Photoresponsive Host-Guest Systems Based on a New Azobenzene-Containing Cryptand

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1. Materials and methods

Bis(5-bromomethyl-\(m\)-phenylene)-32-crown-10,\textsuperscript{S1} 4,4′-dihydroxyazobenzene\textsuperscript{S2} and 2,7-diazapyrenium (DAP) derivatives\textsuperscript{S3} (2\textsuperscript{a} and 2\textsuperscript{b}) were prepared according to literature procedures. Solvents were either employed as purchased or dried according to procedures described in the literature. Photo irradiation experiments were carried on a CHF-XM35 mercury lamp with suitable filters (Beijing Trusttech Co. Ltd, P. R. China). The distance between the lamp and the sample cell was 20 cm.\textsuperscript{1}H NMR spectra were collected on a Varian Unity INOVA-400 spectrometer with internal standard TMS. \textsuperscript{13}C NMR spectra were recorded on a Bruker AVANCE DMX-500 spectrometer at 125 MHz. Low-resolution electrospray ionization mass spectra (LRESIMS) were performed on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with ESI interface and ion trap analyzer. High-resolution electrospray ionization mass spectra (HRMS) were obtained on a Bruker 7-Tesla FT-ICRMS equipped with an electrospray source (Billerica, MA, USA).

2. Synthesis and characterization of 1

A solution of bis(5-bromomethyl-\(m\)-phenylene)-32-crown-10 (750 mg, 1.04 mmol) and 4,4′-dihydroxyazobenzene (222 mg, 1.04 mmol) in CH\(_3\)CN (50 mL) was added via a syringe pump at 1.5 mL/h to a suspension of K\(_2\)CO\(_3\) (2.76 g, 20.0 mmol) in CH\(_3\)CN (0.80 L) at reflux under nitrogen gas protection. After complete addition, the mixture was stirred at reflux for 3 days. The color of the reaction turned deep yellow gradually. The mixture was filtered and CH\(_3\)CN was removed with a rotary
evaporator. Then CH$_2$Cl$_2$ (500 mL) was added and filtered. After the removal of CH$_2$Cl$_2$, flash column chromatography [petroleum ether/ethyl acetate, (1:1, v/v)→(1:2, v/v)] was used to obtain 1 as a red solid, 413 mg (53%), M.p. > 300 °C (decomp.). The proton NMR spectrum of 1 is shown in Figure S1. $^1$H NMR (500 MHz, CD$_3$CN, room temperature) $\delta$ (ppm): 3.43–3.49 (m, 16H), 3.64 (t, $J = 4.5$ Hz, 8H), 4.02 (t, $J = 4.5$ Hz, 8H), 5.27 (s, 4H), 6.25 (t, $J = 2.5$ Hz, 2H), 6.49 (d, $J = 2.5$ Hz, 4H), 7.04 (d, $J = 9.0$ Hz, 4H), 7.67 (d, $J = 9.0$ Hz, 4H). $^{13}$C NMR (125 MHz, acetone-$d_6$, room temperature) $\delta$ (ppm): 160.0, 159.5, 146.7, 139.2, 123.6, 122.0, 117.6, 114.9, 107.1, 106.5, 105.8, 100.4, 70.7, 70.4, 69.7, 69.5, 69.2, 67.7, 67.3. LRESIMS: $m/z$ 775.3 [M + H]$^+$ (64%), 797.3 [M + Na]$^+$ (100%), 813.3 [M + K]$^+$ (35%). HRMS: $m/z$ calcd for [M + Na]$^+$ C$_{42}$H$_{50}$N$_2$O$_{12}$Na, 797.3261, found 797.3232, error 4.0 ppm. $m/z$ calcd for [M + K]$^+$ C$_{42}$H$_{50}$N$_2$O$_{12}$K, 813.3001, found 813.2961, error 5.0 ppm.

Figure S1. $^1$H NMR (500 MHz, CD$_3$CN, rt) of 1 after being heated in the dark for 1 h.
Figure S2. $^1$H NMR (500 MHz, CD$_3$CN, rt) of trans-1 after being irradiated at 350 nm for 5 min.

Figure S3. $^{13}$C NMR (125 MHz, (CD$_3$)$_2$CO, room temperature) of 1.
3. UV-vis spectroscopy studies of 1 and 1\(\rightarrow\)2a

**Figure S4.** UV-vis spectra of (a) trans-1, (b) irradiation of trans-1 with light at 350 nm for 1 min, (c) then irradiation of b with light at 450 nm for 10 min (4\(\times\)10\(^{-5}\) mol/L, MeCN, 25 °C).

**Figure S5.** UV-vis spectra of (a) an equimolar mixture of trans-1 and 2a (2\(\times\)10\(^{-5}\) mol/L), (b) the same mixture after irradiation with light at 350 nm for 1 min. It seems that there is a broad and weak charge transfer band appearing as a tail extending up to 550 nm.\(^{13b}\)
4. Kinetic measurements of thermal isomerization of 1 from cis to trans.
The trans-1 is more stable than the cis-1, so cis-1 will transform to the more stable trans form gradually because of the molecular thermal motion. The rate constant \(k\) was measured, which can give information about the stability of 1 and the influence from the guest molecule. The sample was sealed in a quartz UV cell with a cap. Rate constants of isomerization from the cis to trans in the dark were determined by the increase of intensity at the wavelength of maximum absorption of trans from the cis photostationary state. The cis state was rapidly reached under UV irradiation (\(\lambda = 350\) nm) for 10 min. In the process of irradiation, the temperature of the samples was kept the same as the room temperature.

![Graph](image)

**Figure S6.** Absorption at 360 nm of 1 vs Time in MeCN at rt (283 K).

As shown in Figure S6, the isomerization obeyed first-order kinetics in MeCN. The rate constant \((k)\) in MeCN at room temperature is \(1.20 \times 10^{-4}\) min\(^{-1}\). When an equivalent of 2a was added, the rate constant \((k)\) dropped to \(8.04 \times 10^{-5}\) min\(^{-1}\). The rate of the thermal isomerization (cis to trans) was suppressed by added guest molecule 2a. That is to say, 2a has some interactions with cis-1.
5. Determination of the stoichiometry cis-1⊃2a

In most cases, the sample of 1 contains both the trans and cis form, so ¹H NMR is a more accurate technique to determine the stoichiometry and association constants compared with UV-Vis spectroscopy and fluorescence spectroscopy.

A Job plot based on ¹H NMR chemical shift changes of one complexed proton (H₂) proved that the complex of cis-1 with 2a was of 1:1 stoichiometry in solution (Figure S7).

![Figure S7](image)

**Figure S7.** A Job plot showing the 1:1 stoichiometry of the complex between cis-1 (H) and 2a (G) in acetonitrile by plotting the chemical shift changes of H₂ against the molar fraction of the guest. [H]₀ and [G]₀ are initial concentrations of H and G. [H]₀ + [G]₀ = 8.00 mM.

6. Determination of the association constant of cis-1⊃2a by ¹H NMR

Kₐ,cis-1⊃2a was determined based on ¹H NMR data. Firstly, 1.05 mg (2.00 mmol) of guest 2a was added to a 2 mL volumetric flask. Then acetonitrile was added to give a 1.00 mM solution of 2a (G). A precisely weighed amount (15.4 mg, 20.0 mmol) of host 1, which has been irradiated by light at 350 nm for 5 min, was dissolved in 1 mL of this 1.00 mM 2a solution to afford a 20.0 mM host solution. Titration of the host solution into a specified volume of the guest solution results in an increase of the
chemical shift change of H₂. Treatment of the chemical shift change data with a non-linear curve-fitting program afforded the corresponding association constant.

The non-linear curve-fitting was based on the equation:\(^4\)

\[
A = \left( \frac{A_\infty}{[G]_0} \right) \left( 0.5[H]_0 + \frac{1/\kappa_a}{2([H]_0^2 + 2[H]_0(1/[\kappa_a] - [G]_0)) + ([1/\kappa_a + [G]_0])^{0.5}} \right) \]  

(Eq. S1)

Where \(A\) is the chemical shift change of H₂ on guest 2a at \([H]_0\), \(A_\infty\) is the chemical shift change of H₂ when the guest is completely complexed, \([G]_0\) is the fixed initial concentration of the guest, and \([H]_0\) is the initial concentration of the host cis-1.

**Figure S8.** The \(^1H\) NMR spectral changes of guest 2a (1.00 mM) upon addition of (a) 0, (b) 0.17, (c) 0.34, (d) 0.63, (e) 0.87, (f) 1.23, (g) 1.88, (h) 2.21, and (i) 2.48 mM cis-1.
Figure S9. The chemical shift changes of H$_2$ on 2a (G) upon addition of cis-1 (H). The red solid line was obtained from the non-linear curve-fitting using Eq. S1. The association constant ($K_a$) of $\text{cis-1} \supseteq 2\text{a}$, $3.3 \pm 2.2 \times 10^4$, is close to the value of $K_a$ determined based on fluorescence spectroscopic data.

7. Determination of the association constant of trans-1$\supseteq 2\text{a}$ by isothermal titration calorimetry experiment.

Isothermal titration calorimetric measurements were performed on a VP-ITC micro calorimeter (Microcal, USA), which is composed of a reference cell and a sample cell of 1.43 mL. Stock solutions of 2a (0.50 mM, 10 mL) and 2b (0.50 mM, 10 mL), and the titrant trans-1 (15.0 mM, 5 mL, has been heated in the dark for 1h) in acetonitrile were prepared using volumetric glassware. Before each titration, all the solutions were degassed and kept constant temperature. In a typical run, a 250 µL syringe was full of trans-1 solution (15.0 mM) and the cell was loaded with either 2a or 2b (0.50 mM, 1.43 mL) or acetonitrile. The titrations of 2a/2b with trans-1 solution were carried out at 298.15 K with constant rate of 307 rpm, 35 injections of 3.3µL, time interval of 240 s and duration of 2 s per µL. The enthalpy change per mole of each added trans-1 solution in the sample cell was recorded continuously. The control titrations of trans-1 solution into acetonitrile were also completed under the same conditions. The enthalpy changes of the titrations of the blank test were subtracted from the original titration. All the data were analyzed with Microcal Origin 7.0 software provided by the manufacturer. The final integration data obtained from the
titration were not fit any model, thus, the results show that there should no interaction between the \textit{trans}-1 and 2a/2b.

\textbf{Figure S10.} Titration of 2a (0.50 mM) with \textit{trans}-1 (15.0 mM) in MeCN at 298.15 K

\textbf{Figure S11.} Titration of 2b (0.50 mM) with \textit{trans}-1 (15.0 mM) in MeCN at 298.15 K
8. $^1$H NMR study of the complexation between 1 and 2b.

**Figure S12.** Partial $^1$H NMR spectra (500 MHz, MeCN-$d_3$, 295 K) of (a) trans-1, (b) a 1.00 mM equivalent mixture of trans-1 and 2b, (c) irradiation of b with light at 350 nm for 1 min, (d) irradiation of trans-1 with light at 350 nm for 1 min, and (e) 2b.

Figure S13. Partial NOESY NMR spectrum (500 MHz, MeCN-d₃, 295 K, 300 ms for the mixing time) of a mixture of trans-1, cis-1 and 2a.

10. Partial NOESY NMR spectrum of a mixture of trans-1, cis-1 and 2b.

Figure S14. Partial NOESY NMR spectrum (500 MHz, MeCN-d₃, 295 K, 300 ms for the mixing time) of a mixture of trans-1, cis-1 and 2b.
11. Minimized-energy structures of trans-1 and cis-1.

All calculations of energy-minimized structures were run with the GAUSSIAN 03 software,\textsuperscript{85} based on the arithmetic method B3LYP/6-31G(D). The modeling computation was run based on the reported X-ray crystal structures of 2a and trans-1.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{X-ray crystal structure of trans-1 (a) and energy-minimized structures of trans-1 (b) and cis-1 (c).}
\end{figure}

12. X-ray crystal data for 1

Crystallographic data: orange, C\textsubscript{45.71}H\textsubscript{55.01}N\textsubscript{3.86}O\textsubscript{12.14}, FW 852.79, monoclinic, space group C\textsubscript{2}c, \(a = 18.093(4)\) Å, \(b = 9.0114(18)\) Å, \(c = 28.029(6)\) Å, \(\alpha = 90.00°\), \(\beta = 101.57(3)°\), \(\gamma = 90.00°\), \(V = 4477.1(17) Å^3\), \(Z = 4\), \(T = 293 K\), \(\mu = 0.092 mm^{-1}\), 17271 measured reflections, 5047 independent reflections, 306 parameters, 69 restraints, \(F(000) = 1813.4\), \(R_1 = 0.0518\), \(wR_2 = 0.1270\) (all data), \(R_1 = 0.0465\), \(wR_2 = 0.1224\) [\(I > 2\sigma(I)\)], max. residual density 0.686 e•Å\(^{-3}\), and goodness-of-fit \((F^2) = 1.052\).

13. X-ray crystal data for 2a

Crystallographic data: yellow, C\textsubscript{16}H\textsubscript{14}F\textsubscript{12}N\textsubscript{2}P\textsubscript{2}, FW 524.23, monoclinic, space group P\textsubscript{2}_1/n, \(a = 6.7733(5)\) Å, \(b = 10.6708(6)\) Å, \(c = 13.4177(6)\) Å, \(\alpha = 90.00°\), \(\beta = 91.054(5)°\), \(\gamma = 90.00°\), \(V = 969.63(9) Å^3\), \(Z = 2\), \(T = 293 K\), \(\mu = 3.203 mm^{-1}\), 5255 measured reflections, 1712 independent reflections, 147 parameters, 0 restraints, \(F(000) = 524\), \(R_1 = 0.0728\), \(wR_2 = 0.1906\) (all data), \(R_1 = 0.0465\), \(wR_2 = 0.1765\) [\(I > 2\sigma(I)\)], max. residual density 0.524 e•Å\(^{-3}\), and goodness-of-fit \((F^2) = 1.054\).
References:


