Supporting Information

for

Advanced Materials, adma.200600235

© Wiley-VCH 2006
69451 Weinheim, Germany
Supporting Information

A Double “INHIBIT” Logic Gate Employing Configuration and Fluorescence Changes

Da-Hui Qu, Feng-Yuan Ji, Qiao-Chun Wang, and He Tian *

General: H NMR spectra were measured on a Brücker AM 500 spectrometer. Elemental analysis was performed on a Perkin-Elmer 2400C instrument. MALDI-TOF spectrum was recorded a 4700-Propeomics analyzer. UV/Vis spectra were done on a Varian Cary 500 spectrophotometer (1-cm quartz cell used) at 25 ºC. Fluorescent spectra were recorded on a Varian Cary Eclipse Fluorescence Spectrophotometer (1-cm quartz cell used) at 25 ºC. The photo-irradiation was carried on a CHF-XM 500-W high-pressure mercury lamp with suitable filters (313 nm, 280 nm, 380 nm, type FAL, made in Germany) in a sealed Ar-saturated 1 cm quartz cell. The distance between the lamp and the sample cell is 20 cm.

The synthesis of intermediates and Co-Conformation Identification of [2]Rotaxane 1

5-[2-(4-Bromo-phenyl)-vinyl]-isophthalic acid dimethyl ester (1a): A solution of 5-(bromo-methyl)-isophthalic acid dimethyl ester (28.6 g, 0.1 mol) in trimethyl
phosphite (50 mL, 424 mmol) was heated under reflux for 4 h. The excess trimethyl phosphite was removed in vacuo, the yellow residue was dissolved in dried DMF (50 mL) and THF (50 mL), the resulting solution was cooled to 0 °C, a solution of sodium methoxide (5.4 g, 0.1 mol) in methanol (50 mL) was added dropwise, and the mixture was stirred for 1.5 h at room temperature. Another solution of \( p \)-bromo-benzaldehyde (18.4 g, 0.1 mol) in DMF (80 mL) was then added dropwise and stirring was continued for another 3 h. More sodium methoxide solution (1.6 g, 30 mmol) in methanol (20 mL) was added and the resulting mixture was stirred for another 18 h, then poured into water (300 mL), The precipitate was collected by filtration, washed with water, dried, and recrystallized from methanol and dichloromethane to give \( \text{1a} \) (22 g, 60 %) as a white solid. M.p. 132-134 °C. \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS): \( \delta = 8.56 \) (s, 1H), 8.34 (s, 2H), 7.51 (d, \( J = 8.4 \) Hz, 2H), 7.40 (d, \( J = 8.4 \) Hz, 2H), 7.19 (d, \( J = 16.4 \) Hz, 1H), 7.13 (d, \( J = 16.4 \) Hz, 1H), 4.0 (s, 6H).

5-[2-(4-Bromo-phenyl)-vinyl]-isophthalic acid (\( \text{1b} \)): \( \text{1a} \) (7.5 g, 20 mmol) was dissolved in methanol (70 mL) and THF (70 mL), then CH\(_3\)ONa (5.4 g, 0.1 mol) was added and the resulting solution was refluxed for 8 h, cooled and poured into water (800 mL), acidified with concn. HCl, the precipitate was collected by filtration, washed with water and dried to give \( \text{1b} \) (6.7 g, 96%) as white solid. M.p.>250 °C. \(^1\)H NMR (500 MHz, [D\(_6\)]DMSO, 25 °C, TMS): \( \delta = 8.37 \) (s, 2H), 8.35 (s, 1H), 7.64 (d, \( J = 8.6 \) Hz, 2H), 7.58 (d, \( J = 8.6 \) Hz, 2H), 7.50 (d, \( J = 16.5 \) Hz, 1H), 7.43 (d, \( J = 16.5 \) Hz, 1H).

5-[2-(4-Boronic acid phenyl)-vinyl]-isophthalic acid (\( \text{1c} \)): \( \text{1b} \) (3.35 g, 9.67 mmol) was lithilated by n-BuLi (1.6 M, 21 mL, 33.6 mmol) in dry THF (60 mL) at -78 °C for 3 h, to the stirred suspension trimethyl boronate (4 mL, 35.0 mmol) was added, the resulting mixture was allowed to warm up to room temperature and stirred for another
8 h, then acidified with 10% HCl, after concentration, a great deal of yellow solid precipitated, which was collected by filtration, washed with water and dried, recrystallized from CCl₄:CH₂OH = 6:1 to give 1c (1.3 g, 43%). M.p. 212 ºC (decomp).

¹H NMR (500 MHz, [D₆]DMSO, 25 ºC, TMS): δ = 8.38 (s, 2H), 8.36 (s, 1H), 8.02 (s, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 16.6 Hz, 1H), 7.20 (d, J = 16.6 Hz, 1H).

Scheme S1. The synthetic routes to [2]rotaxane 1. The α-cyclodextrin is drawn with a wide 2,3-rim and a narrow 6-rim; 2 is the free dumbbell.

The [2]rotaxane 1 was synthesized from the Pd catalyzed Suzuki coupling of 1d with 1e in an alkaline aqueous α-CD solution, and it was confirmed that only one
isomer, where the 2,3-rim of the α-CD faces the isophthalic acid stopper, was obtained in the synthesis of 1. The other possible isomer where the 2,3-rim of the α-CD faces the other stopper was not present. This conclusion could be confirmed from the two-dimensional $^1$H ROESY NMR spectrum (500 MHz in D$_2$O at 298 K; mixing time 300 ms) of rotaxane 1 (Figure S1). It is known that with the aid of an alkaline a monoboronic acid can form complexes with a diol$^{[2]}$ which results in the change of neutral sp$^2$-hybridized boronic acid into an anionic sp$^3$-hybridized boronic ester. A molecule of α-CD contains six sugar units and the 2,3-rim of which consists of diol units. In the Na$_2$CO$_3$ aqueous solution, when the boronic acid goes near to the α-CD, an ester between the acid and the 2,3-diol of the α-CD originates. More detail about the direction mechanism of the boronic acid were shown in our previous report.$^{[1f]}$ $^{[2]}$Rotaxane 1 is indeed a locked molecular shuttle, in which the hydrogen-bonding between the α-CD macrocycle and two carboxyl groups stops the shuttling motion of the α-CD macrocycle between the binding sites. As shown in Figure S1, the NOEs between the stilbene protons and H3, H5 and H6 protons on the interior of the α-CD annulus were found (from H$_g$, H$_h$, H$_i$ to H3 and from H$_g$, H$_f$, H$_h$, H$_i$ to H5 and H6), and no NOEs between the azobenzene protons and α-CD protons was found. Moreover, irradiation at 313 nm on $^{[2]}$Rotaxane 1 could not induce the photoisomerization of the stilbene unit and the shuttling motion of α-CD ring on the molecular thread.

The state (E,E)-1$^2$ shown in Figure 1 is a dynamic state (namely DS) at room temperature in D$_2$O, in which the α-CD bead moves back and forward between the
azobenzene station and the stilbene station with a rate that cannot be followed on the NMR time scale at room temperature. Rational nuclear overhauser effects (NOEs) can be obviously observed between the resonance of the azobenzene and stilbene protons and the H3 and H5 protons located inside the cyclodextrin annuli. This set of NOEs is not consistent with any single static geometry, and shows that the cyclodextrin rapidly glides on the dumbbell (Figure S2a).

**Figure S1.** The two-dimensional $^1$H ROESY NMR spectrum (500 MHz in D$_2$O at 298 K; mixing time 300 ms) of rotaxane 1.
Figure S2. The two-dimensional $^1$H ROESY NMR spectra (500 MHz in D$_2$O at 298 K) of [2]rotaxane $^1$: a) before irradiation, $E,E$ isomer (DS state); b) after irradiation at 380 nm for 2 h, $Z_{N=N},E_{C=C}$ isomer (PSS-ZE state); c) after irradiation at 313 nm for 3 h, $E_{N=N},Z_{C=C}$ isomer (PSS-EZ state); d) after irradiation on (b) solution for 3 h or after irradiation on (c) solution for 2 h, $Z,Z$ isomer (PSS-ZZ state).
\((E,E)-\text{I}^2\) converted into \((Z_N=N,E_C=C)-\text{I}^2\) by photoisomerization under irradiation at 380 nm, which leads to two new signals of equal intensity for Hc and Hd (Figure 1b) appearing at \(\delta = 6.70\) and 6.85 ppm, respectively, correspondingly the initial peaks appearing at \(\delta = 7.76\) and 7.89 ppm. The ratio of the integrals of the two signals of Hd suggest that at the photostationary state of azobenzene isomerization (namely \textbf{PSS-ZE}) about 68 % of \((E,E)-\text{I}^2\) was transformed to \((Z_N=N,E_C=C)-\text{I}^2\) isomer. A completely different pattern of NOEs (Figure S2b) is observed in the \(Z_N=N,E_C=C\) isomer. Here the NOEs are more selective, and the NOEs from the protons of the stilbene unit to the protons of \(\alpha\)-CD are much stronger than these from the protons of the azobenzene unit. All these NOEs are consistent with the geometry of the \(Z_N=N,E_C=C\) isomer, where the \(\alpha\)-CD ring stays at the stilbene unit (\textbf{PSS-ZE}).

\((E,E)-\text{I}^2\) converted into \((E_N=N,Z_C=C)-\text{I}^2\) by photoisomerization under irradiation at 313 nm, which results in the fact that the signals of aromatic protons of stilbene unit generally shift to upfields, for Hh, Hi (Figure 1c) appearing at \(\delta \sim 6.5\) (initially \(\delta \sim 7.05\)), Hj appearing at \(\delta = 7.24\) (initially \(\delta = 8.28\)), Hg appearing at \(\delta = 6.85\) (initially \(\delta = 7.42\)). Also, the coupling constant in the \textit{cis}-stilbene protons Hh and Hi in Figure 1c (14.7 Hz) is smaller than that in the \textit{trans}-stilbene protons Hh and Hi in Figure 1a (16.5 Hz). The ratio of the integrals of the two signals of Hh suggest that at the photostationary state of the stilbene isomerization (namely \textbf{PSS-EZ}) about 62 % of \((E,E)-\text{I}^2\) was transformed to \((E_N=N,Z_C=C)-\text{I}^2\) isomer in that case. The NOEs are more selective, and the NOEs from the protons of the azobenzene unit to the protons of \(\alpha\)-CD are much stronger than these from the protons of the stilbene unit (Figure S2c).
All these NOEs are consistent with the geometry of the $E_{N=N,Z=C}$ isomer, where the $\alpha$-CD ring stays at the azobenzene unit (PSS-EZ).

Irradiation by 313 nm on $(Z_{N=N},E_{C=C})$-I$^2$ or irradiation by 380 nm on $(E_{N=N},Z_{C=C})$-I$^2$ generated $Z,Z$ isomer, which results in the fact that the signals of aromatic protons of stilbene unit and azobenzene unit generally shift to upfields similarly (Figure S1d), indicating generation of $(Z,Z)$-I$^2$. Strong NOEs are observed from the protons of the biphenyl unit and the protons H3, H5 of $\alpha$-CD (Figure S2d), which can indicate that the structure of rotaxane 1$^2$ are consistent with the geometry of the $Z,Z$ isomer, where the $\alpha$-CD ring stays at the biphenyl unit (PSS-ZZ).

All these NMR spectra indicate that [2]rotaxane 1 is a five-state molecular shuttle—a locked state (LS), a dynamic state (DS), and three static states (PSS-ZE, PSS-EZ, PSS-ZZ).

Figure S3. The partial $^1$H-NMR spectrum of dumbbell 2 (500 MHz in [D$_6$]DMSO at 298 K).
Absorption spectra of dumbbell 2, rotaxane 1 and 1^{2-}

Figure S4. The absorption spectra of [2]rotaxane 1 in H₂O (1×10⁻⁵ M) at 25 ºC. The black line is the spectrum without irradiation ((E,E)-1), the red line is the spectrum after irradiation at 380 nm for 20 min ((Z_N=N,E_C=C)-1). The orange line is the spectrum by irradiation at 313 nm for 55 min (Z2-1), there is little change relative to the (E,E)-1, which is due to the hydrogen-bonding between the α-CD macrocycle and two carboxyl groups that prevents the isomerization of the stilbene unit.

Figure S5. The absorption spectra of [2]rotaxane 1^{2-} in sodium carbonate aqueous solution (1×10⁻⁵ M, pH = 10.5) at 25 ºC. The black line is the spectrum without irradiation, the red line is the spectrum after irradiation at 313 nm for 55 min, the blue line is the spectrum by irradiation at 380 nm for 20 min, and the green line is after 380 nm for 20 min, then irradiation at 313 nm for 55 min, respectively.
Figure S6. The absorption spectra of dumbbell 2 in H$_2$O (1×10$^{-5}$ M) at 25 °C. The black line is the spectrum without irradiation, the red line is the spectrum after irradiation at 313 nm for 40 min, the blue line is the spectrum by irradiation at 380 nm for 15 min, and the green line is after 380 nm for 15 min, then irradiation at 313 nm for 40 min, respectively.

Fluorescence spectra

Figure S7. Fluorescence emission spectra ($\lambda_{exc} = 438$ nm, emission at $\lambda_{max} = 520$ nm, 1.0×10$^{-5}$ M, H$_2$O, 298 K) of (E,E)-2 (olive), (Z$_{N=N}$E$_{C=C}$)-2 (PSS-ZE, red), (E$_{N=N}$Z$_{C=C}$)-2 (black), (Z,Z)-2 (blue). There is little change among these lines.
Figure S8. Fluorescence emission spectra ($\lambda_{\text{exc}} = 438 \text{ nm}$, emission at $\lambda_{\text{max}} = 520 \text{ nm}$, $1.0 \times 10^{-5} \text{ M}, \text{H}_2\text{O}, 298 \text{ K}$) of locked rotaxane 1. The black line is the spectrum without irradiation, the red line is the spectrum after irradiation at 313 nm for 2 h, the olive line is the spectrum after irradiation at 380 nm for 30 min, and the blue line is the spectrum after irradiation at 313 nm for 2 h and irradiation at 380 nm for 30 min. There is also little change among these lines.

Figure S9. Fluorescence emission spectra ($\lambda_{\text{exc}} = 438 \text{ nm}$, emission at $\lambda_{\text{max}} = 520 \text{ nm}$, $1.0 \times 10^{-5} \text{ M}, \text{Na}_2\text{CO}_3 \text{ aqueous solution, pH = 10.5, 298 K}$) of ($E,E$)-1$^{2-}$ (DS, olive), ($Z_N=N,E_{C=C}$)-1$^{2-}$ (PSS-ZE, black), ($E_{N=N,Z_C=C}$)-1$^{2-}$ (PSS-EZ, red), ($Z,Z$)-1$^{2-}$ (PSS-ZZ, blue).
References:
