Reversible operation of chiral molecular scissors by redox and UV light†

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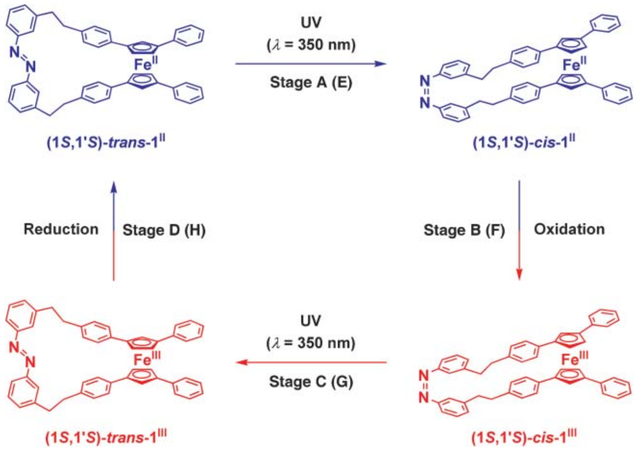
Upon changing the oxidation state, a reversible open–close motion of chiral molecular scissors, composed of a redox-active ferrocene pivot and an isomerizable azobenzene strap, can be realized only by UV light.

Stimuli-responsive reversible motions of molecules are an interesting subject in relation to the development of molecular machines[1] and actuator materials.[2] Representative examples of external stimuli include light, redox, heat, protons and binding guests.[3–8] We have reported light-driven chiral molecular scissors $\mathbf{1}^{\mathrm{II}}$, composed of a 1,1′,3,3′-tetrasubstituted ferrocene module with a planar chirality, strapped by an azobenzene group (Scheme 1).[9,10] Here, the reversible *trans*–*cis* isomerization of the azobenzene strap, induced by irradiation with UV and visible light, brings about opening and closing motions of the blade phenyl groups of $\mathbf{1}^{\mathrm{II}}$ through an angular motion of the ferrocene pivot. Upon incorporation of an appropriate guest-binding site into its blade part, this photoinduced scissoring motion leads to a conformational change of a trapped guest molecule.[11] Through these studies, we were interested in how the oxidation state of the ferrocene unit affects the scissoring motion of **1**.[12–14] In this communication, we report that, by changing the redox state of the ferrocene pivot, the reversible open–close motion of **1** can be realized only by UV light.



Scheme 1 Schematic representation of the sequential operations of **1** on UV irradiation (λ = 350 ± 10 nm) and redox of the ferrocene pivot.

Electronic absorption and circular dichroism (CD) spectral studies, along with cyclic voltammetry, showed that scissors $\mathbf{1}^{\mathrm{II}}$ in CH_2Cl_2 can be reversibly oxidized at 20 °C with neither isomerization nor racemization.‡ In cyclic voltammetry, the *trans* and *cis* (contaminated by 16% with *trans*-**1**) isomers displayed reversible Fe^{III}/Fe^{II} redox waves at $E^{0\prime} = 0.04$ and 0.03 V *versus* ferrocenium/ferrocene (Fc^+/Fc), respectively (see Supplementary Information Fig. S1). Based on these redox potentials, we chose 1,1′-dichloroferrocenium hexafluorophosphate (**2**)‡ ($E^{0\prime} = 0.19$ V *versus* Fc^+/Fc)[13] as an oxidant for $\mathbf{1}^{\mathrm{II}}$. Upon addition of **2** to a CH_2Cl_2 solution of (1*S*,1′*S*)-*trans*-$\mathbf{1}^{\mathrm{II}}$ at 20 °C, a very broad absorption band appeared at 320–600 nm with distinct isosbestic points at 245, 272, 289 and 328 nm (see Fig. 1a, upper). This spectral change is characteristic of the oxidation of ferrocene derivatives.[15] The oxidized form of the scissors displayed a broad CD band around 500 nm, while the original CD bands at 215–300 nm did not show any marked shifts but became less intensified (see Fig. 1a, lower). On the other hand, upon addition of bis(pentamethylcyclopentadienyl)iron(II) (**3**)‡ ($E^{0\prime} = -0.54$ V *versus* Fc^+/Fc) as a reductant, the broad absorption band at 350–600 nm almost disappeared with a retrieval of the original CD bands (see Supplementary Information Fig. S2a). The *cis* form of (1*S*,1′*S*)-$\mathbf{1}^{\mathrm{II}}$ showed similar absorption (see Fig. 2a, upper) and CD (see Fig. 2a, lower) spectral changes upon oxidation with **2** followed by reduction with **3** (see Supplementary Information Fig. S2b).

Analogously to the case in THF,[9] the azobenzene strap of (1*S*,1′*S*)-*trans*-$\mathbf{1}^{\mathrm{II}}$ underwent photoisomerization in CH_2Cl_2 to its *cis* form ((1*S*,1′*S*)-*cis*-$\mathbf{1}^{\mathrm{II}}$) upon exposure to UV light (λ = 350 ± 10 nm), while the backward isomerization took place under irradiation with visible light ($\lambda > 400$ nm).§ As determined by HPLC, the *trans*/*cis* isomer ratios at the photostationary state were 16/84 and 90/10 under irradiation at 20 °C with UV (180 s) and visible (15 s) light, respectively. Quite interestingly, when the photoisomerized mixture (*cis* content = 84%), obtained from (1*S*,1′*S*)-*trans*-$\mathbf{1}^{\mathrm{II}}$ under irradiation with UV light, was oxidized by a stoichiometric amount of **2** and then subjected to further irradiation with UV light, a backward isomerization, in turn, took place to give a *cis* content of 35% in 60 s (see Supplementary Information Fig. S3). Electronic absorption spectroscopy of the photoisomerization system showed an enhancement of the absorption at 323 nm at the expense of the absorption around 460 nm, exhibiting isosbestic points at 247, 288 and 370 nm

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† Electronic supplementary information (ESI) available: Cyclic voltammetry of $\mathbf{1}^{\mathrm{II}}$, absorption and CD spectral changes of (1*S*,1′*S*)-$\mathbf{1}^{\mathrm{II}}$ upon reduction, HPLC analysis of an isomer mixture of (1*S*,1′*S*)-**1**. See DOI: 10.1039/b618248h

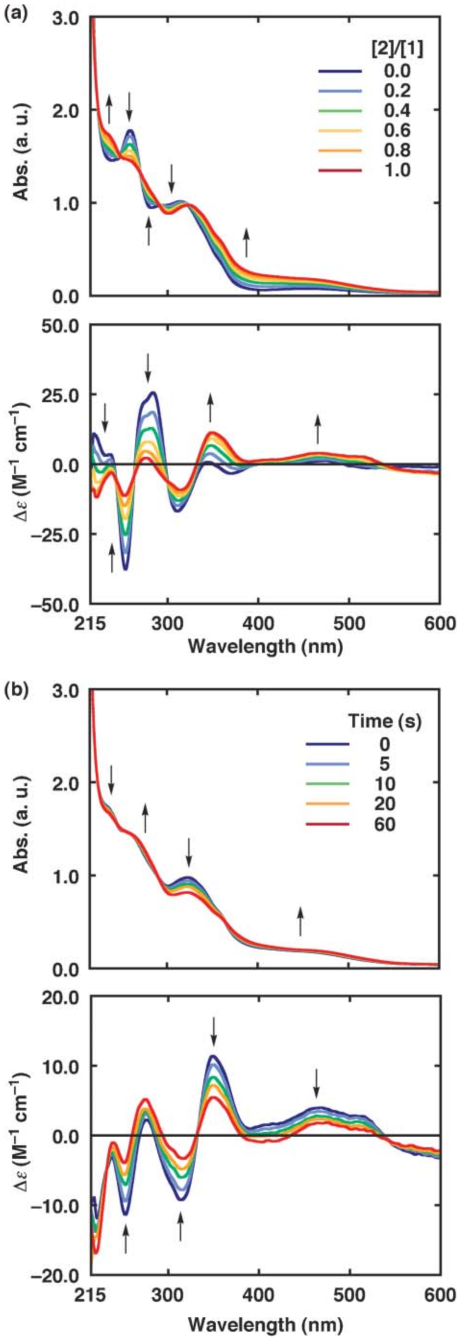

Fig. 1 (a) Absorption (upper) and CD (lower) spectral changes of (1S,1′S)-*trans*-$\mathbf{1}^{\mathrm{II}}$ (1.9×10^{-4} M) in CH_2Cl_2 at 20 °C upon addition of oxidant **2**. [**2**]/[$\mathbf{1}^{\mathrm{II}}$] = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0. (b) Absorption (upper) and CD (lower) spectral changes of *trans*-$\mathbf{1}^{\mathrm{III}}$ (1.9×10^{-4} M, [**2**]/[$\mathbf{1}^{\mathrm{III}}$] = 1.0) in CH_2Cl_2 at 20 °C upon UV irradiation ($\lambda = 350 \pm 10$ nm) for 0, 5, 10, 20 and 60 s. Arrows indicate the directions of spectral changes.

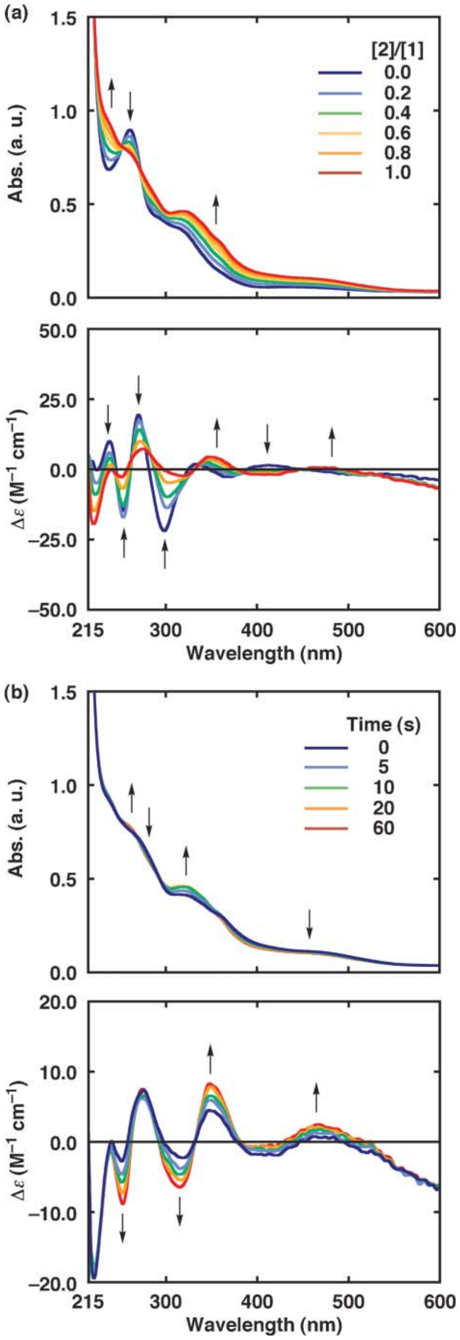

Fig. 2 (a) Absorption (upper) and CD (lower) spectral changes of (1S,1′S)-*cis*-$\mathbf{1}^{\mathrm{II}}$ ([*cis*]/[*trans*] = 84/16; [$\mathbf{1}^{\mathrm{II}}$] = 1.1×10^{-4} M) in CH_2Cl_2 at 20 °C upon addition of oxidant **2**. [**2**]/[$\mathbf{1}^{\mathrm{II}}$] = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0. (b) Absorption (upper) and CD (lower) spectral changes of (1S,1′S)-*cis*-$\mathbf{1}^{\mathrm{III}}$ ([*cis*]/[*trans*] = 84/16; [$\mathbf{1}^{\mathrm{III}}$] = 1.1×10^{-4} M, [**2**]/[$\mathbf{1}^{\mathrm{III}}$] = 1.0) in CH_2Cl_2 at 20 2°C upon UV irradiation ($\lambda = 350 \pm 10$ nm) for 0, 5, 10, 20 and 60 s. Arrows indicate the directions of spectral changes.

(see Fig. 2b, upper). This spectral change leveled off in 60 s to reach a new photostationary state. Consistently, an attempted photoisomerization of the oxidized *trans* form, (1S,1′S)-*trans*-$\mathbf{1}^{\mathrm{III}}$, upon exposure to UV light ($\lambda = 350 \pm 10$ nm) resulted in exactly the same *cis* content (35%) in 60 s, where the electronic absorption spectrum changed oppositely to that shown in Fig. 2b (upper) (see Fig. 1b, upper). Just for confirmation, when the isomerized mixture was reduced by a stoichiometric amount of **3** and then exposed to UV light, the *cis* content increased further to reach 84%, a value finally attained in the UV-induced isomerization of neutral (1S,1′S)-*trans*-$\mathbf{1}^{\mathrm{II}}$.

The fact that the oxidation of the ferrocene pivot of **1** causes a shift of the photostationary state of its azobenzene isomerization suggests an interesting possibility that the scissoring motion of **1** can be realized only by UV light (Scheme 1). As a demonstration

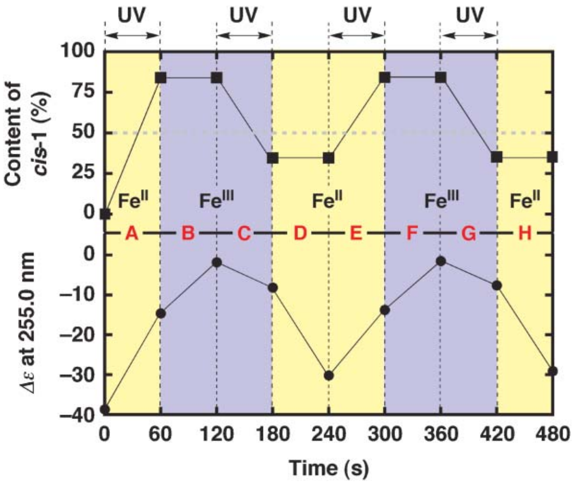

Fig. 3 Changes in isomer ratio (upper) and CD intensity at 255.0 nm (lower) of (1*S*,1′*S*)-*trans*-**1** upon irradiation with UV light (λ = 350 ± 10 nm) in CH_2Cl_2 at 20 °C for 60 s in a sequential redox process. Mauve and yellow regions feature the oxidized and neutral states of **1**, respectively.

of this, we carried out the following sequence of experiments. First, a CH_2Cl_2 solution of (1*S*,1′*S*)-*trans*-**1**^{II} was irradiated with UV light (λ = 350 ± 10 nm) for 60 s to allow the system to reach the photostationary state ([*trans*-**1**^{II}]/[*cis*-**1**^{II}] = 16/84, stage A), and then a stoichiometric amount of oxidant **2** was added to the resulting mixture. After being stirred for 60 s to complete the oxidation of (1*S*,1′*S*)-**1**^{II} (stage B), the resultant solution was exposed again to UV light (λ = 350 ± 10 nm, stage C). In this *cis*-to-*trans* photoisomerization step, the Cotton effects in the CD spectrum became entirely enhanced (see Fig. 2b, lower), indicating that the isomerization of the azobenzene strap in the oxidized scissors is accompanied by an angular motion of the ferrocene pivot. Subsequently, a stoichiometric amount of reductant **3** was added to this photostationary state mixture (stage D, see Supplementary Information Fig. S2c). After the completion of the reduction (60 s) of (1*S*,1′*S*)-**1**^{III}, a small portion of the resulting solution was subjected to HPLC, where the *trans*/*cis* isomer ratio was determined as 65/35. The residual solution was subjected to irradiation with UV light (λ = 350 ± 10 nm) for 60 s (stage E), followed by oxidation with **2** for 60 s (stage F). Then, the resultant solution was again exposed to UV light (λ = 350 ± 10 nm) for 60 s (stage G). As shown in Fig. 3, the *trans*/*cis* isomer ratio of (1*S*,1′*S*)-**1** in these two cycles switched reversibly between 16/84 and 65/35 only with the use of UV light. Synchronously, the CD spectral profile changed in a reversible way.

There have been reported some examples of azobenzene derivatives bearing transition metal complex moieties, where the isomerization profiles of their photochromic parts are altered by changing the oxidation state of the metal center.[12,13,16] In these cases, the metal centers are directly bonded with the photochromic part, and their through-bond electronic interaction has been claimed to play an important role. In sharp contrast, our system carries the redox active ferrocene unit non-directly bonded to the photochromic part. Since these two chromophores are also spatially separated because of the rigid cyclic structure, their ground-state electronic interactions are very unlikely. Nevertheless, upon photoexcitation, some through-space energetic or electronic communication[12,16] might be possible intramolecularly. While photophysical studies are needed to substantiate this possibility, we tentatively think that preferential quenching of either the *cis* or *trans* isomer of the excited azobenzene moiety by such a through-space communication is a likely candidate for the redox-induced shift of the photostationary state, observed for the isomerization of **1** with UV light.

In conclusion, by taking advantage of the redox activity of the ferrocene pivot, we have demonstrated a reversible scissoring motion of chiral molecular scissors **1** only with UV light. This is owing to the fact that the *trans*/*cis* isomer ratio of **1** at the photostationary state is altered by changing the oxidation state of the ferrocene pivot.[12,13] Namely, scissors **1** can now be regarded as a molecular machine that responds to redox as well as light.

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Notes and references

‡ Compound (1*S*,1′*S*)-*trans*-**1** was prepared by the method described in our previous reports.[9,10] 1,1′-Dichloroferrocenium hexafluorophosphate (**2**) was synthesized according to the literature methods.[17] Bis(pentamethylcyclopentadienyl)iron(II) (**3**) was purchased from Aldrich and recrystallized from methanol.

§ Photoirradiation was carried out at 20 °C on degassed and dry CH_2Cl_2 solutions of samples in a 1-mm thick quartz cell under Ar, using a xenon arc lamp (100 W, LAX-102, Asahi Spectra) with a bandpass filter (HQBP350-UV ϕ25, Asahi Spectra) of λ = 350 ± 10 nm.

1 K. Kinbara and T. Aida, *Chem. Rev.*, 2005, **105**, 1377; J.-P. Collin, C. Dietrich-Buchecker, P. Gaviña, M. C. Jimenez-Molero and J.-P. Sauvage, *Acc. Chem. Res.*, 2001, **34**, 477; V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348.
2 T. Fukushima, K. Asaka, A. Kosaka and T. Aida, *Angew. Chem., Int. Ed.*, 2005, **44**, 2410; E. Smela, *Adv. Mater.*, 2003, **15**, 481; E. W. H. Jager, E. Smela and O. Inganäs, *Science*, 2000, **290**, 1540.
3 S. Shinkai, T. Ogawa, T. Nakaji, Y. Kusano and O. Manabe, *Tetrahedron Lett.*, 1979, **20**, 4569.
4 D. A. Leigh, J. K. Y. Wong, F. Dehez and F. Zerbetto, *Nature*, 2003, **424**, 174.
5 N. Koumura, R. W. J. Zijistra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152.
6 J. D. Badjic, V. Balzani, A. Credi, S. Silvi and J. F. Stoddart, *Science*, 2004, **303**, 1845.
7 M. C. Jimenez, C. Dietrich-Buchecker and J.-P. Sauvage, *Angew. Chem., Int. Ed.*, 2000, **39**, 3284.
8 T. Muraoka, K. Kinbara and T. Aida, *J. Am. Chem. Soc.*, 2006, **128**, 11600.
9 T. Muraoka, K. Kinbara, Y. Kobayashi and T. Aida, *J. Am. Chem. Soc.*, 2003, **125**, 5612.
10 T. Muraoka, K. Kinbara, A. Wakamiya, S. Yamaguchi and T. Aida, *Chem.–Eur. J.*, 2007, **13**, 1724.
11 T. Muraoka, K. Kinbara and T. Aida, *Nature*, 2006, **440**, 512.
12 K. Osakada, T. Sakano, M. Horie and Y. Suzaki, *Coord. Chem. Rev.*, 2006, **250**, 1012; H. Nishihara, *Coord. Chem. Rev.*, 2005, **249**, 1468.
13 S. Kume, M. Kurihara and H. Nishihara, *Chem. Commun.*, 2001, 1656.
14 I. Nowik and R. H. Herber, *Inorg. Chim. Acta*, 2000, **310**, 191; R. J. Webb, M. D. Lowery, Y. Shiomi, M. Sorai, R. J. Wittebort and D. N. Hendrickson, *Inorg. Chem.*, 1992, **31**, 5211.
15 M. Rosenblum, *Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, Osmocene*, Interscience Publishers, New York, 1965, part 1, pp. 40–42; Y. S. Sohn, D. N. Hendrickson and H. B. Gray, *J. Am. Chem. Soc.*, 1971, **93**, 3603.
16 S. Kume, M. Kurihara and H. Nishihara, *J. Korean Electrochem. Soc.*, 2002, **5**, 189.
17 D. W. Slocum, T. R. Engelmann, C. Ernst, C. A. Jennings, W. Jones, D. M. Duggan and D. N. Hendrickson, *Inorg. Chem.*, 1975, **14**, 955.