

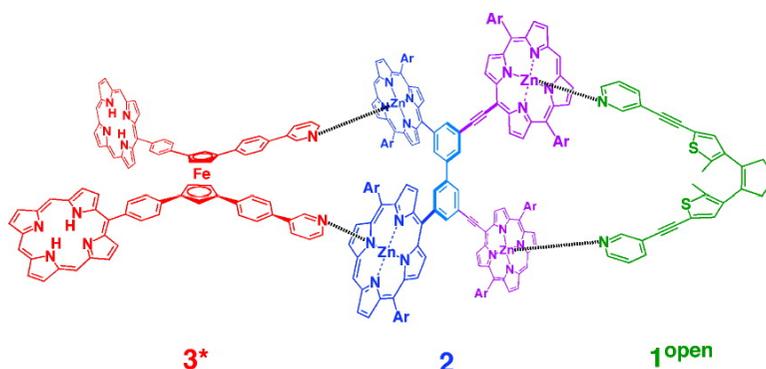
Communication

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

Hiroyuki Kai, Shinji Nara, Kazushi Kinbara, and Takuzo Aida

*J. Am. Chem. Soc.*, **2008**, 130 (21), 6725-6727 • DOI: 10.1021/ja801646b • Publication Date (Web): 01 May 2008

Downloaded from <http://pubs.acs.org> on February 8, 2009



**More About This Article**

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 3 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)

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

Hiroyuki Kai, Shinji Nara, Kazushi Kinbara,\* and Takuzo Aida\*

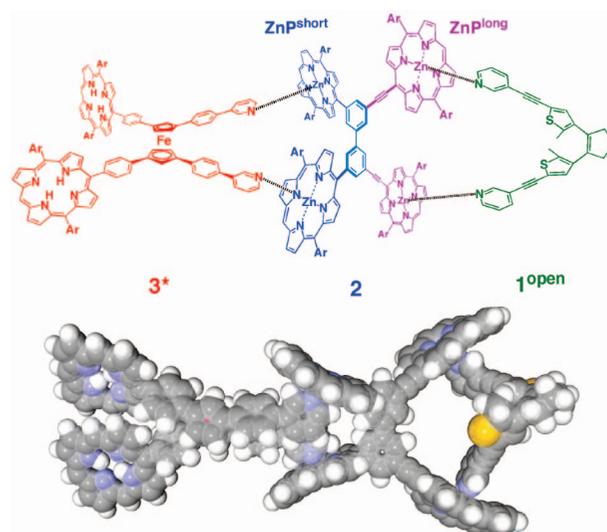
Department of Chemistry and Biotechnology, School of Engineering and Center for NanoBio Integration, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

Received March 5, 2008; E-mail: kinbara@macro.t.u-tokyo.ac.jp; aida@macro.t.u-tokyo.ac.jp

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.<sup>1</sup> Then, G-protein, located away from retinal, senses this configurational change. Despite a rapid progress in the field of synthetic molecular machines,<sup>2,3</sup> it is still a big challenge to design molecularly interconnected systems allowing for the transmission of mechanical motions to a remote place.<sup>3b</sup> 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),<sup>4</sup> 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**.

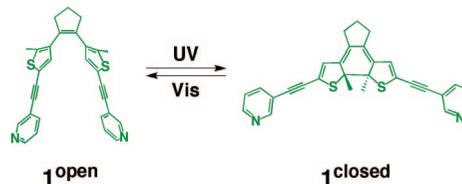
Signaling unit **1** is a pyridine-appended dithienylethene derivative, which is known as a superb photochromic molecule, whose open and closed forms (**1<sup>open</sup>**, **1<sup>closed</sup>**), photochemically generated, do not interconvert thermally (Figure 1).<sup>5</sup> Upon irradiation with 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<sup>open</sup>** and **1<sup>closed</sup>** to furnish molar ratios [**1<sup>open</sup>**]/[**1<sup>closed</sup>**] 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.<sup>3</sup> Bridging module **2** is a biaryl derivative bearing four zinc porphyrin handles, where two of them (ZnP<sup>short</sup>) are shortly connected to the biaryl core, while the other two (ZnP<sup>long</sup>) are attached via an ethynylene spacer to the core. Due to a very small energetic barrier for the axial rotation,<sup>6</sup> **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 literature<sup>3</sup> 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<sup>short</sup> and ZnP<sup>long</sup>, respectively, by reference to the spectral features of **4** and **5** (see Supporting Information, Figure S3). When **2** was mixed in toluene with **1<sup>open</sup>** and an enantiomer of **3\*** at a molar ratio [**1<sup>open</sup>**]:[**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



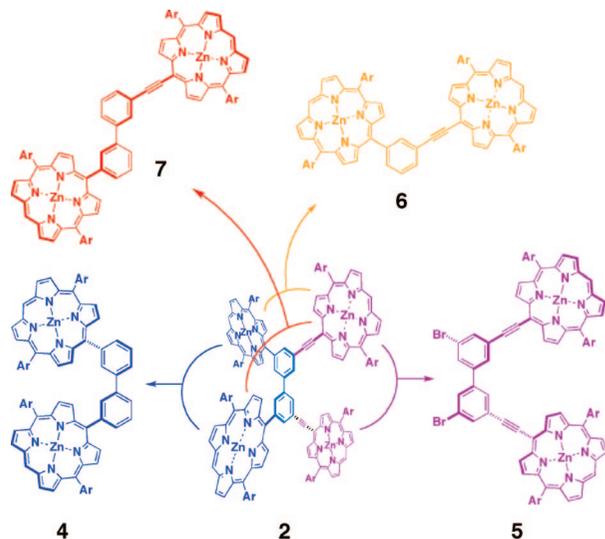
**Figure 1.** Schematic illustration of the expected ternary complex of **1<sup>open</sup>**, **2**, and **3\*** (Ar: 3,5-dioctyloxyphenyl).

### Scheme 1. Isomerization of Photochromic Module 1

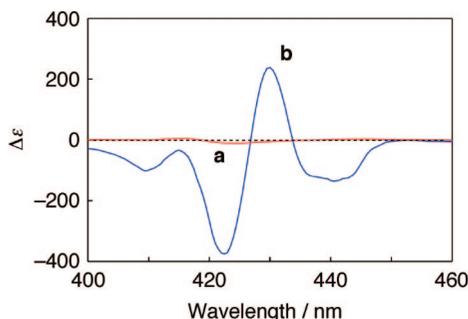


mixture showed clear Cotton effects in a visible absorption region from 400 to 460 nm. Of interest, the CD spectrum (Figure 3b) is much more intense than that of chiral **3\*** (Figure 3a) and extended to a longer wavelength region involving the Soret bands of the zinc porphyrin handles. These observations 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**.<sup>3b</sup>

When the ternary mixture was irradiated with UV light ( $\lambda = 350 \pm 10$  nm) for the purpose of isomerizing **1<sup>open</sup>** into **1<sup>closed</sup>**, 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<sup>closed</sup>** back to **1<sup>open</sup>**, 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<sup>open</sup>** ( $[\mathbf{1}^{\text{open}}]/([\mathbf{1}^{\text{open}}] + [\mathbf{1}^{\text{closed}}])$ ) in the ternary



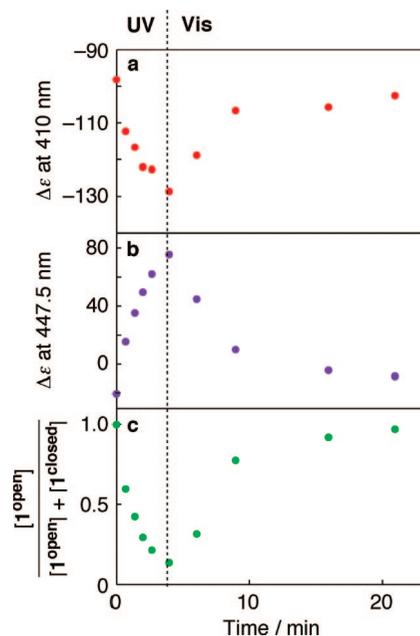
**Figure 2.** Structures of reference compounds 4–7 for imitating four possible binding modes of bridging **2**.



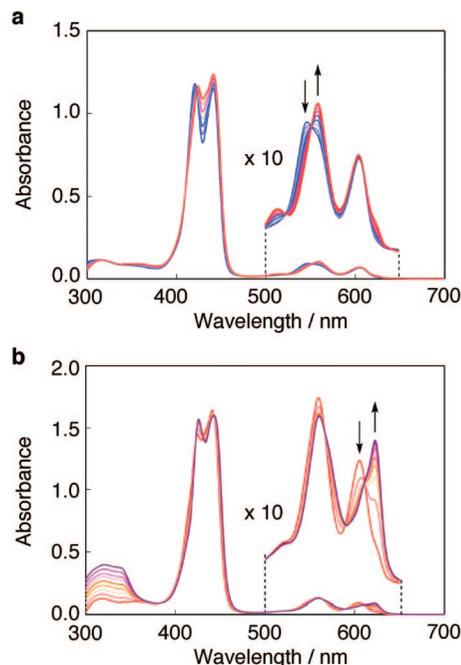
**Figure 3.** Circular dichroism (CD) spectra of (a) **3\*** ( $3.8 \mu\text{M}$ ) and (b) a ternary mixture of **1**<sup>open</sup>, **2**, and **3\*** ( $[\mathbf{3}^*] = 2.2 \mu\text{M}$ ,  $[\mathbf{3}^*]/[\mathbf{2}]/[\mathbf{1}^{\text{open}}] = 1.0/1.0/10.0$ ) in toluene at  $20^\circ\text{C}$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

mixture (Figure 4c).<sup>7</sup> 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 <sup>1</sup>H DOSY spectroscopy at  $27^\circ\text{C}$ , 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).<sup>8</sup> 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  $\text{ZnP}^{\text{long}}$  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 <sup>1</sup>H NMR spectroscopy, the signals due to the meso-substituents of  $\text{ZnP}^{\text{short}}$  showed an upfield shift, but those of  $\text{ZnP}^{\text{long}}$  remained almost unchanged (see Supporting Information, Figure S10). Thus, the short  $\text{ZnP}$  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  $K_{\text{assoc}}$  value of **3\*** with **2** was unable to evaluate spectroscopically due to the concomitant occurrence

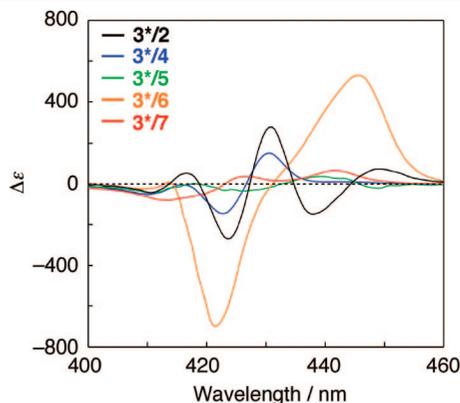


**Figure 4.** Circular dichroism (CD) intensity changes at  $20^\circ\text{C}$  of a ternary mixture of **1**, **2**, and **3\*** ( $[\mathbf{2}] = 2.2 \mu\text{M}$ ,  $[\mathbf{3}^*]/[\mathbf{2}]/[\mathbf{1}] = 1.0/1.0/10.0$ ) in toluene at (a) 410 nm for **3\*** and (b) 447.5 nm for **2**, as a function 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**<sup>open</sup> (0–10.0 equiv) in toluene at  $20^\circ\text{C}$ .

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  $K_{\text{assoc}}$  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 ( $\text{P}_{\text{Fb}}$ ) units in **3\***, the  $K_{\text{assoc}}$  value of **3\*** with **5** was again unavailable. So, we titrated **5** with a modified version of **3\*** without  $\text{P}_{\text{Fb}}$  and confirmed that the  $K_{\text{assoc}}$  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  $1^{\text{open}}$ , where the absorption bands of the ligand-free  $\text{ZnP}^{\text{long}}$  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  $^1\text{H}$  DOSY experiments (vide ante), such a stepwise spectral change indicates the formation of a single heterotropic complex from  $1^{\text{open}}$  and binary complex  $2/3^*$ . The  $K_{\text{assoc}}$  value observed for the complexation of  $2/3^*$  with  $1^{\text{open}}$  ( $4 \times 10^5 \text{ M}^{-1}$ ; 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  $\text{ZnP}^{\text{long}}$  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  $1^{\text{open}}$  gave rise to a CD spectral change at the Soret band of  $\text{ZnP}^{\text{long}}$  (441 nm), as a possible consequence of the complexation of  $1^{\text{open}}$  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  $\text{ZnP}$  handles to bind  $3^*$ , while the remaining long handles are used for grasping  $1^{\text{open}}$  on the other side (Figure 1). Use of closed isomer  $1^{\text{closed}}$  instead of  $1^{\text{open}}$  resulted in almost identical absorption<sup>9</sup> and CD spectral features (see Supporting Information, Figures S15b and S18), indicating the same mode of heterotropic binding of  $1^{\text{closed}}$  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  $K_{\text{assoc}}$  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.<sup>3,6</sup> 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.

**Acknowledgment.** We thank Prof. M. Fujita, Dr. M. Yoshizawa, and Mr. K. Ono for generous assistance for  $^1\text{H}$  DOSY spectral measurements. This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Scientific Research on Priority Areas “Life Surveyors” (to K.K.) and Scientific Research (B), #19350065 (to K.K.).

**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  $K_{\text{assoc}}$  values. Absorption spectral titration of  $3^*/2$  with  $1^{\text{closed}}$ .  $^1\text{H}$  NMR spectra of **2**,  $\text{rac}-3^*/2$  and  $\text{rac}-3^*/2/1^{\text{open}}$ , and  $^1\text{H}$  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>.

## References

- Ridge, K. D.; Palczewski, K. *J. Biol. Chem.* **2007**, *282*, 9297–9301.
- (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348–3391. (b) Kinbara, K.; Aida, T. *Chem. Rev.* **2005**, *105*, 1377–1400. (c) Browne, W. R.; Feringa, B. L. *Nat. Nanotechnol.* **2006**, *1*, 25–35. (d) Kay, E. R.; Leigh, D. A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2007**, *46*, 72–191. (e) Champin, B.; Mobian, P.; Sauvage, J.-P. *Chem. Soc. Rev.* **2007**, *36*, 358–366. (f) Shinkai, S.; Ikeda, M.; Sugasaki, A.; Takeuchi, M. *Acc. Chem. Res.* **2001**, *34*, 494–503.
- (a) Muraoka, T.; Kinbara, K.; Kobayashi, Y.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 5612–5613. (b) Muraoka, T.; Kinbara, K.; Aida, T. *Nature* **2006**, *440*, 512–515. (c) Muraoka, T.; Kinbara, K.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 11600–11605. (d) Muraoka, T.; Kinbara, K.; Wakamiya, A.; Yamaguchi, S.; Aida, T. *Chem.—Eur. J.* **2007**, *13*, 1724–1730. (e) Muraoka, T.; Kinbara, K.; Aida, T. *Chem. Commun.* **2007**, 1441–1443. (f) Muramatsu, S.; Kinbara, K.; Taguchi, H.; Ishii, N.; Aida, T. *J. Am. Chem. Soc.* **2006**, *128*, 3764–3769.
- $3^*$  represents an enantiomer with a positive CD sign at 415 nm, while  $\text{rac}-3^*$  denotes the racemic form.
- Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
- (a) Grein, F. *J. Phys. Chem. A* **2002**, *106*, 3823–3827. (b) Tsuzuki, S.; Tanabe, K. *J. Phys. Chem.* **1991**, *95*, 139–144. (c) Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 115.
- 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  $K_{\text{assoc}}$  value of  $3^*/2$  with  $1^{\text{closed}}$  was evaluated as  $2 \times 10^5 \text{ M}^{-1}$  (see Supporting Information, Figure S15b).

JA801646B