Electronic Supplementary Information

Photo-responsive Cyclodextrin/Anthracene/Eu^{3+} Supramolecular Assembly for a Tunable Photochromic Multicolor Cell Label and Fluorescent Ink

Weilei Zhou,[a] Yong Chen,[a] Qilin Yu,[a,c] Peiyu Li,[a] Xuman Chen[a] and Yu Liu*[a,b]

[a]College of Chemistry, State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

[b]Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, P. R. China

[c]Key Laboratory of Molecular Microbiology and Technology, College of Life Sciences, Nankai University, Tianjin 300071, P. R. China

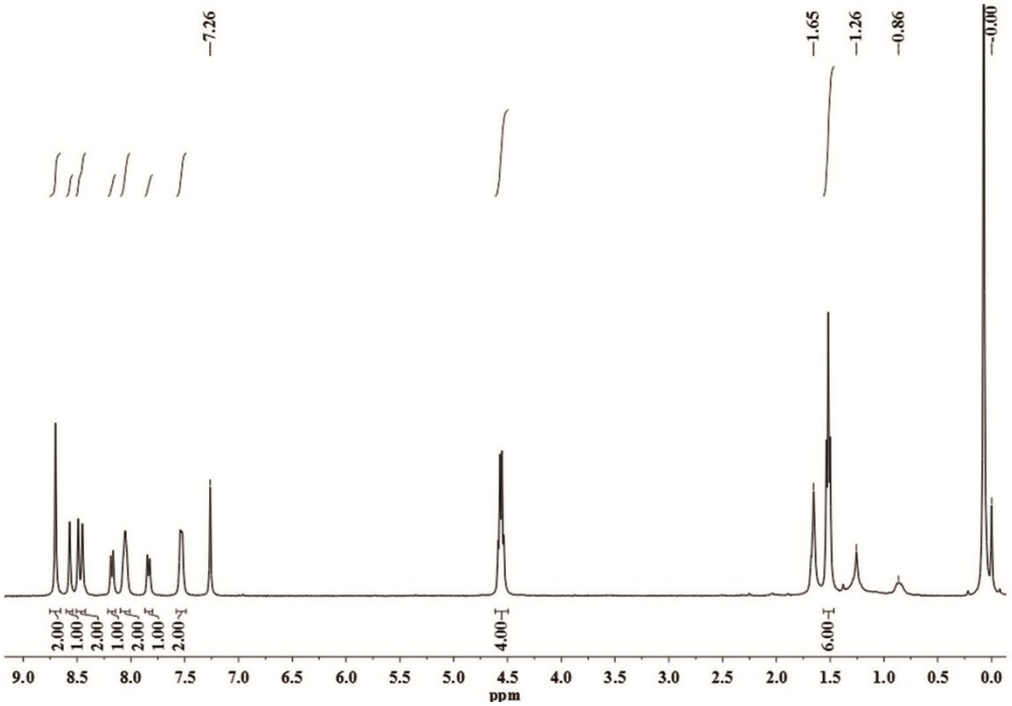


Fig. S1 ^{1}H NMR (400 MHz) spectrum of **3** in $CDCl_3$ at 25 °C.

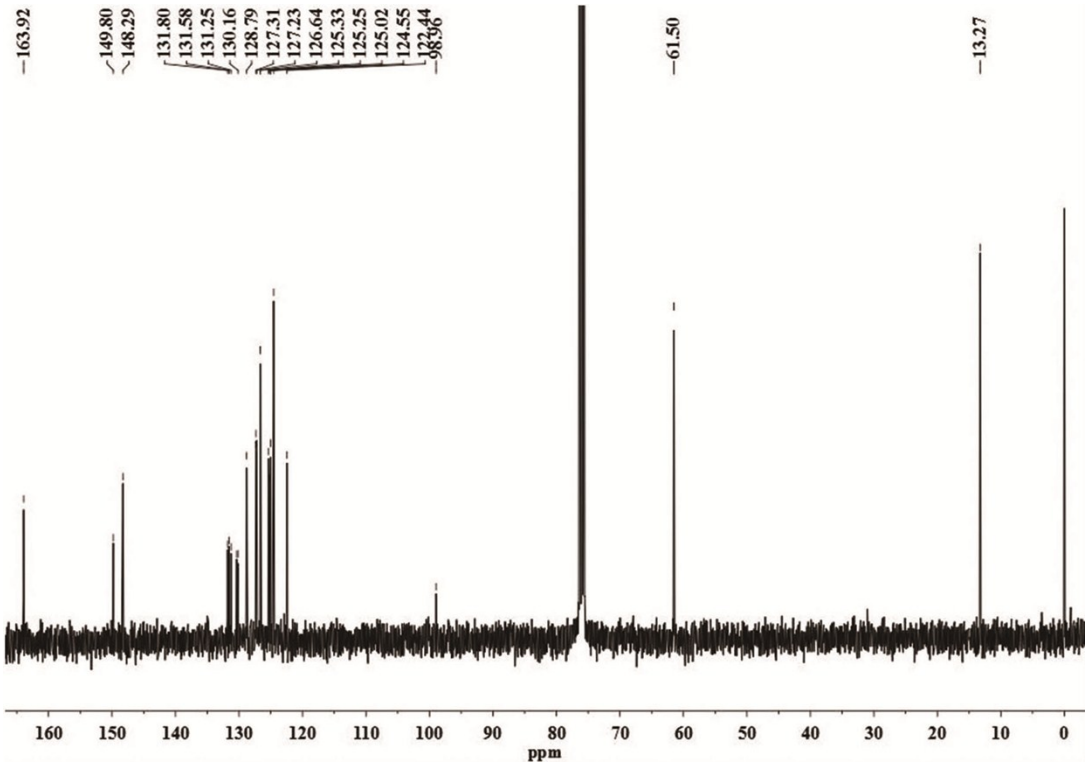
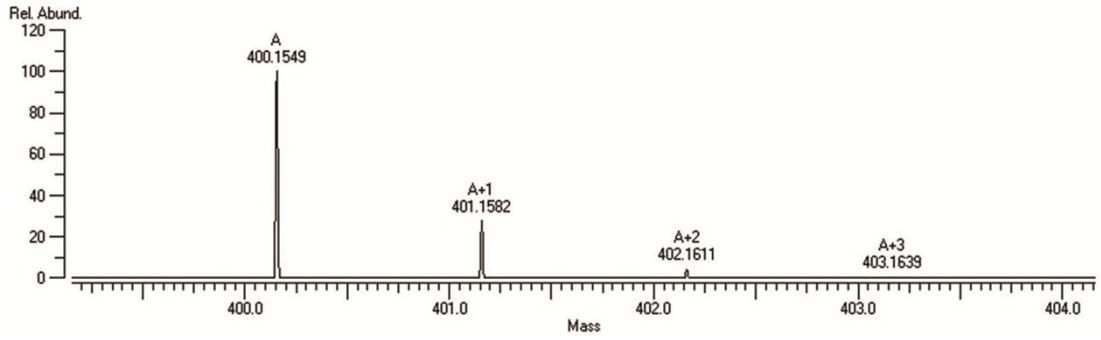


Fig. S2 ^{1}H NMR (400 MHz) spectrum of **3** in $CDCl_3$ at 25 °C.

Cal.



Exp.

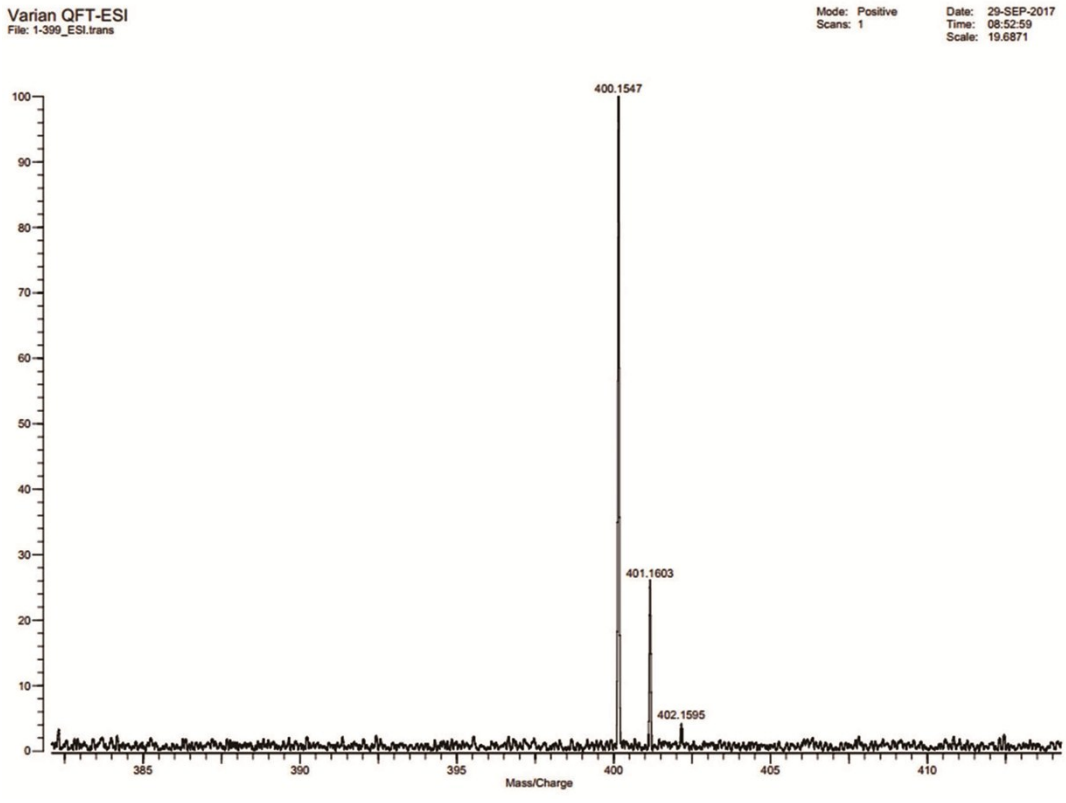


Fig. S3 HR-MS (ESI) spectrum of **3**.

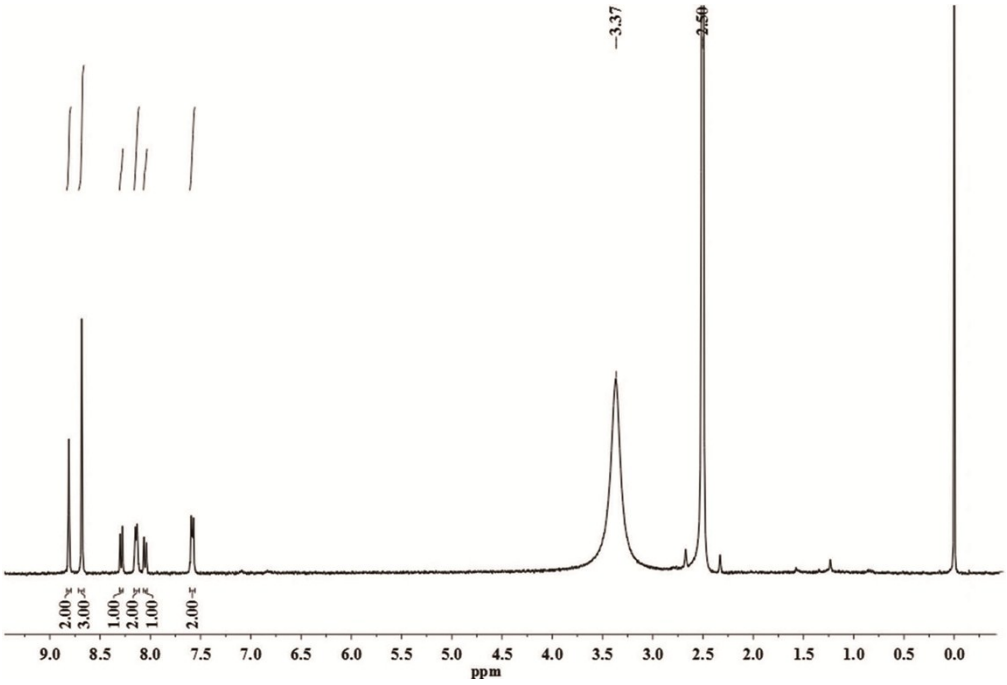


Fig. S4 ^{1}H NMR (400 MHz) spectrum of **1** in DMSO-d_6 at 25 °C.

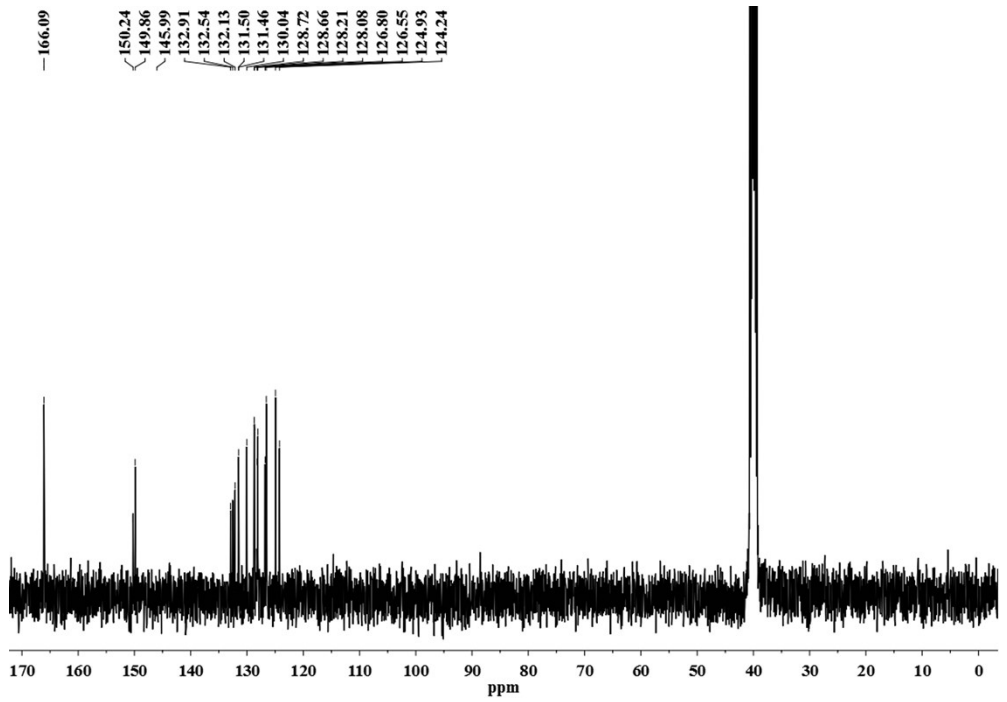
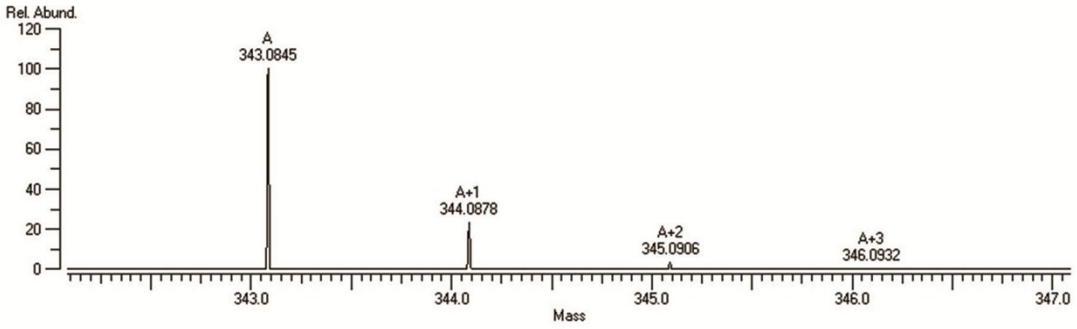


Fig. S5 ^{13}C (400 MHz) spectrum of **1** in DMSO-d_6 at 25 °C.

Cal.



Exp.

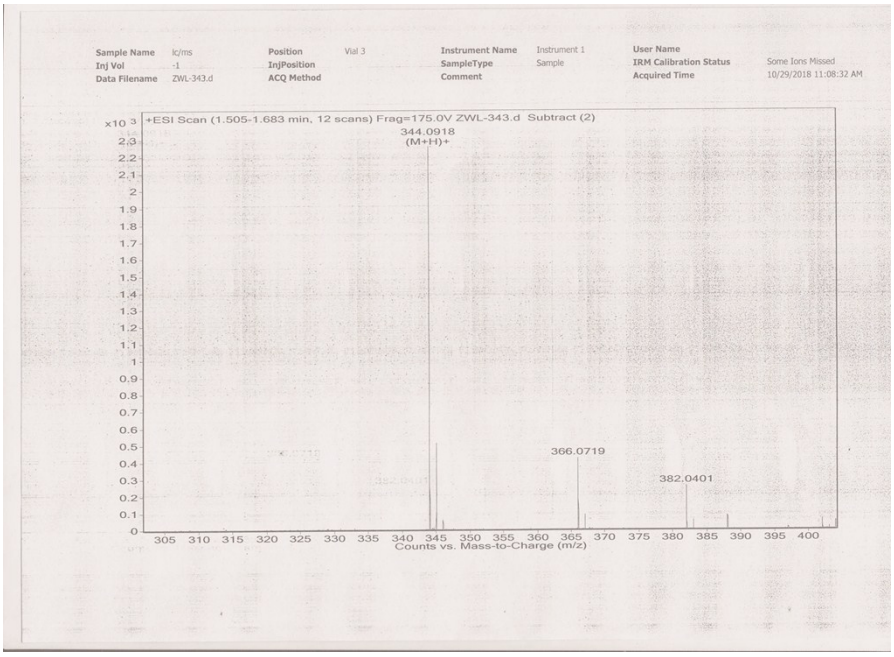


Fig. S6 HR-MS (ESI) spectrum of **1** at 25 °C.

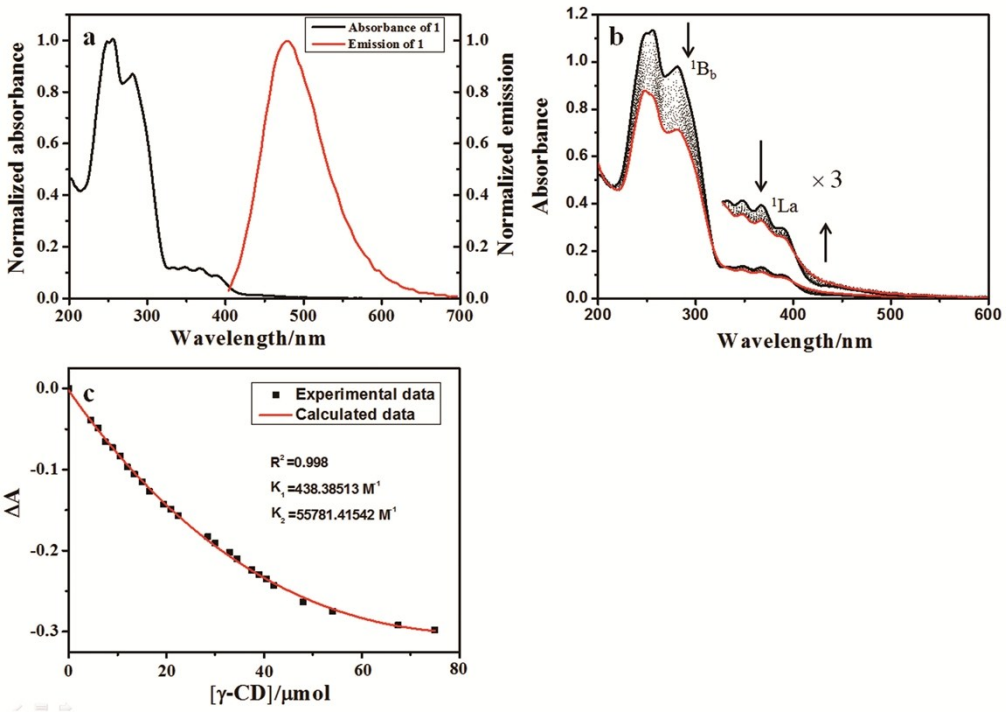


Fig. S7 (a)Normalized emission spectrum and absorption spectrum of **1** in water at 25 °C. (b) Absorption spectra of **1** (0.03 mM) with (red) and without (black) γ-CD (0.045 M) in water at 25 °C. (c) Plots of the absorbance change at 281 nm versus γ-CD concentration in water.

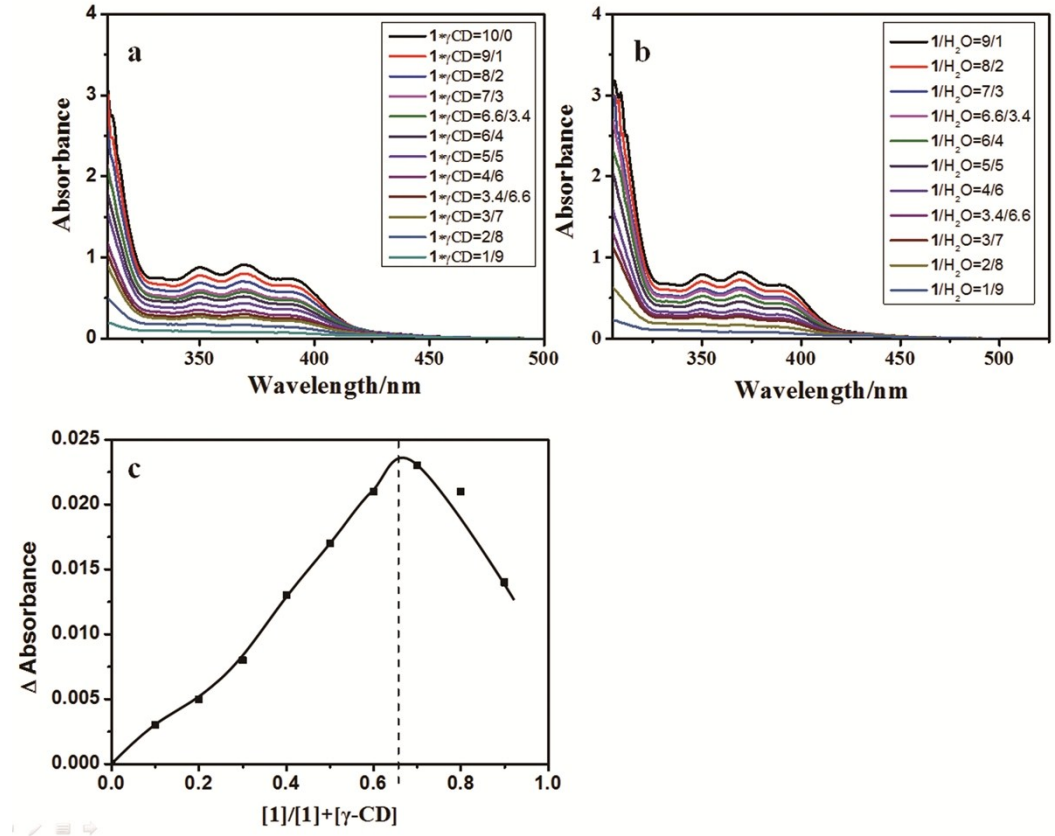


Fig. S8 Absorption spectra of (a) **1** + γ-CD(pH 9.0), (b) **1** + H_2O (pH 9.0); (c) Job's plots for guest molecule **1** and host in pH=9.0 aqueous solution at 25 °C.

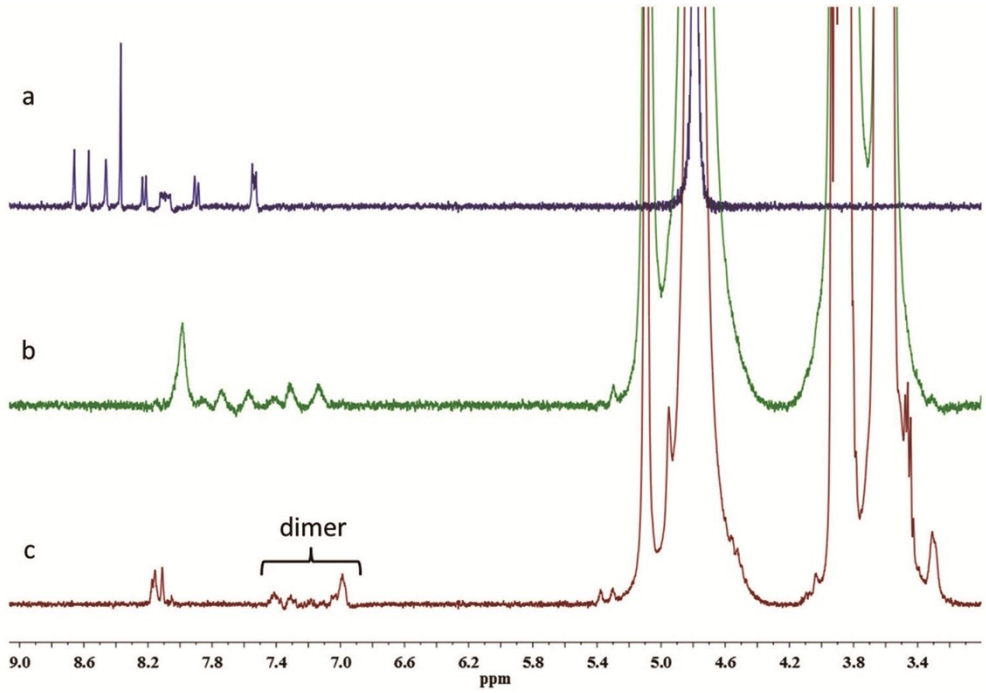


Fig. S9 ^{1}H NMR spectra of (a) **1** (0.2 mM), (b) **1** (0.2 mM) + γ-CD (2 mM) and (c) after 365 nm UV light irradiation of **1** (0.2 mM) + γ-CD (2 mM) in D_2O (pD 9.0) at 25 °C.

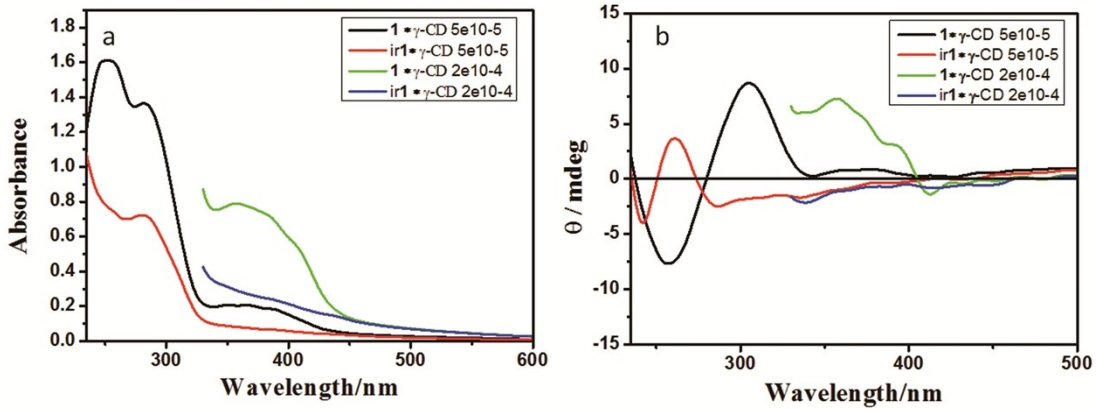


Fig. S10 (a) UV-vis spectra and (b) circular dichroism spectra with γ-CD in pH=9.0 aqueous solution (before irradiation of γ-CD·$\mathbf{1}_2$ (0.05 mM, black),γ-CD·$\mathbf{1}_2$ (0.2 mM, green), and after 365 nm UV light irradiation of γ-CD·$\mathbf{1}_2$ at 25 °C ([2]rotaxane, 0.05 mM, red), γ-CD·$\mathbf{1}_2$ ([2]rotaxane 0.2 mM, blue)).

The partial absorption of anthracene is low, and the structure changes before and after dimerization. The absorption in the aromatic zone is 230-280 nm and the absorption in the anthracene is obviously changed in 330-440 nm. In order to better prove the inclusion behavior before and after dimerization, we selected the

concentration of 0.2 mM to observe the change of 330-440 nm, and selected the concentration of 0.05 mM to observe the change of 230-280 mM aromatic zone.

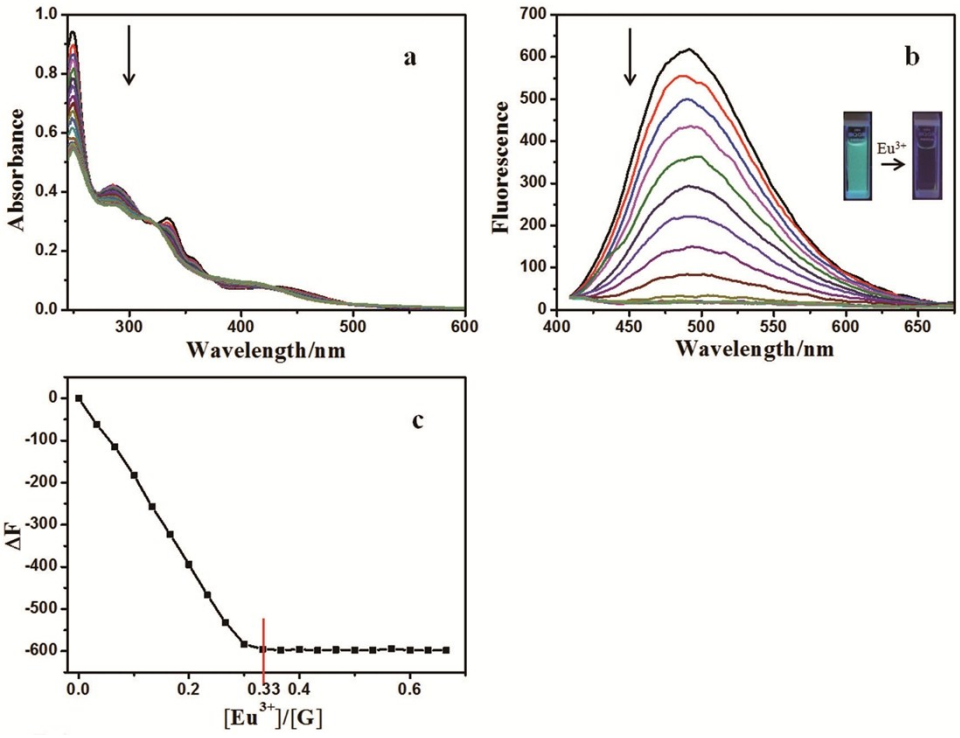


Fig. S11 (a) Absorption spectra and (b) emission spectra of **1** (0.02 mM) upon addition of Eu^{3+} (from 0 to 2eq) in water at 25 °C. (λ_{ex} =365 nm); (c) The curve of ΔF vs Eu^{3+}/[G] molar ratio in water at 25 °C.

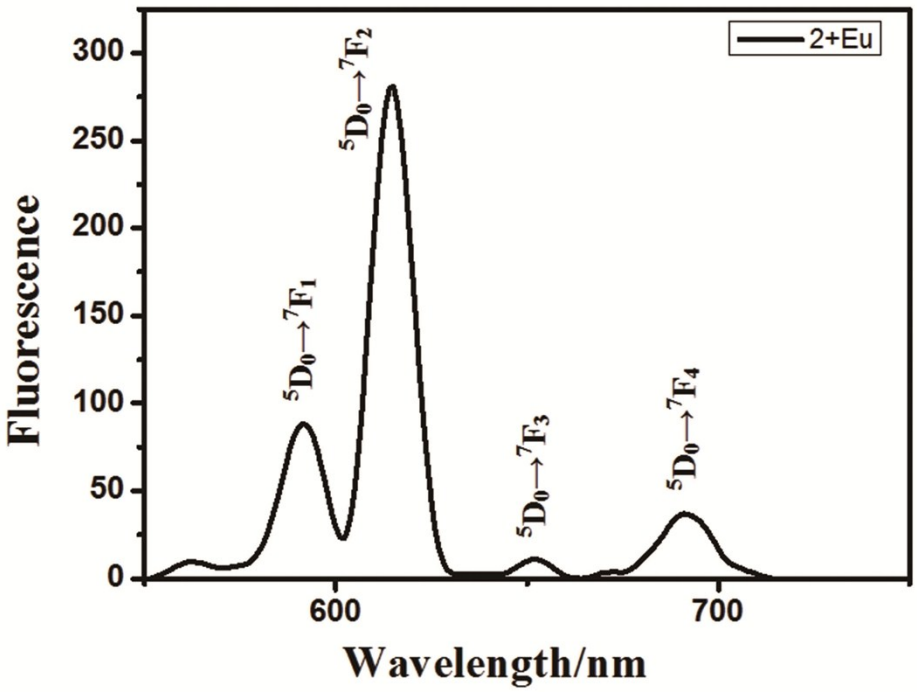


Fig. S12 Emission spectra of $Eu^{3+}\subset\mathbf{2}_3$ in pH=9.0 aqueous solution at 25 °C (λ_{ex} = 254 nm, 254 nm used as an excitation source).

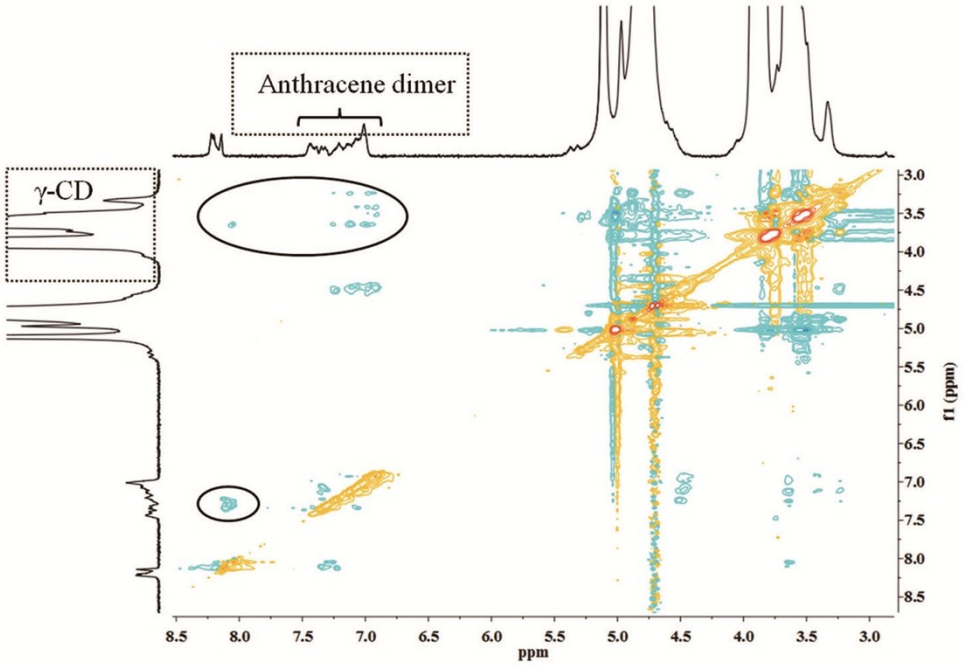


Fig. S13 2D ROESY spectrum of [2]rotaxane in D_2O (pD 9.0, 400 MHz, 25 °C).

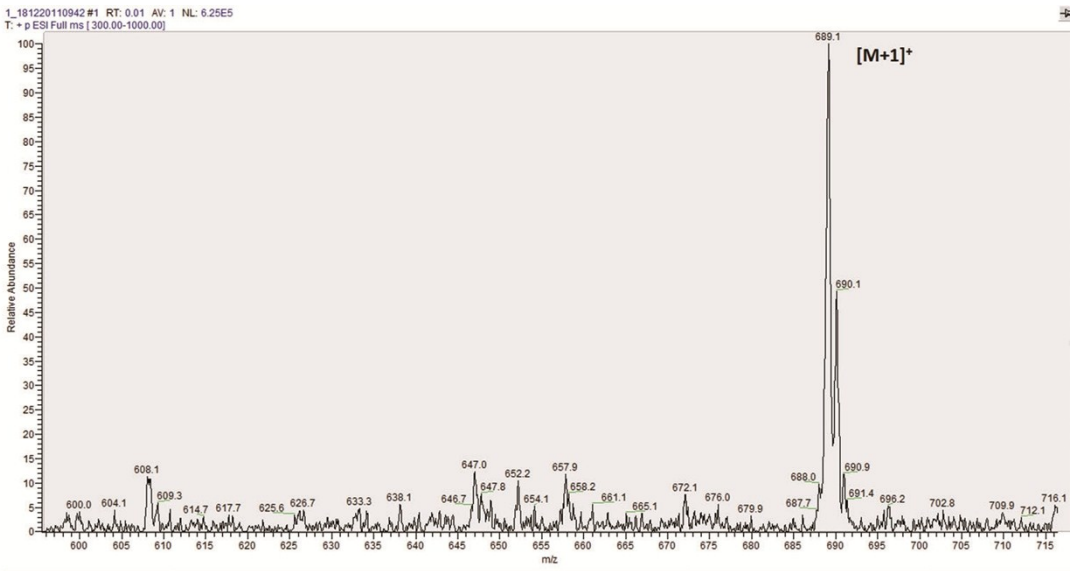


Fig. S14 ESI-MS spectrum of photodimer of **1** under 365 nm at 25 °C.

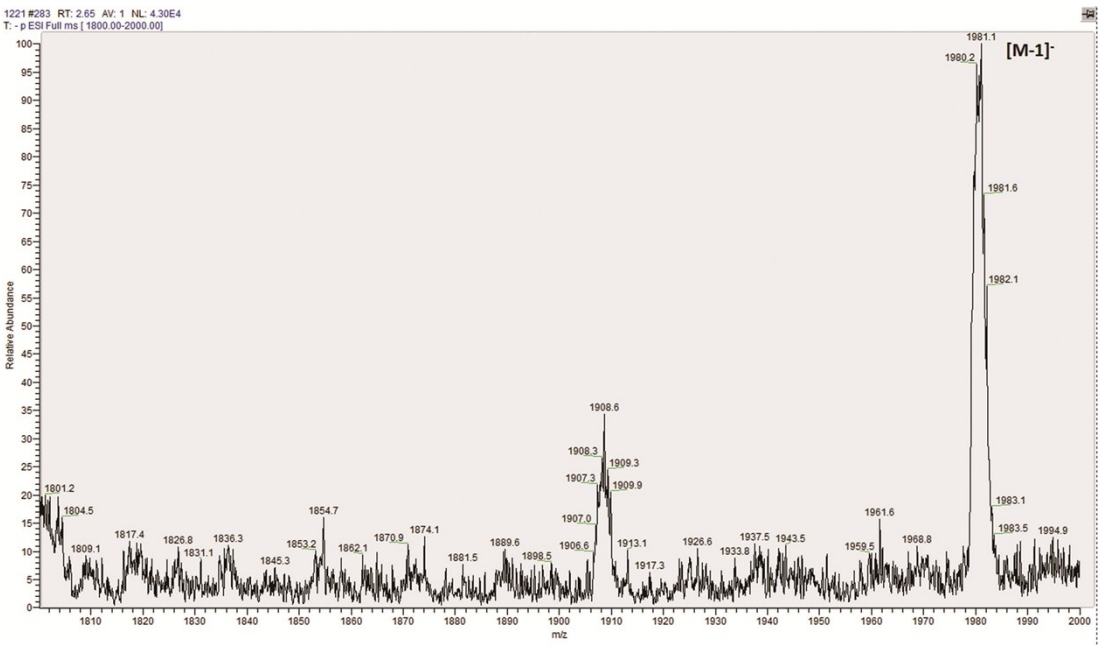
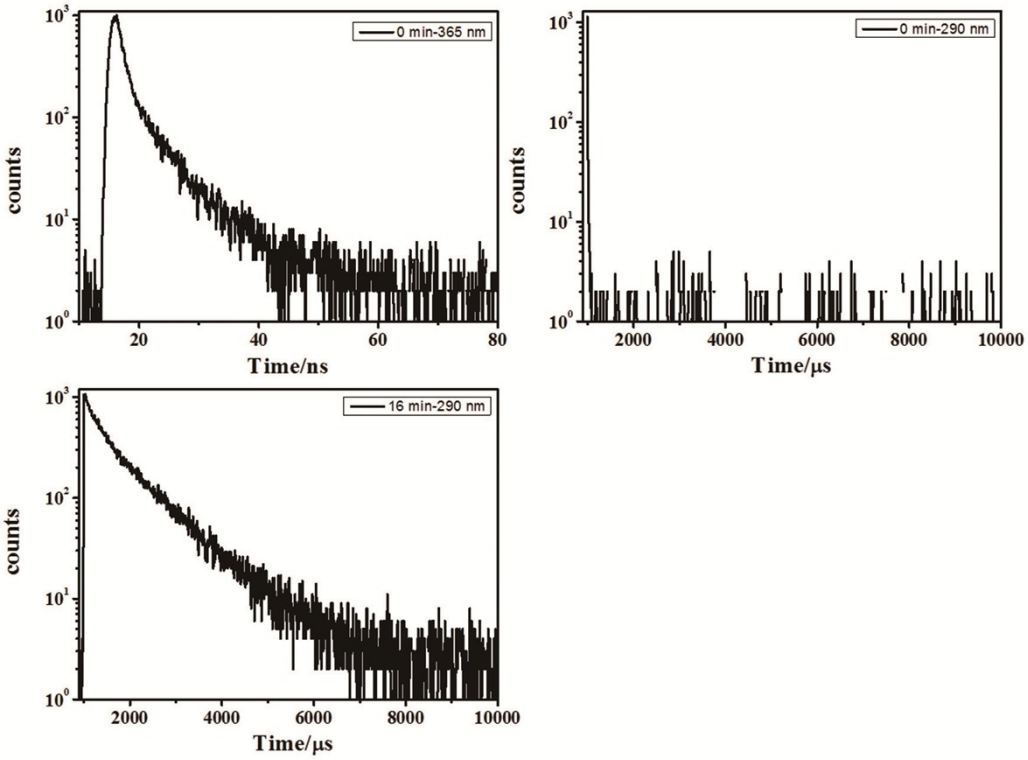


Fig. S15 ESI-MS spectrum of [2]rotaxane at 25 °C.



Time	Lifetime (%contribution)				
	λ_{em}	τ_1	τ_2	τ	χ^2
0 min	480 nm	1.10 ns(45.97%)	5.97 ns(54.03%)	3.73 ns	1.116
	617 nm	0	0	0	0
16 min	617 nm	251.88 μs(19.52%)	993.46 μs(80.48%)	848.70 μs	1.133

Fig. S16 The fluorescence lifetime of Eu^{3+}⊂γ-CD·**1**$_2$ for photoirradiation at 0 min and 16 min in pH=9.0 water at 25 °C (0.1 mM, λ_{ex}=365 nm and 290 nm).

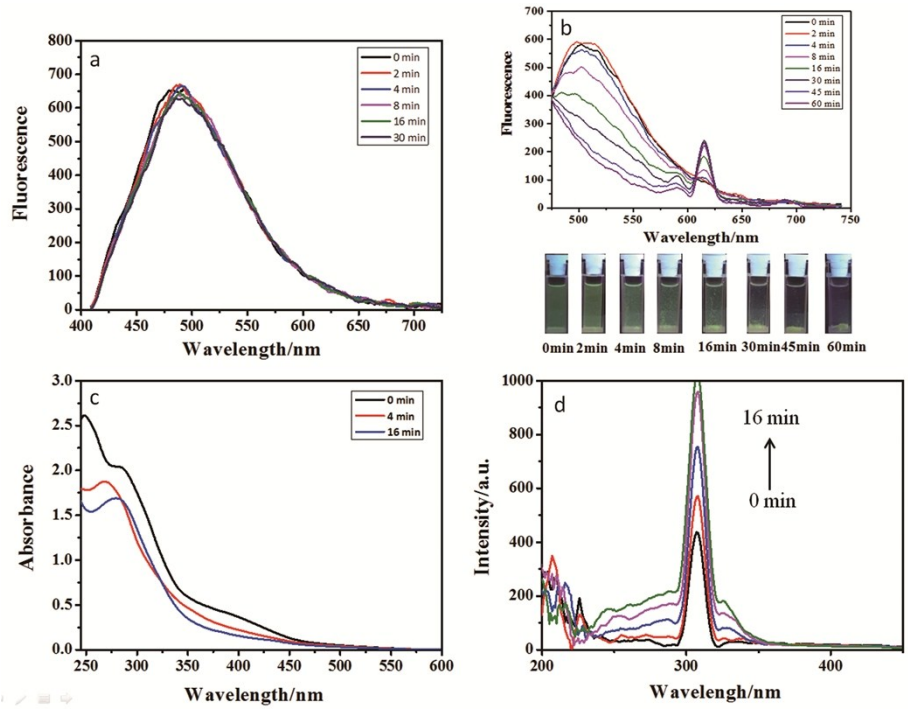


Fig. S17 (a) Emission spectra (λ_{ex} = 300 nm) of $Eu^{3+}\subset$γ-CD·$\mathbf{1}_2$ (0.1 mM) at initial state and without photoirradiation for 2 min, 4 min, 8 min, 16 min, 30 min in pH=9.0 aqueous solution at 25 °C (b) Emission spectra (λ_{ex} = 300 nm) of $Eu^{3+}\subset$ $\mathbf{1}_3$ (0.1 mM, without γ-CD) at initial state and after photoirradiation for 2 min, 4 min, 8 min, 16 min, 30 min, 45 min, 60 min in pH=9.0 aqueous solution at 25 °C and the images of the corresponding states under UV irradiation (λ_{ex} = 365 nm) (c) the change of absorption spectra of $Eu^{3+}\subset$γ-CD·$\mathbf{1}_2$ (0.1 mM) upon photoirradiation in water at 25 °C. (d) the excitation spectra of the $Eu^{3+}\subset$γ-CD·$\mathbf{1}_2$ systems upon photoirradiation in water at 25 °C. (λ_{em} = 615 nm)

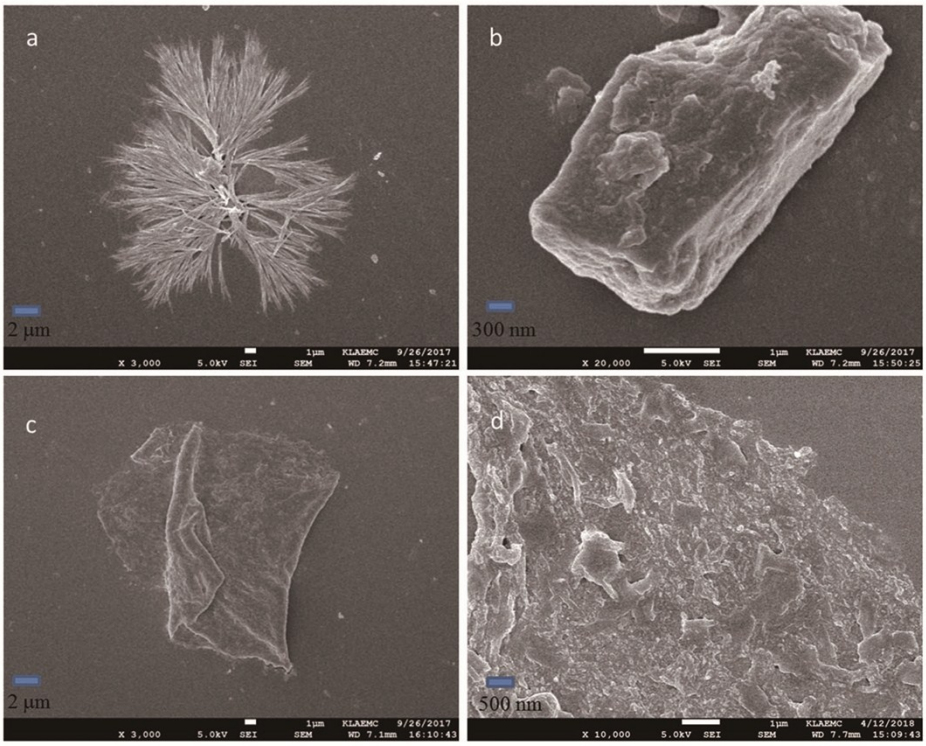


Fig. S18 SEM images of (a) **1** (0.02 mM), (b) **1** ⊂ H (0.02 mM), (c) $Eu^{3+}\subset$γ-CD·$\mathbf{1}_2$ (0.02 mM) and (d) $Eu^{3+}\subset$[2]rotaxane (0.02 mM) at 25 °C.

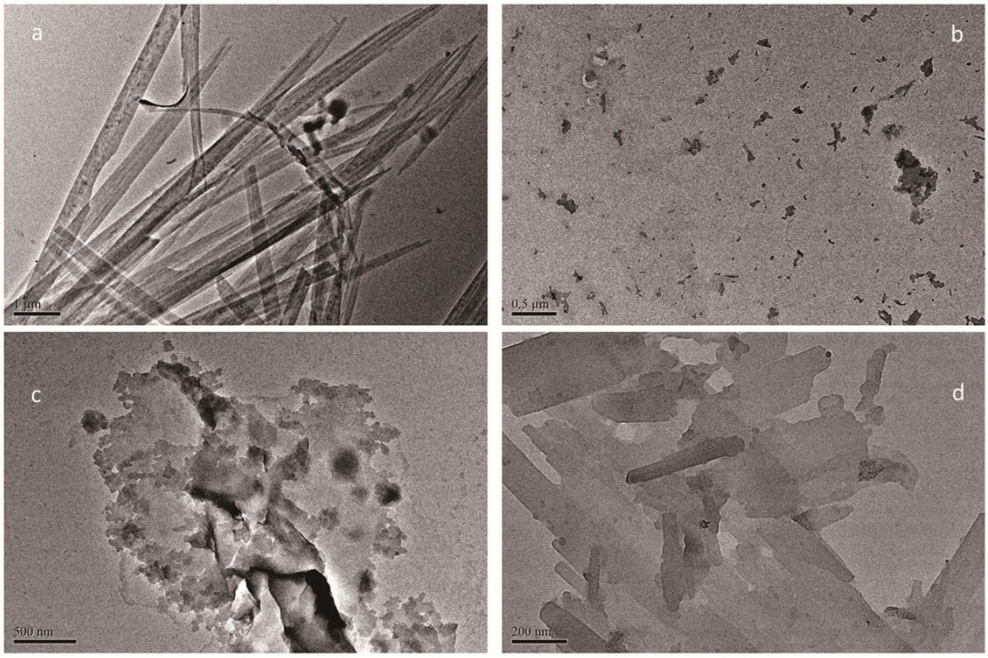


Fig. S19 TEM images of (a) **1** (0.02 mM), (b) **1** ⊂ H (0.02 mM), (c) Eu^{3+}⊂γ-CD·$\mathbf{1}_2$ (0.02 mM) and (d) Eu^{3+}⊂[2]rotaxane (0.02 mM) at 25 °C.

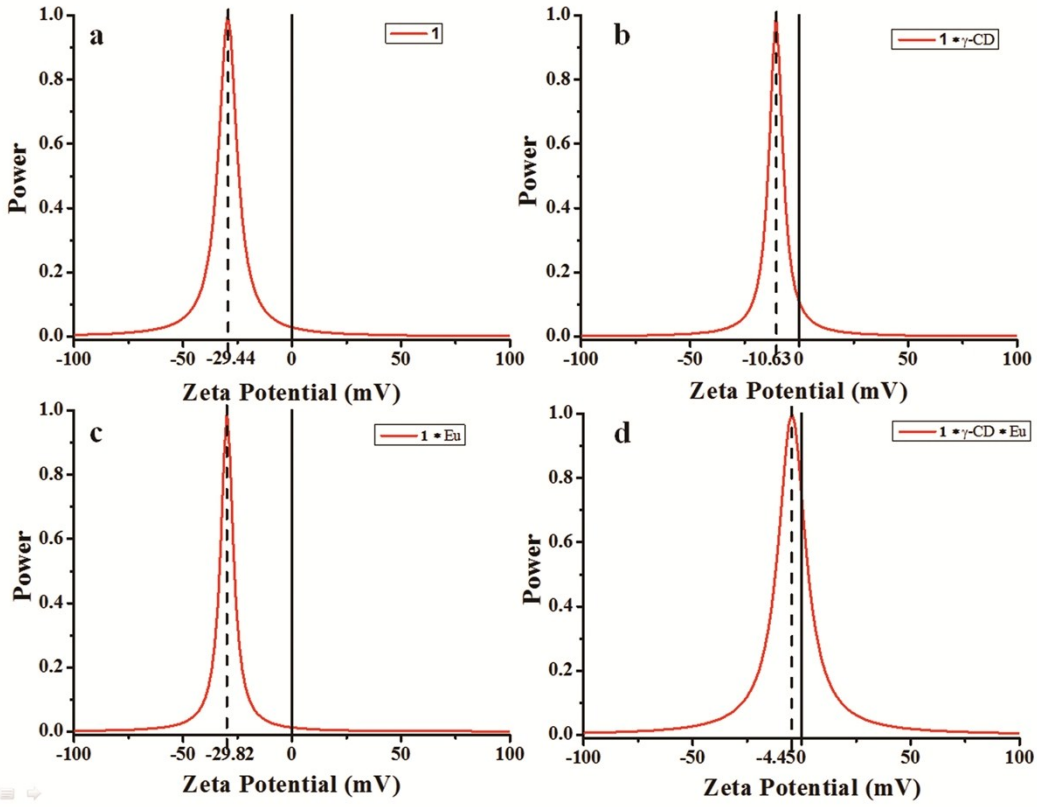


Fig. S20 Zeta potential of (a) **1** (0.02mM), (b) **1** ⊂ H (0.02 mM), (c) Eu^{3+} ⊂$\mathbf{1}_3$ (0.02 mM) and (d) Eu^{3+}⊂γ-CD·$\mathbf{1}_2$ (0.02 mM) in water at 25 °C.

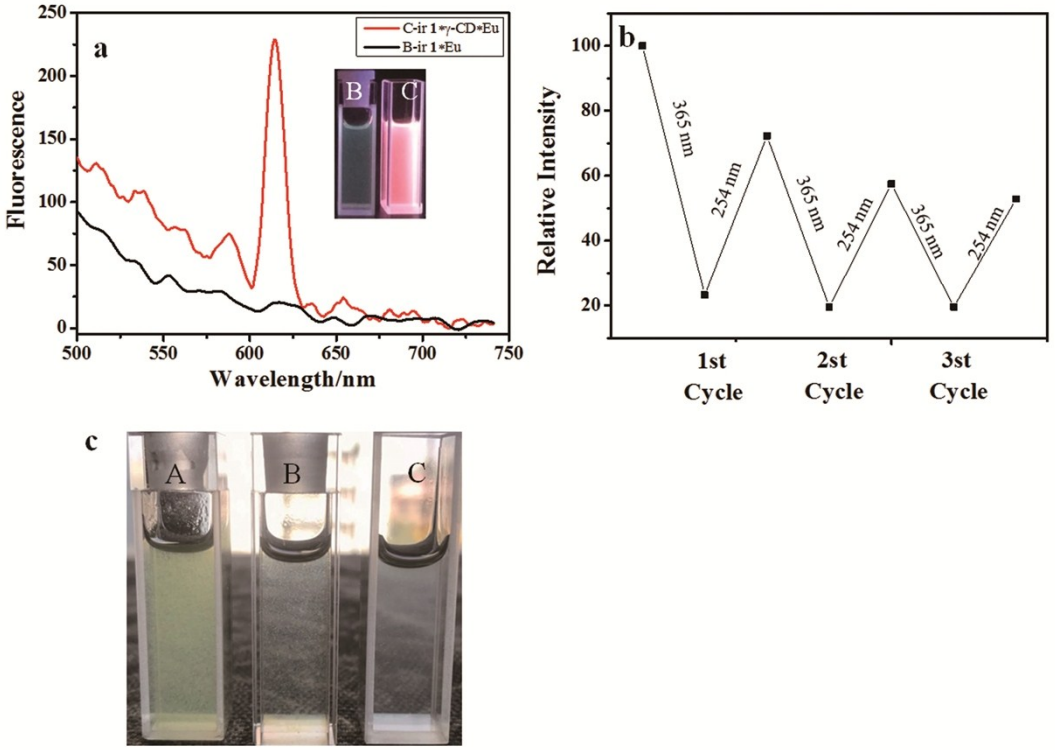
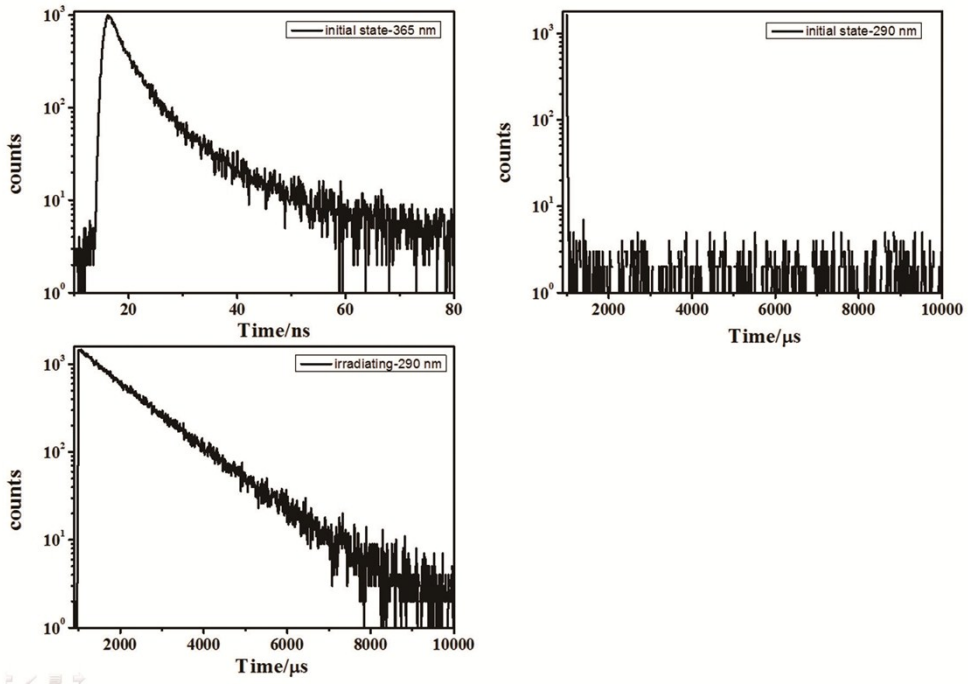


Fig. S21 (a) Emission spectra of Eu^{3+}⊂γ-CD·$\mathbf{1}_2$ (red) and Eu^{3+}⊂$\mathbf{1}_3$ (black) after irradiating at 365 nm (25 °C). Inset: photo image of fluorescence in PBS under a UV light. (pH=7.2, λ_{ex}=254 nm); (b) Cycle performance as revealed by normalized fluorescence change; (c) the photo image under nature light in PBS (A: free **1**, B: Eu^{3+}⊂$\mathbf{1}_3$, C: Eu^{3+}⊂γ-CD·$\mathbf{1}_2$).



Time	Lifetime (%contribution)				
	λ_{em}	τ_1	τ_2	τ	χ^2
Initial state	480 nm	3.02 ns(59.79%)	11.38 ns(40.21%)	6.38 ns	1.192
	617 nm	0	0	0	0
Irradiating	617 nm	543.5028 μs(4.42%)	1204.9155 μs(95.58%)	1175.68 μs	1.232

Fig. S22 The fluorescence lifetime of Eu^{3+}⊂γ-CD·**1**$_2$ for photoirradiation at Initial state and Irradiating in PBS at 25 °C (pH=7.2, 0.1 mM, λ_{ex}=365 nm and 290 nm).

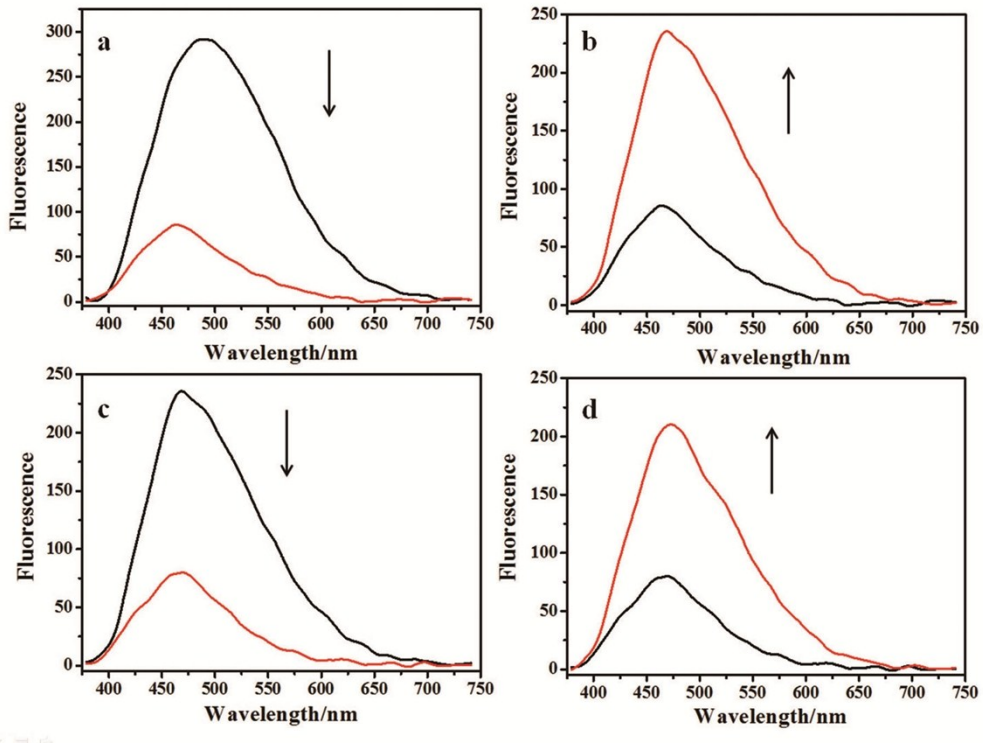


Fig. S23 Cycle test as monitored by fluorescence spectral changes of (a) 2nd photoirradiation at 365 nm and (b) at 254 nm, (c) 3rd photoirradiation at 365 nm and (d) at 254 nm.(25 °C) The spectral changes upon 1st photoirradiation were presented in Figure 4.

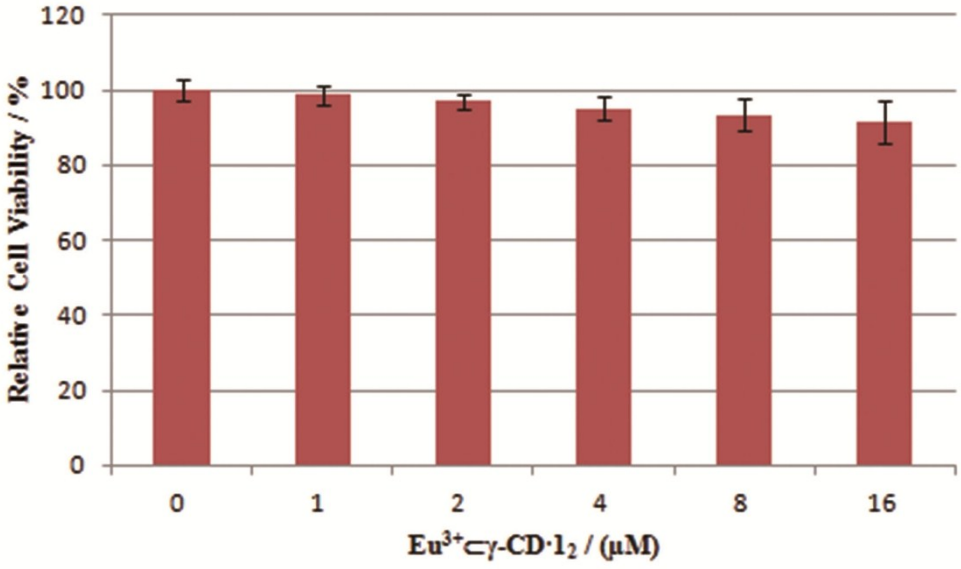


Fig. S24 Relative cell viabilities of Eu^{3+}⊂γ-CD·$\mathbf{1}_2$ with different $\mathbf{1}_2$ concentrations at 25 °C (the molar ratio of Eu^{3+}, γ-CD and $\mathbf{1}_2$ = 1 : 2 : 4)