a new class of photochromic diarylethenes that show open- and closed-form isomers with high thermal stability and high fatigue resistance.[14] However, diarylethenes have two conformations, parallel or antiparallel, and cyclization can proceed only from the antiparallel conformer. The population ratio of the two conformations is essentially 1 : 1, so the cyclization quantum yield cannot exceed 0.5.[14] When the ratio of the antiparallel conformation is increased, the quantum yield is also expected to increase. An interesting approach to achieving selective cyclization is to use chiral diarylethenes that show highly diastereoselective ring closure.[15] On the other hand, the advantage of using azobenzenes is their simple isomerization reversibility, which ensures dynamic change in the molecular structure as mentioned above. It is believed that cyclic linkage of the molecular structure would be a simple and effective approach to realize photochromic compounds with higher thermal stability. New cyclic molecules with good performance are expected to be developed using this line of molecular design.

In conclusion, novel chiral cyclic compounds containing binaphthyl and azobenzene functionalities were demonstrated to behave uniquely as non-destructive erasable chiroptical memory through photoinduced switching of the dihedral angle of the binaphthyl moiety. Chiroptical switches that exhibited high fatigue resistance and stable information storage for over 1.7 months in 1,4-dioxane at 298 K were achieved by alternating the photoirradiation wavelength. Furthermore, the values of the optical rotations of the neat film can be switched without deterioration of the stored information by means of the dynamic molecular twisting motions of the photoresponsive chiral compounds. Because both isomers of the compounds show good film-forming properties and high thermal stability, they will allow the fabrication of high-performance solid molecular devices that are driven by incident light.

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