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Crystallographic and Chiroptical Studies on Tetraarylferrocenes for Use as Chiral Rotary Modules for Molecular Machines

**Takahiro Muraoka,[a] Kazushi Kinbara,*[a, b] Atsushi Wakamiya,[c]
Shigehiro Yamaguchi,[c] and Takuzo Aida*[a]**

Abstract: A crystal structure of the racemic form of chiral molecular scissors **1** with a *trans* configuration at the azobenzene unit (*rac-trans*-**1**), in which the scissors adopt a closed geometry with two blade phenyl groups that overlap each other, was successfully determined. X-ray crystallographic determination of the structure of (1*S*,1′*S*)-**10**, which is a derivative of the key precursor of *trans*-**1**, was also successful. On the basis of the crystal structure of (1*S*,1′*S*)-**10**, the absolute configuration of **1** and related molecular machines, such as molecular pedal **2**, and self-locking rotor **3**, which all contain a chiral tetrasubstituted ferrocene module, were determined. A correlation between the absolute configuration and the circular dichroism properties of these molecular machines and their synthetic precursors was also determined.

Keywords: absolute configuration · chirality · circular dichroism · metallocenes · molecular devices

Introduction

Ferrocene, which was discovered in 1951,[1] is the oldest example of a metallocene.[2] Ferrocene derivatives have attracted much attention owing to their distinctive chemical properties that arise from their unique metal-sandwich double-decker structures, and they are utilized for a variety of applications. Representative examples include the molecular design of redox-active materials and homogeneous catalysts,[3,4] which take advantage of the structural robustness of ferrocene derivatives. Aside from these applications, the rotary motions of the two facing cyclopentadienyl (Cp) rings in ferrocene derivatives have also attracted attention. Gardner et al. have reported that the Cp rings of ferrocene rotate very rapidly at a rate of $3.4\times10^{8}\,s^{-1}$ in solution even at low temperatures, such as 154 K.[5] Orrell et al. have reported that a substituted ferrocene molecule containing 1,3-diphenylcyclopentadienyl rings also undergoes a rapid rotary motion, even at 173 K.[6] Therefore, ferrocene derivatives can be regarded as free-rotating modules. In relation to these unique dynamic motions, we have demonstrated recently that a ferrocene derivative composed of disubstituted Cp rings can be utilized as a novel rotary module for molecular machines,[7,8] such as molecular scissors (**1**),[9] a molecular pedal (**2**),[10] and a self-locking rotor (**3**).[11] Despite their free-rotating feature, the rotary motion of the Cp rings is geometrically restricted, which results in the ferrocene-based rotary modules behaving like a ball-bearing unit.[12] For example, **1** is composed of three interlocked components, namely, a handle, a pivot, and blade units, in which a chiral 1,1′,3,3′-tetrasubstituted ferrocene derivative serves as the pivot, whereas the handle consists of Cp-attached phenylene groups strapped together by a photoresponsive azobenzene unit. Through an angular motion of the ferrocene module, elongation and contraction of the handle is operated by means of the *trans–cis* photoisomerization reaction of the azobenzene unit, which is translated into an open–close scissoring motion of the other Cp-attached phenyl groups that act as the blade. As the chiroptical properties of the ferrocene pivot are entirely dependent on the dihedral angular moments of the substituted Cp rings, the scissoring motion

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[a] T. Muraoka, Prof. Dr. K. Kinbara, Prof. Dr. T. Aida
Department of Chemistry and Biotechnology, School of Engineering
Center for NanoBio Integration, The University of Tokyo
7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656 (Japan)
Fax: (+81) 3-5841-7310
E-mail: kinbara@macro.t.u-tokyo.ac.jp
aida@macro.t.u-tokyo.ac.jp

[b] Prof. Dr. K. Kinbara
PRESTO, Japan Science Technology Agency (JST), 4-1-8 Honcho
Kawaguchi, Saitama 332-0012 (Japan)

[c] Dr. A. Wakamiya, Prof. Dr. S. Yamaguchi
Department of Chemistry, Graduate School of Science
Nagoya University, Chikusa
Nagoya 464-8602 (Japan)

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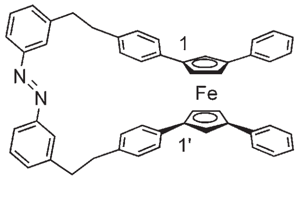
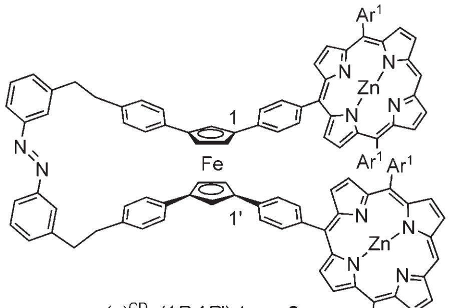
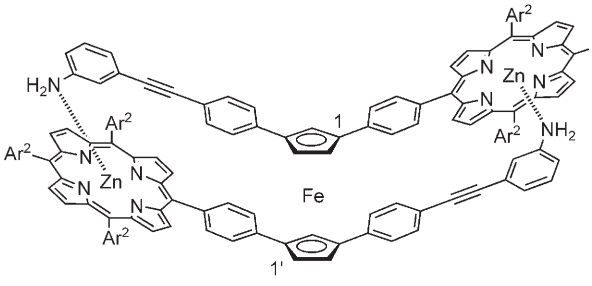


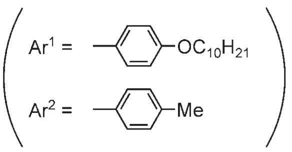
$(-)^{\mathrm{CD}}_{260}$-(1*S*,1'*S*)-*trans*-**1**



$(-)^{\mathrm{CD}}_{260}$-(1*R*,1'*R*')-*trans*-**2**

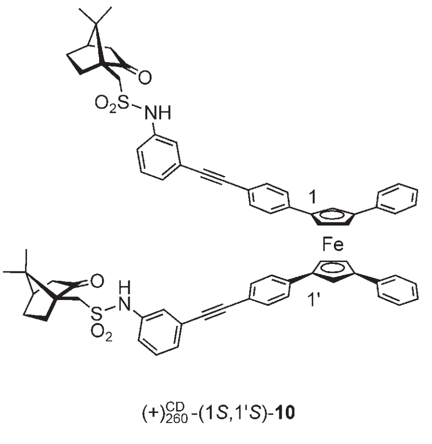


$(-)^{\mathrm{CD}}_{260}$-(1*R*,1'*R*)-**3**



of **1** can be monitored by means of its circular dichroism (CD) response.

Despite the potential for chiral 1,1′,3,3′-tetrasubstituted ferrocenes to act as rotary modules for molecular machines, their chiroptical properties and absolute configurations have not yet been correlated to each other. This absence of data is partly because of a limited success in determining the crystal structure of such highly substituted ferrocene derivatives with a planar chirality.[13] In this paper, we report the determination of the crystal structures for the racemic form of *trans*-**1** and optically pure (1*S*,1′*S*)-**10**, which is a derivative of the important precursor of **1**. We also discuss stereochemical aspects of related molecular machines and their precursors based on their chiroptical properties[14] and absolute configurations deduced from that of (1*S*,1′*S*)-**10**.



$(+)^{\mathrm{CD}}_{260}$-(1*S*,1'*S*)-**10**

Results and Discussion

Crystal structure of molecular scissors *trans*-1: As compound **1** adopts a highly unsymmetrical structure, it was rather hard to obtain a single crystal of **1** that was suitable for X-ray crystallography. However, after numerous attempts, we finally obtained a needlelike thin crystal by means of slow evaporation of a solution of the racemic form of *trans*-**1** in $CHCl_3$. The crystal structure of *trans*-**1** belonged to space group $P2_1/c$, in which an asymmetric unit involving one molecule of *trans*-**1** included 0.5 molecules of $CHCl_3$.[15] As shown in Figure 1, the crystal structure indicates that the two Cp-attached phenylene groups in the handle section form an angle of 62.78° and are separated from one another to accommodate the *trans*-azobenzene unit with almost a planar and extended geometry. Consequently, the Cp-attached phenyl groups in the blade section

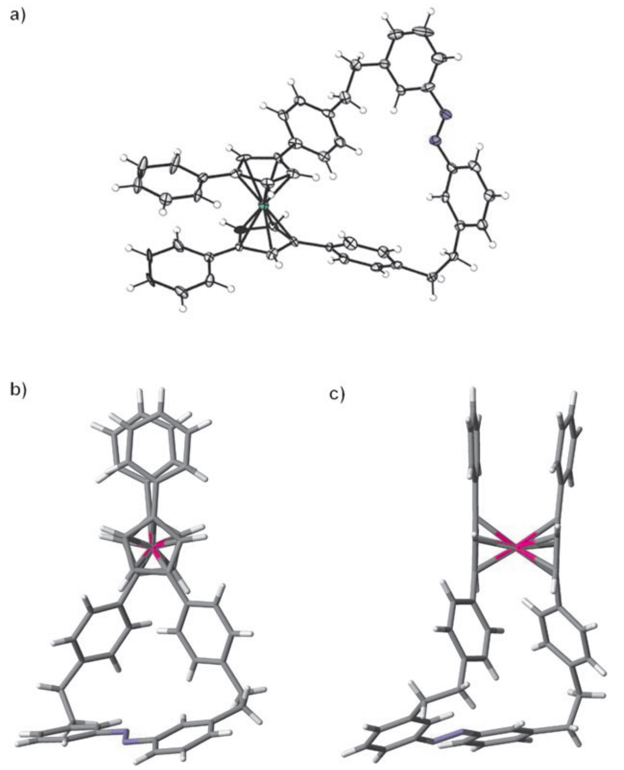


Figure 1. a) ORTEP drawing of molecular scissors *trans*-**1** (50 % thermal ellipsoids). Crystal structures of *trans*-**1** viewed from b) the top and c) the side of the ferrocene unit.

are positioned close to one another with a twisting angle of only 8.75°, and therefore, the scissors with a *trans*-azobenzene unit is in a closed form, as predicted by means of DFT calculations.[9] The phenylene groups in the handle are twisted by 49.25 and 37.84° relative to the attached Cp planes, whereas those in the blade part are almost coplanar with the Cp planes. We also found that the two Cp rings are almost parallel to each other with a plane-to-plane separation of 3.334 Å.

Crystal structure of $(+)^{CD}_{260}$-(1*S*,1′*S*)-10: The enantiomers of **4**, which is a precursor of **10**, are separable by means of recycling chiral HPLC on a Chiralpak IA column by using a mixture of toluene and hexane (1:4 v/v) as the eluent. As the first and second fractions of **4** exhibited positive- and negative-signed CD bands, respectively, at $\lambda = 260$ nm in CH_2Cl_2, they are denoted as $(+)^{CD}_{260}$-**4** and $(-)^{CD}_{260}$-**4**, respectively. Precursor $(+)^{CD}_{260}$-**4** was then treated with 2-[3-(1*S*,4*R*)-(10-camphorsulfonyl)aminophenyl]ethynylbenzene (**11**) to give $(+)^{CD}_{260}$-**10**, which also displayed a positive-signed CD band at $\lambda = 260$ nm in CH_2Cl_2. We successfully obtained a needlelike single crystal of $(+)^{CD}_{260}$-**10**, which was suitable for X-ray crystallography, by means of vapor diffusion of hexane into a solution of $(+)^{CD}_{260}$-**10** in acetone. The crystal structure of this compound belonged to space group *C*2, in which an asymmetric unit involving one molecule of $(+)^{CD}_{260}$-**10** included two different kinds of symmetrically independent acetone molecules.[15] As shown in Figure 2, $(+)^{CD}_{260}$-**10** in the crystal adopts a *syn* geometry, in which the two bulky camphorsulfonyl substituents are located close to each other. The interatomic distance between the amide nitrogen and carbonyl oxygen atoms is 2.905 Å. This conformation most likely results from an intramolecular hydrogen-bonding interaction of the camphor carbonyl on a Cp ring with the amide NH on the other Cp ring. In fact, an infrared spectrum of $(+)^{CD}_{260}$-**10** displayed a vibrational band corresponding to the camphor carbonyl group at $\tilde{\nu} = 1734$ cm^{-1}, which is lower than that of camphor ($\tilde{\nu} = 1743$ cm^{-1}) used as a reference. By taking advantage of the presence of (1*S*,4*R*)-camphorsulfonyl groups as a stereochemically defined internal reference, the absolute configuration of the ferrocene module in $(+)^{CD}_{260}$-**10** was unambiguously determined as 1*S*,1′*S*. Accordingly, the absolute configuration of precursor $(+)^{CD}_{260}$-**4** could be assigned as $(+)^{CD}_{260}$-(1*S*,1′*S*)-**4**.

Absolute configuration of molecular scissors *trans*-1 and those of related ferrocene-based precursors: As *trans*-**1** is derived from **4** (Scheme 1)—with retention of the stereochemistry around the ferrocene unit—the absolute configuration of *trans*-**1**, along with those of intermediates **5** and **6**, was also determined. Interestingly, although unstrapped (1*S*,1′*S*)-**5** and (1*S*,1′*S*)-**6**, which are analogous to (1*S*,1′*S*)-**4**, both have positive-signed CD bands at $\lambda = 260$ nm, the resulting (1*S*,1′*S*)-*trans*-**1** with an azobenzene strap gives a negative CD band at the same wavelength ($(-)^{CD}_{260}$-(1*S*,1′*S*)-*trans*-**1**) (Figure 3a and Figure S1 in the Supporting Information).

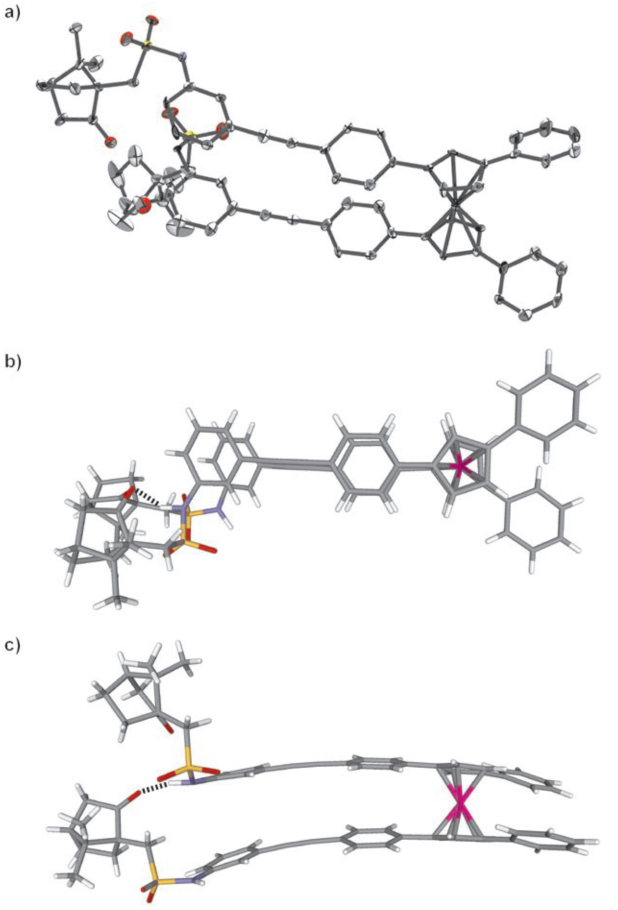
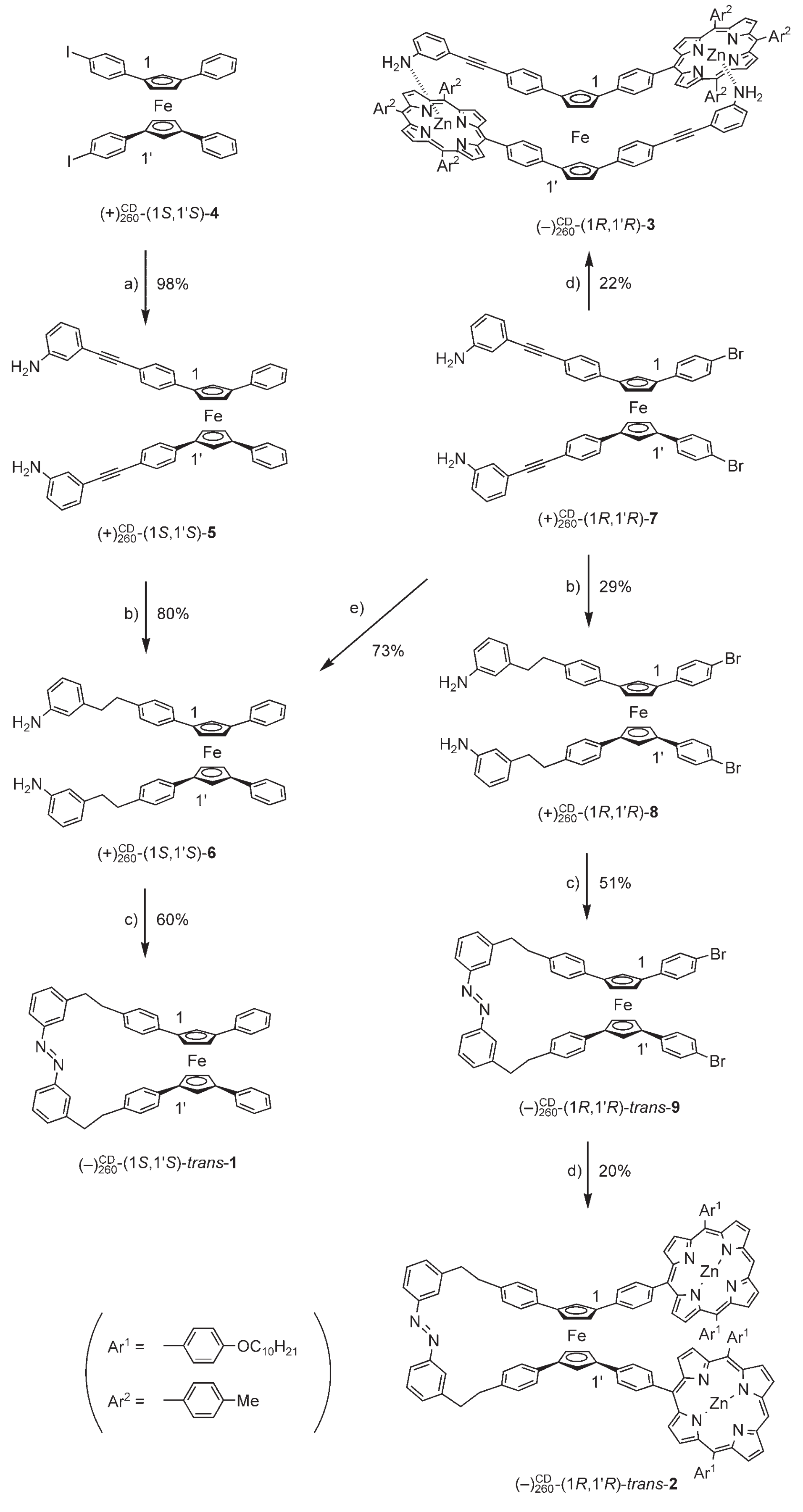


Figure 2. a) ORTEP drawing of $(+)^{CD}_{260}$-(1*S*,1′*S*)-**10** (50% thermal ellipsoids) for determination of the absolute configuration of its 1,1′,3,3′-tetraarylferrocene module. Hydrogen atoms are omitted for clarity. Crystal structures of $(+)^{CD}_{260}$-(1*S*,1′*S*)-**10** viewed from b) the top and c) the side of the ferrocene unit. Broken lines in b) and c) represent an intramolecular hydrogen bond between the camphor carbonyl and amide NH.

Absolute configuration of molecular pedal *trans*-2 and those of related ferrocene-based precursors: The absolute configuration of molecular pedal *trans*-**2** and self-locking rotor **3** could be determined from that of **6**. As shown in Scheme 1, *trans*-**2** can be synthesized from brominated **7** via intermediates **8** and **9**. Compound **7** can also be converted into **6** by means of palladium-catalyzed hydrogenation of the acetylene units with retention of the stereochemistry. Thus, by comparing the CD spectral profile of hydrogenated derivative **6**, obtained from **7**, with those of its configurationally defined enantiomers (1*S*,1′*S*)-**6** and (1*R*,1′*R*)-**6**, the absolute configuration of **7** can be determined. Thus, enantiomers $(-)^{CD}_{260}$-**7** and $(+)^{CD}_{260}$-**7**, which display negative- and positive-signed CD bands at $\lambda = 260$ nm in CH_2Cl_2, respectively, were obtained as the first and second fractions, respectively, from recycling chiral HPLC of *rac*-**7** on a Chiralpak IA column by using a mixture of CH_2Cl_2, toluene, and triethylamine (1:2:0.01 v/v/v) as an eluent. Hydrogenenation of $(-)^{CD}_{260}$-**7** gave **6**, which exhibited a negative-signed CD band at $\lambda = 260$ nm and was therefore designated (1*R*,1′*R*)-**6**. From this, precursor **7** was designated (1*S*,1′*S*)-**7**, whose absolute configuration with respect to the ferrocene module is identical to that of (1*R*,1′*R*)-**6**. Subsequently, the enantiomers of *trans*-**2**, $(+)^{\mathrm{CD}}_{260}$-*trans*-**2** and $(-)^{\mathrm{CD}}_{260}$-*trans*-**2**, which exhibit positive- and negative-signed CD bands at $\lambda = 260$ nm, can be assigned as (1*S*,1′*S*)-*trans*-**2** and (1*R*,1′*R*)-*trans*-**2**, respectively. As in the case of *trans*-**1**, unstrapped (1*R*,1′*R*)-**7** and (1*R*,1′*R*)-**8** exhibited positive-signed CD bands at 260 nm, whereas strapped (1*R*,1′*R*)-*trans*-**9** and (1*R*,1′*R*)-*trans*-**2** both displayed a negative-signed CD band at the same wavelength ($(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-*trans*-**9**, $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-*trans*-**2**) (Figure 3b and Figure S2 in the Supporting Information).

Absolute configuration of molecular self-locking rotor 3: As shown in Scheme 1, **3** can be synthesized from **7** with retention of the stereochemistry. Thus, the absolute configuration of compound **3** was consequently determined. We prepared enantiomer (1*R*,1′*R*)-**3** from $(+)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**7**, and found that it shows a negative-signed CD band at $\lambda = 260$ nm in CH_2Cl_2. Hence, this enantiomer can be denoted as $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**3**, whereas its enantiomeric counterpart is denoted as $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**3**. The CD signs of $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**3** and $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**3** are opposite to those of their precursors $(+)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**7** and $(-)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**7**, respectively (Figure 3c).



Scheme 1. Synthetic pathways toward molecular scissors *trans*-**1**, molecular pedal *trans*-**2**, and molecular self-locking rotor **3**. Reagents and conditions: a) 3-ethynylaniline, $[PdCl_2(PPh_3)_2]$, CuI, Et_3N, THF, RT; b) H_2, PtO_2, EtOH, THF, RT; c) O_2, CuI, pyridine, RT; d) zinc 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10,20-bis(4-decyloxyphenyl)porphyrin, $[Pd(PPh_3)_4]$, Cs_2CO_3, toluene, H_2O, reflux; e) H_2, Pd/C, EtOH, THF, reflux.

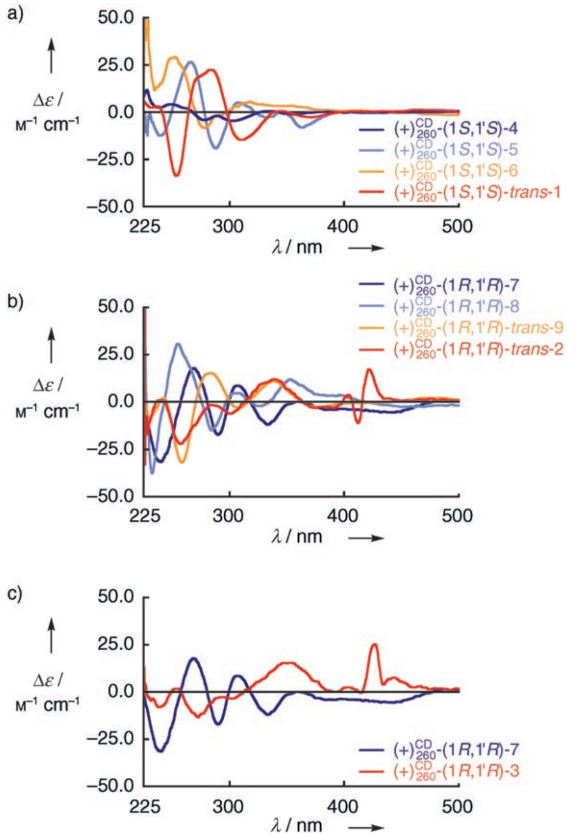


Figure 3. CD spectra recorded in CH_2Cl_2 at 20°C of a) $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**4**, -**5**, and -**6**, and $(-)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-*trans*-**1**; b) $(+)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**7**, -**8**, and -*trans*-**9**, and $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-*trans*-**2**; and c) $(+)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**7** and $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**3**.

Conclusion

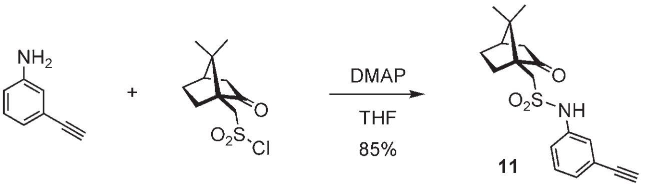
We have succeeded in determining the crystal structure of molecular scissors *trans*-**1** and $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**10**, which is a derivative of the key intermediate of *trans*-**1**. In particular, the clarification of the absolute configuration of (1*S*,1′*S*)-**4**, via the (1*S*,4*R*)-camphor derivative (1*S*,1′*S*)-**10**, made it possible to determine the absolute configurations of a series of ferrocene-based molecular machines and their precursors. This achievement enables precise stereochemical design of molecular-scale rotary machines based on chiral 1,1′,3,3′-tetrasubstituted ferrocenes.

Experimental Section

General methods: ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ by using a JEOL GSX-270 spectrometer, in which chemical shifts were determined with respect to $CHCl_3$ as an internal reference. Fast-atom-bombardment high-resolution mass spectrometry (FAB-HRMS) was performed by using 3-nitrobenzyl alcohol as a matrix by using a JEOL JMS-AX505H mass spectrometer. Electronic absorption spectra were recorded by using a JASCO U-best 560 spectrometer. CD spectra were recorded by using a JASCO J-720 spectropolarimeter. Infrared spectra were recorded by using a JASCO FTIR-610 spectrometer. X-ray crystallography was performed by using a Rigaku Single Crystal CCD X-ray Diffractometer (Saturn 70 with MicroMax-007) with $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The structures were solved and refined by applying the Rigaku Crystal Structure package:[16] the direct method (SIR 92) followed by normal heavy-atom procedures, and a full-matrix least-squares refinement with all anisotropic non-hydrogen atoms except for solvent and hydrogen atoms in calculated positions.

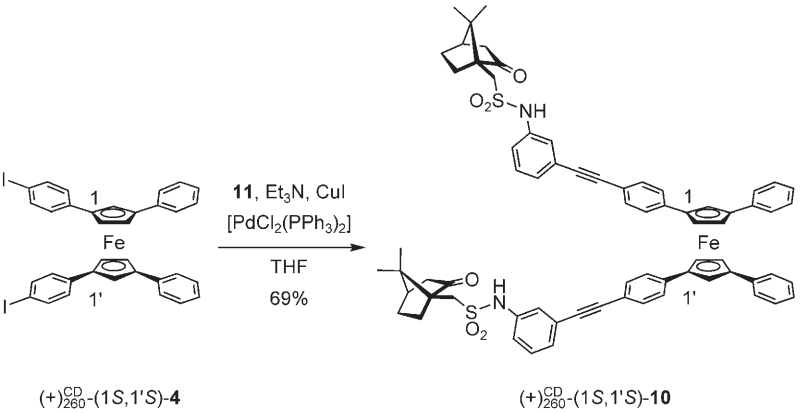
Materials: Compounds **1**–**9** were prepared by using the methods described in our previous reports.[9–11] (1*S*,4*R*)-(+)-10-Camphorsulfonyl chloride, 4-dimethylaminopyridine (DMAP), 3-ethynylaniline, and $[PdCl_2(PPh_3)_2]$ were purchased from Tokyo Chemical Industry (TCI), while CuI was purchased from Kanto Kagaku. These commercially available reagents were used without further purification. Dehydrated THF (stabilizer-free) was purchased from Kanto Kagaku. NEt_3 was distilled over KOH under an Ar atmosphere. For column chromatography, Wakogel C-300HG (particle size 40–60 μm, silica gel) was used.

2-[3-(1*S*,4*R*)-(10-Camphorsulfonyl)aminophenyl]ethynylbenzene (11): A solution of (1*S*,4*R*)-(+)-10-camphorsulfonyl chloride (6.25 g, 24.9 mmol) dissolved in THF (50 mL) was added to a solution of 3-ethynylaniline (2.65 g, 22.7 mmol) and DMAP (3.32 g, 27.2 mmol) dissolved in THF (50 mL) at 0°C under an Ar atmosphere (Scheme 2). The reaction mixture was stirred for 1 h at 0°C and then 6 h at room temperature to give a white precipitate. The reaction mixture was then quenched with water and extracted by using diethyl ether (3×30 mL). The combined organic extract was washed with 0.5 M aqueous HCl solution, saturated aqueous $NaHCO_3$ solution, and brine, and then dried over anhydrous $MgSO_4$. The solvent was evaporated to leave a yellowish-white residue, which was recrystallized from acetone/hexane to afford **11** as a white crystalline solid (6.40 g, 19.3 mmol, 85%). ^{1}H NMR (270.05 MHz, $CDCl_3$, 24°C): $\delta = 0.84$ (s, 3H), 0.94 (s, 3H), 1.40–2.50 (m, 7H), 2.67 (d, $J = 15.2$ Hz, 1H), 2.90 (s, 1H), 3.32 (d, $J = 15.3$ Hz, 1H), 7.26–7.29 (m, 3H), 7.40 (s, 1H), 7.83 ppm (brs, 1H); ^{13}C NMR (67.80 MHz, $CDCl_3$, 31°C): $\delta = 19.4$, 20.0, 27.2, 27.8, 43.0, 43.2, 49.2, 49.5, 59.8, 77.8, 77.9, 82.8, 122.4, 123.3, 129.1, 129.4, 137.7, 217.3 ppm; IR (KBr): $\tilde{\nu} = 3440$, 3256, 2960, 2108, 1745, 1603, 1580, 1496, 1469, 1409, 1393, 1334, 1310, 1278, 1241, 1217, 1163, 1144, 1068, 1053, 1002, 970, 863, 799, 688, 563, 537, 499 cm^{-1}; CD (EtOH, 20°C): λ_{ext} ($\Delta\varepsilon$) = 297 nm (+1.14); FABMS (3-nitrobenzyl alcohol): *m*/*z*: 331 [M^+].



Scheme 2. Synthetic pathway for **11**.

(1*S*,1′*S*)-Bis{2-[3-(1*S*,4*R*)-(10-camphorsulfonyl)aminophenylethynylphenyl]-(3*R*,3′*R*)-diphenylferrocene ($(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-10): A solution of **11** (344 mg, 1.04 mmol) dissolved in dry THF (10 mL) was added to a suspension of $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**4** (24.5 mg, 33.0 μmol), $[PdCl_2(PPh_3)_2]$ (5.4 mg, 7.69 μmol), and CuI (2.7 mg, 14.2 μmol) in dry NEt_3 (2.5 mL) under an Ar atmosphere, and the mixture was stirred for 10 h at room temperature (Scheme 3). Water (50 mL) was added to the reaction mixture, which was then extracted by using CH_2Cl_2 (2×100 mL). The combined organic extract was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The orange powdery residue was purified by means of column chromatography by using a silica gel column with CH_2Cl_2/hexane (2:1) as the eluent. Crude $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**10**, thus obtained, was purified by recycling preparative HPLC with a Chemcosorb 5Si column by using CH_2Cl_2/hexane (2:1) as the eluent at a flow rate of 10.0 mL min^{-1}, to allow the isolation of $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**10** (26 mg, 22.6 μmol, 69%). ^{1}H NMR (500.00 MHz, $CDCl_3$, 20°C): $\delta = 0.87$ (s, 6H), 0.96 (s, 6H), 1.46–2.50 (m, 14H), 2.91 (d, $J = 15.4$ Hz, 2H), 3.37 (d, $J = 15.4$ Hz, 2H), 4.47 (s, 2H), 4.52 (s, 2H), 4.70 (s, 2H), 7.11 (d, $J = 8.6$ Hz, 4H), 7.20–7.33 (m, 16H), 7.30 (d, $J = 8.6$ Hz, 4H), 7.45 (s, 2H), 7.82 ppm (brs, 2H); ^{13}C NMR (67.80 MHz, $CDCl_3$, 27°C): $\delta = 19.5$, 20.0, 27.2, 27.8,



Scheme 3. Synthetic pathway for $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**10**.

43.0, 43.2, 49.3, 49.5, 59.9, 67.3, 70.0, 70.8, 86.4, 88.1, 88.8, 90.6, 120.2, 121.6, 124.6, 124.8, 125.4, 125.8, 128.2, 128.3, 128.6, 129.4, 131.6, 136.7, 137.4, 137.7, 217.3 ppm; IR (KBr): $\tilde{\nu}=3442$, 2958, 2209, 1734, 1601, 1578, 1527, 1463, 1394, 1377, 1335, 1212, 1151, 1130, 1108, 1068, 1053, 1000, 968, 834, 789, 764, 689 cm^{-1}; UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 472 (4430), 293 nm (75 900 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): λ_{ext} ($\Delta\varepsilon$) = 485 (+2.61), 366 (−4.96), 345 (+5.33), 332 (−1.38), 312 (+13.71), 288 (−26.02), 266 nm (+24.94 mol^{-1}dm^{3}cm^{-1}); FAB-HRMS (3-nitrobenzyl alcohol): *m*/*z* calcd for $C_{70}H_{64}FeN_2O_6S_2$: 1148.3555; found: 1148.3582.

Electronic absorption and CD spectral data of *trans*-1, *trans*-2, 3–8, and *trans*-9

Compound trans-***1***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 455 (2900), 314 (31 700), 296 (30 600), 259 nm (55 400 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(-)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-*trans*-**1**: λ_{ext} ($\Delta\varepsilon$) = 371 (−2.73), 345 (+0.66), 311 (−14.73), 284 (+22.44), 253 nm (−33.64); $(+)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-*trans*-**1**: λ_{ext} ($\Delta\varepsilon$) = 370 (+3.01), 344 (−1.12), 310 (+15.40), 286 (−22.27), 254 nm (+35.04).

Compound trans-***2***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 586 (2620), 545 (23 100), 418 (318 000), 308 nm (31 200 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-*trans*-**2**: λ_{ext} ($\Delta\varepsilon$) = 420 (−14.31), 411 (+10.25), 403 (−2.89), 373 (+2.52), 341 (−11.46), 299 (+6.77), 257 nm (+23.70); $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-*trans*-**2**: λ_{ext} ($\Delta\varepsilon$) = 421 (+17.20), 412 (−11.29), 404 (+3.68), 375 (−3.24), 339 (+11.90), 300 (−6.29), 257 nm (−22.06).

Compound ***3***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 563 (26 900), 432 (350 000), 286 nm (57 700 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**3**: λ_{ext} ($\Delta\varepsilon$) = 444 (+7.56), 427 (+25.41), 403 (+2.53), 354 (+15.46), 303 (−3.57), 272 (−13.39), 254 (+1.80), 238 nm (−8.17).

Compound ***4***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 471 (926), 268 nm (58 100 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**4**: λ_{ext} ($\Delta\varepsilon$) = 356 (−1.33), 336 (+0.65), 303 (−4.61), 278 (−4.17), 249 nm (+4.18); $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**4**: λ_{ext} ($\Delta\varepsilon$) = 354 (+1.08), 334 (−0.69), 303 (+4.52), 277 (+6.35), 247 nm (−2.71).

Compound ***5***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 468 (3350), 289 nm (75 200 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**5**: λ_{ext} ($\Delta\varepsilon$) = 363 (−8.22), 334 (−2.71), 308 (+5.12), 288 (−19.14), 266 (+26.62), 241 nm (−12.34); $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**5**: λ_{ext} ($\Delta\varepsilon$) = 363 (+9.04), 335 (+4.11), 308 (−4.94), 288 (+17.02), 267 (−32.97), 240 nm (+15.21).

Compound ***6***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 467 (2030), 260 nm (51 100 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**6**: λ_{ext} ($\Delta\varepsilon$) = 318 (+6.20), 292 (−1.72), 253 nm (+28.15); $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**6**: λ_{ext} ($\Delta\varepsilon$) = 319 (−3.36), 294 (+2.83), 252 nm (−27.21).

Compound ***7***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 474 (1680), 295 nm (71 700 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(-)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**7**: λ_{ext} ($\Delta\varepsilon$) = 488 (−3.56), 435 (+4.88), 334 (+12.93), 307 (−6.31), 290 (+23.21), 267 (−14.13), 239 nm (+37.41); $(+)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**7**: λ_{ext} ($\Delta\varepsilon$) = 487 (+1.65), 441 (−5.28), 333 (−12.06), 307 (+8.22), 290 (−17.22), 268 (+17.88), 240 nm (−32.71).

Compound ***8***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 462 (1680), 267 nm (44 300 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(-)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**8**: λ_{ext} ($\Delta\varepsilon$) = 354 (−7.49), 329 (+4.03), 308 (−4.86), 284 (+14.16), 260 (−26.57), 233 nm (+42.56); $(+)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-**8**: λ_{ext} ($\Delta\varepsilon$) = 353 (+11.98), 328 (−2.28), 308 (+4.63), 284 (−14.87), 260 (+28.74), 232 nm (−37.63).

Compound trans-***9***: UV/Vis (CH$_2$Cl$_2$, 20 °C): λ_{ext} (ε) = 454 (2320), 317 (28 500), 264 nm (52 300 mol^{-1}dm^{3}cm^{-1}); CD (CH$_2$Cl$_2$, 20 °C): $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-*trans*-**9**: λ_{ext} ($\Delta\varepsilon$) = 472 (−1.86), 377 (+1.77), 339 (−11.80), 308 (+2.61), 284 (−15.49), 258 (+31.44), 242 (−3.12), 231 nm (+7.85); $(-)^{\mathrm{CD}}_{260}$-(1*R*,1′*R*)-*trans*-**9**: λ_{ext} ($\Delta\varepsilon$) = 472 (+2.26), 379 (−2.69), 337 (+11.01), 308 (−3.16), 284 (+15.31), 258 (−31.95), 242 (+2.00), 231 nm (−9.14).

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[14] To represent the chiroptical features of chiral compounds, the sign of the CD band at $\lambda = 260$ nm is utilized because this band is commonly observed for all the compounds that contain a chiral ferrocene unit.

[15] Crystal data and structural refinement parameters: *trans*-**1**$\cdot$(CHCl$_3$)$_{0.5}$: $C_{50.5}H_{40.5}Cl_{1.5}FeN_2$; $M_r = 784.42$; monoclinic; space group $P2_1/c$; $a = 20.092(12)$, $b = 5.907(3)$, $c = 33.09(2)$ Å; $\alpha = \gamma = 90$, $\beta = 96.052(2)°$; $V = 3906(4)$ Å^3; $Z = 4$; $R = 0.0714$; $wR = 0.0755$ (for 11 970 data and 555 refined parameters). $(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**10**$\cdot$acetone: $C_{73}H_{70}FeN_2O_7S_2$; $M_r = 1207.33$; monoclinic; space group $C2$; $a = 32.997(6)$, $b = 8.4674(13)$, $c = 24.442(4)$ Å; $\alpha = \gamma = 90$, $\beta = 113.0452(7)°$; $V = 6284.1(18)$ Å^3; $Z = 4$, $R = 0.0587$; $wR = 0.0668$ (for 13 056 data and 839 refined parameters). CCDC-611823 (*trans*-**1**$\cdot$(CHCl$_3$)$_{0.5}$) and -611824 ($(+)^{\mathrm{CD}}_{260}$-(1*S*,1′*S*)-**10**$\cdot$acetone) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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