

## Supplementary Information

# A Light-Driven [1]Rotaxane via self-complementary and Suzuki-Coupling Capping

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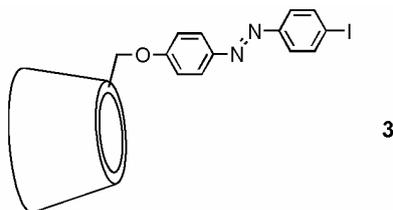
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**General:**  $^1\text{H}$  NMR spectra were measured on a Brücker AM 500 spectrometer. Elemental analysis was performed on a Perkin-Elmer 2400C instrument. MALDI-TOF spectrum was recorded on a 4700-Propeomics analyzer. UV/Vis spectra were done on a Varian Cary 500 spectrophotometer (1-cm quartz cell used) at 25 °C. ICD spectrum was measured on a Jasco J-815 CD spectrophotometer (1-cm quartz cell used) at 25 °C. The photo-irradiation was carried on a CHF-XM 500-W high-pressure mercury lamp (Lambda Physics, Germany) in a sealed Ar-saturated 1 cm quartz cell. The distance between the lamp and the sample cell is 20 cm.

### Experimental Section

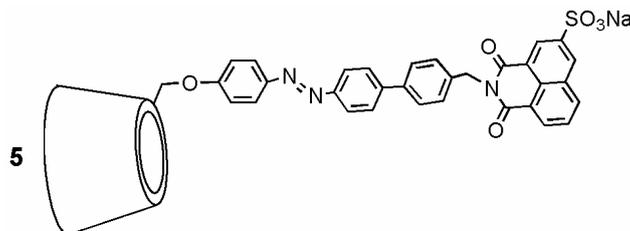
#### Mono{6-O-[4-((4-indo-phenyl)azo)phenyl]}- $\beta$ -cyclodextrin (**3**):



To a solution of DMF (15 mL) containing 1.0 g of 6-OTs- $\beta$ -CD (**1**)<sup>1</sup> and 0.2 g of  $\text{K}_2\text{CO}_3$  was added 0.3 g of 4-indo-phenyl-azo-phenol (**2**). The resultant mixture was stirred at 90 °C for 3 days under nitrogen. The solution was poured into 100 mL of water, and the precipitate was collected by filtration to give a yellow powder. The crude product was washed with water (100 mL), then with acetone (40 mL) and dried in vacuo to give a pure sample 0.8 g (yield 71 %).  $^1\text{H}$  NMR (500 MHz,  $[\text{D}_6]\text{DMSO}$ , 25 °C, TMS):  $\delta$  =

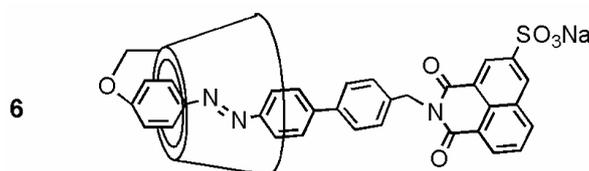
8.70 (s, 1H), 8.67 (s, 1H), 8.57 (d, J=8.2 Hz, 1H), 8.53 (d, J=7.0 Hz, 1H), 7.85 (d, J=8.2 Hz, 2H), 7.77 (m, 4H), 7.08 (d, J=8.2 Hz, 2H), 5.8~5.6 (m, 14H), 4.90~4.70 (m, 7H), 4.45~4.05 (m, 6H), 3.8~3.2 (m, 42H).

### Compound 5:



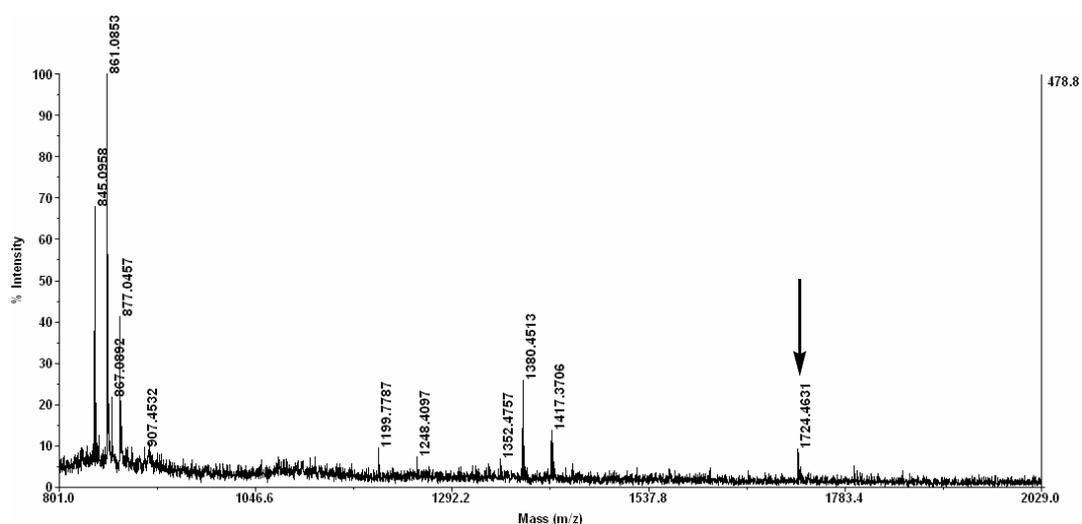
Compound **3** (0.2 g, 0.140 mmol), 2-[(4-boronic acid)-yl]-benzyl)-benzo[de]isoquinoline-1,3-dione-5-sulfonic acid sodium salt **4**<sup>2</sup> (0.12 g, 0.27 mmol), and palladium(II) acetate (8.0 mg, 0.038 mmol) were dissolved in DMSO (25 mL) and Ar-saturated sodium carbonate aqueous solution (5 mL, 0.4 mol/L), then the mixture was stirred at 85 °C for 20 h under Ar atmosphere. Cooled and acidified with acetic acid, after concentrated in vacuo, the resulting dark solid was purified by column chromatography (silica gel, the upper layer of 1:2:5 acetic acid/n-butanol/water) to give pure **5** (10 mg, 4.2%) as yellow powder. M.p.> 250°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO, 25 °C, TMS): δ= 8.71 (s, 1H), 8.68 (s, 1H), 8.58 (d, J=8.2 Hz, 1H), 8.53 (d, J=7.0 Hz, 1H), 7.95~7.80 (m, 7H), 7.69 (d, J=8.2 Hz, 2H), 7.48 (d, J=8.2 Hz, 2H), 7.14 (d, J=8.0 Hz, 2H), 6.0~5.8 (m, 14H), 5.32 (s, 2H), 4.90~4.70 (m, 7H), 4.40~4.0 (m, 6H), 3.8~3.2 (m, 42H). MALDI-TOF: m/z (%): 1724.41 (22) [M<sup>+</sup>+Na]; elemental analysis calcd (%) for C<sub>73</sub>H<sub>88</sub>N<sub>3</sub>NaO<sub>40</sub>S·6H<sub>2</sub>O: C 48.42, H 5.57, N 2.32; found C 48.63, H 5.73, N 2.45.

### [1]Rotaxane 6:



Compound **3** (0.2 g, 0.140 mmol) was dissolved in DMSO (5 mL) and Ar-saturated sodium carbonate aqueous solution (20 mL, 0.2 mol/L), then the mixture was stirred at 60 °C for 20 h.<sup>3</sup> Compound **4** (0.12 g, 0.27 mmol), and palladium(II) acetate (8.0 mg, 0.038 mmol) were added and the mixture was stirred at

85 °C for 20 h under Ar atmosphere. Cooled and acidified with acetic acid, after concentrated in vacuo, the resulting dark solid was purified by column chromatography (silica gel, the upper layer of 1:2:5 acetic acid/n-butanol/water) to give pure **6** (50 mg, 21%) as yellow powder. M.p. > 250°C. <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO, 25 °C, TMS): δ= 8.68 (s, 2H), 8.57 (d, J=8.1 Hz, 1H), 8.50 (d, J=7.2 Hz, 1H), 7.90~7.85 (m, 3H), 7.80~7.75 (m, 4H), 7.51 (d, J=8.2 Hz, 2H), 7.35 (d, J=8.2 Hz, 2H), 7.18 (d, J=8.0 Hz, 2H), 6.25 (m, 14H), 5.27 (s, 2H), 4.95~4.70 (m, 7H), 4.45~4.05(m, 6H), 3.85~3.25 (m, 42H). <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 25 °C, TMS): δ= 9.04 (s, 1H), 8.92 (s, 1H), 8.87 (d, J=7.0 Hz, 1H), 8.68 (d, J=8.2 Hz, 1H), 8.11(dd, J=8.2 Hz, J=7.0 Hz, 1H), 7.90~7.70 (m, 10H), 6.94 (d, J=7.6 Hz, 2H), 5.58 (s, 2H), 5.2~4.9 (m, 7H), 4.35~3.3 (m, 41H). MALDI-TOF: m/z (%): 1724.46 (12) [M<sup>+</sup>+Na]; elemental analysis calcd (%) for C<sub>73</sub>H<sub>88</sub>N<sub>3</sub>NaO<sub>40</sub>S·6H<sub>2</sub>O: C 48.42, H 5.57, N 2.32; found C 48.58, H 5.43, N 2.40.



**Figure S1.** MALDI-TOF spectrum of [1]rotaxane **6**, the vertical arrow points at the m/z 1724.4.

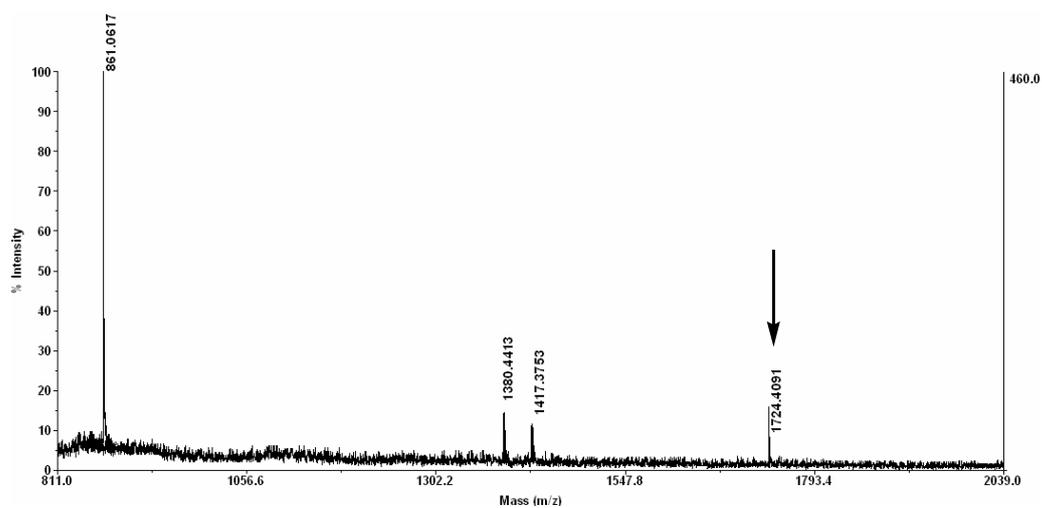


Figure S2. MALDI-TOF spectrum of compound **5**, the vertical arrow points at the  $m/z$  1724.4.

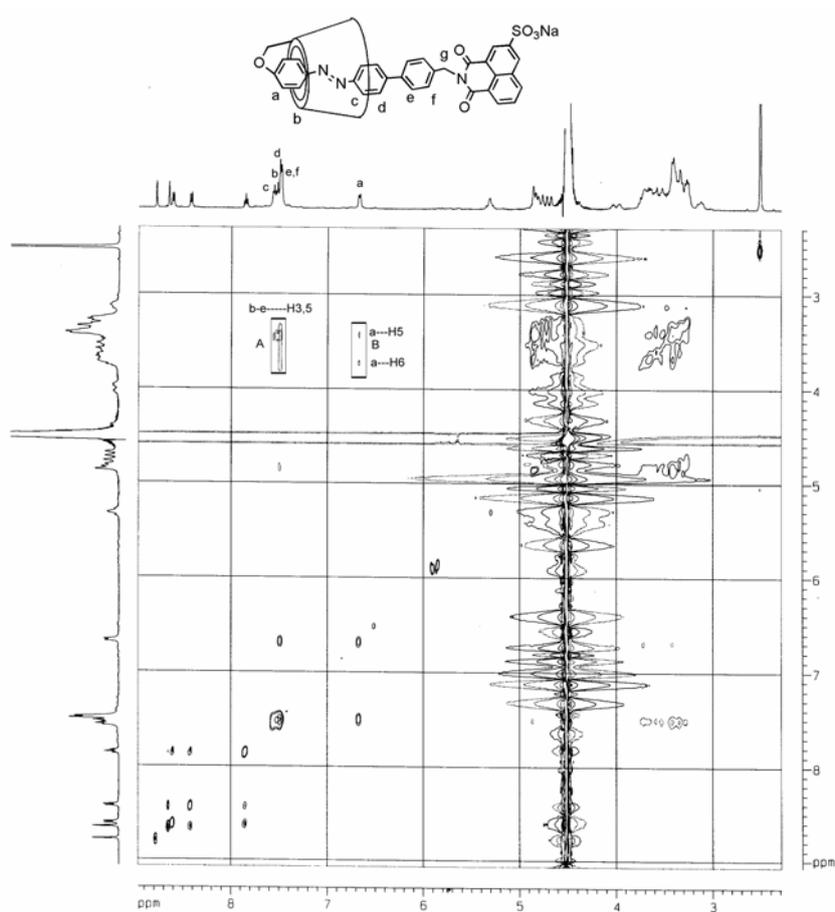
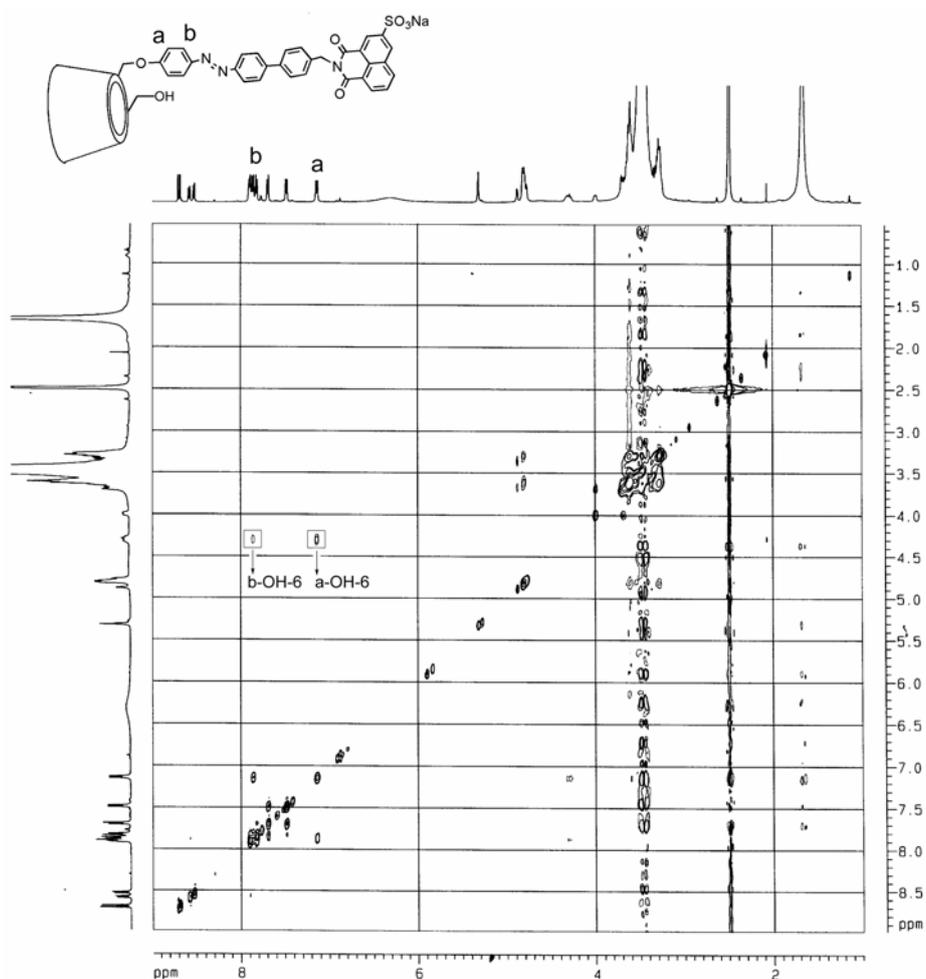


Figure S3. The two-dimensional  $^1\text{H}$  ROESY NMR spectrum of [1]rotaxane **6** (500 MHz in  $\text{D}_2\text{O}$  at 298 K, at a mixing time of 300 ms).



**Figure S4.** The two-dimensional <sup>1</sup>H ROESY NMR spectrum of **5** (500 MHz in [D<sub>6</sub>]DMSO at 298 K, at a mixing time of 300 ms).

The yield of the Suzuki coupling to prepare the reference compound **5** is low, this may be due to the different reaction media from that of [1]rotaxane **6**. The solvent system consisted of DMSO (25 ml) and H<sub>2</sub>O (5 ml) may not be very favorable for the catalysis of Pd(OAc)<sub>2</sub>, other organic Pd catalysts might work better in this solvent media.

## References

- [1] Y. Liu, Y.-L. Zhao, H.-Y. Zhang, Z. Fan, G.-D. Wen and F. Ding, *J. Phys. Chem. B* 2004, **108**, 8836.
- [2] D.-H. Qu, Q.-C. Wang, J. Ren and H. Tian, *Org. Lett.* 2004, **6**, 2085.
- [3] T. Fujimoto, Y. Sakata and T. Kaneda, *Chem. Commun.* 2000, 2143.