Light-driven twisting behaviour of chiral cyclic compounds†

Masuki Kawamoto,* Takuya Aoki and Tatsuo Wada*

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Chiral cyclic compounds exhibited light-driven twisting by means of *trans–cis* photoisomerization in 1,4-dioxane solution, a neat film, and a liquid-crystalline host.

Molecular machines have received a great deal of attention because they play a role in life and materials science.[1] One of the most important natural molecular machines is coupled to adenosine triphosphate (ATP) synthesis. Since a rotary motion of ATP synthesis occurs in a stepwise manner in response to hydrolysis of ATP, it is regarded as a biological rotor.[1f–h] On the other hand, several groups have demonstrated artificial molecular machines, showing tweezers,[2a,f,j] actuators,[2b,d,k] shuttles,[2c,e,l] and rotors[2g–i,m,n] could change their motion in response to a variety of external stimuli such as an electric field, temperature, pH, ionic strength, and light. Recently, Aida *et al.* synthesized light-driven scissor-like moieties containing pivot, blade, and handle parts.[3] The photoresponsive moiety exhibited control of mechanical twisting of a guest molecule with the aid of coordination between a zinc porphyrin and nitrogenous compounds.[3b]

Light-driven cyclic compounds, especially rotaxanes and catenanes, have attracted much attention in the past decade: their high sensitivity and fast response are of great interest for molecular machines.[1a–c] To drive these compounds, a photoisomerization reaction is one of the most promising strategies and enables control of molecular structures in an elegant way.[4] Azobenzene is a typical photochromic compound, which shows a significant change in molecular length upon photoisomerization: the distance between 4- and 4′-carbons decreases from 9.0 Å (*trans* form) to 5.5 Å (*cis* form).[5] The moiety changes its molecular shape, which leads to control of other properties such as polarity and refractive index even in a thin film including the azobenzene moiety.[6] On the other hand, 2,2′-disubstituted binaphthyl moieties have been used as asymmetric catalysts and chiral recognition agents because of their stable chiral configuration.[7] Furthermore, the moiety is observed to show a change in dihedral angle between two naphthalene rings at various external fields without racemization. We consider if the molecular shape of the azobenzene moiety is changed by light efficiently, the dihedral angle of the binaphthyl moiety may be controlled by *trans–cis* photoisomerization. From the molecular design aspect, cyclic linkage of alkyl chains in a compound gives a correlation among terminal groups of the azobenzene moiety attached to those of the binaphthyl moiety.

In this study, we designed and synthesized a novel type of a cyclic compound containing azobenzene and binaphthyl moieties. The compound shows change in a twisting motion in solution, a neat film, and a liquid-crystalline (LC) host by alternating irradiation of UV and visible light.

Fig. 1 shows the chemical structures of **(*R*)-Azo** and **(*S*)-Azo** used in this study. **(*R*)-Azo** and **(*S*)-Azo** have the same molecular characteristics except for opposite chirality. Thermal behaviour of the moieties was checked by differential scanning calorimetry at a heating rate of 10 °C min^{-1}. On first heating, an endothermic peak (ΔH: 39 kJ mol^{-1}) due to the melting point was observed at 187 °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 86 °C on second heating. The formation of the glassy state was also evidenced by X-ray diffraction patterns. Before thermal treatment the moiety exhibited sharp diffraction peaks due to crystalline characteristics. On the other hand, the sample obtained by thermal treatment above the melting point showed only a broad halo. These compounds tend to show the glassy state based on a stellar structure of two naphthalene rings in the binaphthyl moiety similarly to starsburst molecules.[8]

Maximum absorption wavelengths (λ_{max}/nm) of **(*R*)-Azo** and **(*S*)-Azo** in 1,4-dioxane were 231 (ε/M^{-1} cm^{-1} 111 200), 293 (15 100), 336 (12 500), 365 sh (6300) and 452 (1200). These can be assigned as ^1B_b (231 nm), ^1L_a (293 nm), and ^1L_b (336 nm) transitions of the binaphthyl group. ^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.[9] In contrast, the *trans* form of the azobenzene moiety in the compounds exhibited absorption maxima at 365 nm due to a π–π* transition and at 452 nm due to a n–π* transition. CD spectra of these compounds in

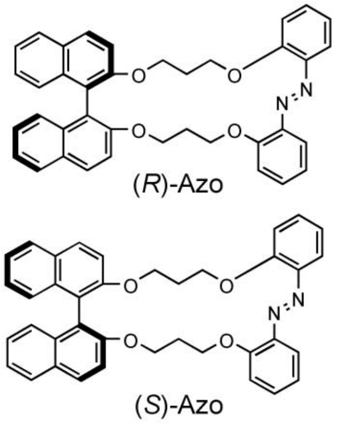

Fig. 1 Chemical structures of **(*R*)-Azo** and **(*S*)-Azo** in this study.

RIKEN, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan.
E-mail: mkawamot@riken.jp; tatsuow@riken.jp; Fax: 81 48 467 9389; Tel: 81 48 467 2745

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1,4-dioxane exhibited symmetrical structures. Exciton couplets at *ca.* 240 nm and *ca.* 440 nm were derived from ^1B_b transitions of the two naphthyl moieties and n–π* transitions of the azobenzene moieties, respectively.[9]

Irradiation at 365 nm induced a decrease in the π–π* band and an increase in the n–π* band. This indicates *trans–cis* isomerization of **(*R*)-Azo** and **(*S*)-Azo** in 1,4-dioxane on photoirradiation. We determined the ratio of *trans* : *cis* in the photostationary state to be 20 : 80 by ^{1}H NMR.[10] Furthermore, first-order rate constants (k) and thermodynamic parameters such as enthalpy of activation ($\Delta H^\ddagger$) and entropy of activation ($\Delta S^\ddagger$) for thermal *cis–trans* isomerization in 1,4-dioxane were determined according to Eyring equations[11] (k at 298 K: 2.3×10^{-6} s^{-1}; $\Delta H^\ddagger$: 26 kcal mol^{-1}; $\Delta S^\ddagger$: -1.3 cal mol^{-1} K^{-1}). To compare thermodynamic parameters we selected 2,2′-dipropoxyazobenzene as a model compound (k at 298 K: 2.7×10^{-6} s^{-1}; $\Delta H^\ddagger$: 22 kcal mol^{-1}; $\Delta S^\ddagger$: -12 cal mol^{-1} K^{-1}). $\Delta S^\ddagger$ reflects the difference in a degree of freedom between ground and transition states. The value of $\Delta S^\ddagger$ was derived from the cyclic structure by assuming that the moiety may show a limited formation in comparison with the model compound. In fact, an optimum structure of a *trans* form exhibited a strained structure according to the results of MOPAC.[12] On the other hand, a *cis* form has a steric hindrance or a distorted conformation. This difference in molecular shapes of cyclic and model compounds gives rise to a change in the stabilization of the molecular structure through *cis–trans* isomerization.

The value of $\Delta\varepsilon$ in a binaphthyl moiety is dependent on the dihedral angle between the two naphthyl moieties. If the value of $\Delta\varepsilon$ of the compound is changed by *trans–cis* photoisomerization of the azobenzene moiety, a molecular rotation of the binaphthyl moiety can be observed. After irradiation at 365 nm, the values of the exciton couplets of the compounds were increased. Changes in the values of $|\Delta\varepsilon_{\text{after}} - \Delta\varepsilon_{\text{before}}|$ at 238 and 440 nm were 45 and 15, respectively. Rosini *et al.* calculated a relation between the value of $\Delta\varepsilon$ and the dihedral angle.[13] By the results of the calculation, the change in the dihedral angle of the compound is estimated to be about 10° after photoirradiation.

Next, we investigated switching behaviour of $\Delta\varepsilon$ values of **(*R*)-Azo** and **(*S*)-Azo** in 1,4-dioxane upon irradiation with light. It was found that the dihedral angle of the compound could be controlled repeatedly by alternating irradiation at 365 and 436 nm. As described above, azobenzene exhibits a change in its molecular length. The cyclic moieties readily propagate change in the molecular structure of the azobenzene moiety through the alkyl chain. As a result, cyclic linkages in the moieties give a correlation and results in the motion of the twist upon photoisomerization of the azobenzene moiety. We also prepared neat films (thickness: 100 nm) of **(*R*)-Azo** and **(*S*)-Azo**, and then checked the switching behaviour. Fig. 2(a) shows a reversible change in absorbance of **(*R*)-Azo** induced by alternating irradiation at 365 and 436 nm in a thin film at room temperature. Since the absorbance recovers when the sample is irradiated at 436 nm, it is assumed that the switching observed is based on *trans–cis* photoisomerization of the azobenzene moiety in the thin film. Fig. 2(b) shows switching behaviour of ellipticities of **(*R*)-Azo** and **(*S*)-Azo** in the thin films. We observed changes in ellipticities of the compounds at 245 and 440 nm of 100 and 80 mdeg μm^{-1}, respectively.

Chiral compounds, which show right- or left-handed helical structures, were dissolved in a nematic (N) LC to produce a chiral N phase.[14] Recently, Feringa *et al.* reported that a light–driven molecular rotor acts as a chiral dopant that can induce a chiral N phase.[15] The molecular rotor could rotate an object placed on a chiral NLC film that exceeded the size of the dopant by a factor of 10^4.

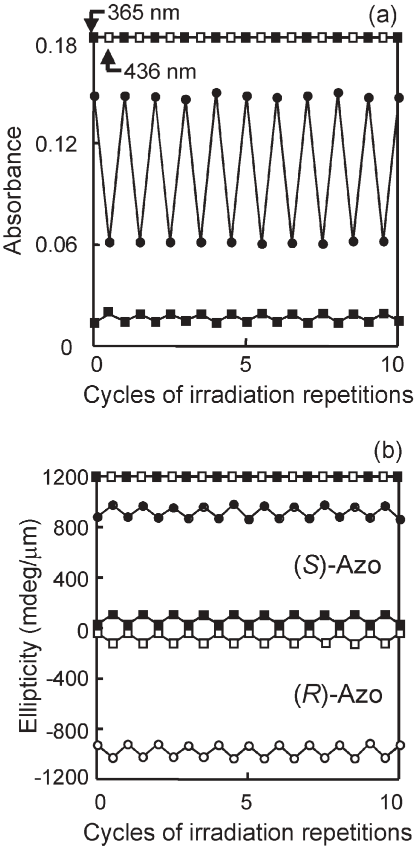

Fig. 2 Change in absorbance of **(*R*)-Azo** (monitoring wavelength: 365 nm (circles) and 452 nm (squares)) (a) and ellipticities of **(*R*)-Azo** (open symbols) and **(*S*)-Azo** (closed symbols) (monitoring wavelength: 245 nm (circles) and 440 nm (squares)) (b) in neat films at room temperature. Irradiation wavelength: 365 nm (6 mW cm^{-2}, 60 s) and 436 nm (14 mW cm^{-2}, 60 s), respectively.

(*R*)-Azo was added to a NLC host (ZLI-3282, Merck) at a concentration of 1 wt% to induce a chiral N phase with a left-handed helical structure. We checked the photoresponsive behaviour of the chiral cyclic compound in the LC host by using the Grandjean–Cano technique.[16] The mixture was put into a wedge cell, which had been coated with polyimide and rubbed to align the LC moieties. The ability of a chiral dopant to induce a helical pitch is defined as helical twisting power (β) according to the following equation: $\beta = 1/pc$, where p and c are helical pitch length and concentration of a chiral dopant, respectively. The values of β before and after irradiation at 365 nm in a photostationary state were -10 and -14 μm^{-1}, respectively.[17] Fig. 3 shows change in the LC texture of the chiral N phase in the cell upon continuous UV irradiation. Before irradiation Grandjean–Cano lines were observed with a polarizing microscope, indicating that the LC moieties are aligned parallel to the rubbing direction (Fig. 3(a)). During photoirradiation at 365 nm, the Grandjean–Cano line diminished and fingerprint textures were observed (Fig. 3(b)). The photoinduced LC texture may be interpreted as a

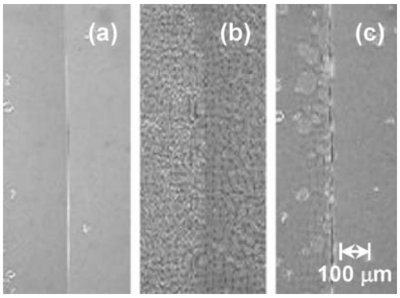

Fig. 3 Change in LC texture of a chiral nematic phase in a wedge cell upon continuous UV irradiation. Before irradiation (a), after 5 s (b), after 30 s (c). Irradiation wavelength: 365 nm (10 mW cm^{-2}).

result of change in orientation of the LC moiety and a tendency of LC directors to become aligned nearly perpendicular to the rubbing direction.[18] Shortly afterwards an appearance of the Grandjean–Cano line is due to a reorientation of the chiral NLC in the photostationary state (Fig. 3(c)). Moreover, the helical pitch length of 40% was reduced by a change in the twisting motion of the cyclic compound with the aid of *trans–cis* photoisomerization. Finally a recovery of an initial state could be achieved by irradiation at 436 nm to cause *cis–trans* backisomerization. We found that the cyclic compound possesses an ability of a chiral dopant, especially, LC alignment behaviour based on the reorientation process upon continuous UV irradiation is an interesting phenomenon. A further detailed investigation of the origin of the LC alignment mechanism is now in progress.

In conclusion, we investigated light-driven molecular twisting behaviour of novel cyclic compounds containing azobenzene moieties. It was clear that the chiral cyclic compound shows a reversible change in the dihedral angle of the binaphthyl moiety by means of photoisomerization of the azobenzene moiety. Cyclic moieties could be promising in view of their ease in molecular design, synthesis, and the formation of thin films. Since there are many other functional groups, which can be connected with binaphthyl or azobenzene units, we expect new cyclic molecules with good performance to be further developed in this line of molecular design.

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