Supporting Information

Unexpected fluorescent behavior of an 4-amino-1,8-naphthalimide derived β-cyclodextrin: Conformation analysis and sensing properties

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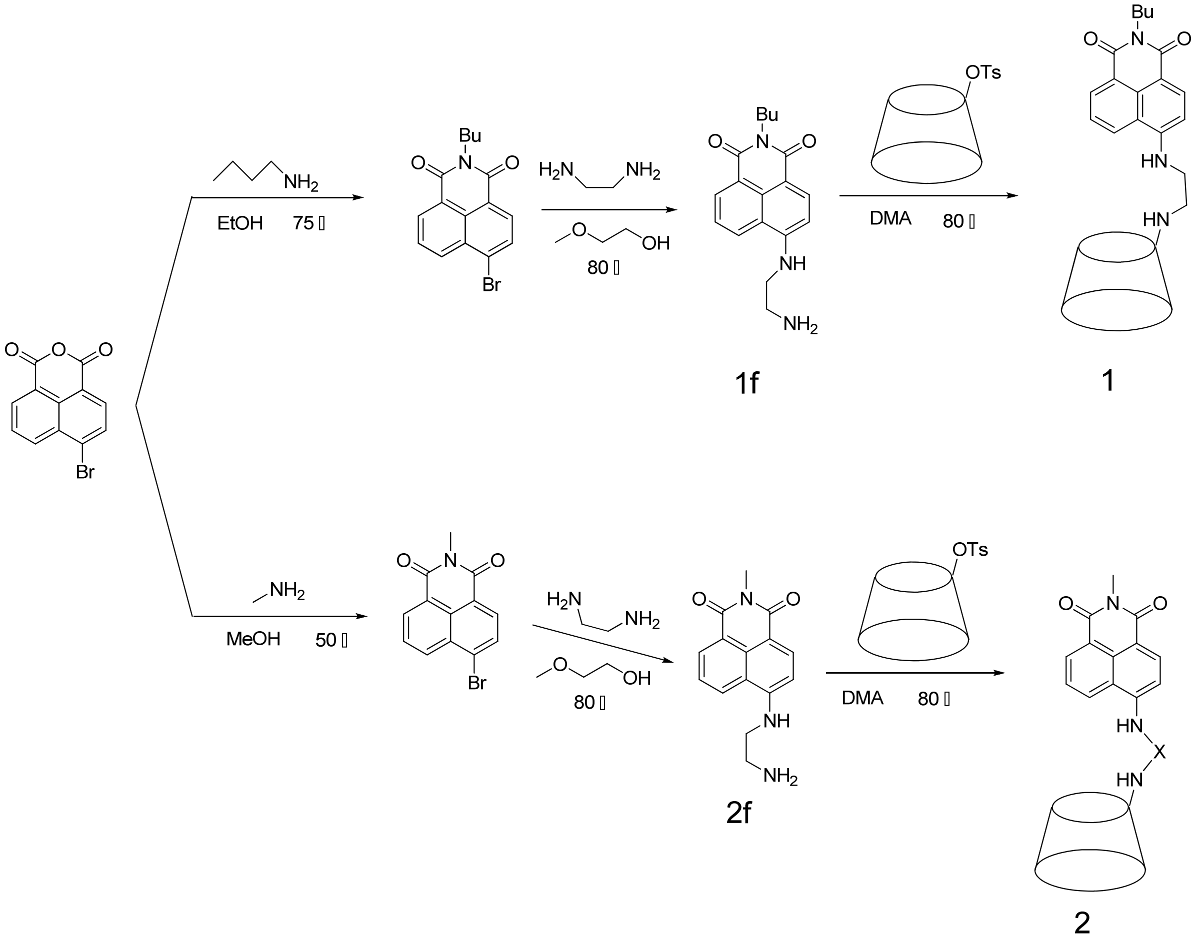
Contents

1. Experimental procedures



Scheme S1. Synthetic route for **1, 2**

1-1. Synthesis of 1 and 2

1f, 2f These compounds were prepared according to the literature[1,2].

6-O-p-Toluenesulfonyl-β-Cyclodextrin This compound was prepared according to the literature[3].

Compound 1 1 g (3.22 mmol) N-butyl-4-(2-aminoethylamino)-1, 8-naphthalimide was added to 6 mL DMF solution containing 2 g (1.55 mmol) 6-O-p-Toluenesulfonyl-β-Cyclodextrin. The resulting solution was stirred for 6 h at 80 ºC and cooled to room temperature. Afterward, the solution was added to 200 mL acetone dropwise to form precipitates. The precipitates were collected, washed with acetone followed by ether, and dried in vacuum. The product was dissolved in water and the solution was layered on a column packed with YMC GEL ODS-A (2.5 x 10 cm, pre-equilibrated with water). Step gradient elution (5, 10, 15, 20 and 25% EtOH containing 1% hydrochloric acid) was applied. The title compound was eluted at 20%-25% EtOH. The fractions containing 1 were combined and further purified and desalted on a SP Sephadex C-25 column with 1M aqueous ammonia as eluent. After drying in vacuo, a pure sample was obtained in 15% yield. MS (ESI): m/z 1428.5 ([M+H]+). 1H NMR (DMSO-d6, 300 MHz, TMS, ppm): δ 0.91 (t, 3H), 1.29-1.36 (m, 2H), 1.55-1.58 (m, 2H), 3.0-4.0 (m, 48H),4.52 (s, 6H), 4.83-4.90 (m, 7H), 5.60-5.90 (m, 14H), 6.85 (d, 1H), 7.69 (t, 1H), 8.28 (d, 1H), 8.44 (d, 1H), 8.68 (d, 1H). Anal.Calcd for C60H89N3O36·5H2O: C, 47.46; H, 6.57; N, 2.77%. Found: C, 47.52; H, 6.78; N, 2.71%.

Compounds 2 was synthesized in the same manner as that for **1** from 6-Ts-β-CD and fluorophore 2f. MS (ESI): m/z 1386.5 ($[M+H]^+$). 1H NMR (DMSO-*d*6, 300 MHz, TMS, ppm): δ 3.1-3.9 (m, 46H), 3.97 (s, 3H), 4.5-4.7 (m, 6H), 4.7-5.0 (m, 7H), 5.60-5.90 (m, 14H), 6.88 (d, 1H), 7.69 (t, 1H), 8.29 (d, 1H), 8.44 (d, 1H), 8.67 (d, 1H). Anal.Calcd for C57H83N3O36·6H2O: C, 45.81; H, 6.41; N, 2.81%. Found: C, 45.86; H, 6.38; N, 2.95%.

1-2. Spectroscopic Measurements

2D NOESY NMR spectra were obtained with D_2O as the solvent at 10 ºC on a 400 MHz bruker Avance-400 spectrometer. Chemical shifts were referenced to the solvent values. Fluorescence spectra were recorded on a HITACHI FL-4500 spectrofluorometer (1-cm quartz cell used), and excitation wavelength was set at 450 nm. The Circular dichroism spectra and UV spectra were recorded on a JASCO J810 spectrometer in water with 1 cm cell at 10 ºC.

2. Calculation of absorption spectra and transition dipole moment

The geometrical and electronic properties of the compounds were performed with the Gaussian 03 program package[4]

1. Optimization of the ground-state geometry at the DFT B3LYP/6-31G+(d) level of theory

2. Determination of the vertical electronic excitation energies and direction of transition dipole moment using the TD-DFT B3LYP/6-31G+(d) framework with PCM (polarized continuum model) as solvation model

Table S1 Excitation energies and oscillator strengths of the molecules calculated with TDDFT

Absorption wavelength (λ)	oscillator strengths (f)	Experiment result (λ)
251nm	0.2272	256nm
273nm	0.2457	284nm
279nm	0.2225	
421nm	0.2812	450nm

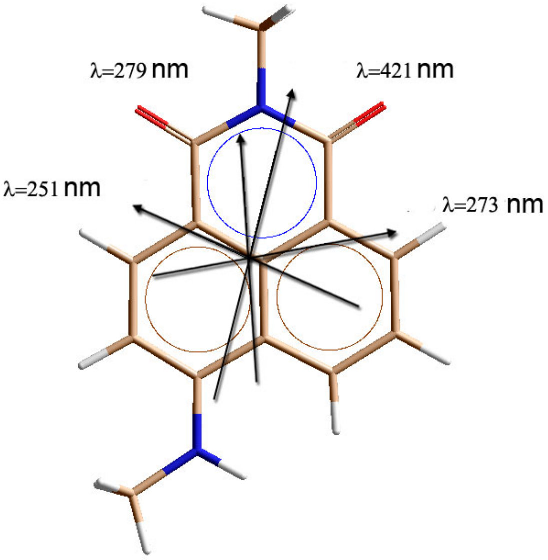


Figure S2-1 illustration of calculated direction of transition dipole moment

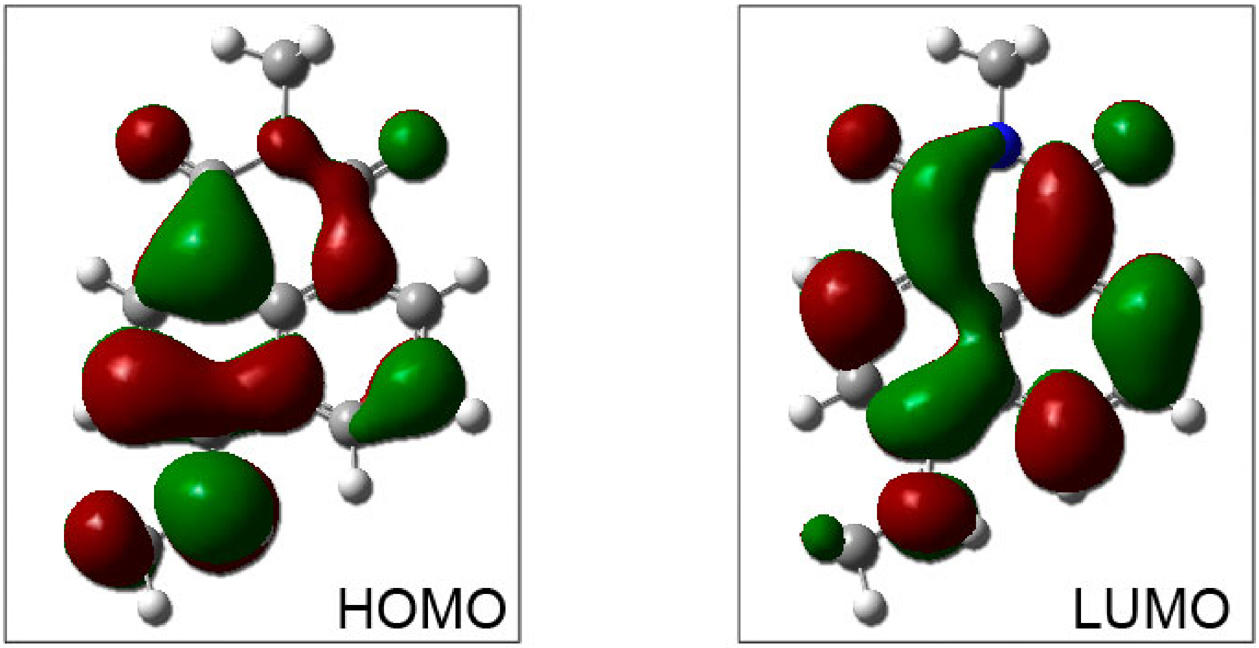


Figure S2-2 HOMO (left) and LUMO (right) computed on the ground state geometry with the PCM(water)-DFT B3LYP/6-31G+(d) scheme.

3. Molecular modeling results

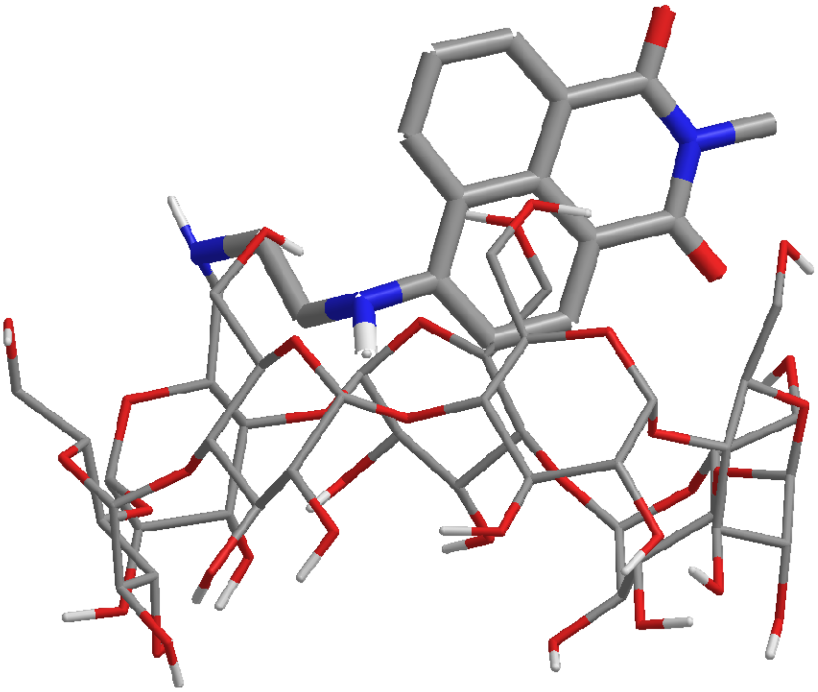


Figure S3-1 Molecular modeling of **2** derived from 2D NOESY NMR and energy minimization with amber force field calculation.

4. Additional fluorescence spectral data

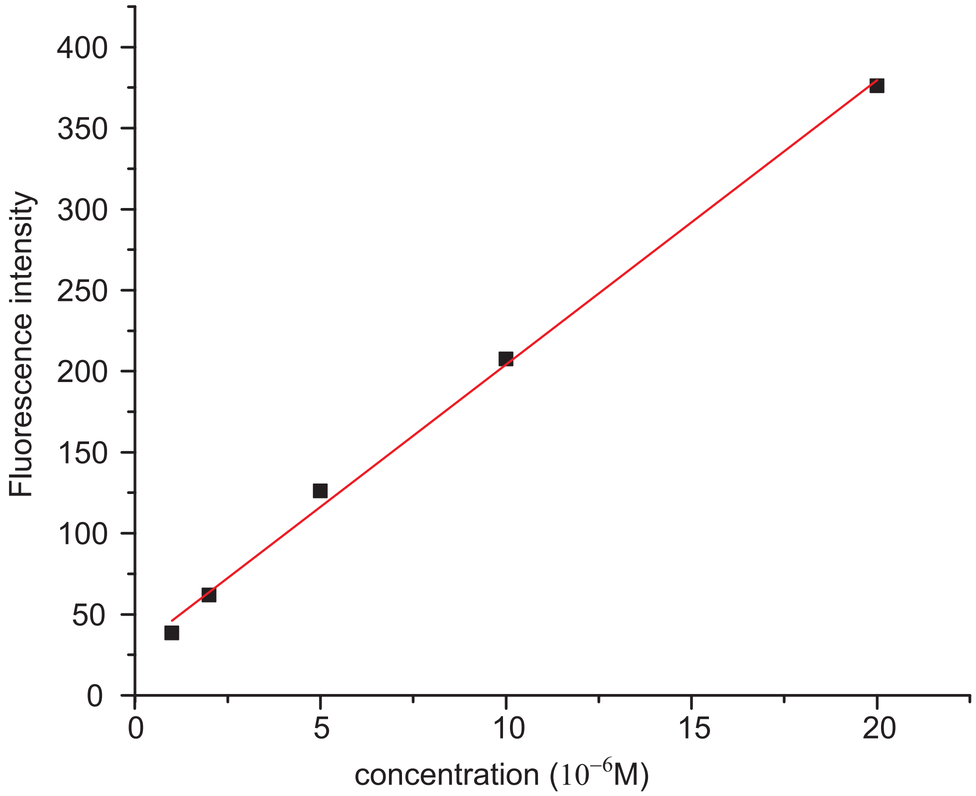


Figure S4-1 Fluorescence intensity at 530nm of compound **1** at various concentrations (1, 2, 5, 10, 20 μM)

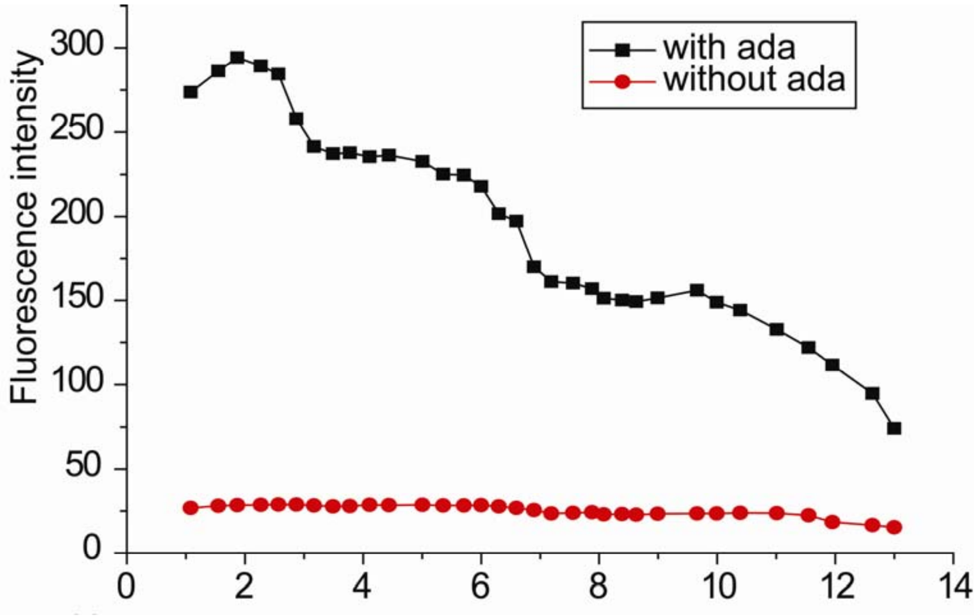
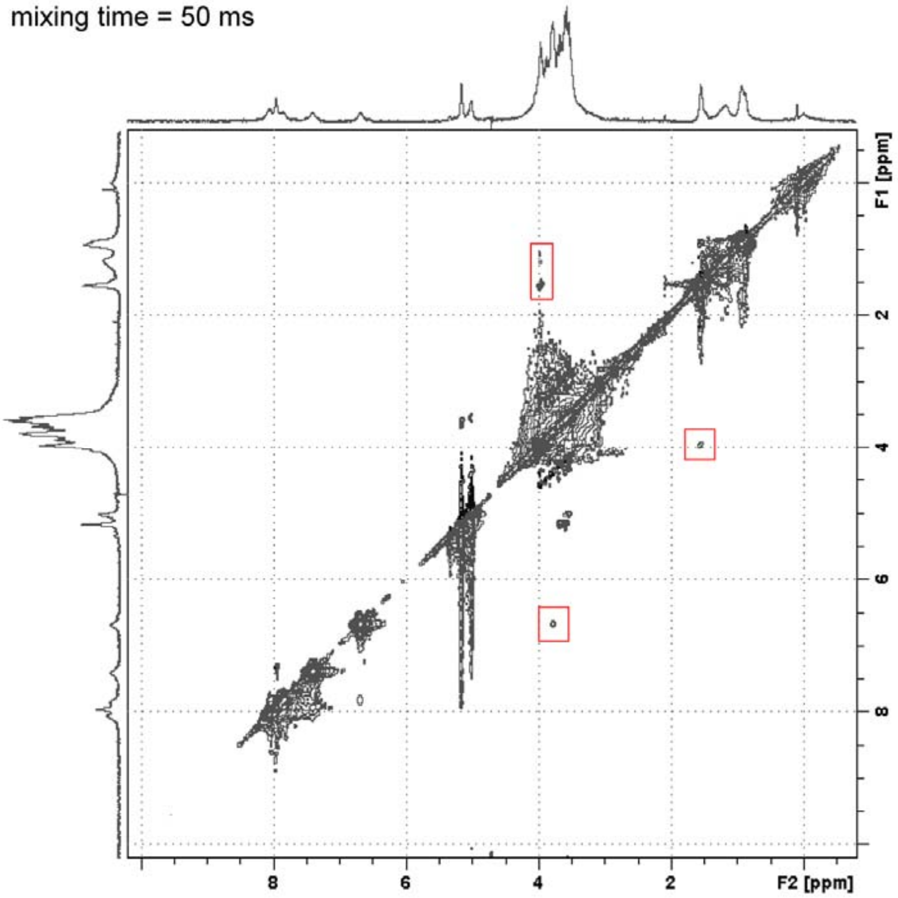
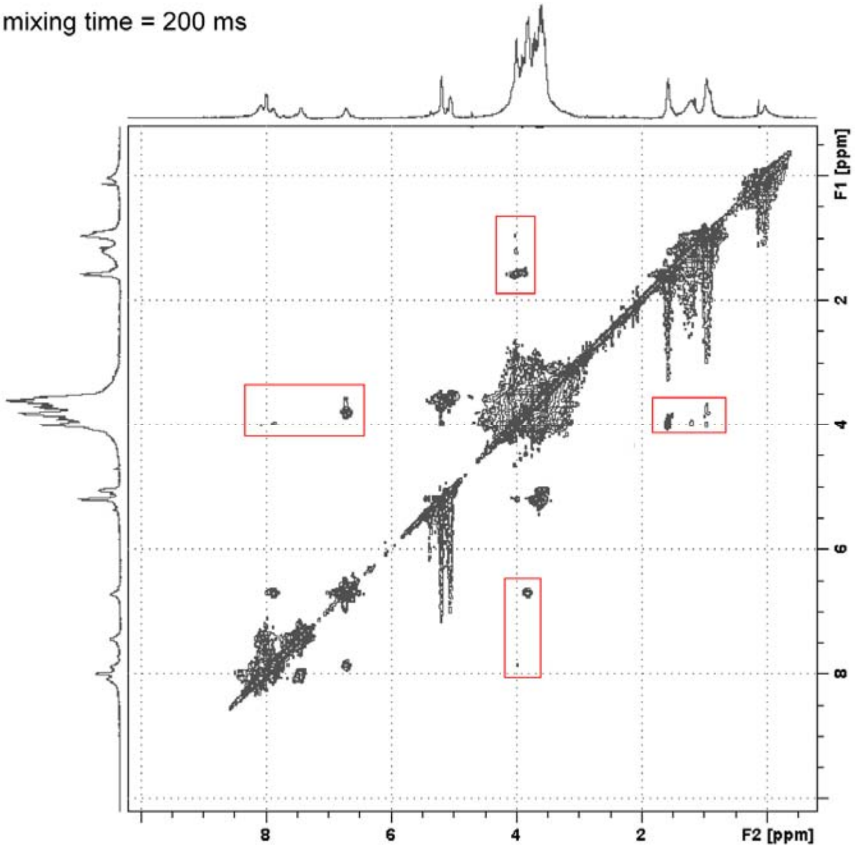


Figure S4-2. pH dependency of the fluorescence intensities and fluorescence maximum of **1** alone (10 μM) and in the presence of adamantane-1-carboxylate (200 μM).

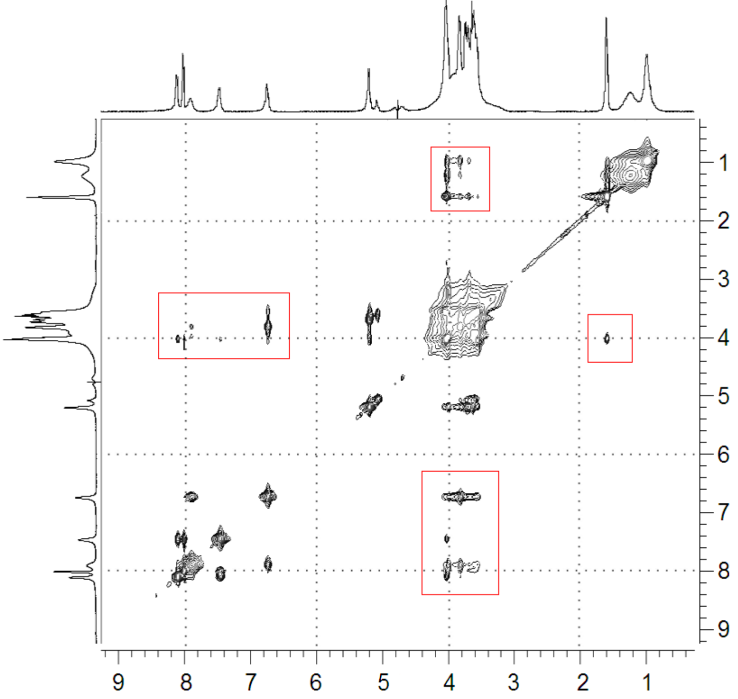
As shown in Fig. S4-2, the fluorescence of compound **1** is enhanced upon addition of the guest molecule at various pH values. Which suggest this behavior is not caused by the change of protonation degree of the ethylendiamine chain.

5. Additional NMR data


mixing time = 50 ms


mixing time = 200 ms

mixing time = 400 ms



ROESY

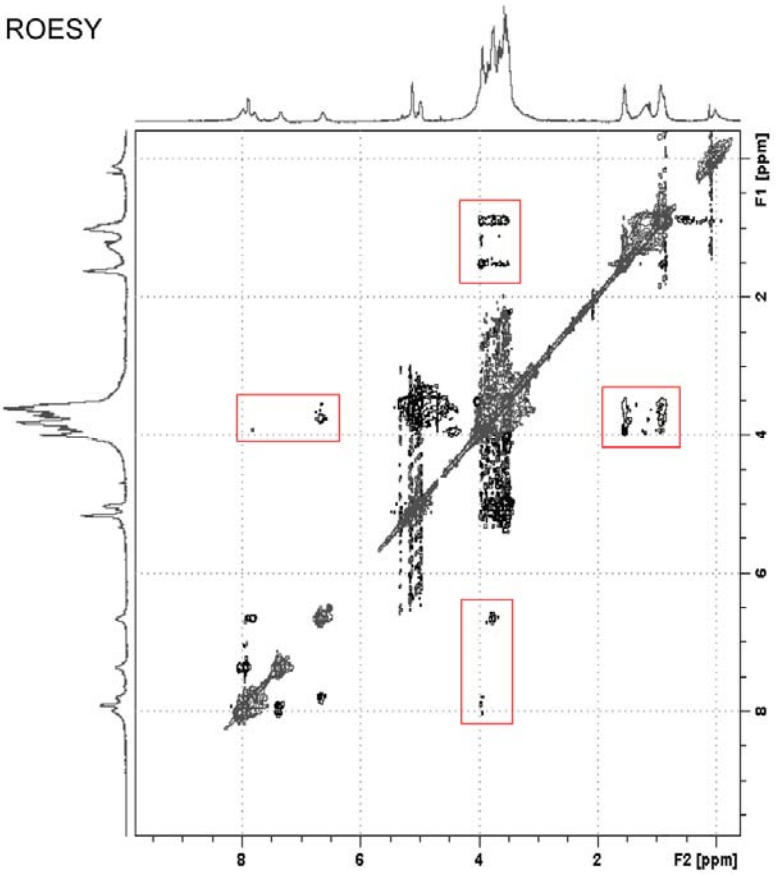


Figure S5-1 400MHz 2D NOESY NMR spectrum with water suppression of **1** in D_2O with mixing time of 50 msec (first), 200 msec (second), 400 msec (third) and 400MHz 2D ROESY NMR spectrum with water suppression of **1** in D_2O (fourth).

reference

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(2) Fan, J.; Peng, X.; Wu, Y.; Lu, E.; Hou, J.; Zhang, H.; Zhang, R.; Fu, X. *J. Lumin.* **2005**, *114*, 125-130.

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