

Supplementary Information

Photocontrolled Reversible Room Temperature Phosphorescence (RTP) Encoding β -Cyclodextrin Pseudorotaxane Complex

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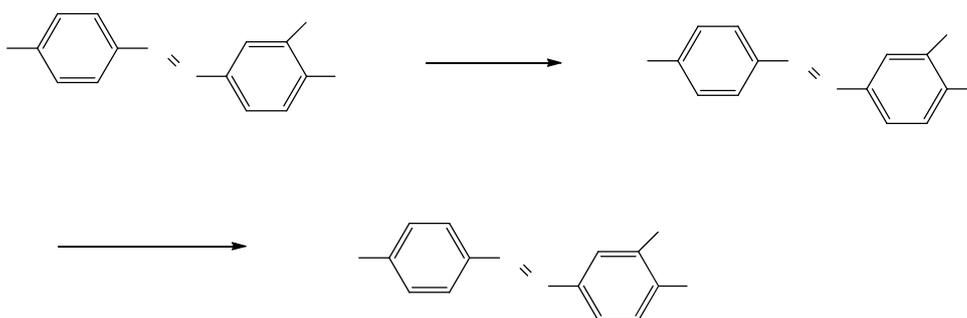
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Materials and methods

Chemicals

Sodium 2-hydroxy-5-((4-nitrophenyl)diazenyl)benzoate (Alizarine Yellow R), α -bromonaphthalene (α -BrNp) and CH₃CN were commercially available and used without further purification. β -Cyclodextrin (β -CD) was purchased from Acros and used as received. H₂O was distilled twice before use.

Synthesis of sodium 2-methoxy-5-((4-nitrophenyl)diazenyl)benzoate (DAYR)



A solution of Alizarine Yellow R (0.31g, 1 mmol) and iodomethane (0.43 g, 3 mmol) in MeCN (10 mL) was heated to 80 °C under Ar for 4 h. The solution was then cooled to room temperature and then added in water (50 mL). The resulting precipitate was filtered and washed with water. The yellow solid was then dissolved in a H₂O/C₂H₅OH (3:1) mixture (15 mL) containing NaOH (0.4g, 1mmol) and heated to

reflux for 1 h. The solvent was evaporated under vacuum pressure and dried to give **DAYR** (0.31g, 95%) as a yellow solid. M.p. 207-209°C (dec.). ^1H NMR (400 MHz, D_2O) δ 8.35 (d, 2H), 7.92 (dt, 4H), 7.13 (s, 1H), 3.89 (s, 3H). MS (ESI): $m/z = 300.0618$ [**DAYR** - Na^+] $^-$.

Instruments

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. RTP spectra were recorded on a Varian Cary Eclipse spectrophotometer (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. ^1H NMR spectra were measured on a Bruker AV-400 spectrometer. 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.

^1H NMR spectra of **DAYR** and its pseudorotaxane included by β -CD.

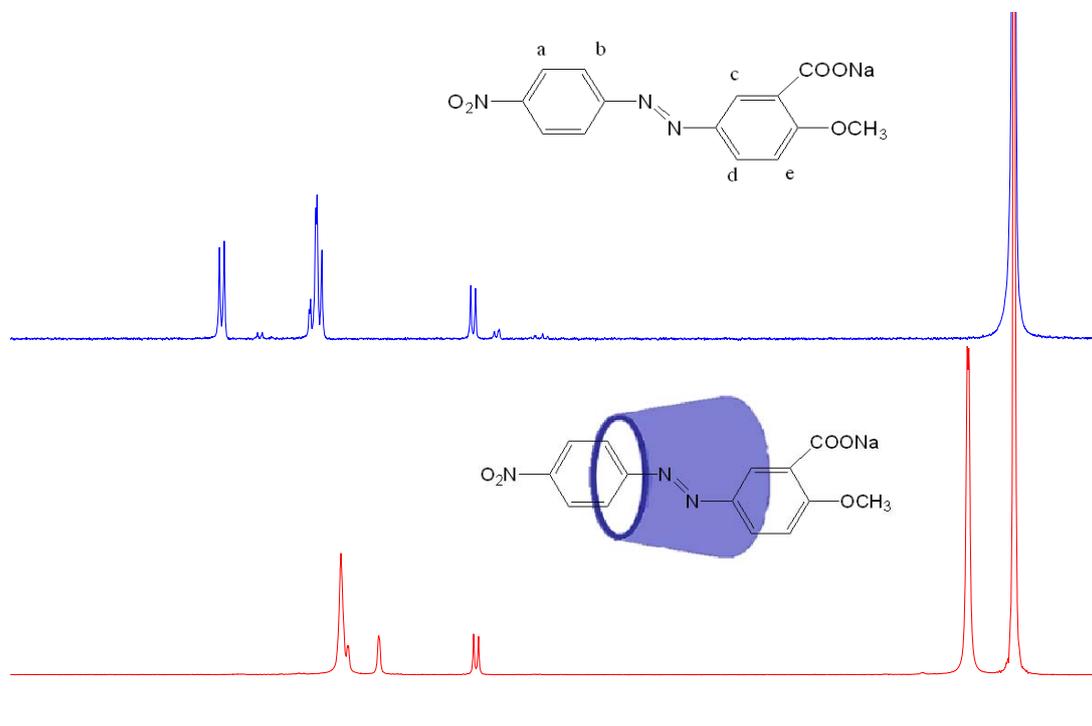


Figure S1. ^1H NMR spectra of **DAYR** (top) and its inclusion complex with β -CD (bottom) in D_2O at 298K.

The ^1H NMR spectra of **DAYR** is shown in Figure S1 (top). After mixing with β -CD in D_2O , the aromatic protons H_a , H_b , H_e , H_c and H_d of **DAYR** move upfield about 0.55, 0.09, 0.12, 0.31 and 0.06 ppm respectively, which shows the formation of pseudorotaxane between them.

RTP measurement

RTP spectra were recorded on a Varian Cary Eclipse spectrophotometer (1-cm quartz cell used) at 25 °C. Phosphorescence mode; Excitation slit =20nm; Emission slit = 20nm; Delay time = 0.1 ms; Gate time = 2.0 ms; Exciting light (286 nm).

Preparation of the aqueous ternary β -CD/DAYR/ α -BrNp solution: Mixing 0.2 mL aqueous α -BrNp solution (40% CH_3CN , 2.0×10^{-3} mol/L), 2 mL aqueous **DAYR** solution (1.0×10^{-2} mol/L) and 5 mL aqueous β -CD solution (4×10^{-3} mol/L) together in a 10 mL colorimeter tube, and then using water to dilute the ternary solution to 10 mL. Airproof the colorimeter tube and shake up the solution for 1.5 mins. Then in the ternary solution, the concentration of the respective component was as following: $[\alpha\text{-BrNp}] = 4.0 \times 10^{-5}$ mol/L, $[\text{DAYR}] = [\beta\text{-CD}] = 2.0 \times 10^{-3}$ mol/L.

After standing for 30 mins, the solution was displaced in a 1cm quartz cell with sealed cover for UV, ICD and RTP testing.

The aqueous binary β -CD/**DAYR** and β -CD/ α -BrNp solution was prepared in a similar way: firstly mixing the two component solution together in specific concentration respectively, shaking for a while and then standing for 30 mins.

UV spectra

UV spectra of α -BrNp and β -CD/ α -BrNp

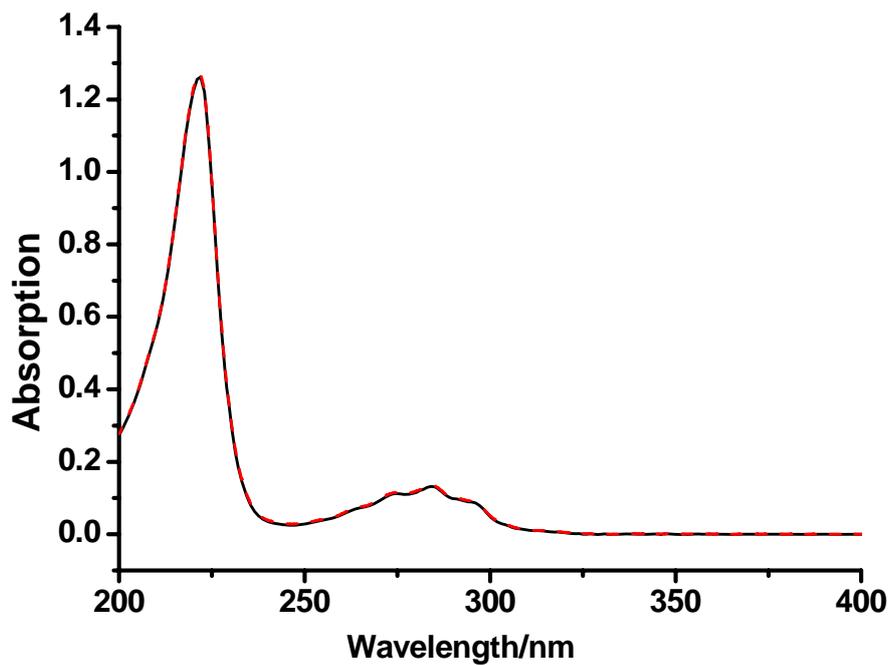


Figure S2. UV spectrum of aqueous α -BrNp solution (solid and blank, containing little CH_3CN , 2.0×10^{-5} mol/L) and UV spectrum of aqueous β -CD/ α -BrNp solution (dash and red, containing little CH_3CN , 2.0×10^{-5} mol/L). The two spectra are very similar.

UV spectra of DAYR solution after irradiation with different lights

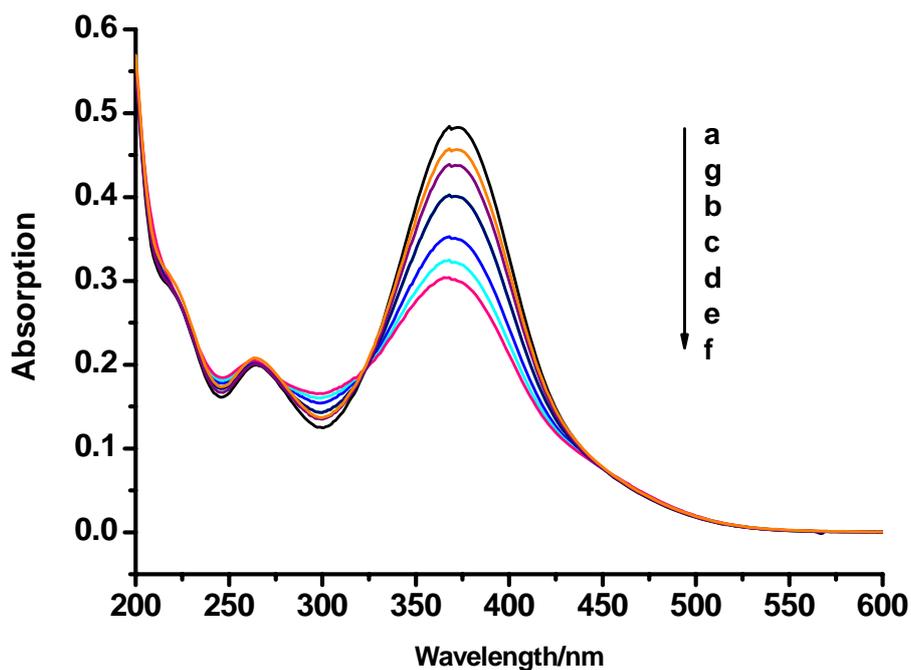


Figure S3. UV spectra of aqueous **DAYR** solution (**a**, containing little CH_3CN , 2.0×10^{-5} mol/L), and after irradiation by 360 nm light for 3 min (**b**), 6 min (**c**), 9 min (**d**), 12 min (**e**), 15 min (**f**). And the spectral change can be almost shifted back by 430 nm for 15 min (**g**)

Owing to the *trans-cis* isomerization of **DAYR**, the prolonged irradiation with 360nm light to the aqueous **DAYR** solution leads to an gradual intensity decrease of the maximal absorption peak at about 368nm, as shown in Figure S3 (curve **a**,, **f**). The UV spectral changes can be almost shifted back by irradiation at 430 nm for 15 min (curve **g**).

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

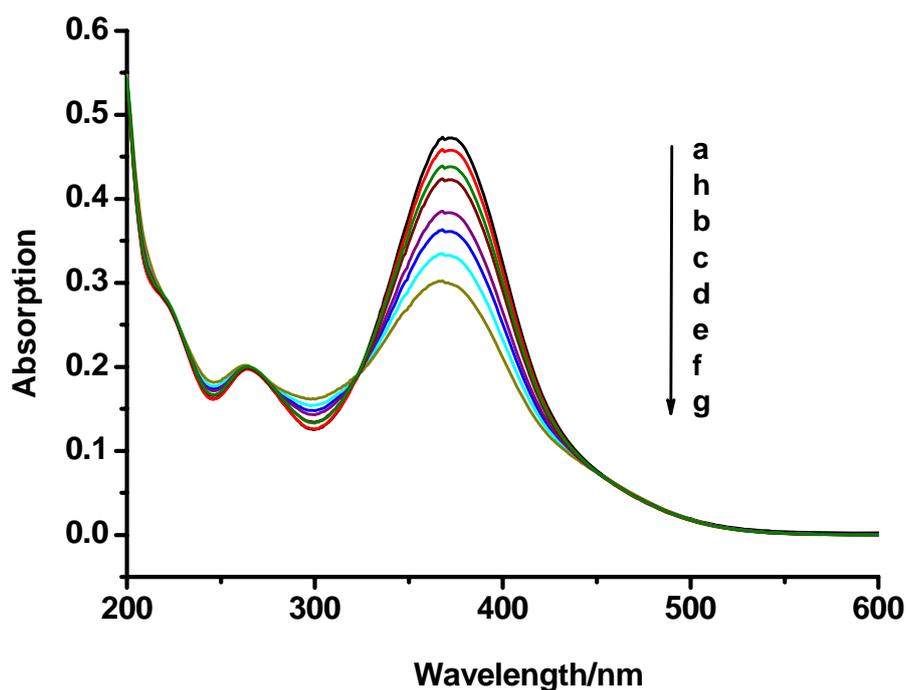


Figure S4. UV spectra of aqueous ternary β -CD/**DAYR**/ α -BrNp solution (**a**, containing little CH_3CN , $[\alpha\text{-BrNp}] = 4.0 \times 10^{-7}$ M, $[\text{DAYR}] = [\beta\text{-CD}] = 2.0 \times 10^{-5}$ M), and after irradiation by 360 nm light for 3 min (**b**), 6 min (**c**), 9 min (**d**), 12 min (**e**), 15 min (**f**), 18 min (**g**). And the spectral change can be almost shifted back by 430 nm for 15 min (**h**).

The prolonged irradiation with 360nm light to the ternary β -CD/DAYR/ α -BrNp solution leads to an gradual intensity decrease of the maximal absorption peak at about 368nm, as shown in Figure S4 (curve **a**,, **g**). The UV spectral changes can be shifted back by irradiation at 430 nm for 15 min (curve **h**). It should be noted that in this ternary solution, the absorption signal of α -BrNp is very low and changes little after irradiation with UV lights because of its relatively lower concentration (4.0×10^{-7} M) than the other two components ($[\text{DAYR}] = [\beta\text{-CD}] = 2.0 \times 10^{-5}$ M). So we just paid special attention to the maximal absorption peak of DAYR at about 368 nm here.

ICD spectra

ICD spectra of α -BrNp and binary β -CD/ α -BrNp solution

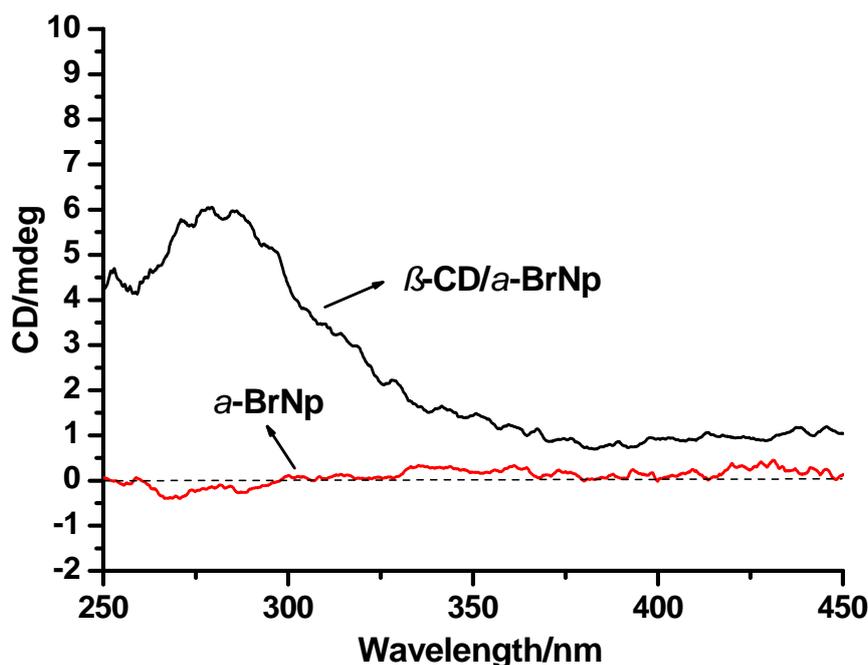


Figure S5. ICD spectrum of aqueous β -CD/ α -BrNp solution (top, containing little CH_3CN , $[\alpha\text{-BrNp}] = [\beta\text{-CD}] = 2.0 \times 10^{-4}$ M). The reference aqueous α -BrNp solution (bottom, $[\alpha\text{-BrNp}] = 2.0 \times 10^{-4}$ M) shows no Cotton effect but only the system error of the measurement.

As Figure S5 shown, the aqueous α -BrNp solution shows no obvious ICD signal

because there is no chair center in the α -BrNp molecule. However, in the aqueous binary β -CD/ α -BrNp solution, β -CD and α -BrNp form inclusion complex. And α -BrNp was induced to originate positive Cotton peak at about 285 nm by β -CD with its asymmetry cavity. This ICD property can be evidence of the formation of complex.

ICD spectrum of binary β -CD/DAYR solution

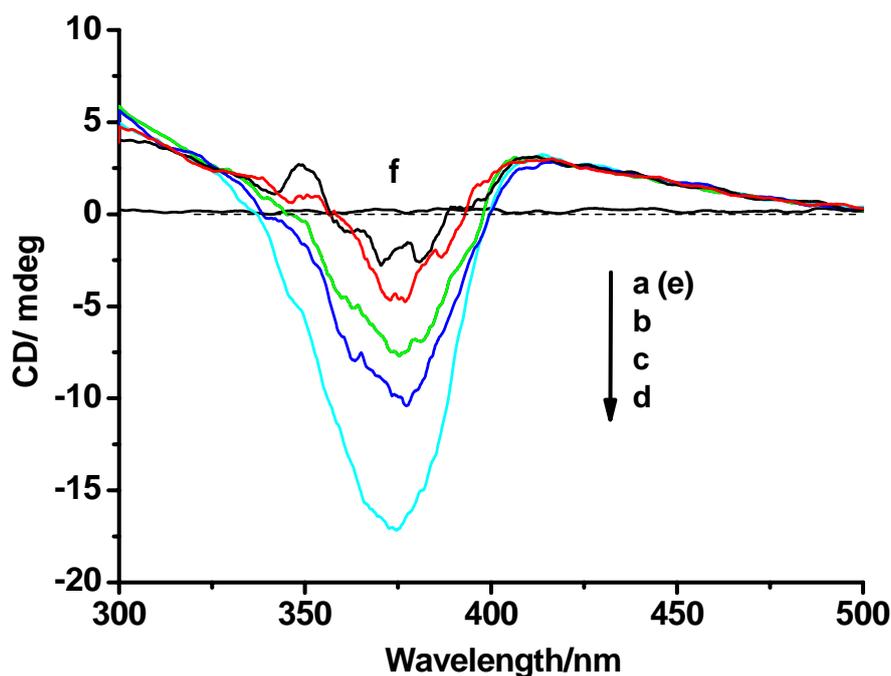


Figure S6. ICD spectrum of aqueous β -CD/DAYR solution (a, [DAYR]=[β -CD]= 2.0×10^{-4} M), and after irradiation by 360 nm light for 3 min (b), 9 min (c), 15 min (d). And the spectral change can be shifted back by 430 nm for 15 min (e). The reference aqueous DAYR solution (f, [DAYR]= 2.0×10^{-4} M) shows no Cotton effect but only the system error of the measurement.

DAYR can be induced to generate ICD signal when it is included into the cavity of β -CD. [1] A negative Cotton peak exists at about 374 nm after mixing together of DAYR and β -CD and standing for a short time (Figure S6). Owing to the *trans-cis* photoisomerization of DAYR, the prolonged irradiation with 360nm light to this binary system leads to a gradual intensity increase of the Cotton peak at 374 nm (curve b, c, d). And the ICD spectral changes can be shifted back by irradiation at 430

nm (curve e). Without the inclusion inducement effect of β -CD, the reference aqueous DAYR solution shows no obvious ICD signal, as shown in Figure S6 (curve f).

RTP spectrum of aqueous β -CD/ α -BrNp solution ^[2]

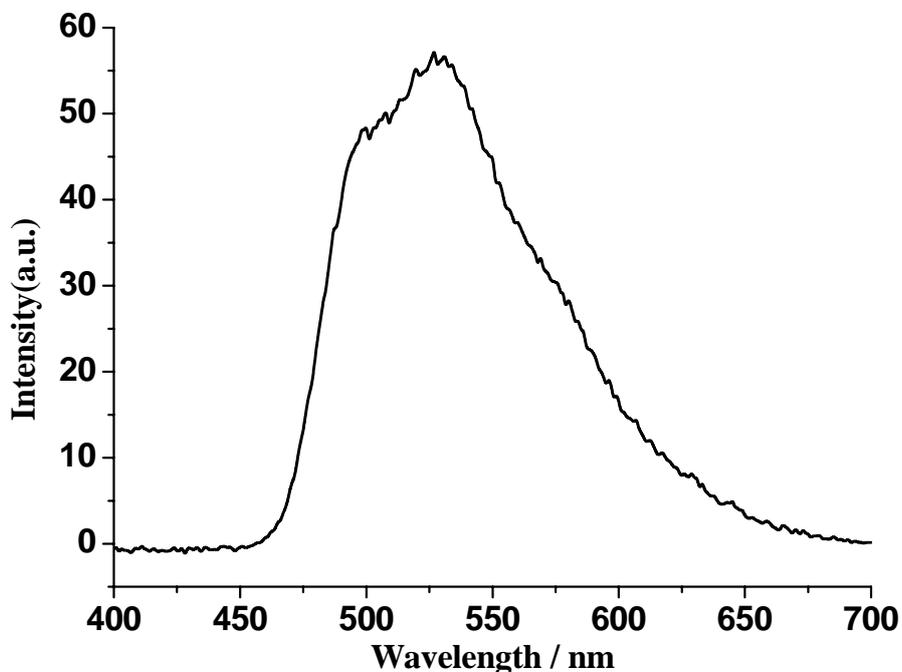


Figure S7. RTP spectrum of aqueous β -CD/ α -BrNp solution (containing little CH_3CN , $[\alpha\text{-BrNp}] = 4.0 \times 10^{-5}$ M, $[\beta\text{-CD}] = 2.0 \times 10^{-3}$ M)

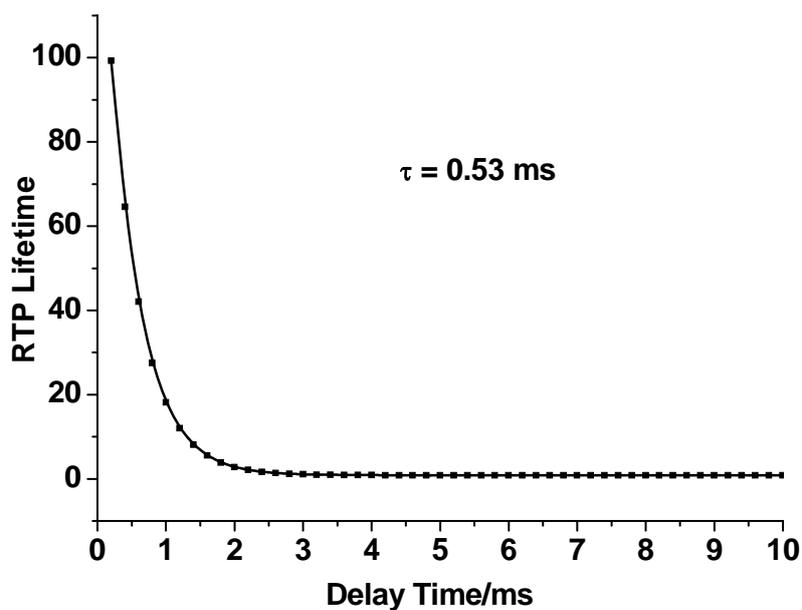


Figure S8. RTP lifetime of aqueous β -CD/ α -BrNp solution (containing little CH_3CN ,

$$[\alpha\text{-BrNp}] = 4.0 \times 10^{-5} \text{ M}, [\beta\text{-CD}] = 2.0 \times 10^{-3} \text{ M}$$

References

- S1. (a) X. Ma, Q. Wang, D. Qu, Y. Xu, F. Ji and H. Tian. *Adv. Funct. Mater.*, 2007, **17**, 829; (b) H. Murakami, A. Kawabuchi, K. Kotoo, M. Kunitake, N. Nakashima. *J. Am. Chem. Soc.*, 1997, **119**, 7605.
- S2. The aqueous β -CD/ α -BrNp solution has no fluorescence emission when excited at 286 nm because of the heavy atom effect of the α -BrNp.