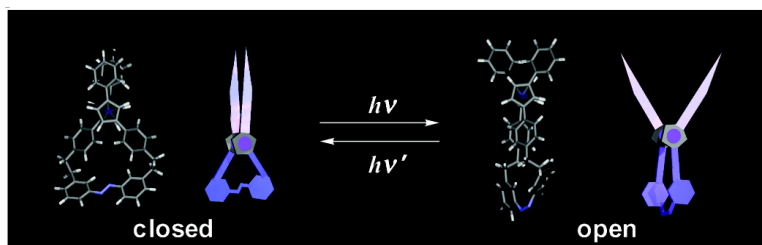


Light-Driven Open–Close Motion of Chiral Molecular Scissors

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Light-Driven Open–Close Motion of Chiral Molecular Scissors

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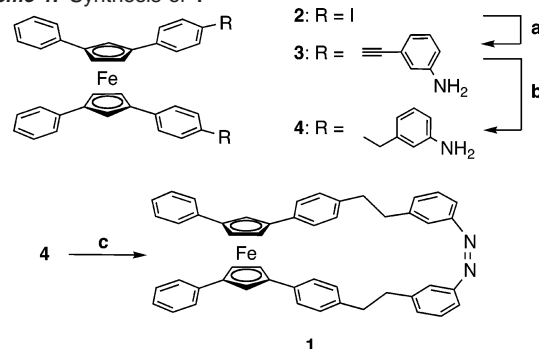
Control of mechanical motions of single molecules by external stimuli has attracted great attention, not only in relation to biological supramolecular machines but also for the development of molecular machines and devices. Until now, a variety of molecular machineries including motors, shuttles, switches, and tweezers has been reported.¹ Herein we report on “light-driven chiral molecular scissors,” where a motion of a photoisomerizable part is transformed into an open–close motion of the blade moieties. Examples of such an interlocking mechanical motion are very rare² in the precedent molecular machineries, which are mostly operative by individual motions of driving parts.

A pair of scissors consists of three different essential components, i.e., handles, pivot, and blades. A change in a distance between the two handles should be transformed, through an angular motion of the pivot, into an open–close motion of the blades. The pivot should be comprised of two parallel planes, which can rotate freely. We chose ferrocene as the candidate for the pivot part, since the two cyclopentadienyl (*Cp*) rings are parallel to each other and rotate freely even at low temperature.³ As the driving group to operate the handles azobenzene was chosen because it expands and contracts reversibly upon irradiation with visible and ultraviolet lights, respectively. Thus, we designed molecular scissors **1**, consisting of two phenyl groups (A) as the blade moieties, 1,1',3,3'-tetrasubstituted ferrocene as the pivot part, and two phenylene groups (B) as the handle parts, which are strapped by an azobenzene unit through ethylene linkages (Scheme 1). Compound **1** is asymmetric due to the planar chirality of the 1,1',3,3'-tetrasubstituted ferrocene unit, and allows us to evaluate the angular motion of the pivotal ferrocene unit by means of circular dichroism (CD) spectroscopy.

A DFT calculation of **1** predicted that the blade parts are closed when the connecting azobenzene unit adopts a *trans* configuration, while they are open in *cis*-**1** (Figure 1). In *trans*-**1**, the expanded conformation of the azobenzene unit places the two-phenylene groups in the handle parts apart from one another, while the phenyl groups in the blade parts are in close proximity to each other with a bite angle of 9.2°. On the other hand, the blade phenyl groups in *cis*-**1** are separated from each other with a bite angle of 58.2°. Thus, the photoisomerization of the azobenzene unit can be expected to induce the angular motion of the ferrocene unit, resulting in the open–close motion of the blade parts.

Scheme 1 shows the synthetic route to molecular scissors **1** (for details, see Supporting Information). Tetrasubstituted ferrocene **2**,⁴ obtained as a mixture of *meso* and *racemic* isomers from 1-aryl-4-phenylcyclopenta-1,3-diene, was reacted with 3-ethynylaniline to afford **3** in 98% yield.⁵ Compound **3**, thus obtained, was subjected to preparative HPLC to isolate the *racemic* isomer in 45% yield. The configuration of **3** in the *racemic* form was successfully confirmed by the X-ray crystallographic analysis of **4**, obtained by hydrogenation of **3** with Adam's reagent (80% yield).⁶ Finally,

Scheme 1. Synthesis of **1**^a



^a (a) 3-Ethynylaniline, Pd(PPh₃)₂Cl₂, CuI, Et₃N, rt, 98%. (b) PtO₂, H₂, EtOH, THF, rt, 80%. (c) CuCl, air, pyridine, rt, 60%. See Supporting Information for details of the synthesis of **1**–**4**.

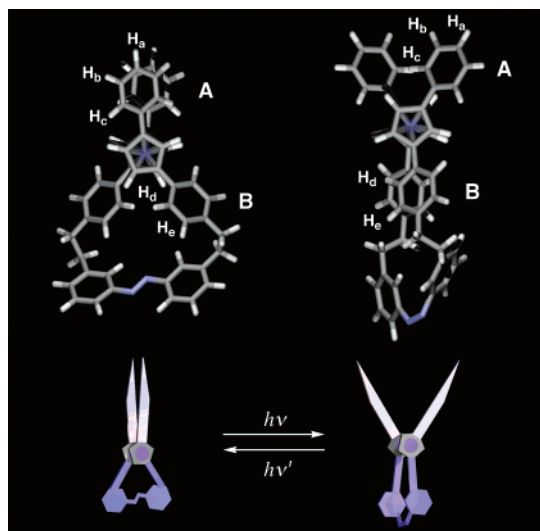


Figure 1. Molecular structures of *trans*-**1** (left) and *cis*-**1** (right), optimized with DFT calculation (B3LYP/3-21G*) (top), and schematic representation of its open–close motion induced by photoisomerization of the azobenzene unit (bottom).

oxidative coupling of the aniline amino groups in **4**, in the presence of CuCl, gave desired product **1** in 60% yield as a mixture of *trans* and *cis* isomers with respect to the azobenzene unit.⁷ Then, **1** was subjected to preparative HPLC to isolate *trans*-**1** and *cis*-**1** at a molar ratio of 67:33. The optically active forms of *trans*-**1** ([CD(–)280]-*trans*-**1** and [CD(+)-280]-*trans*-**1**) were successfully resolved by chiral HPLC with Daicel Chiralpak OT (+).

When *trans*-**1** in tetrahydrofuran (THF) was irradiated with a UV light (150-W xenon arc lamp, $\lambda = 350$ nm) for 180 s at 20 °C, the intensity of the absorption band centered at 420 nm was increased, while that of the absorption band centered at 330 nm was decreased (Figure 2a). ¹H NMR spectroscopy after irradiation showed an upfield shift of the signals due to the aromatic protons

† Responsible for theoretical calculation of **1**.

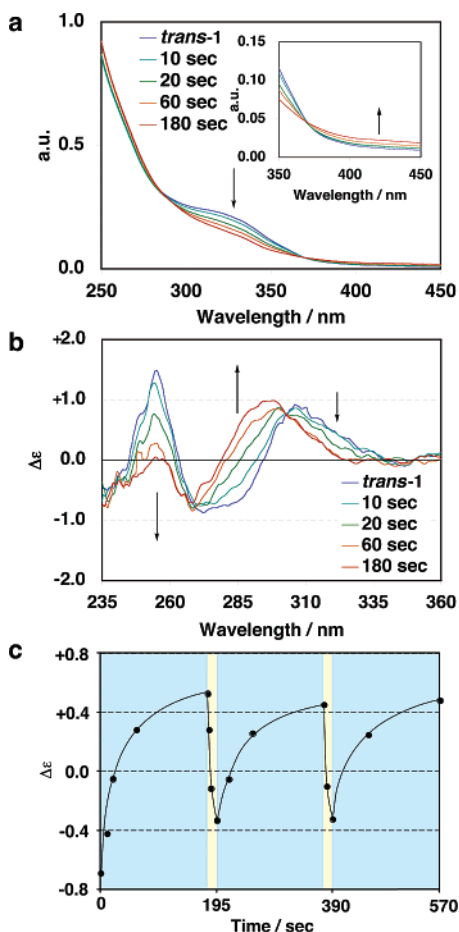


Figure 2. (a) Absorption and (b) circular dichroism (CD) spectral changes of *trans*-**1** (3.5×10^{-5} mol dm $^{-3}$) in THF at 20 °C upon irradiation with a UV light ($\lambda = 350$ nm). (c) Light-induced CD intensity change at 285 nm, upon sequential irradiation with a UV light ($\lambda = 350$ nm) for 180 s (blue areas) and a visible light ($\lambda > 400$ nm) for 15 s (yellow areas).

of the azobenzene unit. These spectral changes are typical of those for the *trans*-to-*cis* isomerization of azobenzene derivatives.⁸ The molar ratio of *trans*-**1** to *cis*-**1**, as determined by HPLC, was 11:89 after photoirradiation. On the other hand, upon irradiation with a visible light ($\lambda > 400$ nm) for 15 s at 20 °C, a backward isomerization took place to furnish the *cis*/*trans* isomer ratio of 54:46. Thus, the azobenzene unit in compound **1** can reversibly isomerize in response to UV and visible lights.

The enantiomers of *trans*-**1** displayed characteristic CD spectra. For example, [CD(-)280]-*trans*-**1** showed a negative Cotton effect at 272.5 nm and positive Cotton effects at 256.0 and 315.5 nm (Figure 2b). The *trans*-to-*cis* isomerization of [CD(-)280]-*trans*-**1**, upon UV-irradiation ($\lambda = 350$ nm) for 180 s, was accompanied by a CD spectral change at 240–300 nm due to the major absorption of the tetraarylferrocene unit. On the other hand, upon irradiation with visible light, ($\lambda > 400$ nm), a reverse CD spectral change occurred, where the system quickly reached a photo-stationary state in 15 s. On sequential irradiation with UV and visible lights in an alternating manner, the sign of the Cotton effect, e.g., at 280–290 nm was inverted from negative to positive and then from positive to negative (Figure 2c). These results suggest a

reversible angular motion of the Cp rings of the ferrocene unit induced by the photoisomerization of the azobenzene unit.

¹H NMR spectroscopy was conducted to investigate a possible interlocking motion of **1**, associated with the pivotal motion around the ferrocene unit on the isomerization of the azobenzene part. After the *trans*-to-*cis* isomerization of **1**, the ¹H NMR signals due to aromatic protons H_{a,b} (δ 6.99 ppm) and H_c (δ 7.12 ppm) in the blade phenyl groups (Figure 1) showed downfield shifts by 0.09 and 0.13 ppm, respectively. On the other hand, aromatic signals due to H_d and H_e in the handle phenylene groups, observed respectively at 7.16 and 7.13 ppm for *trans*-**1**, showed upfield shifts by 0.30 and 0.58 ppm, after the isomerization to the *cis* form. These spectral change profiles are quite reasonable for the molecular models of the *trans* and *cis* isomers of **1** (Figure 1). Namely, the two blade phenyl groups in *trans*-**1**, which are in close proximity to each other, become apart from one another on the isomerization to the *cis* form. This motion will lead to the lowering of a magnetic shielding effect from one phenyl group to the other (downfield shift). On the other hand, the two handle parts in **1** come closer to each other on the *trans*-to-*cis* isomerization of the azobenzene part, so that each phenylene unit can receive a magnetic effect more efficiently from the counterpart. Hence, it can now be concluded that compound **1** undergoes a scissors-like open–close motion upon light stimuli.

In conclusion, we have succeeded in the molecular design of the first “light-driven molecular scissors”, where the open–close motion of the blade parts is interlocked by that of the handle parts strapped by a photoisomerizable azobenzene unit, due to the pivotal motion of the connecting ferrocene unit. This work provides a basis for the development of the next-generation molecular machineries, which realize further complex motions interlocked by many joint parts.

Supporting Information Available: Synthesis of **1–4**, details of crystal structure determination of **4**, ¹H NMR spectra of **1**, and details of DFT calculation of *trans*-**1** and *cis*-**1** (PDF). X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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