

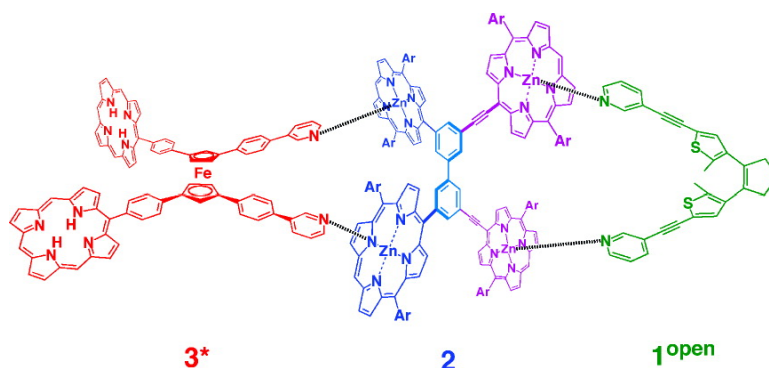
Communication

Toward Long-Distance Mechanical Communication: Studies on a Ternary Complex Interconnected by a Bridging Rotary Module

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Toward Long-Distance Mechanical Communication: Studies on a Ternary Complex Interconnected by a Bridging Rotary Module

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In biological signal transduction systems, an external stimulus acquired by a receptor is converted into a mechanical motion, which is transmitted intermolecularly over a long distance via a physical interconnection. For example, in a vision system, a light-triggered configurational change of retinal is transmitted to rhodopsin.¹ Then, G-protein, located away from retinal, senses this configurational change. Despite a rapid progress in the field of synthetic molecular machines,^{2,3} it is still a big challenge to design molecularly interconnected systems allowing for the transmission of mechanical motions to a remote place.^{3b} Here we report a signal transmission system (Figure 1) consisting of three different movable components; a photochromic “signaling” unit (**1**; green), a chiral “scissoring” unit (**3***; red),⁴ and an intermediately “bridging” unit (**2**; blue/purple). These components are mechanically interconnected with one another by the connection with bidentate coordination bonds, so that a configurational change of **1**, induced by UV or visible light, is transmitted over a long distance to **3*** through an angular motion of **2**.

Signaling unit **1** is a pyridine-appended dithienylethene derivative, which is known as a superb photochromic molecule, whose open and closed forms (**1^{open}**, **1^{closed}**), photochemically generated, do not interconvert thermally (Figure 1).⁵ Upon irradiation with UV ($\lambda = 350 \pm 10$ nm, 7 min) and visible ($\lambda = 546 \pm 10$ nm, 24 min) lights in toluene at 20 °C, compound **1** isomerized between **1^{open}** and **1^{closed}** to furnish molar ratios [**1^{open}**]/[**1^{closed}**] of 3/97 and 92/8 at the photostationary states, respectively (Scheme 1). Scissoring component **3*** involves a chiral tetrasubstituted ferrocene core bearing two pyridyl groups, capable of accommodating the zinc porphyrin handles of bridging module **2**. Two free-base porphyrin units in **3*** are intended to monitor the conformational change of **3*** by means of circular dichroism (CD) spectroscopy.³ Bridging module **2** is a biaryl derivative bearing four zinc porphyrin handles, where two of them (ZnP^{short}) are shortly connected to the biaryl core, while the other two (ZnP^{long}) are attached via an ethynylene spacer to the core. Due to a very small energetic barrier for the axial rotation,⁶ **2** as well as **3*** can serve as a friction-free rotary module.

Compounds **1–3** were synthesized according to methods similar to those reported in the literature³ and unambiguously characterized (see Supporting Information). For spectral understanding of the complexation, we also synthesized reference compounds **4–7** (Figure 2; see Supporting Information), which are expected to spectroscopically imitate four possible binding modes of **2**. Electronic absorption spectroscopy of **2** in toluene at 20 °C displayed two sets of Soret and Q bands at 421/545 and 441/605 nm, which are assigned to ZnP^{short} and ZnP^{long}, respectively, by reference to the spectral features of **4** and **5** (see Supporting Information, Figure S3). When **2** was mixed in toluene with **1^{open}** and an enantiomer of **3*** at a molar ratio [**1^{open}**]:[**2**]:[**3***] of 10.0:1.0:1.0, the two sets of zinc porphyrin Soret/Q bands were red-shifted to 426.5/560 and 443/622.5 nm, suggesting that all the zinc porphyrin handles of **2** in the ternary mixture accommodate an axial ligand (see Supporting Information, Figure S4). The ternary

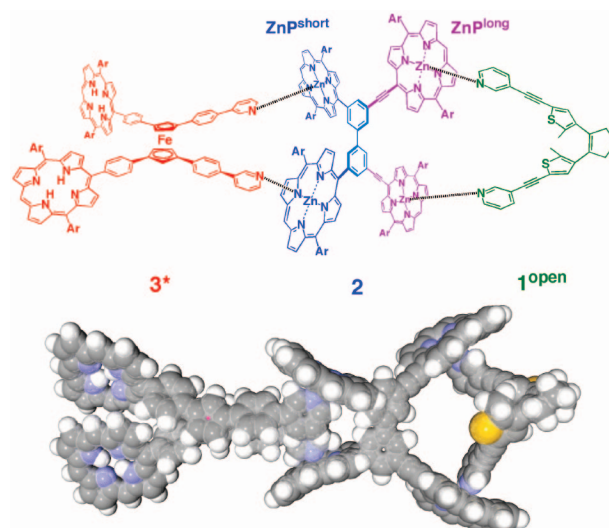
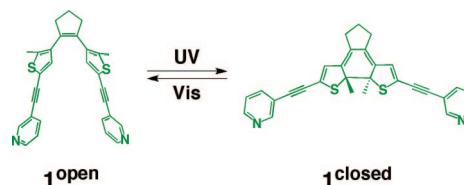


Figure 1. Schematic illustration of the expected ternary complex of **1^{open}**, **2**, and **3*** (Ar: 3,5-dioctyloxyphenyl).

Scheme 1. Isomerization of Photochromic Module 1



mixture showed clear Cotton effects in a visible absorption region from 400 to 460 nm. Of interest, the CD spectrum (Figure 3b) is much more intense than that of chiral **3*** (Figure 3a) and extended to a longer wavelength region involving the Soret bands of the zinc porphyrin handles. These observations indicate that compound **2** adopts a twisted chiral geometry upon complexation with chiral **3*** (Figure 1). The notable enhancement of the CD band at the free-base porphyrin Soret band (411 nm) indicates that the conformation of the ferrocene moiety of **3*** is fixed as a result of the complexation with **2**.^{3b}

When the ternary mixture was irradiated with UV light ($\lambda = 350 \pm 10$ nm) for the purpose of isomerizing **1^{open}** into **1^{closed}**, the CD band at the zinc porphyrin Soret band of **2** (447.5 nm) was gradually enhanced and reached a plateau in 4 min, while that of **3*** at 410 nm decreased synchronously (Figure 4a,b, see also Supporting Information, Figure S5a). On the other hand, upon exposure of the resulting mixture to visible light ($\lambda = 546 \pm 10$ nm) to allow the isomerization of **1^{closed}** back to **1^{open}**, a backward CD spectral change took place and subsided in 17 min (see Supporting Information; Figure S5b). We also confirmed that these CD spectral changes are synchronous to a change in the mole fraction of **1^{open}** ($[\mathbf{1}^{\text{open}}]/([\mathbf{1}^{\text{open}}] + [\mathbf{1}^{\text{closed}}])$) in the ternary

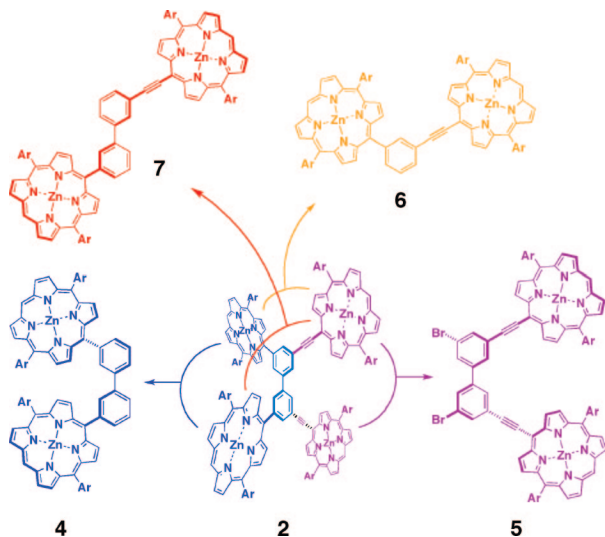


Figure 2. Structures of reference compounds 4–7 for imitating four possible binding modes of bridging **2**.

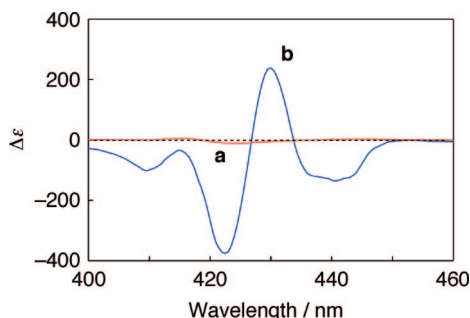


Figure 3. Circular dichroism (CD) spectra of (a) **3*** ($3.8 \mu\text{M}$) and (b) a ternary mixture of **1**^{open}, **2**, and **3*** ($[\mathbf{3}^*] = 2.2 \mu\text{M}$, $[\mathbf{3}^*]/[\mathbf{2}]/[\mathbf{1}^{\text{open}}] = 1.0/1.0/10.0$) in toluene at 20°C .

mixture (Figure 4c).⁷ Therefore, three components **1**, **2**, and **3*** are mechanically interconnected. In sharp contrast, when bridging **2** was absent, neither CD enhancement of **1** nor light-induced CD spectral change resulted for a mixture **1** and **3*** (13:1) (see Supporting Information, Figure S6). These results clearly demonstrate that scissoring **3*** is able to communicate with photochromic **1** but only in the presence of bridging **2** (Figure 1).

In order to investigate if components **1**–**3*** indeed form a ternary assembly (Figure 1), we carried out ¹H DOSY spectroscopy at 27°C , where a 1:1:1 mixture of **1**, **2**, and *rac*-**3***, as expected, showed a smaller diffusion constant ($\log_{10}[D/\text{m}^2 \text{s}^{-1}] = -9.75$) than individual monomeric components and even 1:1 binary mixtures *rac*-**3***/**2** and **1**/**2** (see Supporting Information, Figures S7–S9).⁸ Then, for further structural understanding, some selected binary mixtures were investigated spectroscopically. Of interest, when **2** was titrated with **3***, only the absorption bands of $\text{ZnP}^{\text{short}}$ were red-shifted with clear isosbestic points at 422.5 and 552 nm, while those of ZnP^{long} remained substantially unchanged until the molar ratio $[\mathbf{3}^*]/[\mathbf{2}]$ reached 0.9 (Figure 5a). In conformity with this observation, when the titration was followed by ¹H NMR spectroscopy, the signals due to the meso-substituents of $\text{ZnP}^{\text{short}}$ showed an upfield shift, but those of ZnP^{long} remained almost unchanged (see Supporting Information, Figure S10). Thus, the short ZnP handles of **2** selectively accommodate an axial ligand. The site-selective complexation between **2** and **3***, thus observed, indicates that the pyridyl groups of **3*** coordinate very tightly to the short handles of **2**. Although the K_{assoc} value of **3*** with **2** was unable to evaluate spectroscopically due to the concomitant occurrence

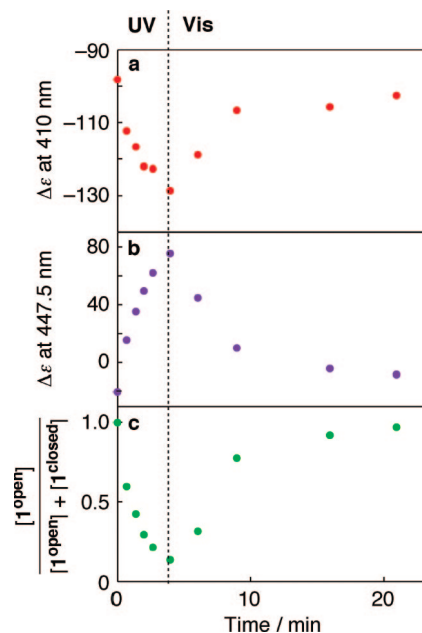


Figure 4. Circular dichroism (CD) intensity changes at 20°C of a ternary mixture of **1**, **2**, and **3*** ($[\mathbf{2}] = 2.2 \mu\text{M}$, $[\mathbf{3}^*]/[\mathbf{2}]/[\mathbf{1}] = 1.0/1.0/10.0$) in toluene at (a) 410 nm for **3*** and (b) 447.5 nm for **2**, as a function of (c) the extent of isomerization of **1** upon irradiation with UV ($\lambda = 350 \pm 10 \text{ nm}$, 4 min) and visible ($\lambda = 546 \pm 10 \text{ nm}$, 17 min) lights.

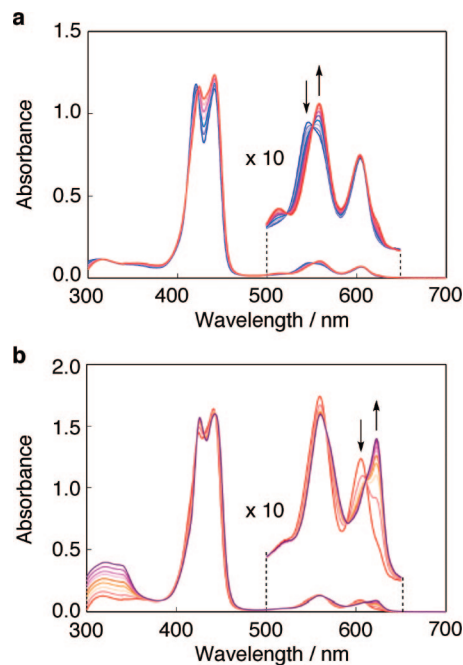


Figure 5. Absorption spectral changes upon titration of (a) **2** ($1.5 \mu\text{M}$) with **3*** (0–0.9 equiv) and (b) a binary mixture of **2** and **3*** ($[\mathbf{2}] = 2.2 \mu\text{M}$, $[\mathbf{2}]/[\mathbf{3}^*] = 1.0$) with **1**^{open} (0–10.0 equiv) in toluene at 20°C .

of a secondary complexation at $[\mathbf{3}^*]/[\mathbf{2}] > 1$, model studies with reference compounds 4–7 (Figure 2) allowed us to conclude that the K_{assoc} value of **3*** with **4** carrying only $\text{ZnP}^{\text{short}}$ handles ($4 \times 10^7 \text{ M}^{-1}$) is indeed greater than those of **3*** with **6** ($9 \times 10^5 \text{ M}^{-1}$) and **7** ($4 \times 10^6 \text{ M}^{-1}$, see Supporting Information, Figures S11–S13). Due to a spectral interference by the free-base porphyrin (P_{Fb}) units in **3***, the K_{assoc} value of **3*** with **5** was again unavailable. So, we titrated **5** with a modified version of **3*** without P_{Fb} and confirmed that the K_{assoc} value ($1 \times 10^7 \text{ M}^{-1}$) of **5**/**3*** is again smaller than that of **4**/**3*** (see Supporting Information, Figure S14).

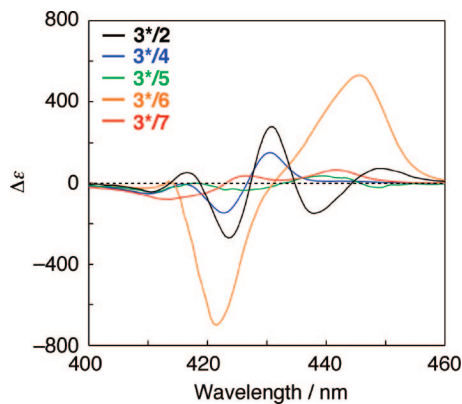


Figure 6. Circular dichroism (CD) spectra in toluene at 20 °C of binary mixtures $3^*/2$ (black; $[2] = 2.2 \mu\text{M}$, $[3^*]/[2] = 1.0$), $3^*/4$ (blue; $[4] = 4.6 \mu\text{M}$, $[3^*]/[4] = 1.9$), $3^*/5$ (green; $[5] = 1.0 \mu\text{M}$, $[3^*]/[5] = 1.7$), $3^*/6$ (orange; $[6] = 1.8 \mu\text{M}$, $[3^*]/[6] = 3.0$), and $3^*/7$ (red; $[7] = 2.4 \mu\text{M}$, $[3^*]/[7] = 2.2$).

For spectral characterization of the ternary mixture, binary complex $2/3^*$ (1:1) was titrated with 1^{open} , where the absorption bands of the ligand-free ZnP^{long} handles of **2** became red-shifted (Figure 5b). Noteworthy, this spectral change displayed clear isosbestic points at 443 and 610.5 nm. Together with the ^1H DOSY experiments (vide ante), such a stepwise spectral change indicates the formation of a single heterotropic complex from 1^{open} and binary complex $2/3^*$. The K_{assoc} value observed for the complexation of $2/3^*$ with 1^{open} ($4 \times 10^5 \text{ M}^{-1}$; see Supporting Information, Figure S15a) was reasonably small compared with that of **4** (alternative to **2**) with 3^* ($4 \times 10^7 \text{ M}^{-1}$).

CD spectral titration of **2** with 3^* resulted in the appearance of intense Cotton effects at the Soret bands of both noncoordinated ZnP^{long} and coordinated $\text{ZnP}^{\text{short}}$ handles of **2** (see Supporting Information, Figure S16). Noteworthy, the CD spectral pattern at $[3^*]/[2] = 1.0$ (black curve, Figure 6) was analogous to that of the heterotropic $1^{\text{open}}/2/3^*$ ternary complex (Figure 3b). Nevertheless, at a closer look, titration of binary complex $2/3^*$ with 1^{open} gave rise to a CD spectral change at the Soret band of ZnP^{long} (441 nm), as a possible consequence of the complexation of 1^{open} with the long handles of 3^* -bound **2** (see Supporting Information, Figure S17). CD spectral features of reference **4**–**7** upon complexation with 3^* are likely informative of the mode of ternary complexation. While they considerably differ from one another (Figure 6), we found that the one observed for $4/3^*$ (blue curve) quite resembles that of the ternary complex. Considering that reference **4** possesses only $\text{ZnP}^{\text{short}}$, it is now obvious that bridging module **2** in the heterotropic ternary complex uses its short ZnP handles to bind 3^* , while the remaining long handles are used for grasping 1^{open} on the other side (Figure 1). Use of closed isomer 1^{closed} instead of 1^{open} resulted in almost identical absorption⁹ and CD spectral features (see Supporting Information, Figures S15b and S18), indicating the same mode of heterotropic binding of 1^{closed} and 3^* mediated by **2**. This is essential for photoisomerizing **1** to mechanically communicate with 3^* .

In conclusion, we succeeded in the construction of a heterotropic ternary complex, using a photochromic component (**1**) on one end,

a scissoring component (3^*) on the other, and a bridging component (**2**) in the middle (Figure 1). The three components are connected together with bidentate coordination bonds and therefore mechanically interconnected. Upon photoirradiation, **1** undergoes an opening/closing motion, which gives rise to a rotary motion of **2** and a synchronous scissoring motion of 3^* on the other end. The system involves certain dissociation/association dynamics. However, considering the large K_{assoc} values, the dissociation events must occur much more slowly than the isomerization of the photochromic component and rotary motions of the ferrocene and biaryl moieties.^{3,6} Thus, the light-induced motion of **1** can be transmitted to 3^* before the ternary complex dissociates. In this context, the heterotropic ternary complex illustrated in Figure 1 can be regarded as a prototype of “molecular reacher” and may be extended to polymeric systems of larger size regimes that could allow remote manipulation of molecular events.

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Supporting Information Available: Synthesis of $1^{\text{open}}-7$, absorption spectra of **2** and reference compounds **4** and **5**. Absorption and CD spectral titrations of **4**–**7** with 3^* (19^* for **5**), and their curve fitting profiles for evaluation of K_{assoc} values. Absorption spectral titration of $3^*/2$ with 1^{closed} . ^1H NMR spectra of **2**, $\text{rac}-3^*/2$ and $\text{rac}-3^*/2/1^{\text{open}}$, and ^1H DOSY spectra of $1^{\text{open}}-\text{rac}-3^*$, $1^{\text{open}}/2$, $\text{rac}-3^*/2$, and $\text{rac}-3^*/2/1^{\text{open}}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- 3^* represents an enantiomer with a positive CD sign at 415 nm, while $\text{rac}-3^*$ denotes the racemic form.
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- Determined by HPLC.
- Values of $\log_{10}D$ (D : diffusion constant in $\text{m}^2 \text{ s}^{-1}$) were evaluated as follows: $1^{\text{open}} = -9.15$, $2 = -9.65$, $\text{rac}-3^* = -9.51$, $\text{rac}-3^*/2 = -9.68$, $1^{\text{open}}/2 = -9.63$, $\text{rac}-3^*/2/1^{\text{open}} = -9.75$.
- Assuming the formation of a heterotropic ternary complex, the K_{assoc} value of $3^*/2$ with 1^{closed} was evaluated as $2 \times 10^5 \text{ M}^{-1}$ (see Supporting Information, Figure S15b).

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