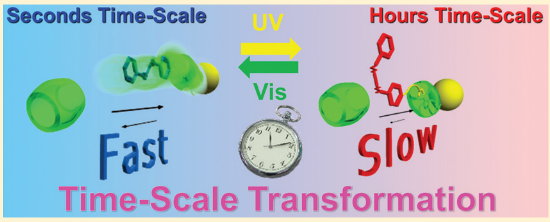
JOC The Journal of Organic Chemistry
Article
pubs.acs.org/joc

Photoreversible Transformation between Seconds and Hours Time-Scales: Threading of Pillar[5]arene onto the Azobenzene-End of a Viologen Derivative

Tomoki Ogoshi,* Daiki Yamafuji, Takamichi Aoki, and Tada-aki Yamagishi

Graduate School of Natural Science and Technology, Kanazawa University, Kakuma-machi, Kanazawa, 920-1192, Japan

S *Supporting Information*



ABSTRACT: Photoswitching of the transformation between seconds and hours time-scales is demonstrated using the threading of *per*-hydroxylated pillar[5]arene onto the azobenzene-end of a viologen derivative. When the azobenzene moiety was in the trans form, the threading of *per*-hydroxylated pillar[5]arene quickly took place at 25 °C and could not be monitored directly. The exchange rate (k) and half-life time ($t_{1/2}$) examined by 2D EXSY NMR spectroscopy were found to be $0.209 \pm 0.013\ \mathrm{s}^{-1}$ and 3.33 ± 0.21 s, respectively. In contrast, the cis form of the azobenzene moiety required very long time ($k = 2.14 \pm 0.27 \times 10^{-5}\ \mathrm{s}^{-1}$, $t_{1/2} = 9.13 \pm 1.2$ h) to thread *per*-hydroxylated pillar[5]arene at 25 °C. Photoisomerization from the trans to the cis form generated the following increment of free energy of activation at 25 °C: $\Delta G_{\mathrm{in}}^{\ddagger}$ (cis form) − $\Delta G_{\mathrm{in}}^{\ddagger}$ (trans form) = $22.8 \pm 0.24\ \mathrm{kJ\ mol^{-1}}$, which led to the time-scale transformation. The tuning of the threading was also accomplished by heating/cooling: the rate constants increased on heating and decreased on cooling.

INTRODUCTION

Typically, chemical reactions proceed for several minutes/hours and can be directly monitored by various analog spectroscopic analyses. In contrast, host−guest complexation usually occurs very quickly (several seconds/microseconds) and cannot be directly monitored. To monitor fast exchange processes, indirect investigation using dynamic NMR, UV−vis, and fluorescence techniques is necessary.[1] Examples of host−guest exchange processes that occur on minutes/hours time-scales are very rare.[2] Accordingly, transformation of the time-scale of host−guest complexation processes from several seconds/microseconds to several minutes/hours is an interesting research target in host−guest chemistry. In this paper, we report interesting photoreversible transformation of a host−guest exchange between the seconds and hours time-scales. *per*-Hydroxylated (**1**, Figure 1a) and *per*-ethylated pillar[5]arenes (**2**, Figure 1a) were used as host molecules, and a viologen derivative was used as an axis. They are cyclic pentamers composed of electron-donating hydroquinone units connected by methylene bridges at the para-positions to form a unique symmetrical pillar architecture.[3−6] Pillar[5]arenes exhibit very interesting host−guest properties with electron-accepting molecules such as viologen and pyridinium derivatives.[3,4]

In this study, a viologen derivative containing adamantane and azobenzene moieties at either end is used as an axis (**3**, Figure 1b). The size of the cavity of pillar[5]arenes are ca. 4−5 Å;[3a] thus, pillar[5]arenes cannot slip over the bulky adamantyl moiety, which has been used as a permanent stopper to construct **1**-based polyrotaxane.[4] To form a complex with the viologen region (station), threading of pillar[5]arene from the azobenzene end (gate) of **3** is necessary. Azobenzene derivatives undergo a reversible trans−cis photoisomerization of their N═N double bond, and thus photostimulus can change the geometry of the azobenzene gate. The threading processes of **1** onto the trans form of **3** (*trans*-**3**) and the cis form of **3** (*cis*-**3**) were investigated.

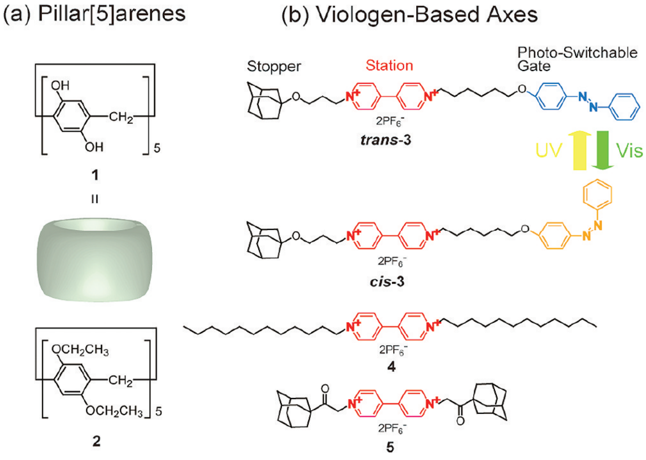


Figure 1. Chemical structures of (a) *per*-hydroxylated (**1**) and *per*-ethylated (**2**) pillar[5]arenes and (b) viologen-based axes containing an adamantane and azobenzene moiety at either end (**3**), dodecyl chains (**4**), or adamantane moieties (**5**) at both ends.

RESULTS AND DISCUSSION

Size relationships between the cavity size of pillar[5]arenes and end groups of axes were investigated by ^{1}H NMR measurements.

Received: October 6, 2011
Published: October 17, 2011

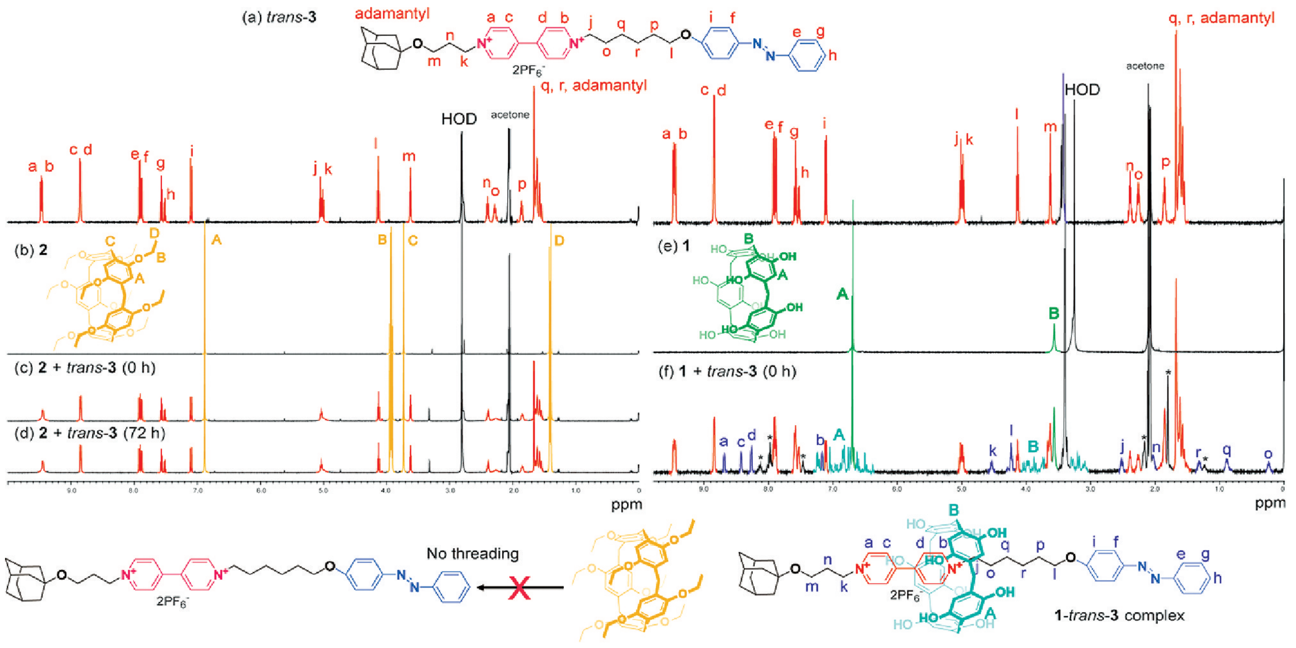


Figure 2. ^{1}H NMR spectra of (a) *trans*-**3**; (b) **2** and a 1:1 mixture of **2** and *trans*-**3** in 5 mM in acetone-d_6 at 25 °C, time after addition of **2** = (c) 0 h and (d) 72 h; (e) **1** and (f) a 1:1 mixture of **1** and *trans*-**3** in 5 mM in acetone-d_6 at 25 °C. Because of the slow rotation of the phenolic units in **1** on NMR time-scale, proton peaks from complexed **1** in (f) were split.[6] Peaks with an asterisk could be not assigned by EXSY and 2D COSY NMR.

When **1** and viologen-based axis containing dodecyl groups at both ends (**4**, Figure 1b) were mixed in acetone-d_6, peak shifts of viologen moieties were observed (Supporting Information, Figure S3). The same peak shifts were observed by adding **2** to **4** in acetone-d_6 (Supporting Information, Figure S4). These results indicate that the viologen moiety of **4** was included in the cavity of **1** and **2**. Upon addition of **1** or **2** to viologen-based axis containing adamantane moieties at both ends (**5**, Figure 1b) at 25 °C, no peak shifts and broadening were observed. Even after the commensurate period of time (72 h), the peaks were hardly changed (Supporting Information, Figures S5 and S6), indicating that **1** and **2** could not be threaded onto the adamantane moiety. Since adamantyl moiety has been used as a stopper for the synthesis of a polyrotaxane composed of **1** and a viologen polymer,[4] it is apparent that pillar[5]arenes (**1** and **2**) cannot slip over the bulky adamantane moiety and the adamantane part acts as a permanent stopper.

When **2** was added to *trans*-**3** in acetone-d_6, the peak shifts and new peaks were not observed after a commensurate period of time (Figure 2c,d), indicating that the trans form of azobenzene cannot thread though the cavity of **2**. In contrast, when **1** was added to *trans*-**3** in acetone-d_6, new additional peaks appeared (blue and light blue peaks, Figure 2f). The data strongly suggest the complexation between **1** and *trans*-**3**. Because of the bulky 10 ethoxy groups at both rims of **2**, the complexation between **2** and *trans*-**3** was inhibited, which was supported by the computational investigations (Supporting Information, Figure S7). Thus, **1** has a cavity large enough to allow threading of **1** onto the trans form of azobenzene end, but **2** does not. The additional peaks observed in the ^{1}H NMR spectrum of the 1:1 mixture of **1** and *trans*-**3** (Figure 2f) were assigned by 2D COSY and 2D exchange spectroscopy (EXSY) measurements. The additional peaks of the viologen moieties (blue peaks, a, c, d) were not overlapped with the other proton peaks and completely assignable, whereas the additional proton peaks from viologen (blue peak, b), methylene linker (blue peaks, l, n, r), and **1** (light blue peaks, A and B) were complex and overlapped. The additional peaks of methylene linker (blue peaks, j, k, o, q) were not overlapped, but these free peaks (red peaks, j, k, o, q) were overlapped. Thus, the free and complexed proton peaks from the viologen moiety (peaks a, c, d, except for peak b) were used for investigation of the threading process. Partial ^{1}H NMR spectra of the proton peaks from the viologen moiety (a, c, d) are presented in Figure 3. Upon addition of **1**, new peaks from the viologen groups were observed (Figure 3b, blue peaks, which were assigned using 2D COSY NMR, Supporting Information, Figure S8), along with the original signals (red peaks). EXSY measurements of the **1**-*trans*-**3** complex at 25 °C showed cross-peaks between the signals of the viologen protons from the complex and free forms (purple squares, Figure 4a), indicating that these species are undergoing chemical exchange and that this chemical exchange is slow on an NMR time-scale. From the Job plot (Supporting Information, Figure S9), the stoichiometry of **1**-*trans*-**3** complex was 1:1. From the integration ratio between complex and free species from ^{1}H NMR, the association constant (K_1) of the 1:1 **1**-*trans*-**3** complex was found to be 234.1 ± 62.7 M^{-1} at 25 °C.[7] The rate constant (k) and half-life time ($t_{1/2}$) at 25 °C for the interconversion estimated using the chemical exchange signals between the complex and free peaks in the EXSY NMR were found to be 0.209 ± 0.013 s^{-1} and 3.33 ± 0.21 s, respectively (Figure 4b). We also investigated effect of temperature on the rate constants. The rate constants (k) increased with increasing temperatures.

The change in the threading of **1** onto *trans*-**3** and *cis*-**3** upon irradiation with light was investigated.

The UV−vis spectrum of an equimolar mixture of **1** and *trans*-**3** displayed a strong absorption band at 350 nm (Figure 5A, a). Upon irradiation with UV light (λ = 340 nm), the absorption at 350 nm decreased (Figure 5A, b), indicating isomerization from *trans*-**3** to *cis*-**3**. But complete isomerization did not occur: at the equilibrium state, the *trans*-**3**/*cis*-**3** ratio

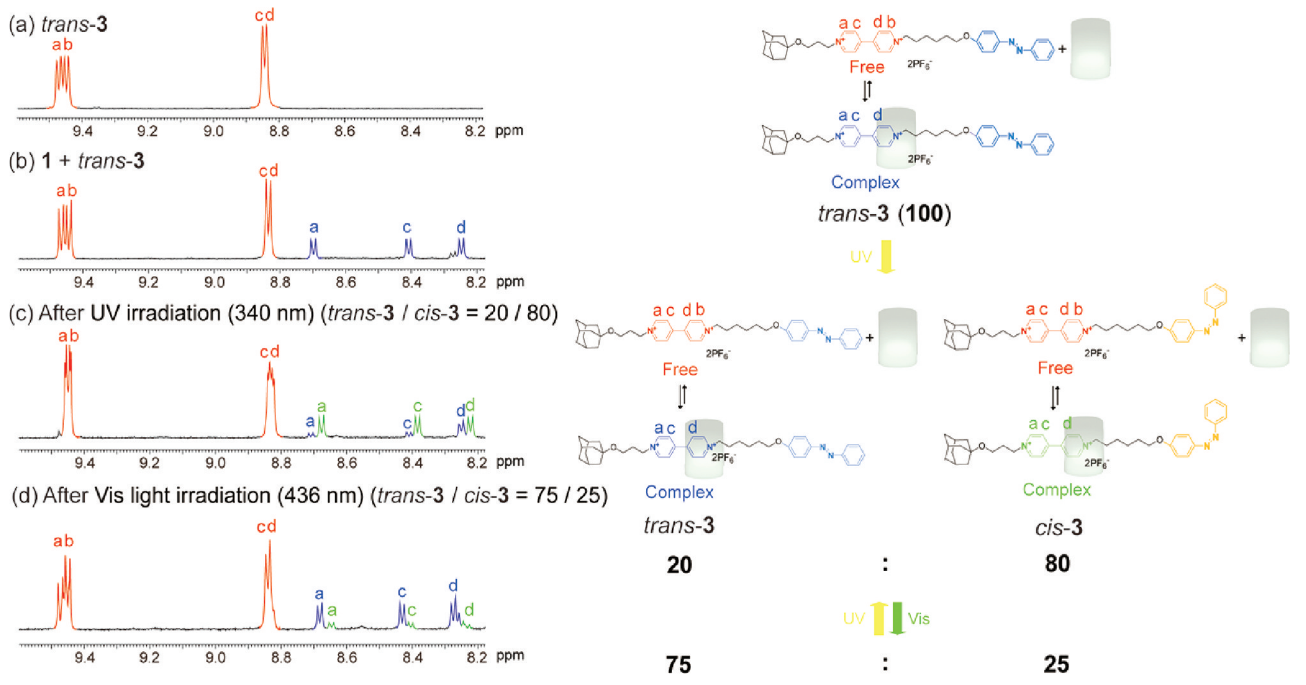


Figure 3. Partial ^{1}H NMR spectra of (a) *trans*-**3** without **1** and *trans*-**3** with **1** (b) before UV irradiation, (c) after UV-irradiation, and (d) after visible light irradiation for 2 h in acetone-d_6 at 25 °C. [**1**] = [*trans*-**3**] = 5 mM.

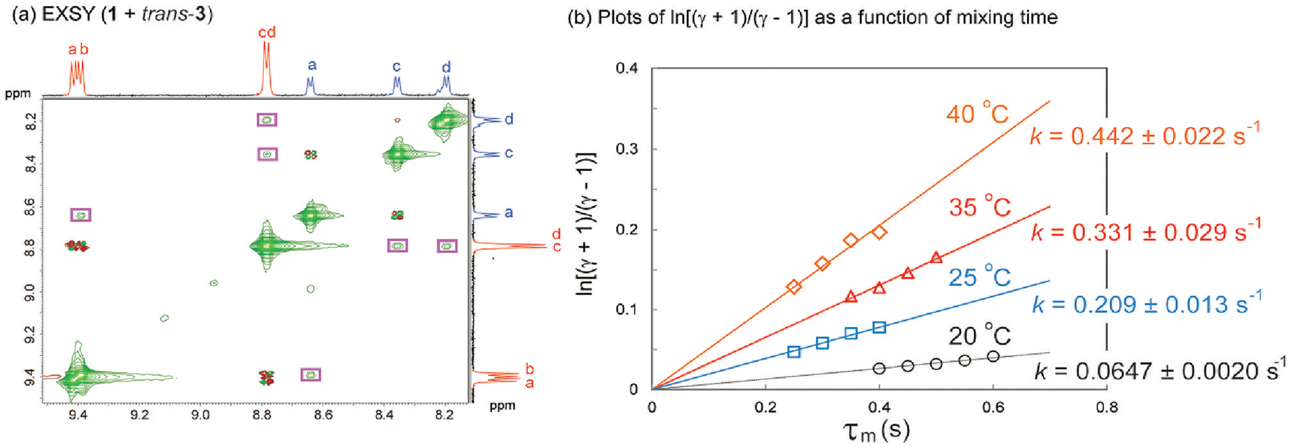


Figure 4. (a) 2D EXSY analysis of an equimolar mixture of **1** and *trans*-**3** in 5 mM in acetone-d_6 at 25 °C. (b) Results of EXSY for an equimolar mixture of **1** and *trans*-**3**. Plots of ln[(γ + 1)/(γ − 1)] as a function of mixing time at several temperatures.

was approximately 20/80. Irradiation of the mixture (*trans*-**3**/*cis*-**3** = 20/80) with visible light (λ = 436 nm) in the presence of **1** allowed recovery of *trans*-**3** but not almost complete recovery. In the equilibrium state after irradiation of the visible light, the *trans*-**3**/*cis*-**3** ratio was approximately 75/25. Photoisomerization between both states is reversible (Figure 5B). The same reversible photoisomerization of *trans*-**3** was observed in the absence of **1** (Supporting Information, Figure S10). *trans*-**3** was mixed with **1** in acetone-d_6 and then irradiated with UV light. Figure 3c shows a ^{1}H NMR spectrum of the mixture after UV irradiation at the equilibrium state. The blue peaks from the complexed *trans*-**3** decreased, and new viologen peaks from the complexed *cis*-**3** were observed (green peaks, which were assigned using 2D COSY NMR, Supporting Information, Figure S11), indicating that the photoisomerization from the **1**-*trans*-**3** complex to the **1**-*cis*-**3** complex took place by irradiation with UV light. Then, by irradiation with visible light, the peaks for the **1**-*cis*-**3** complex decreased and those for the **1**-*trans*-**3** complex increased (Figure 3d), indicating that the switching process is reversible.

To clarify whether **1** can slip over the azobenzene end of the *cis* form, complexation between **1** and *cis*-**3** was examined. First, photoisomerization from *trans*-**3** to *cis*-**3** (*trans*-**3**/*cis*-**3** = 20/80) was carried out. **1** was then added to the solution. After 0.5 h (Figure 6a), viologen peaks from three species were observed: the free *trans*-**3** and *cis*-**3** (red peaks) and the complexed *trans*-**3** (blue peaks). However, peaks consistent with the complexed *cis*-**3** (Figure 3c, green peaks) were not present. It was found that the ^{1}H NMR spectra changed over time. After 2 h (Figure 6b), viologen peaks from the complexed *cis*-**3** appeared (green peaks) and the integration ratio of the peaks from the complexed *cis*-**3** gradually increased over time (Figure 6c). Figure 7 shows the correlation between time and the degree of complex formation of *cis*-**3** and **1**, which was calculated using the integration ratio of the free and complexed *cis*-**3**.[8] At 25 °C (Figure 7, blue squares), complexation of *cis*-**3** with **1** took

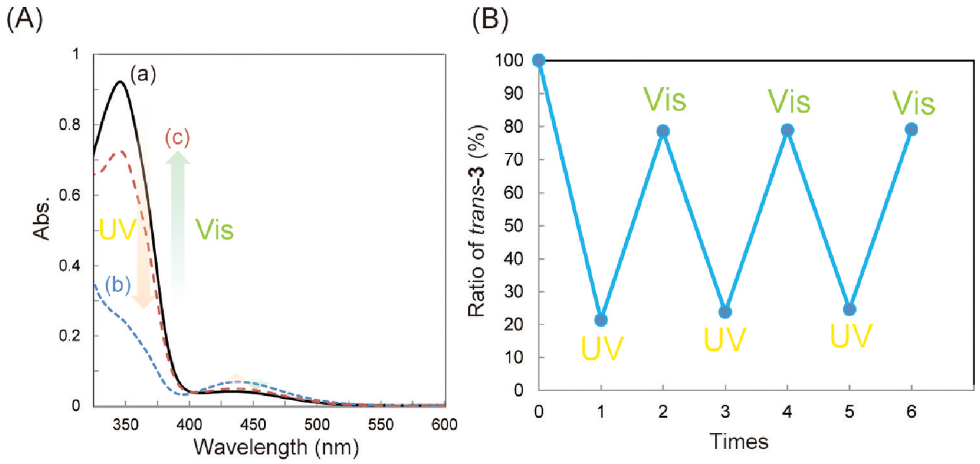


Figure 5. (A) UV−vis spectra of an equimolar mixture of **1** and *trans*-**3** (0.031 mM) before photoirradiation (a), upon irradiation at 340 nm (UV light) for 360 s (b), and successive irradiation at 446 nm (visible light) for 360 s (c) in acetone at 25 °C. (B) Ratio of *trans*-**3** under repetitive irradiations with UV and visible light.

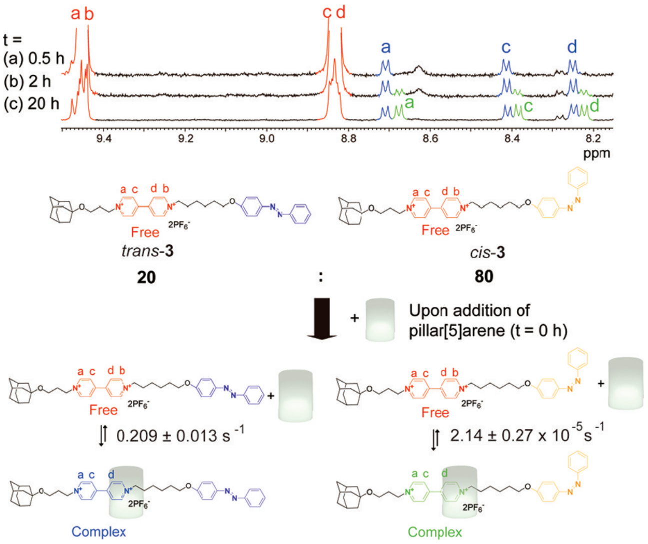


Figure 6. Partial ^{1}H NMR spectra of the mixture (5 mM, *trans*-**3**/*cis*-**3** = 20/80) after addition of **1** (5 mM) in acetone-d_6 at 25 °C; time after addition of **1** = (a) 0.5 h, (b) 2 h, and (c) 20 h.

approximately 20 h to reach equilibrium ($t_{1/2}$ = 9.13 ± 1.2 h), and the rate constant (k) for the threading process was calculated to be 2.14 ± 0.27 × 10^{-5} s^{-1}, which is extremely slow for this kind of reaction. Consequently, a system demonstrating photoswitchable time-scale transformation was produced, as illustrated schematically in the bottom of Figure 6. With *trans*-**3** at 25 °C, **1** could pass over the azobenzene end with the rate constant (k) of 0.209 ± 0.013 s^{-1}, which belongs to the several seconds time-scale. Upon UV irradiation, photoisomerization from *trans*-**3** to *cis*-**3** took place. **1** can also pass over the *cis* form of the azobenzene end, but the rate constant (k) for this process is very slow (2.14 ± 0.27 × 10^{-5} s^{-1}), which is on the several hours time-scale and approximately 9770 times slower than that in the trans form. There are no interactions between **1** and the trans/cis forms of azobenzene (Supporting Information, Figure S12) and between viologen and trans/cis forms of azobenzene (Supporting Information, Figure S13). The association constant at 25 °C for **1**-*trans*-**3** complex (234.1 ± 32.7 M^{-1}) was almost the same as that for **1**-*cis*-**3** complex (204.6 ± 8.34 M^{-1}), which also supports that the azobenzene moiety only acts as a gate and that there is no interaction between **1** and the trans/cis forms of azobenzene moiety. Therefore, the difference in the bulkiness of the trans/cis forms of the azobenzene moiety leads to the time-scale transformation. In conclusion, **1** has a cavity large enough to allow threading of the trans/cis forms of azobenzene, but the threading process of the cis form of the azobenzene takes a long time. The rate constant (k) at 35 °C was found to be 4.02 ± 0.57 × 10^{-5} s^{-1} (Figure 7, red triangle), indicating that the exchange was accelerated by heating. In contrast, at 0 °C, the rate constant decreased largely (5.46 ± 0.55 × 10^{-6} s^{-1}), indicating that the exchange was considerably suppressed by cooling.

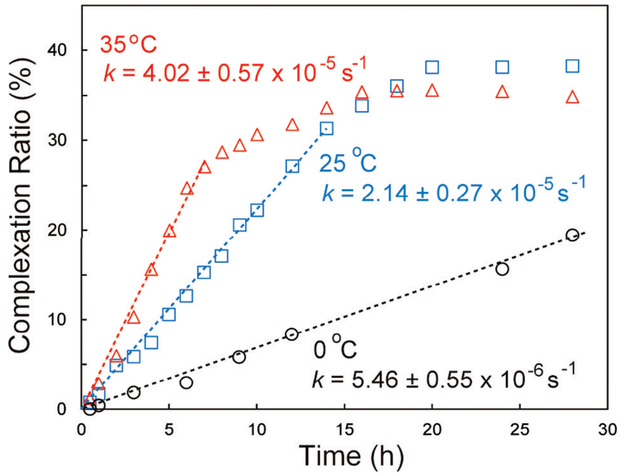


Figure 7. Correlation between time and degree of complex formation between **1** and *cis*-**3** in acetone-d_6 at 0 °C (black circle), 25 °C (blue square) and 35 °C (red triangle).

The threading processes of **1** onto the *trans*-**3** and *cis*-**3** were investigated by a thermodynamics and kinetics study. The thermodynamic parameters (ΔH, ΔS, and ΔG) were determined by van't Hoff plots (Supporting Information, Figure S16). The free energies of activation for the complexation ($\Delta G_{in}^{\ddagger}$, $\Delta G_{out}^{\ddagger}$) were obtained from the Eyring equation. Figure 8 shows the activation parameters for the complexation of *trans*-**3** and *cis*-**3** with **1** at 25 °C. As a typical example, the activation parameters

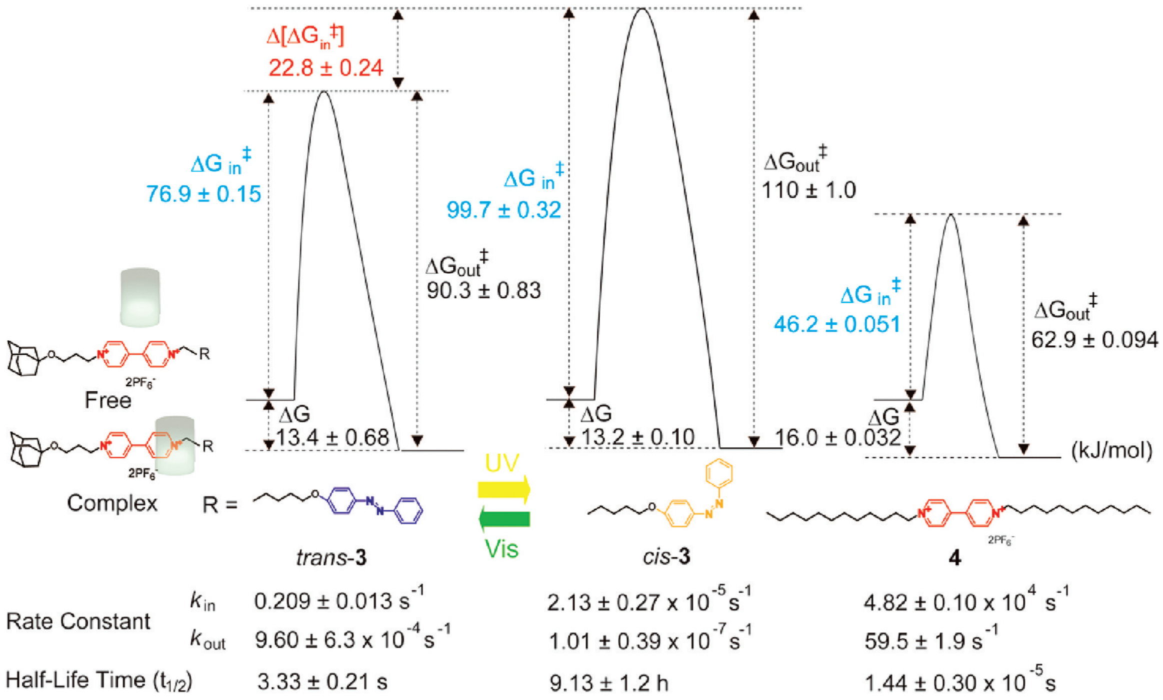


Figure 8. The activation parameters for the complexation for **1**-*trans*-**3** (left), **1**-*cis*-**3** (middle), and **1**–**4** (right) at 25 °C.

for the complexation between **1** and **4** are also shown.[9] The rate constant for the complexation between **1** and **4** was fast on the NMR time-scale at 25 °C ($k = 4.82 \pm 0.10 \times 10^4$ s^{-1}, $t_{1/2} = 1.44 \pm 0.30 \times 10^{-5}$ s). The values of $\Delta G_{in}^{\ddagger}$ for the complexation of **1**-*trans*-**3** (76.9 ± 0.15 kJmol^{-1}) and **1**-*cis*-**3** (99.7 ± 0.32 kJmol^{-1}) were much larger than that of **1**–**4** (46.2 ± 0.051 kJmol^{-1}). This is due to the bulky adamantane and azobenzene ends. The increment of free energy of activation ($\Delta[\Delta G_{in}^{\ddagger}] = 22.8 \pm 0.24$ kJ mol^{-1}) is generated by change in the geometry of the azobenzene gate and results in the time-scale transformation from seconds to hours time-scales.

■ CONCLUSIONS

Photoswitching of the time-scale of the threading process of pillar[5]arene onto a viologen derivative containing an azobenzene end-group was demonstrated. Isomerization of the azobenzene moiety from cis to trans form caused the threading rate to change from seconds to hours time-scales. Thus, the azobenzene end-group acts as a gate to control the rate of complexation with pillar[5]arene. To the best of our knowledge, the photoswitchable time-scale transformation between several seconds and several hours (very slow exchange) time-scales is extremely unusual and little known. This is also the first example of application of photostimuli[10] in host–guest chemistry in pillar[5]arene. Moreover, by changing the temperature, tuning of the dynamic is also accomplished. The threading of **1** onto the cis form of the azobenzene end was considerably suppressed at 0 °C. Switching of the time-scale of exchange processes by combining light and heating/cooling is new concept for controlling the movement of wheel components in supramolecular architectures.

■ EXPERIMENTAL SECTION

Materials. All solvents and reagents were used as supplied. Pillar[5]arenes (**1** and **2**), 1-(3-bromopropoxy)-adamantane (**6**), and 1-(6-bromohexyloxy)azobenzene (**7**) were prepared according to the previous papers.[3b,6a,11,12]

Synthesis of 3. To a solution of 4,4′-dipyridyl (3.12 g, 20.0 mmol) and 1-(3-bromopropoxy)adamantane (**6**, 0.137 g, 0.500 mmol) in acetonitrile (20 mL) at 85 °C, a solution of **6** (0.960 g, 3.50 mmol) in acetonitrile (7 mL) was added dropwise, and the mixture was stirred for 7 h. The resulting solution was concentrated under vacuo. The solution was poured into diethyl ether, and the precipitate was collected by filtration (**8**, 0.802 g, 1.86 mmol, 45%). This product (**8**, 0.802 g, 1.86 mmol) and 1-(6-bromohexyloxy)azobenzene (**7**, 1.34 g, 3.72 mmol) were allowed to react in acetonitrile (100 mL) at 85 °C for 168 h. After cooling, the precipitate was collected by filtration. The crude product was purified by recrystallization from methanol. This obtained product (1.34 g, 1.67 mmol, yield 90%) was dissolved in the mixture of methanol (30 mL) and water (15 mL). To the mixture, NaPF$_6$ (1.40 g, 8.33 mmol) was added. The reaction mixture was stirred at 25 °C for 24 h. The resulting solution was concentrated under vacuo. The residue was poured into water, and the precipitate was collected by filtration (0.969 g, 1.05 mmol, 63%): ^{1}H NMR (acetone-d_6, 500 MHz, ppm) δ 9.48 (d, 2H, viologen group), 9.45 (d, 2H, viologen group), 8.85 (d, 2H, viologen group), 8.84 (d, 2H, viologen group), 7.92 (d, 2H, azobenzene group), 7.88 (d, 2H, azobenzene group), 7.58 (t, 2H, azobenzene group), 7.53 (m, 1H, azobenzene group), 7.11 (d, 2H, azobenzene group), 5.02 (t, 2H, methylene linker), 4.99 (t, 2H, methylene linker), 4.14 (t, 2H, methylene linker), 3.63 (t, 2H, methylene linker), 2.39 (m, 2H, methylene linker), 2.27 (m, 2H, methylene linker), 1.85 (m, 2H, methylene linker), 1.55–1.70 (m, 19H, adamantane group and methylene linker); ^{13}C NMR (acetone-d_6, 125 MHz, ppm) δ 162.0, 152.7, 150.1, 146.5, 146.1, 130.6, 129.2, 127.3, 127.0, 124.7, 122.4, 114.9 (C of azobenzene and viologen groups), 72.0, 68.0, 62.3, 60.7, 56.3, 41.2, 36.1, 31.5, 31.2, 30.4, 25.6, 25.3 (C of methylene linker and adamantane group). Anal. Calcd for $C_{41}H_{50}F_{12}N_4O_2P_2$: C, 53.48; H, 5.47; N, 6.08. Found: C, 53.40; H, 5.60; N, 6.14. MS (FAB) Calcd for $C_{41}H_{50}F_6N_4O_2P$ [M − PF$_6$]$^+$: 775.3570, found 775.

Determination of Association Constants for 1-*trans*-3 and 1-*cis*-3 Complexes. The ^{1}H NMR spectra of mixtures of **1** and *trans*-**3** in different ratios showed two sets of resonances for complexed and free *trans*-**3**. The association constant K_1 for **1**-*trans*-**3** complex was calculated from integrations of complexed and free peaks of viologen moiety of *trans*-**3** (Figure 3b, peaks c and d). K_1 for **1**-*cis*-**3** complex was also determined from integrations of complexed and free peaks of viologen moiety of *cis*-**3** (Figure 6c, peaks c and d). The complexation ratio of the *cis*-**3** is similar to that of *trans*-**3** in the temperature range investigated; thus, K_1 for **1**-*cis*-**3** complex is almost the same as that for **1**-*trans*-**3** complex.

Determination of the Rate Constant for the Threading Process in *trans*-3 by EXSY NMR Measurements. The EXSY measurements were carried out with a phase-sensitive NOESY pulse sequence. The k values, which represent rate constants, were determined by using the following equations:[13]

$$\mathbf{1} + trans\text{-}\mathbf{3} \underset{k_{\mathrm{out}}}{\overset{k_{\mathrm{in}}}{\rightleftharpoons}} \mathbf{1}\text{-}trans\text{-}\mathbf{3}\text{ complex}$$

$$k = k_{\mathrm{in}} + k_{\mathrm{out}} \quad K_1 = \frac{k_{\mathrm{in}}}{k_{\mathrm{out}}}$$

$$k = (1/\tau_{\mathrm{m}})\ln(\gamma + 1/\gamma - 1)$$

where τ_{m} is the mixing time and γ is defined by the following equation:

$$\gamma = 4X_{\mathrm{A}}X_{\mathrm{B}}(I_{\mathrm{AA}} + I_{\mathrm{BB}})/[(I_{\mathrm{AB}} + I_{\mathrm{BA}}) - (X_{\mathrm{A}} - X_{\mathrm{B}})^2]$$

where X_{A} and X_{B} are the mole fraction of free (Figure 3b, red peak a) and complex (Figure 3b, blue peak a) species, respectively, I_{AB} and I_{BA} are the intensities of the cross peaks between the free and complex peaks (Figure 4a), respectively, and I_{AA} and I_{BB} are the intensities of the diagonal signals.

The free energy of activation of the exchange was obtained from the Eyring equation:

$$k = k_{\mathrm{B}}T/h\exp(-\Delta G^{\ddagger}/RT)$$

where k_{B} is the Boltzmann constant, T is the absolute temperature, h is Plank's constant, $\Delta G^{\ddagger}$ is the free energy of activation, and R is the gas constant.

Determination of the Rate Constant for the Threading Process in *cis*-3 by ^{1}H NMR Measurements. The complexation ratio of *cis*-**3** was determined by using following equations:

$$\text{complexation ratio of } cis\text{-}\mathbf{3}\ (\%) = 100([\text{complexed } cis\text{-}\mathbf{3}]/[cis\text{-}\mathbf{3}])$$

$$[\text{complexed } cis\text{-}\mathbf{3}] = [\mathbf{3}]\{(\mathrm{I}_{\text{complexed } cis\text{-}\mathbf{3}})/(\mathrm{I}_{\text{free } \mathbf{3}} + \mathrm{I}_{\text{complexed } trans\text{-}\mathbf{3}} + \mathrm{I}_{\text{complexed } cis\text{-}\mathbf{3}})\}$$

$$[cis\text{-}\mathbf{3}] = \alpha[\mathbf{3}]$$

$$\alpha = I_{cis\text{-}\mathbf{3}}/(I_{trans\text{-}\mathbf{3}} + I_{cis\text{-}\mathbf{3}})$$

where α is isomerization ratio and I is the integral intensity of the complexed *trans*-**3** (Figure 6, blue peaks c and d), complexed *cis*-**3** (Figure 6, green peaks c and d), free **3** (Figure 6, red peaks c and d), *trans*-**3** (Figure S16, peak h), and *cis*-**3** (Figure S16, peak h). The half-life times ($t_{1/2}$) of the cis-form complexation at 25 and 35 °C were found to be $3.24 \pm 0.040 \times 10^4$ s and $1.76 \pm 0.25 \times 10^4$ s, respectively. The rate constants k were determined by using following equation:

$$k = \ln 2/t_{1/2}$$

Determination of the Rate Constant for the Threading Process by Variable-Temperature ^{1}H NMR Measurements. The exchange rate constant (k) at a coalescence temperature was estimated by using the approximate expression:[14]

$$\Delta G^{\ddagger} = 8.314T_{\mathrm{c}}[22.96 + \log(T_{\mathrm{c}}/\delta\nu)]$$

where $\Delta G^{\ddagger}$ is the free energy of activation for the exchange and $\delta\nu$ is the chemical shift difference between the proton signals from complexed and free the viologen protons (Figure S15, signal b). The coalescence temperature T_{c} was estimated on the coalescence signal in the signal b of the viologen protons. The extrapolated value of k at 25 °C (k) was obtained from the Eyring equation.

Study of Thermodynamic Parameters by Variable-Temperature ^{1}H NMR Measurements. The thermodynamic parameters such as ΔH, ΔS, ΔG, and K_1 were determined from the temperature dependence of K_1 by the use of the linear van't Hoff plots:

$$\ln K_1 = -\Delta\mathrm{H}/RT + \Delta S/R$$

The ΔH and ΔS for complexation between **1** and **4** were calculated from the slope and intercept by plotting ln K_1 vs $1/T$ and ΔG was obtained according to the following equation:

$$\Delta G = \Delta\mathrm{H} - T\Delta S$$

Calculated Structures. All DFT calculations were performed at B3LYP/6-31G(d,p) using the Gaussian 09 suite of programs.

■ ASSOCIATED CONTENT

Supporting Information

Spectroscopic data for **3**, calculated structures, Job plot, van't Hoff plot, and determination of thermodynamic and kinetic parameters for **1**−**4** complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel.: +81-76-234-4775. Fax: +81-76-234-4800. E-mail: ogoshi@t.kanazawa-u.ac.jp.

■ REFERENCES

(1) Mugridge, J. S.; Szigethy, G.; Bergman, R. G.; Raymond, K. N. *J. Am. Chem. Soc.* **2010**, *132*, 16256−16264. (b) Raytchev, P. D.; Martinez, A.; Gornitzka, H.; Dutasta, J. P. *J. Am. Chem. Soc.* **2011**, *133*, 2157−2159. (c) Giansante, C.; Mazzanti, A.; Baroncini, M.; Ceroni, P.; Venturi, M.; Klärner, F. G.; Vögtle, F. *J. Org. Chem.* **2009**, *74*, 7335−7343. (d) Nakazawa, J.; Sakae, Y.; Aida, M.; Naruta, Y. *J. Org. Chem.* **2007**, *72*, 9448−9455.

(2) (a) Kawaguchi, Y.; Harada, A. *J. Am. Chem. Soc.* **2000**, *122*, 3797−3798. (b) Miyawaki, A.; Kuad, P.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2008**, *130*, 17062−17069. (c) Oshikiri, T.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2005**, *127*, 12186−12187. (d) Liu, K. L.; Goh, S. H.; Li, J. *Macromolecules* **2008**, *41*, 6027−6034. (e) Kohsaka, Y.; Nakazono, K.; Koyama, Y.; Asai, S.; Takata, T. *Angew. Chem., Int. Ed.* **2011**, *50*, 4872−4875.

(3) (a) Ogoshi, T.; Kanai, S.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *J. Am. Chem. Soc.* **2008**, *130*, 5022−5023. (b) Ogoshi, T.; Aoki, T.; Kitajima, K.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *J. Org. Chem.* **2011**, *76*, 328−331. (c) Ogoshi, T.; Tanaka, S.; Yamagishi, T.; Nakamoto, Y. *Chem. Lett.* **2011**, *40*, 96−98. (d) Li, C.; Xu, Q.; Li, J.; Yao, F.; Jia, X. *Org. Biomol. Chem.* **2010**, *8*, 1568−1576. (e) Li, C.; Zhao, L.; Li, J.; Ding, X.; Chen, S.; Zhang, Q.; Yu, Y.; Jia, X. *Chem. Commun.* **2010**, *46*, 9016−9018.

(4) (a) Ogoshi, T.; Nishida, Y.; Yamagishi, T.; Nakamoto, Y. *Macromolecules* **2010**, *43*, 3145−3147. (b) Ogoshi, T.; Nishida, Y.; Yamagishi, T.; Nakamoto, Y. *Macromolecules* **2010**, *43*, 7068−7072. (c) Ogoshi, T.; Hasegawa, Y.; Aoki, T.; Ishimori, Y.; Inagi, S.; Yamagishi, T. *Macromolecules* **2011**, No. 10.1021/ma2016979.

(5) (a) Ogoshi, T.; Hashizume, M.; Yamagishi, T.; Nakamoto, Y. *Chem. Commun.* **2010**, 3708−3710. (b) Ogoshi, T.; Umeda, K.; Yamagishi, T.; Nakamoto, Y. *Chem. Commun.* **2009**, 4874−4876. (c) Ogoshi, T.; Kitajima, K.; Yamagishi, T.; Nakamoto, Y. *Org. Lett.* **2010**, *12*, 636−638. (d) Ogoshi, T.; Shiga, R.; Yamagishi, T.;

Nakamoto, Y. *J. Org. Chem.* **2011**, *76*, 618−622. (e) Ogoshi, T.; Shiga, R.; Hashizume, M.; Yamagishi, T. *Chem. Commun.* **2011**, 6927−6929. (f) Ogoshi, T.; Demachi, K.; Kitajima, K.; Yamagishi, T. *Chem. Commun.* **2011**, 7164−7166. (g) Ogoshi, T.; Kitajima, K.; Fujinami, S.; Yamagishi, T. *Chem. Commun.* **2011**, 10106−10108. (h) Ogoshi, T.; Demachi, K.; Kitajima, K.; Yamagishi, T. *Chem. Commun.* **2011**, 10290−10292. (i) Strutt, N. L.; Forgan, R. S.; Spruell, J. M.; Botros, Y. Y.; Stoddart, J. F. *J. Am. Chem. Soc.* **2011**, *133*, 5668−5671. (j) Zhang, Z.; Xia, B.; Han, C.; Yu, Y.; Huang, F. *Org. Lett.* **2010**, *12*, 3285−3287. (k) Hu, X. B.; Chen, L.; Si, W.; Yu, Y.; Hou, J. L. *Chem. Commun.* **2011**, 4694−4696.

(6) (a) Ogoshi, T.; Kitajima, K.; Aoki, T.; Fujinami, S.; Yamagishi, T.; Nakamoto, Y. *J. Org. Chem.* **2010**, *75*, 3268−3273. (b) Ogoshi, T.; Kitajima, K.; Aoki, T.; Yamagishi, T.; Nakamoto, Y. *J. Phys. Chem. Lett.* **2010**, *1*, 817−821. (c) Ogoshi, T.; Masaki, K.; Shiga, R.; Kitajima, K.; Yamagishi, T. *Org. Lett.* **2011**, *13*, 1264−1266.

(7) The association constant K_1 of **1**-octyl viologen complex determined by fluorescence measurements was found to be 12 000 M^{-1} in methanol (ref 3a). This is due to the different solvent system and measurements. The association constants of viologen derivatives/pillar[5]arene complexes determined by ^{1}H NMR measurements in acetone-d_6 (ref 3d) were in the same range.

(8) Determination of the degree of the complexation ratio was conducted by considering thermal cis to trans isomerization during the measurements.

(9) The threading process was fast on the NMR time-scale; thus, we measured the rate constant by variable-temperature ^{1}H NMR measurements (Supporting Information).

(10) Photoswitchable transformations of positions of ring segment and supramolecular structures have been reported. However, photoswitching of the time-scale transformation between seconds and hours time-scales has not been reported. (a) Coskun, A.; Friedman, D. C.; Li, H.; Patel, K.; Khatib, H. A.; Stoddart, J. F. *J. Am. Chem. Soc.* **2009**, *131*, 2493−2495. (b) Sidhaye, D. S.; Kashyap, S.; Sastry, M.; Hotha, S.; Prasad, B. L. V. *Langmuir* **2005**, *21*, 7979−7984. (c) Rakotondradany, F.; Whitehead, M. A.; Lebuis, A. M.; Sleiman, H. F. *Chem.—Eur. J.* **2003**, *9*, 4771−4780. (d) Hirose, T.; Matsuda, K.; Irie, M. *J. Org. Chem.* **2006**, *71*, 7499−7508. (e) Mueller, M.; Zentel, R. *Macromolecules* **1994**, *27*, 4404−4406. (f) Maxein, G.; Zentel, R. *Macromolecules* **1995**, *28*, 8438−8440. (g) Mueller, M.; Zentel, R. *Macromolecules* **1996**, *29*, 1609−1617. (h) Mayer, S.; Maxein, G.; Zentel, R. *Macromolecules* **1998**, *31*, 8522−8525. (i) Ciardelli, F.; Fabbri, D.; Pieroni, O.; Fissi, A. *J. Am. Chem. Soc.* **1989**, *111*, 3470−3472. (j) Pieroni, O.; Fissi, A.; Viegi, A.; Fabbri, D.; Ciardelli, F. *J. Am. Chem. Soc.* **1992**, *114*, 2734−2736. (k) Ajayaghosh, A.; Praveen, V. K. *Acc. Chem. Res.* **2007**, *40*, 644−656. (l) Inoue, Y.; Kuad, P.; Okumura, Y.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 6396−6397. (m) Tomatsu, I.; Hashidzume, A.; Harada, A. *J. Am. Chem. Soc.* **2006**, *128*, 2226−2227. (n) Kuad, P.; Miyawaki, A.; Takashima, Y.; Yamaguchi, H.; Harada, A. *J. Am. Chem. Soc.* **2007**, *129*, 12630−12631.

(11) van Bommel, K. J. C.; Metselaar, G. A.; Verboom, W.; Reinhoudt, D. N. *J. Org. Chem.* **2001**, *66*, 5405−5412.

(12) Mitsuoka, T.; Sato, H.; Yoshida, J.; Yamaguchi, A.; Einaga, Y. *Chem. Mater.* **2006**, *18*, 3442−3447.

(13) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935−967.

(14) (a) Sutherland, I. O. *Annu. Rep. NMR Spectrosc.* **1971**, *4*, 71−235. (b) Sandstorm, J. In *Dynamic NMR Spectroscopy*; Academic Press: London, New York, 1982; pp 93−123.