Electronic Supplementary Information

INHIBIT logic operations based on light-driven *β*-cyclodextrin pseudo[1]rotaxane with room temperature phosphorescence addresses

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Experimental section

Materials

All reagents and solvents were commercially available and used without further purification. *β*-Cyclodextrin (*β*-CD) was purchased from Acros and used as received. Mono[6-O-(4-methyl-phenylsulfonyl)]- *β*-cyclodextrin (6-OTs-*β*-CD) was synthesized in our laboratory.[1] H_2O was distilled twice before use.

Instruments

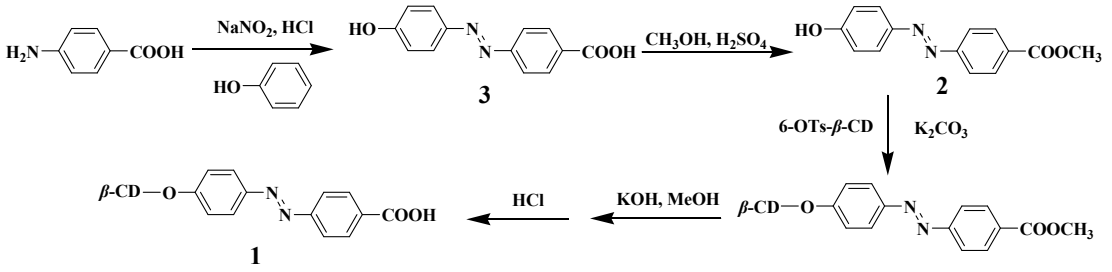
^{1}H-NMR spectra were measured on a Brüker AM 400 spectrometer at 25 °C. UV/Vis spectra were obtained on a Varian Cary 500 spectrophotometer (1 cm quartz cell used) at 25 ºC. The ICD spectra were obtained on a Jasco J-815 CD spectrophotometer with 1 mm quartz cell at 25 ºC. Melting points were determined on a Reichert Thermovar apparatus and reported uncorrected. 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 or 1 mm quartz cell. The distance between the lamp and the sample cell is 20 cm.

RTP spectra were carried out on a Varian Cary Eclipse Fluorescence Spectrophotometer equipped with a phosphorescence attachment at room temperature (1 cm quartz cell used). A 150 W Xenon-pulsed lamp was used as the excitation light source and Obey-Decay application program was used for phosphorescence lifetime measurements. The instrument's main parameters are as follows: delay time 0.1 ms, gate time 2.0 ms, cycle time 20 ms, flash count 1, ex slit 20 nm, em slit 20nm, scan

speed 400 nm min^{-1}.

Procedure for preparation of the aqueous *β*-CD-Azo/BrNp solution: Mixing 0.2 mL aqueous *α*-BrNp solution (40% CH_3CN, 2.0×10^{-3} mol/L), 2mL aqueous solution of *β*-CD-Azo (1.0×10^{-2} mol/L) together in a 10 mL colorimeter tube, and then using water to dilute the solution to 10 mL. Airproof the colorimeter tube and shake up the solution for 1.5 min. Then in the ternary solution, the concentration of the respective component was as following: [*α*-BrNp] =4.0×10^{-5} mol/L, [*β*-CD-Azo] = 2.0×10^{-3} mol/L. After standing for 30 min, the solution was displaced in a 1cm quartz cell with sealed cover for UV and RTP testing, and 1 mm quartz cell for ICD measurement.

Scheme S1 **Synthesis route of *β*-CD-Azo.**



Synthesis of 4-[2-(4-hydroxyphenyl)diazenyl]benzoic acid (3)

4-amino-benzoic acid (4.00g, 29.17mmol) was dissolved in a solution of hydrochloric acid (36%, 4.86 ml) and water (2.60 ml), and then the solution was stirred at 0 °C for 10 min. A solution of sodium nitrite (2.42g, 35.00mmol) in water was added slowly to yield a solution of diazonium salt. The reaction was stirred for another 20 min, and then stopped by adding a litter urea to remove redundant sodium nitrite. The diazonium salt was slowly added to a solution of phenol (3.02g, 32.12 mmol) dissolved in aqueous sodium hydroxide (3.80g) at 0 °C. After stirring for 20 min, diluted HCl solution was added. The orange product was then collected by filtration and recrystallized from ethanol to obtain 4-[2-(4-hydroxyphenyl)diazenyl]-benzoic acid (yield 75%). M.p. 272-273°C (dec.); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (d, *J* = 8.6 Hz, 2H), 7.90 (d, *J* = 11.2, 2H), 7.87 (d, *J* = 8.8 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H). ^{13}C HMR (400 MHz, DMSO-d_6) δ 165.64, 161.75, 154.69, 145.27, 130.49, 130.37, 125.34, 122.15, 116.04. IR: 3600-3100 cm^{-1}, 2976cm^{-1}, 1717 cm^{-1}, 1642 cm^{-1}, 1600-1430 cm^{-1}, 784 cm^{-1},1400 cm^{-1}, 839 cm^{-1}.

Synthesis of 4-[2-(4-hydroxyphenyl)diazenyl]-benzoic acid-methyl ester (2)

A solution of above product **3** (6.00g, 24.77mmol) dissolved in methanol (60ml) was heated and added with conc. sulfuric acid (98%, 6 ml). The mixture was refluxed under Ar for 4 h. After most solvent was evaporated under vacuum pressure, the solution was cooled to room temperature and added in water (50 mL). The resulting precipitate was filtered and washed with water. The desired product was obtained by recrystallization with EtOH as yellow solid. (yield 90%). M.p. 223-225°C (dec.); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.12 (d, ^{3}J=8.6 Hz, 2H,), 7.91 (d, ^{3}J=8.6 Hz, 2H), 7.86 (d, J = 8.9 Hz, 2H), 6.97 (d, ^{3}J=8.9 Hz, 2H), 3.89 (s, 3H). ^{13}C HMR (400 MHz, DMSO-d_6) δ 52.240, 116.039, 122.149, 125.343, 130.368, 130.485, 145.275, 154.684, 161.754, 165.641. IR: 3600-3100 cm^{-1}, 2960cm^{-1}, 1781 cm^{-1}, 1594 cm^{-1}, 1600-1430 cm^{-1}, 789 cm^{-1},1402 cm^{-1}, 939 cm^{-1}. ESI-MS: m/z calcd for $C_{14}H_{13}N_2O_3$ [M + H^+] 257.0926, found 257.0919.

Synthesis of compound *β*-CD-Azo (1) [2]

To a stirred solution of 1.0 g of 6-OTs-*β*-CD and 0.2 g of K_2CO_3 in dry DMF (15 mL) was added 0.3 g of product **2**. The mixture was stirred at 90 °C for 3 days under Ar, and then cooled to room temperature and filtered. The solvent was evaporated, and the residue solid was washed with acetone and purified by column chromatography (silica gel, the upper layer of 1:2:5 acetic acid/*n*-butanol/water). The pure product **1** was obtained by washing with acetone (40 mL) again and drying in vacuo as yellow solid (65%), which was hydrolyzed by the usual method (KOH/CH_3OH). The reaction was refluxed until that TLC indicates that hydrolysis is complete, and the solution was adjusted to pH 3-4 with hydrochloric acid. The desired product **1** was obtained by filtration as yellow solid (95%). M.p. > 250°C. ^{1}H NMR (400 MHz, D_2O) δ 8.14 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 6.70 (d, J = 8.5 Hz, 2H), 4.99 - 4.70 (m, 21H), 4.14 - 2.95 (m, 48H); ^{13}C HMR (400 MHz, D_2O) δ 181.55, 161.24, 130.25, 124.40, 121.42, 114.50, 102.00, 81.93, 80.60, 72.95, 72.02, 71.73, 59.82. Elemental analysisi calcd (%) for $C_{55}H_{78}N_2$: C 48.60, H 5.78, N 2.06, found C 48.27, H 5.46, N 1.04. ESI-MS: m/z calcd for $C_{55}H_{77}N_2O_{37}$ [M – H^+] 1357.4205, found 1357.4031.

^{1}H NMNR spectroscopy and 2D ^{1}H ROESY NMR spectroscopy of *β*-CD-Azo in D_2O

Fig. S1A shows the spectral changes in ^{1}H NMR spectra of *β*-CD-Azo in D_2O solution at 298K after light irradiation for 2h and 4h. Irradiation at 360 nm for 4h leads to several new signals for *cis*-azobenzene unit, appearing at δ 7.94, 7.61, 6.98, 6.76, and 6.32 ppm, respectively. This is reasonable because the signals of the aromatic protons of the azobenzene unit generally shift upfield upon their isomerization form *trans* to *cis* configuration, as a result of the magnetic shielding effect of aromatic rings. Integrals of the two signals for H_a appear with a 2:3 ratio, which suggests that, at the photostationary state, about 60% of *trans* isomer was transformed to *cis* isomer. In addition, the spectral change can be shifted back by irradiation at 430 nm for 4h. It should be noted that a bit decrease of the whole intensity of signals is attributed to the reducing of the water solubility of the *cis*-*β*-CD-Azo in high concentration (about 5.8 $\times 10^{-2}$ M).

Fig. S1B illustrated the ROESY spectrum of *β*-CD-Azo in D_2O, which displayed the clear NOE correlations between the protons of *β*-CD and the $H_a/H_b/H_c/H_d$ protons of the azobenzene moiety (cross-peaks A, B, C, D). These correlations indicated that the azobenzene moiety is deeply self-included in the hydrophobic cavity of the *β*-CD.

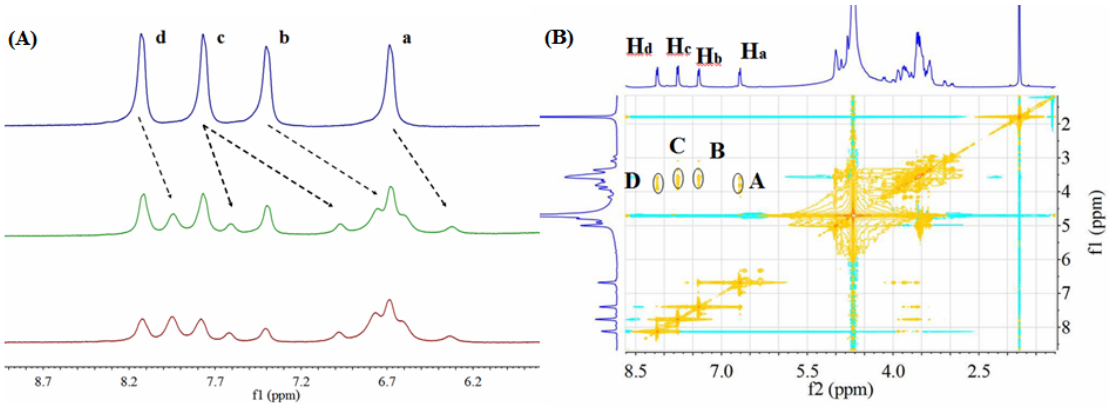


Fig. S1 (A) Partial ^{1}H NMR spectra of *β*-CD-Azo pseudo[1]rotaxane (top, 298K, D_2O), and after irradiation at 360nm for 2h (middle) and 4h (bottom); (B) The two-dimensional ^{1}H ROESY NMR spectrum of *β*-CD-Azo pseudo[1]rotaxane (298K, D_2O, at a mixing time of 300 ms).

UV spectra of aqueous ***α*-BrNp, *β*-CD-Azo, *β*-CD-Azo /*α*-BrNp（1:1）solution**

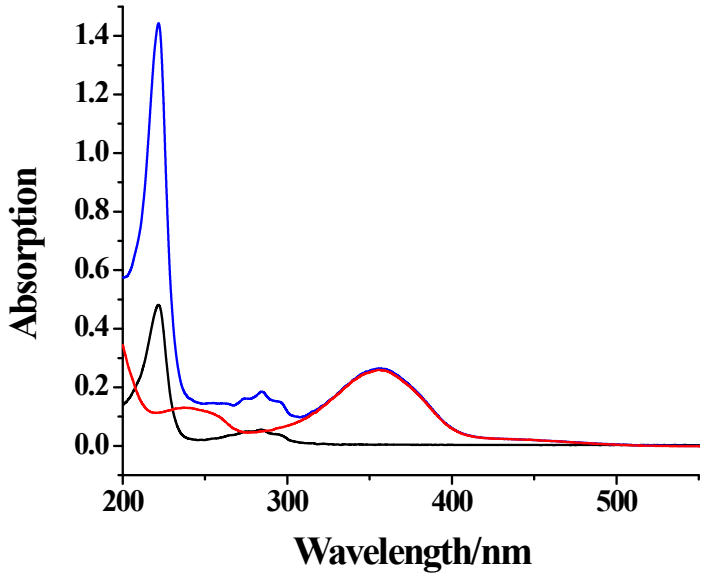


Fig. S2 UV spectra of aqueous α-BrNp solution (black, containing a little CH_3CN, 2.0×10^{-5} mol/L), aqueous β-CD-Azo solution (red, 2.0×10^{-5} mol/L), and aqueous β-CD-Azo/α-BrNp solution (blue, containing a little CH_3CN, [α-BrNp] = 2.0×10^{-5} mol/L, [β-CD-Azo] = 2.0×10^{-5} mol/L)

UV spectra of aqueous solution of β-CD-Azo after irradiation with different lights

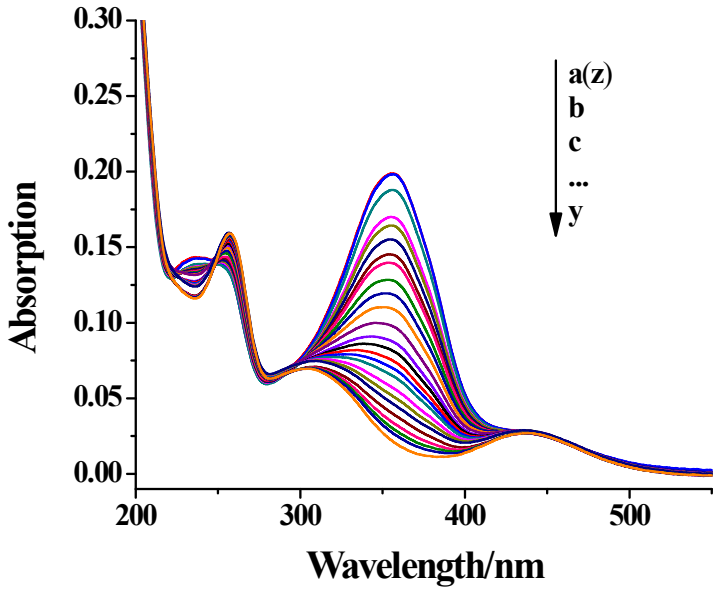


Fig. S3 UV spectra of aqueous β-CD-Azo solution (**a**, 2.0×10^{-5} mol/L), and after

irradiation by 360 nm light for 2s (**b**), 4s (**c**), 6s (**d**), … , 2 min (**y**). And the spectral change can be shifted back by 430 nm for 2 min (**z**)

Owning to the *trans-cis* isomerization of *β*-CD-Azo, the irradiation with 360nm light to the aqueous solution of *β*-CD-Azo leads to a gradual decrease in the intensity of the maximal absorption peak at about 368nm, as shown in Fig. S3 (curve **a**, ……, **y**). The UV spectral changes can be shifted back by irradiation at 430 nm for 60 min (curve **z**).

UV spectra of *β*-CD-Azo /*α*-BrNp solution after irradiation with different lights

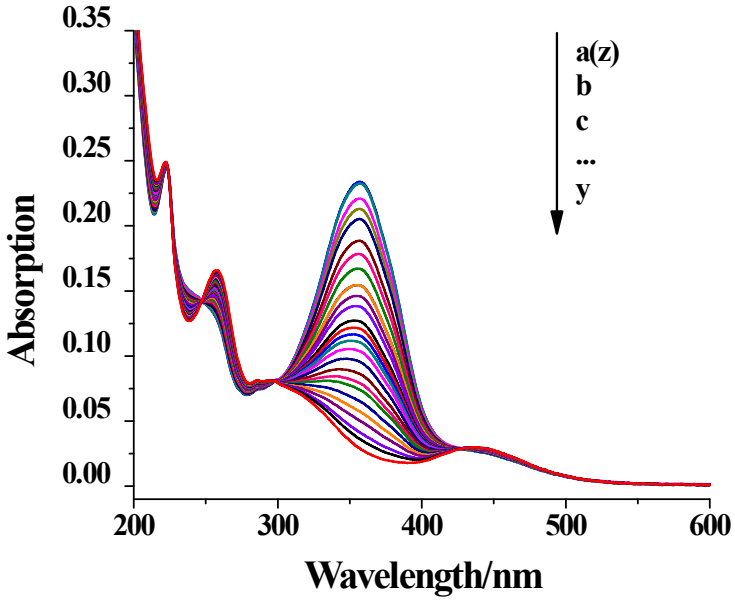


Fig. S4 UV spectra of aqueous *β*-CD-Azo /*α*-BrNp solution (**a**, containing a little CH_3CN, [*α*-BrNp] = 2.0×10^{-5} mol/L, [*β*-CD-Azo] = 2.0×10^{-5} mol/L), and after irradiation by 360 nm light for 2s (**b**), 4s (**c**), 6s (**d**), … , 2 min (**y**). And the spectral change can be shifted back by 430 nm for 2 min (**z**)

As shown in Fig. S4, the absorption spectra of aqueous *β*-CD-Azo/*α*-BrNp solution exhibit dramatic changes after light irradiation for 2 min. Owning to the *trans-cis* isomerization of *β*-CD-Azo, irradiation with 360nm to the aqueous *β*-CD-Azo/*α*-BrNp solution generates some gradual changes, which including a decrease in absorption at around 238 nm, a rise at about 256 nm and an evident decrease at the maximum absorption peak of *β*-CD-Azo around 357 nm, as well as the presence of two

isoabestic points at about 247nm and 298nm(curve **a**, ……, **y**). The absorption signals of *α*-BrNp at 284nm and 222nm experience slight changes after irridation with UV lights, as the relatively lower concentration of *α*-BrNp (4.0×10^{-7} M) than the *β*-CD-Azo (2.0×10^{-5} M), but a little increase at 284nm and 222nmm can still be found assigned to *α*-BrNp included into *β*-CD cavity. Upon irradiation at 430 nm for 2 min, the absorption spectrum shows almost the same equality with that of the original one (curve **z**).

ICD spectra of aqueous solution of *β*-CD-Azo after irradiation with different lights

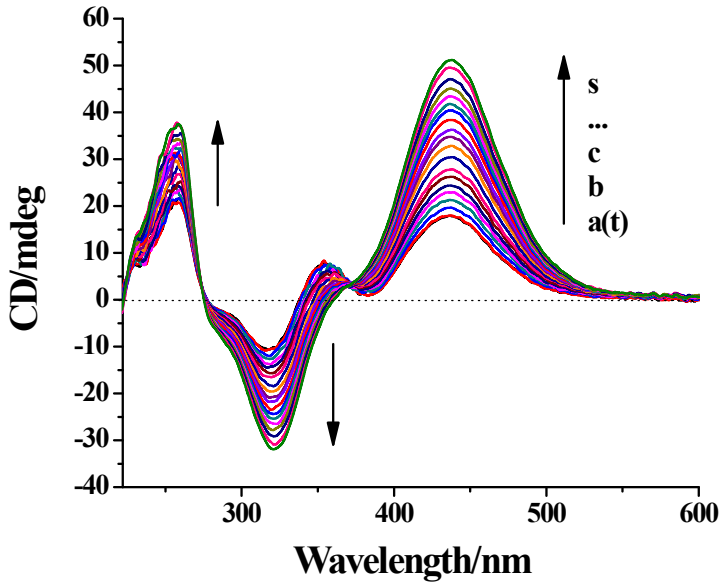


Fig. S5 ICD spectrum of aqueous *β*-CD-Azo solution (**a**, 2.0×10^{-3} mol/L), and after irradiation by 360 nm light for 2s (**b**), 4s (**c**), 6s (**d**), … , 2 min (**s**). And the spectral change can be shifted back by 430 nm for 2 min (**t**). 1mm quartz cell was used.

ICD spectrum of aqueous solution of *β*-CD-Azo/*α*-BrNp after irradiation with different lights

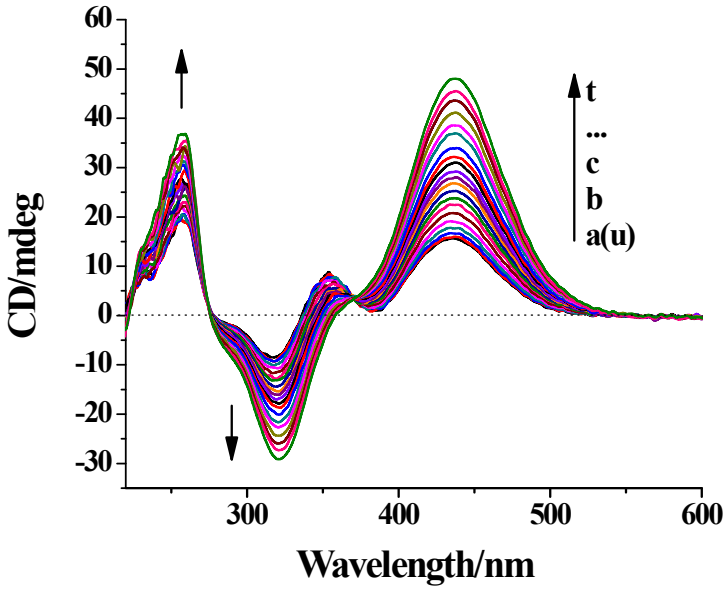


Fig. S6 ICD spectrum of aqueous *β*-CD-Azo/*α*-BrNp solution (**a**, [*β*-CD-Azo] = 2.0×10^{-3} mol/L, [*α*-BrNp] = 4.0×10^{-5} mol/L), and after irradiation by 360 nm light for 2s (**b**), 4s (**c**), 6s (**d**), … , 2 min (**s**). And the spectral change can be shifted back by 430 nm for 2 min (**t**). 1 mm quartz cell was used.

Owing to the *trans-cis* photoisomerization of azobenzene unit in *β*-CD-Azo pseudo[1]rotaxane, and its subsequent dethreading out of the *β*-CD cavity, the irradiation with 360nm light to this binary system results in a gradual increase of the Cotton peak intensity at around 258nm and 436nm, but decrease at about 320nm (Fig. S6, curve **a**, **b**, …, **t**). And the ICD spectral changes can be shifted back by irradiation at 430 nm (curve **u**). It should be noted that the intensity of maximum peak of the ICD spectra in the binary system is beyond the detection limit using 1 cm quartz cell, so 1 mm quartz cell was more appropriate to use at the same concentration with the RTP measurements ([*β*-CD-Azo] = 2.0×10^{-3} mol/L, [*α*-BrNp] = 4.0×10^{-5} mol/L).

The ICD intensity increases at 258 nm by about 197% (from 19.02 mdeg to 37.54 mdeg), at 436 nm by about 286% (from 17.89 mdeg to 51.11 mdeg), the decrease at 320 nm by about 301% (from -10.57 mdeg to -31.85 mdeg) after irradiation within a time of 2 min (curve **t**). The characteristic ICD signal of the *α*-BrNp/CD is unobvious.

RTP spectrum of aqueous solution of *β*-CD-Azo/*α*-BrNp after irradiation with

different lights

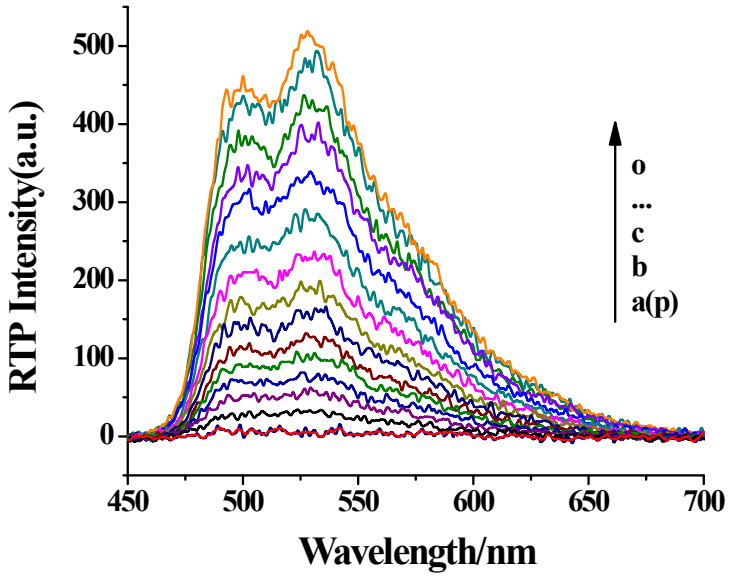


Fig. S7 RTP spectrum of aqueous *β*-CD-Azo/*α*-BrNp solution (**a**, containing a little CH_3CN, [*α*-BrNp]= 4.0×10^{-5} mol/L, [*β*-CD-Azo]= 2.0×10^{-3} mol/L), and after irradiation by 360 nm light for 2 min (**b**), 4 min (**c**), 6 min (**d**), 8 min (**e**), 10 min (**f**), 15 min (**g**), 20 min (**h**), 25 min (**i**) ,30 min (**j**), 35 min (**k**), 40min (**l**), 45 min (**m**), 50 min (**n**), 60 min (**o**); then by 430 nm for 60 min (**p**).

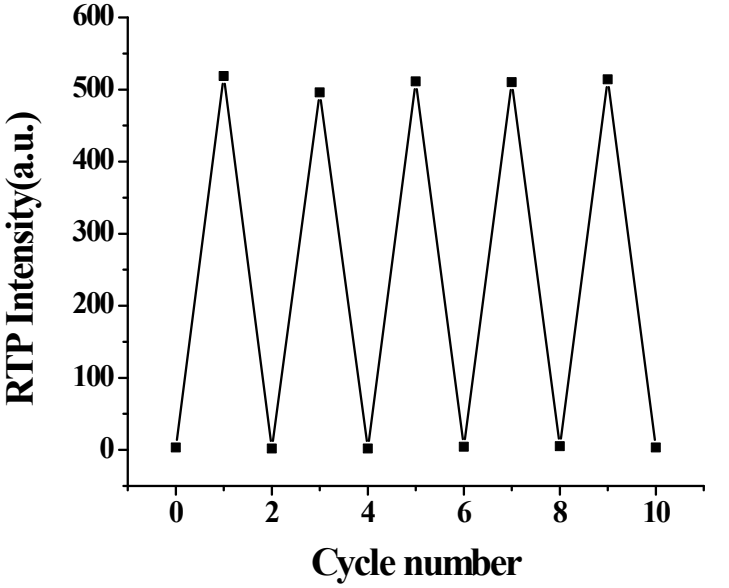


Fig. S8 Changes in the RTP intensity of aqueous *β*-CD-Azo/*α*-BrNp solution at 528

nm along with changes in irradiation time and light source. Light sources of 360 and 430 nm UV light were alternated every 60 min.

RTP lifetime of aqueous *β*-CD-Azo/*α*-BrNp solution

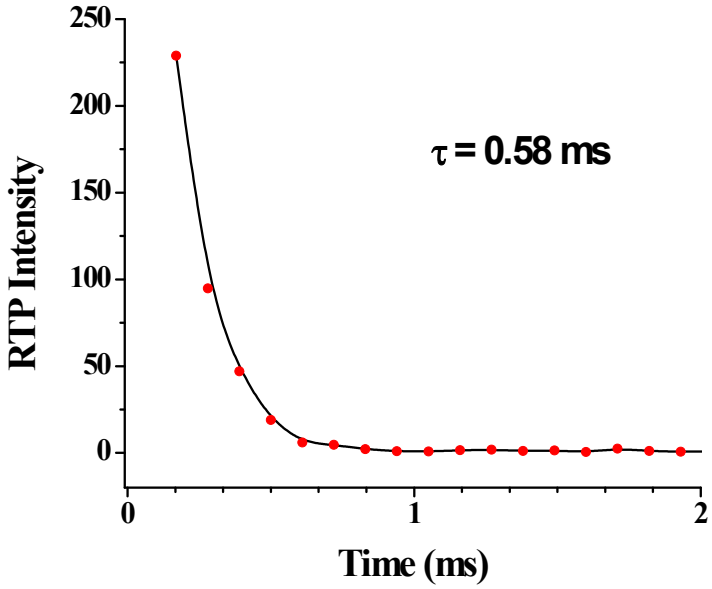


Fig. S9 RTP lifetime of aqueous ternary *β*-CD-Azo/*α*-BrNp solution (containing a little CH_3CN, [*α*-BrNp] =4.0×10^{-5} M, [*β*-CD-Azo] = 2.0×10^{-3} M)

The room temperature phosphorescence spectrum of *β*-CD-Azo/*α*-BrNp binary system in aqueous solution is shown in Fig. S7. At the originate state, this binary system was excited to bring very weak RTP signals. The maximal RTP emission was at around 528 nm, and the intensity was merely about 5.78 a.u. (curve **a**). The reason, as we elucidated above, is that most *β*-CD-Azo pseudorotaxane in aqueous solution prefers forming *trans*- configuration. And only a little *α*-BrNp was included by *β*-CD cavity and thus weak RTP signals were engendered.

An interesting phenomenon was found in the RTP spectrum of the ternary system. UV light (360nm) irradiation of its aqueous solution makes the RTP at around 528nm (due to the *β*-CD/*α*-BrNp) stronger, as illustrated in Fig. S7. As the azo unit is photoisomerized to dethread from *β*-CD and more *α*-BrNp molecules are included into *β*-CD cavity to enhance the RTP obviously. The RTP intensity enhancement is so big as to reach 90.53 times than its original state (523.27 a.u. to 5.78 a.u.). After the

photoisomerization of the *β*-CD-Azo/*α*-BrNp system, the equilibrium can be reversed by irradiation at 430 nm for 60 min (curve **p**). Upon alternating the light sources of 360 and 430 nm UV light every 60 min, changes in the RTP intensity of aqueous *β*-CD-Azo/*α*-BrNp solution at 528 nm experience several cycles (Fig. S8). RTP lifetime of the binary system *β*-CD-Azo/*α*-BrNp in aqueous solution was found about 0.58 ms (Fig. S9), which was consistent with the one of the *β*-CD/*α*-BrNp system. [3]

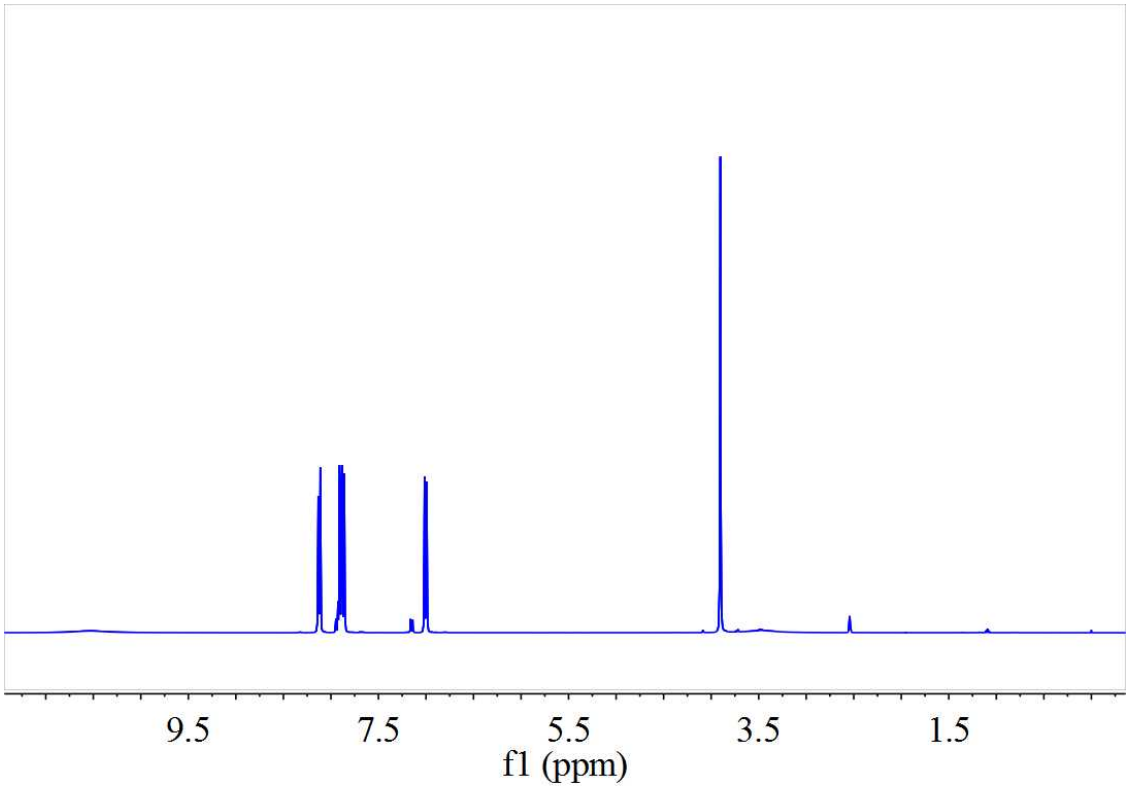


Fig. S9 ^{1}H NMR spectra of compound **2** (D_2O, 298K).

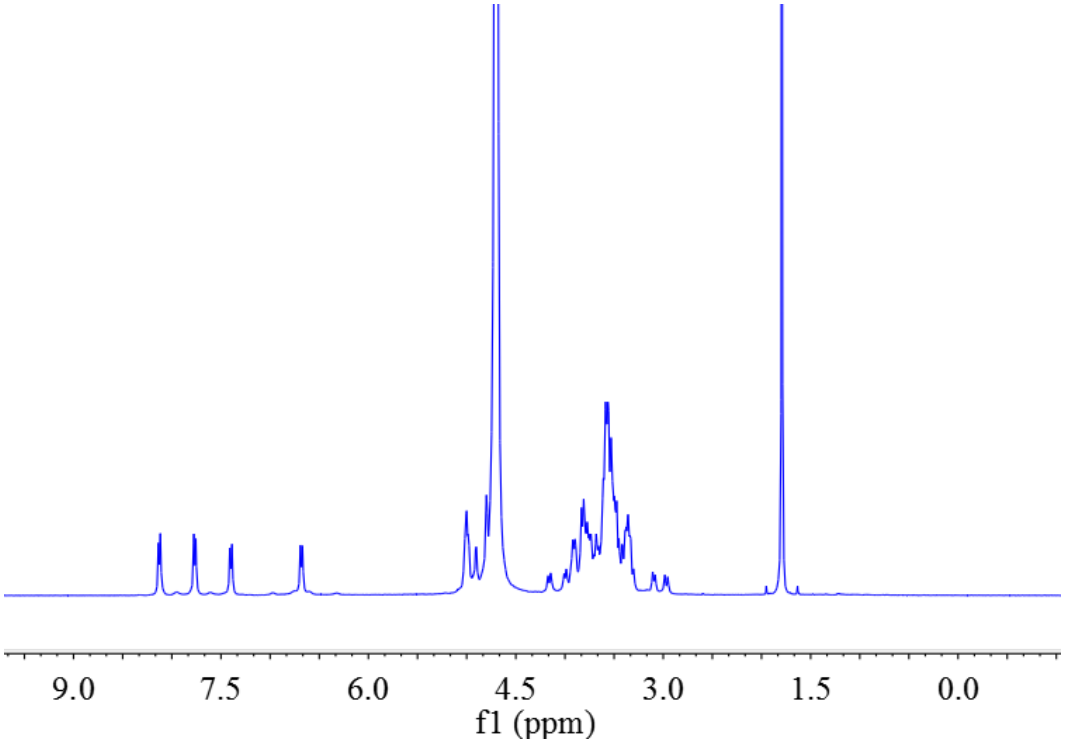


Fig. S10 ^{1}H NMR spectra of compound **1** (D_2O, 298K).

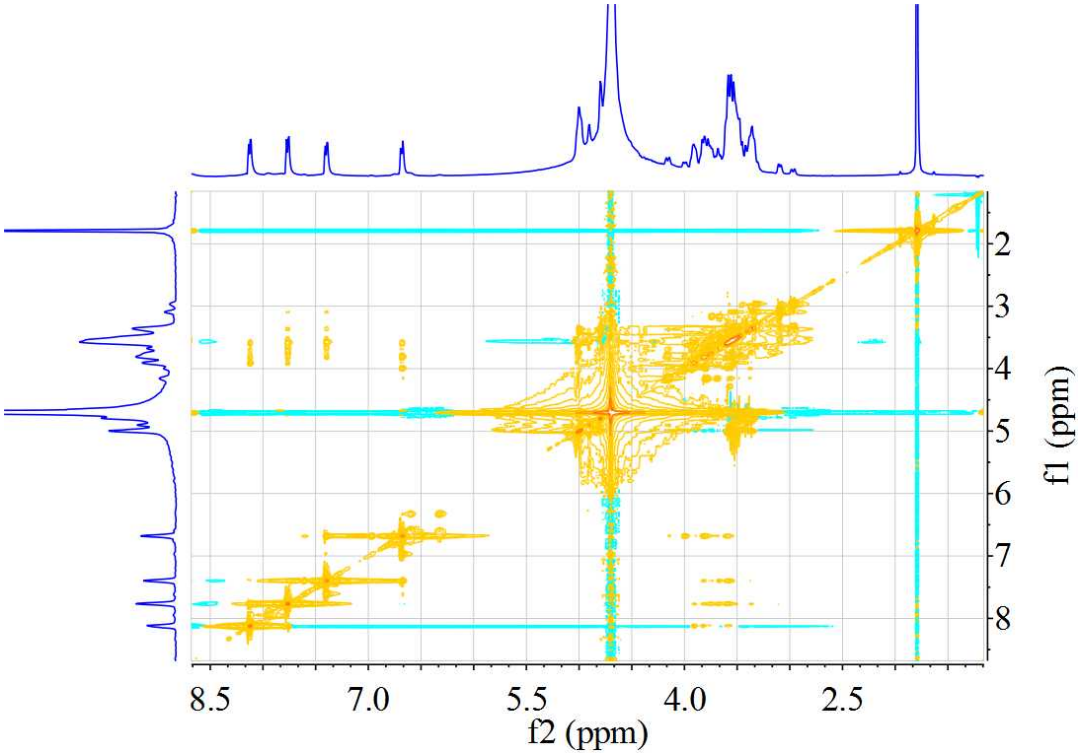


Fig. S11 ^{1}H 2D ROSEY NMR spectra of compound **1** (D_2O, 298K, at a mixing time of 300 ms).

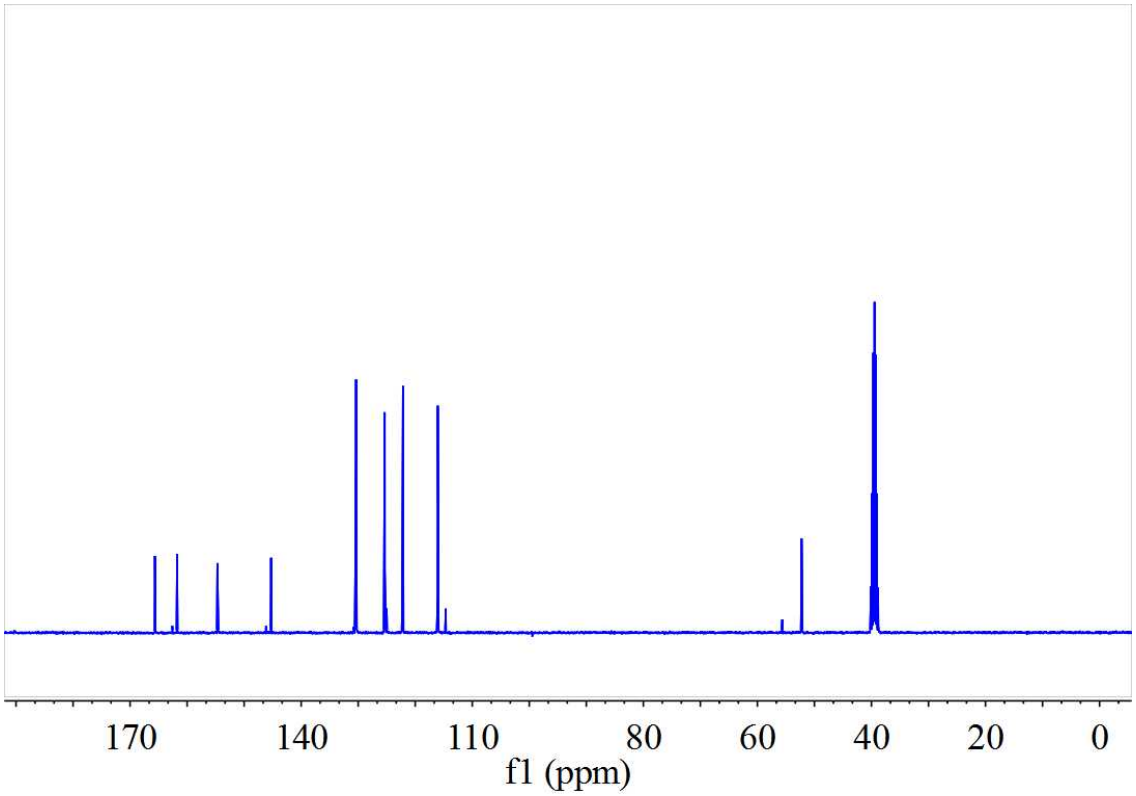


Fig. S12 ^{13}C NMR spectra of compound **2** (D_2O, 298K).

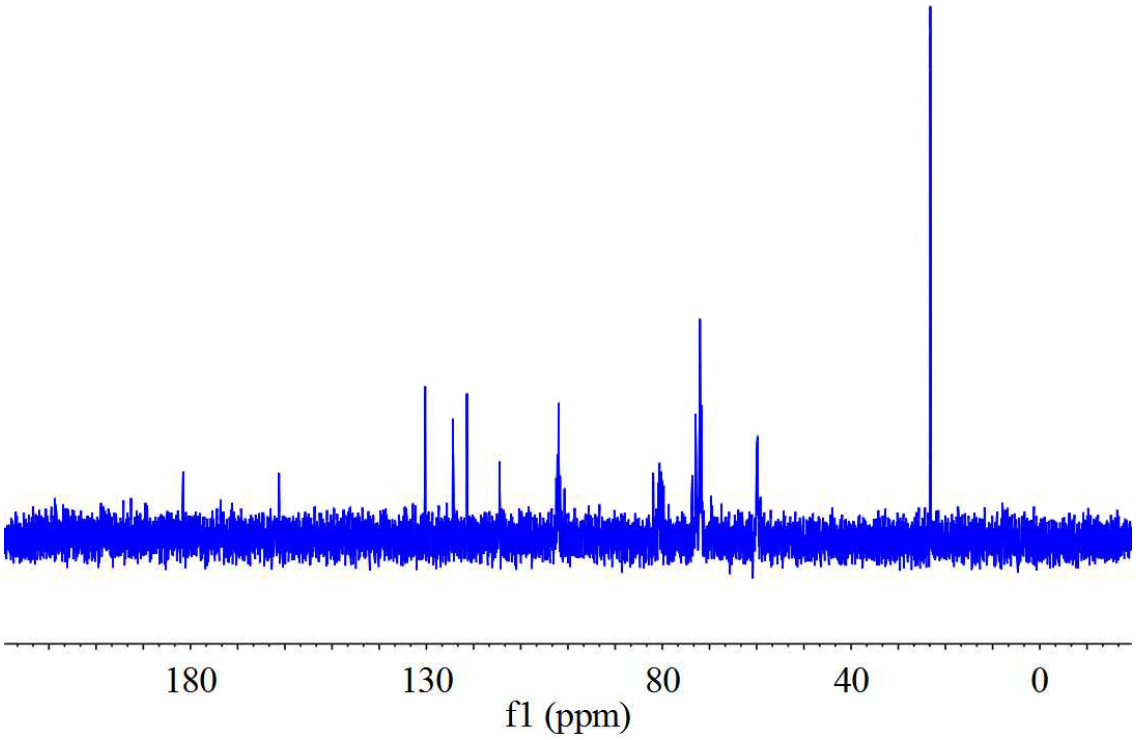
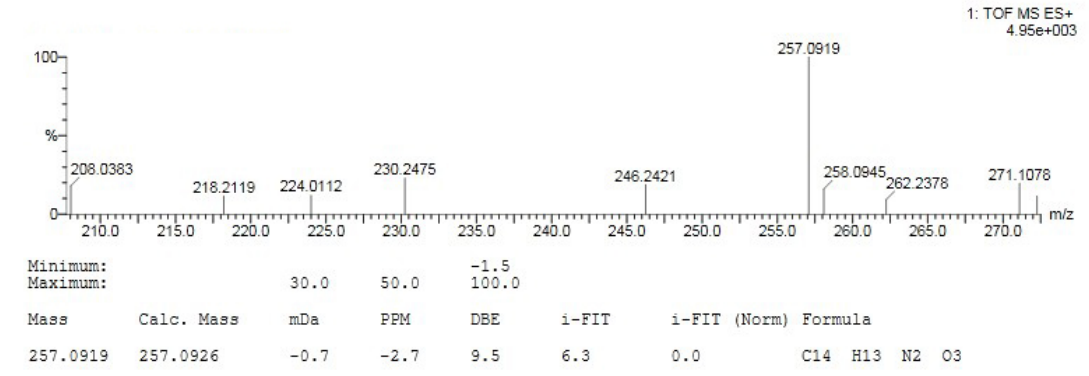


Fig. S13 ^{13}C NMR spectra of compound **1** (D_2O, 298K).



Minimum:				-1.5			
Maximum:		30.0	50.0	100.0			
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
257.0919	257.0926	-0.7	-2.7	9.5	6.3	0.0	C14 H13 N2 O3

Fig. S14 ESI HRMS spectra of compound **2**.

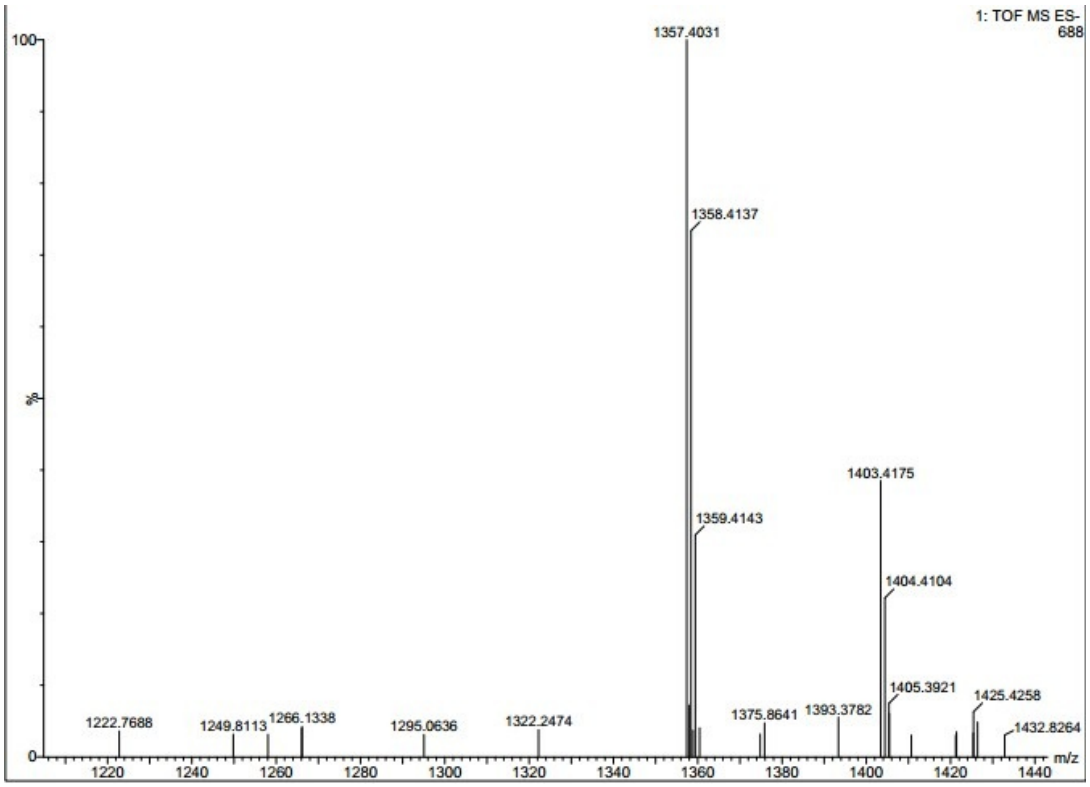


Fig. S15 ESI HRMS spectra of compound **1**.

References

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S2. X. Ma, D. Qu, F. Ji, Q. Wang, L. Zhu, Y. Xu and H. Tian, *Chem. Commun.*, 2007, 1409.

S3. X. Ma, J. J. Cao, Q. C. Wang and H. Tian, *Chem. Commun.*, 2011, **47**, 3559.