

# Supporting Information Available

## A Light-Powered Stretch-contraction Supramolecular System Based on Cobalt Coordinated [1]Rotaxane

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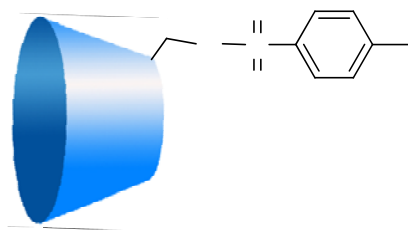
Figure S11. ICD spectral change for **C** ( $25^\circ\text{C}$   $1.2 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ) in  $\text{H}_2\text{O}$  by irradiation at 365 nm.

### Experimental Details

**Instruments:**  $^1\text{H}$  NMR spectra and the  $^{13}\text{C}$  NMR were measured on a Bruker AV-400 spectrometer, and the 2D-NOESY NMR spectra were recorded on a Bruker AV-500 spectrometer. The electronic spray ionization (ESI) mass spectra were tested on a HP5989 mass spectrometer. Elemental analysis was performed on a vario EL III instrument. Absorption spectra were done on a Varian Cary 500 UV/Vis spectrophotometer (1-cm quartz cell used), while the ICD spectra were recorded on a Jasco J-815 CD spectrophotometer in a 1 mm quartz cell. The photoirradiation was carried on a CHF-XM 500-W high-pressure mercury lamp with a filter for 365 nm in a sealed Ar-saturated 1 cm quartz cell. The distance between the lamp and the sample cell was 20 cm. Melting points were determined by using an X-6 micro-melting point apparatus.

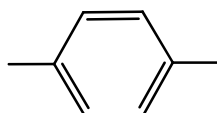
**Materials:**  $\beta$ -cyclodextrin ( $\beta$ -CD), 4-aminobenzoic acid, sodium nitrite, amido-sulfonic acid, salicylaldehyde and ethylene diamine were commercially available and used as received. Ethylene diamine platinum chloride was purchased from Alfa Aesar and used as received. MeOH and acetone were dried with anhydrous magnesium sulfate. Acetonitrile and DMF were dried by 4A molecular sieve and distilled under reduced pressure before used.

**Mono-6-deoxy-6-(*p*-tolylsulfonyl)-  $\beta$ -CyD (**6-TsO- $\beta$ -CyD**)**



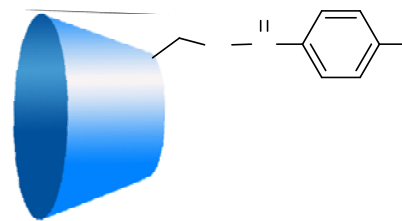
This compound was prepared according to the method reported previously.<sup>1</sup>

**Sodium 4-aminobenzoate (A)**



NaOH (2.92 g,  $7.3 \times 10^{-2}$  mol) and 4-aminobenzoic acid (10 g,  $7.29 \times 10^{-2}$  mol) were dissolved in EtOH (200 mL). The reaction was carried out with stirring under reflux for 1 hour. The precipitated product was filtered and washed with EtOH, then dried under vacuum at 70 °C. (Yield=92%). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO, 25°C, TMS):  $\delta$  = 7.67 (d, 2H), 6.76 (d, 2H).

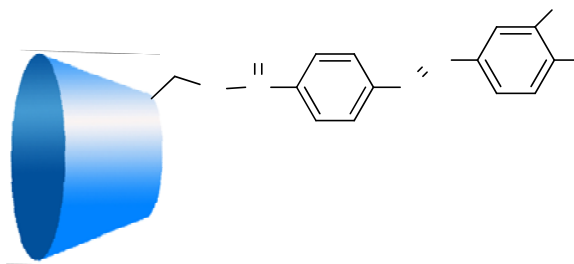
**Mono-6-deoxy-6-(4-aminobenzoyl)- $\beta$ -CyD (**B**)**



To a solution of DMF (40 mL) containing 3.24 g ( $2.51 \times 10^{-3}$  mol) of **6-TsO- $\beta$ -CyD** was added 1.0 g ( $6.28 \times 10^{-3}$  mol) of **A**. The resultant mixture was stirred at 60 °C for 3 days under nitrogen. After filtration the filtrate was concentrated in vacuum. Then 200 mL of acetone was added to give birth to the precipitate. The precipitate was collected by filtration to obtain a white powder. The crude product was washed with acetone (30 mL) and dried in vacuum, then was purified by column chromatography (silica gel, the upper layer of 1:3:5 acetic acid/n-butanol/water) to give pure **B** (yield=51%). <sup>1</sup>H NMR (500 MHz, [D<sub>6</sub>]DMSO, 25°C, TMS):  $\delta$  = 7.49 (d, 2H), 7.12 (d, 2H), 6.15~6.34 (m, 14H), 5.19 (d, 1H), 4.82 (m, 10H), 4.21~4.72 (m, 5H), 3.12~3.92 (m, 40H). ESI: m/z: 1276.3977 [M+Na]<sup>+</sup>

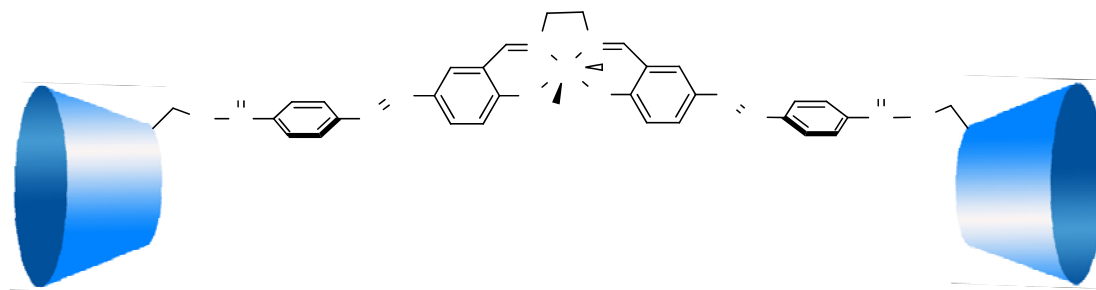
**6-Azo-CyD (C):**

NaOOC



**B** (2.0 g,  $1.6 \times 10^{-3}$  mol) and concd. HCl (0.51 mL) were stirring in water (10 mL) while sodium nitrite (0.12 g,  $1.73 \times 10^{-3}$  mol) was adding dropwise to keep the temperature between  $0^\circ\text{C}$  and  $3^\circ\text{C}$  for half an hour in 50mL flask. Then, some amido-sulfonic acid was added to remove the unreacted sodium nitrite. Sodium hydroxide (0.05 g) and salicylaldehyde (0.21 mL) in distilled water (50 mL) were stirring in a three-necked flask (250 mL). Then the acid solution was slowly added that three-necked flask, which was stirred for another 2 hours at  $0^\circ\text{C}$ . The precipitate was collected and dried to give an orange powder, which was stirred in light petroleum (150 mL) for 1 hour and then filtered to give pure products in a yield of 32 %. M.p.  $264\text{-}267^\circ\text{C}$ .  $^1\text{H NMR}$  (500 MHz,  $\text{D}_2\text{O}$ ,  $25^\circ\text{C}$ , TMS):  $\delta = 10.26$  (s, 1H), 8.33 (s, 1H), 7.96 (d, 1H), 7.70 (d, 2H), 7.38 (d, 2H), 6.90(d, 1H), 5.10(s, 1H), 4.97(m, 6H), 3.10~4.12(m, 42H).  $^1\text{H NMR}$  (500 MHz,  $[\text{D}_6]\text{DMSO}$ ,  $25^\circ\text{C}$ , TMS):  $\delta = 10.13$ (s, 1H), 8.06(d, 2H), 7.92(s, 1H), 7.76(d, 3H), 6.35(d,1H), 5.70~5.76(m, 18H), 4.83~4.91(m, 3H), 4.39~4.60(m, 10H), 4.0(s, 1H), 3.55~3.66(m, 35H). ESI: m/z: 1409.1  $[\text{M}+\text{Na}]^+$  Elemental analysis calcd. for **C** ( $\text{C}_{56}\text{H}_{78}\text{N}_2\text{O}_{38}$ ): C 48.47; H 5.65; N 2.02; O 43.86.

#### RASC-Co :



**C** (0.36 g, 0.256 mmol) and ten equivalents of 1-adamantanol (0.39 g, 2,56 mmol) were dissolved in  $\text{H}_2\text{O}$  (50 mL) and the mixture was stirred at  $60^\circ\text{C}$  for 24 h, then ethylene diamine ( $17\ \mu\text{L}$ , 0.255 mmol) was added in this solution. After 4 hours, another ethylene diamine (0.02 mL) was added and stirred for 1 hour. Finally, the solution was extracted by dichloromethane ( $30\ \text{mL} \times 5$ ) for 5 times, then concentrated and dialyzed through a 2000 MWCO cellulose membrane with distilled water (5 L) for 1 week. Removal of the solvent under reduced pressure and drying under vacuum at  $60^\circ\text{C}$  gave the product as a red solid **RASC** (50 mg). **RASC** (50 mg, 0.011 mmol) was dissolved in  $\text{H}_2\text{O}$  (15 mL),  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (13.3 mg, 0.053 mmol) was dissolved in  $\text{H}_2\text{O}$  (3.0 ml) and added dropwise to the solution then the mixture was stirred at  $60^\circ\text{C}$ . After 3 hours, the

solution was concentrated and dialyzed through a 2000 MWCO cellulose membrane with distilled water (1 L) for 1 day. Removal of the solvent under reduced pressure and drying under vacuum at 60 °C gave the product as a dark red solid (32 mg, 62.7%). M.p. >310 °C. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 25 °C, TMS): δ = 10.07 (s, 1H), 8.06 (s, 1H), 8.01 (d, 2H), 7.88 (d, 1H), 7.73 (d, 2H), 6.87 (d, 1H), 4.95~4.96 (m, 6H), 3.50~3.80 (m, 53H), 2.94 (d, 1H), 2.78 (d, 1H). MALDI-TOF: m/z (%)1451.5283 [M+Na-H<sub>2</sub>O]<sup>2+</sup>.

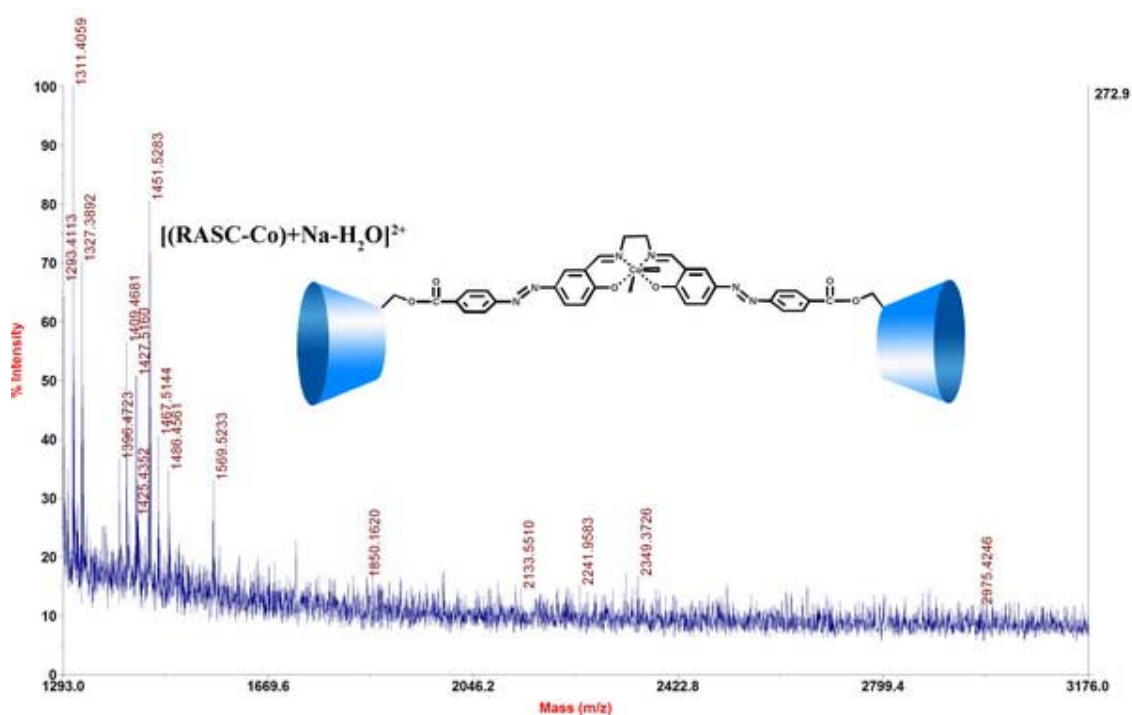
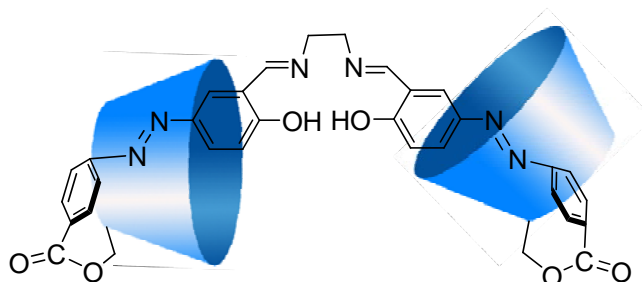


Figure S1. MALDI-TOF spectrum of RASC-Co.

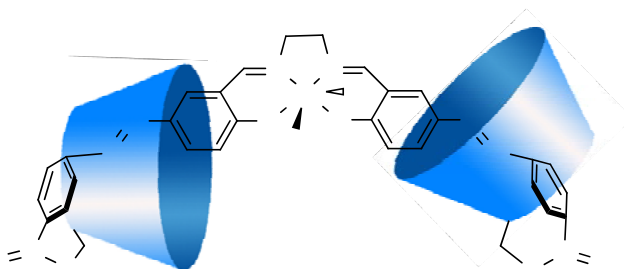
### [1]Rotaxane (ASC) :



C (0.36 g, 0.256 mmol) was dissolved in H<sub>2</sub>O (50 mL) and the mixture was stirred at 60 °C for 24 h, then ethylene diamine (17 μL, 0.255 mmol) was added in this solution. After 4 hours, another ethylene diamine (0.02 mL) was added and stirred for 1 hour. Finally, the solution was concentrated and dialyzed through a 2000 MWCO cellulose membrane with distilled water (5 L) for 1 week. Removal of the solvent under reduced pressure and drying under vacuum at 60 °C gave the product as a dark red solid (103 mg, 28.5%). M.p. >310 °C. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 25 °C, TMS): δ = 9.85 (s, 1H), 8.32 (d, 2H), 7.87 (d, 2H), 7.72 (d, 1H), 7.22 (s, 1H), 7.08 (d, 1H),

4.78~5.25(m, 6H), 3.20~4.70(m, 42H), 2.75(d, 1H), 2.41(d, 1H).

[1]Rotaxane-Co (ASC-Co) :



ASC (90 mg, 0.019 mmol) was dissolved in H<sub>2</sub>O (20 mL), Co(OAc)<sub>2</sub>·4H<sub>2</sub>O (24 mg, 0.096 mmol) was dissolved in H<sub>2</sub>O (3.0 ml) and added dropwise to the solution then the mixture was stirred at 60 °C. After 3 hours, the solution was concentrated and dialyzed through a 2000 MWCO cellulose membrane with distilled water (1 L) for 1 day. Removal of the solvent under reduced pressure and drying under vacuum at 60 °C gave the product as a dark red solid (73 mg, 80.2%). M.p. >310 °C. <sup>1</sup>H NMR (500 MHz, D<sub>2</sub>O, 25°C, TMS): δ = 9.82 (s, 1H), 8.32 (d, 2H), 7.87 (d, 2H), 7.69(d, 1H), 7.52 (s, 1H), 7.05(d, 1H), 4.9~5.1(m, 6H), 3.20~4.40(m, 42H), 2.73(d, 1H), 2.439(d, 1H). MALDI-TOF: m/z: 1451. 5336[M+Na-H<sub>2</sub>O]<sup>2+</sup>

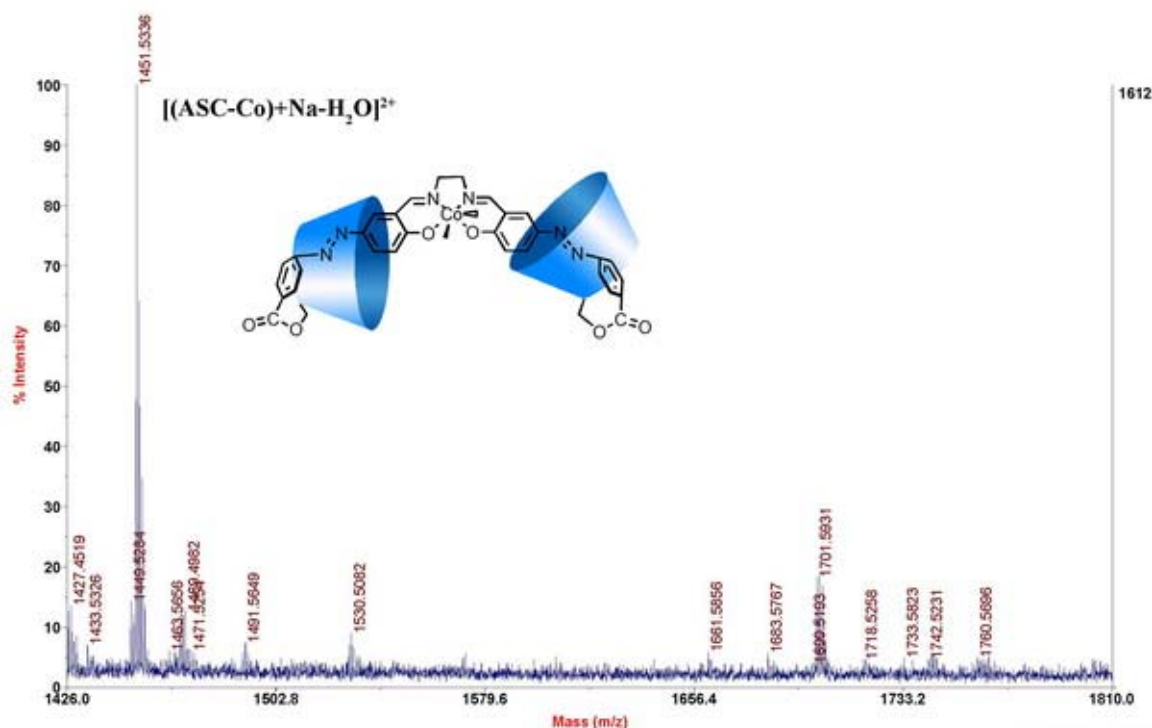


Figure S2. MALDI-TOF spectrum of ASC-Co.

<sup>1</sup>H NOESY NMR analysis

N  
O C

N  
N

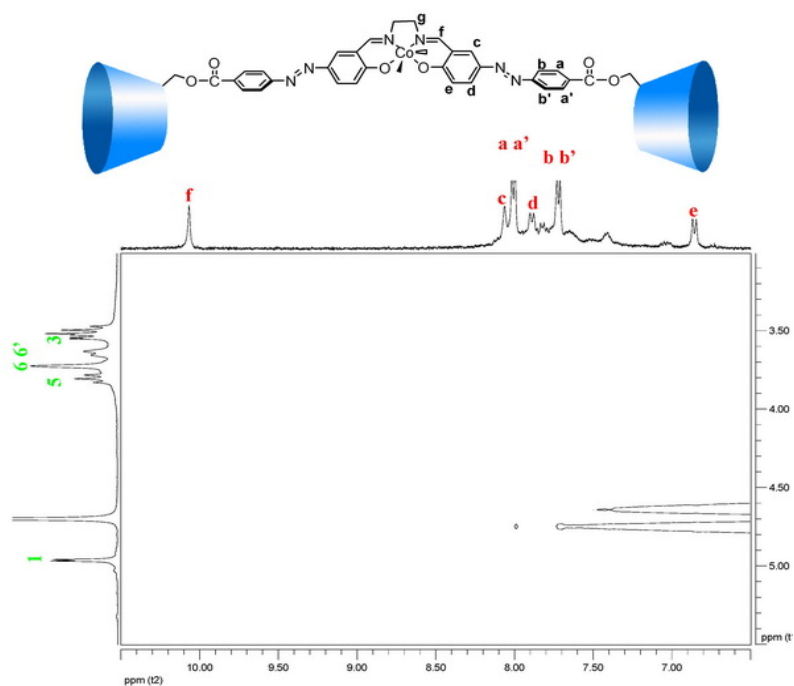


Figure S3.  $^1\text{H}$  NOESY NMR Spectrum of **RASC-Co** in  $\text{D}_2\text{O}$ .

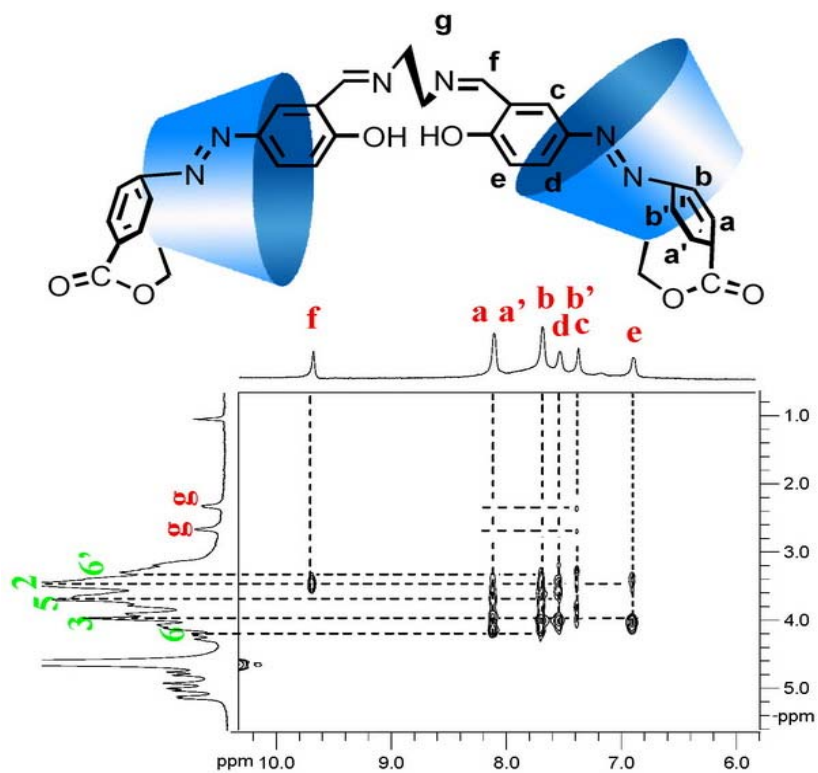


Figure S4. Partial  $^1\text{H}$  NOESY NMR Spectrum of **ASC** in  $\text{D}_2\text{O}$ .

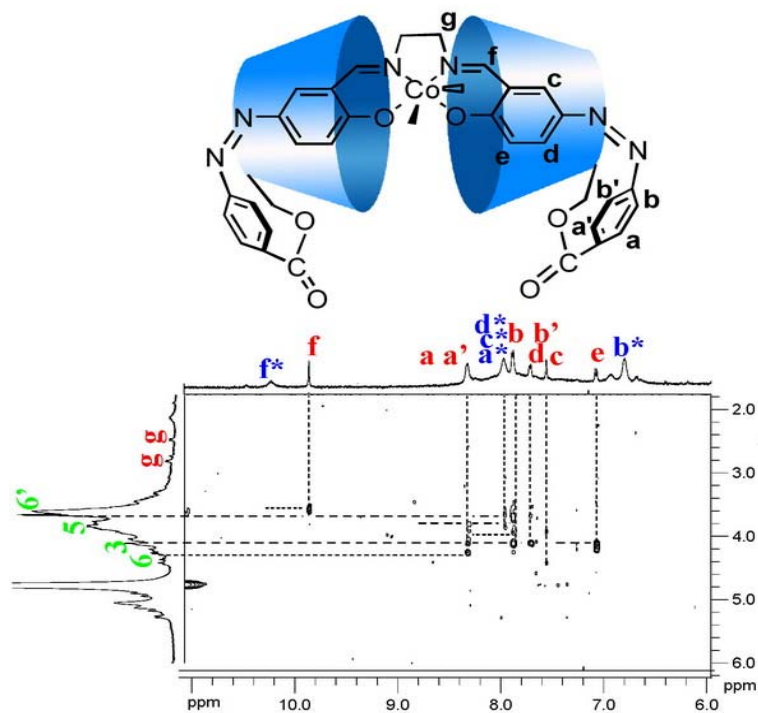


Figure S5. Partial  $^1\text{H}$  NOESY NMR Spectrum of *trans*-ASC-Co in  $\text{D}_2\text{O}$ .

### Calculated structure analysis

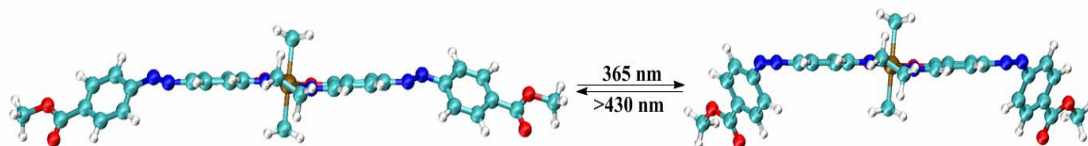


Figure S6. Calculated structure of RASC-Co shaft from *trans*- to *cis*- after irradiation

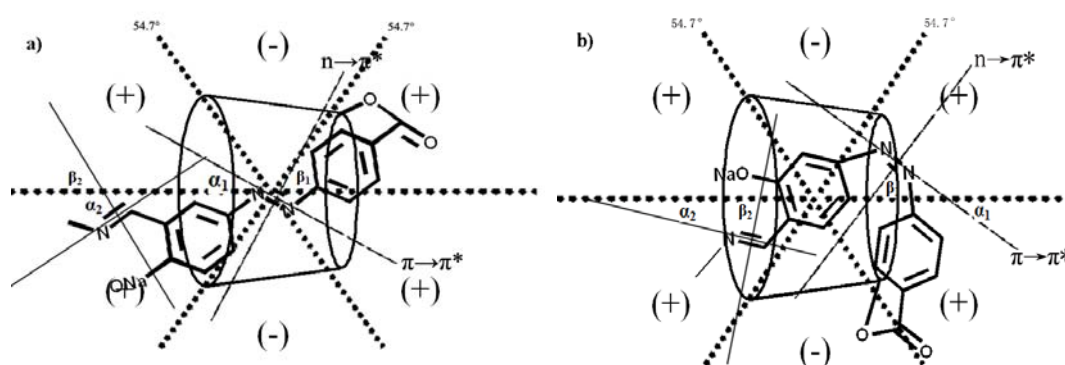


Figure S7. Relationship of the angles  $\alpha_1$ ,  $\beta_1$ ,  $\alpha_2$ ,  $\beta_2$  and positions between  $\beta$ -CyD ring and the linear subunit before (a) and after (b) the photoisomerization of azobenzene moiety and Schiff base unit in aqueous solution about ASC.  $\alpha_1$ ,  $\alpha_2$  are the angles between the axis and the orientation of  $\pi \rightarrow \pi^*$  transition which are separately belong to azobenzene moiety and Schiff base unit while

$\beta_1, \beta_2$  are the angles between the axis and the orientation of  $n \rightarrow \pi^*$  transition.

### Optical spectrum analysis

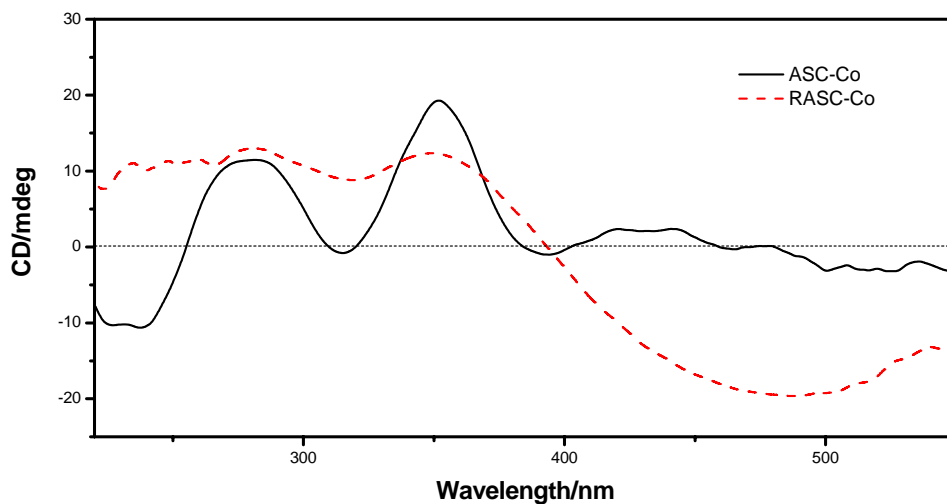


Figure S8. ICD spectra for **RASC-Co** and **ASC-Co** (25°C,  $1.2 \times 10^{-4}$  mol·dm<sup>-3</sup>) in aqueous solution.

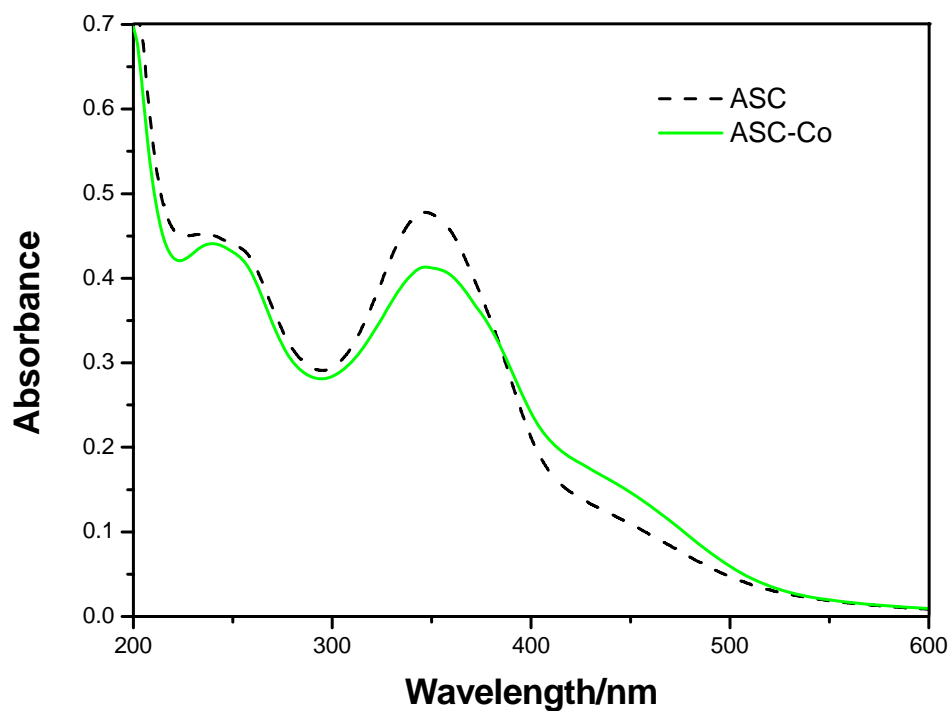


Figure S9. UV/Vis absorption spectra of **ASC-Co** ( $1.1 \times 10^{-5}$  mol·dm<sup>-3</sup>, solid) and **ASC** ( $1.1 \times 10^{-5}$  mol·dm<sup>-3</sup>, dish) in H<sub>2</sub>O at 298K.



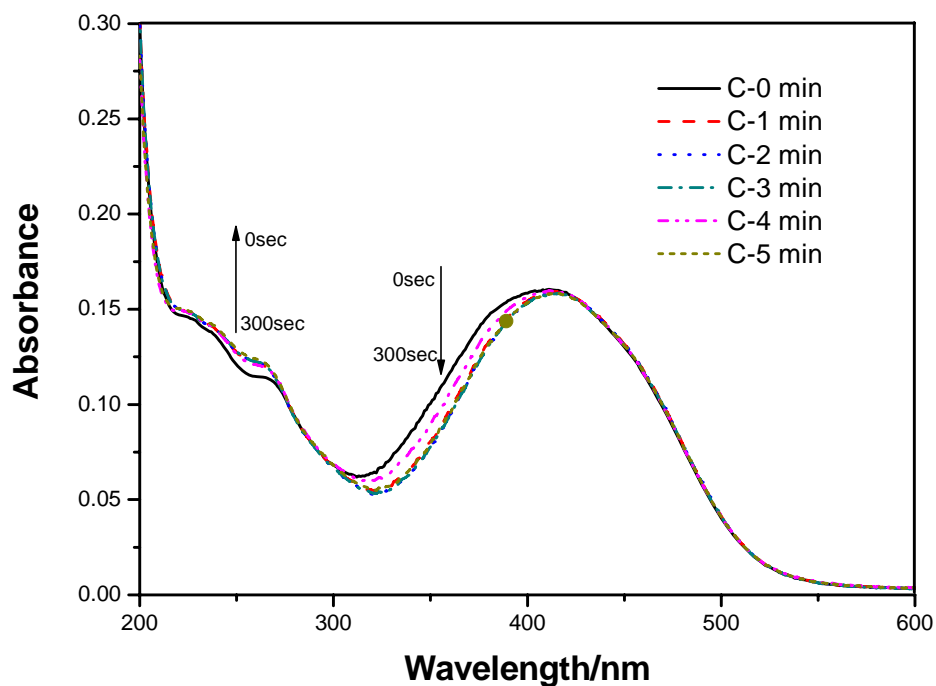


Figure S10. UV/Vis spectral ( $25^{\circ}\text{C}$ ,  $1.3 \times 10^{-5} \text{ mol}\cdot\text{dm}^{-3}$ ) change for **C** in  $\text{H}_2\text{O}$  by irradiation at 365 nm

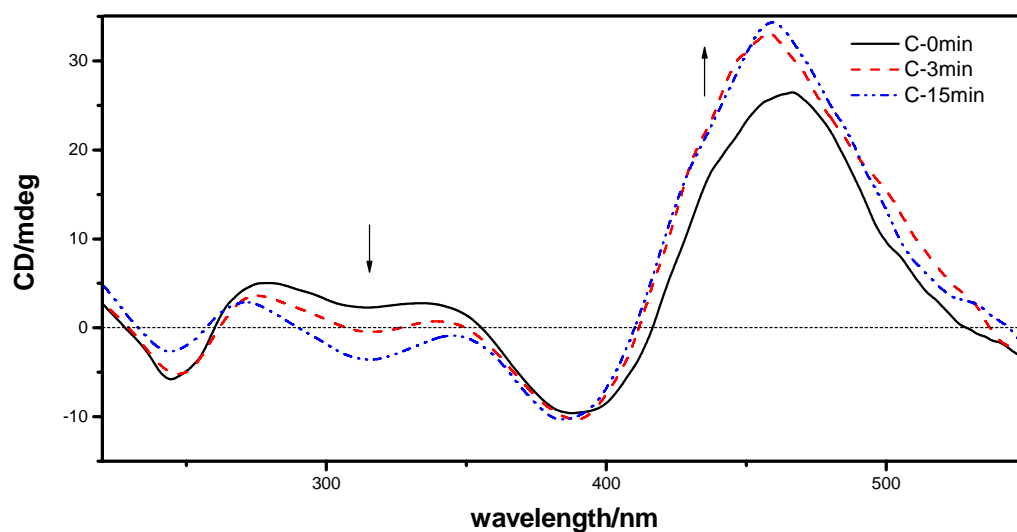


Figure S11. ICD spectrum change for **C** ( $25^{\circ}\text{C}$ ,  $1.2 \times 10^{-4} \text{ mol}\cdot\text{dm}^{-3}$ ) in  $\text{H}_2\text{O}$  by irradiation at 365 nm.

### References

- (1) K. Takahashi, K. Hattori and F. Toda, *Tetrahedron Lett.* 1984, **25**, 3331-3334.
- (2) Y. Liu, Y.-L. Zhao, H.-Y. Zhang, Z. Fan, G.-D. Wen and F. Ding, *J. Phys. Chem. B* 2004, **108**, 8836-8843.
- (3) D.-H. Qu, Q.-C. Wang, J. Ren and H. Tian, *Org. Lett.* 2004, **6**, 2085-2088.
- (4) X. Ma, D.-H. Qu, F.-Y. Ji, Q.-C. Wang, L.-L. Zhu, Xu, Y. and H. Tian, *Chem. Commun.* 2007, 1409-1411.