

**A novel cascade strategy of supramolecular and  
chemodosimetic methods for designing  
fluorescence ratiometric detector hypersensitive  
to trace water†**

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**(Electronic Supplementary Information)**

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## **Experimental section**

### **Materials**

All the materials for synthesis and spectra were purchased from commercial suppliers (analytical grade) and used without further purification. Freshly purchased THF and methanol were purchased from Acros Organic (Super Dehydrated, > 99.8%, H<sub>2</sub>O < 50 ppm) and standardized with the Karl-Fischer method. These solvents were taken by syringe under dry N<sub>2</sub>, and used for spectral measurements. Other solvents were HPLC grade (> 99%, Tianjin Guangfu Fine Chemical Research Institute) and dried over molecular sieves prior to use. Ultrapure water (18.25 MΩ\*cm) from a Millipore Milli-Q purification system was used throughout the work.

### **Instrumentation**

The UV-vis absorption spectra were taken on a Shimadzu 3600 UV-VIS-NIR recording spectrophotometer using a 3 nm slit width. The fluorescence spectra were determined with a Shimadzu RF-5301PC spectrofluorophotometer. Unless otherwise mentioned, the excitation slit width was 3 nm and the emission slit width was 3 nm. <sup>1</sup>H-NMR (TMS) and <sup>13</sup>C-NMR were recorded on a Bruker UltraShield 500MHz spectrometer. Mass spectra were measured on a Thermo Scientific ITQ 1100<sup>TM</sup> GC/MSn and an autoflex speed<sup>TM</sup> MALDI-TOF mass spectrometer (Bruker, daltonics Inc., USA). Elemental analyses were carried out with a vario MICRO cube elementar. All measurements were taken at room temperature and repeated at least once.

### **Spectral measurements**

Incremental amounts of water were added to the solutions of **1** and **1-Zn(II)** in different anhydrous organic solutions (THF and methanol) by a micropipette, obtaining the organic-aqueous solutions with the required dye concentration as well as the water contents. After being

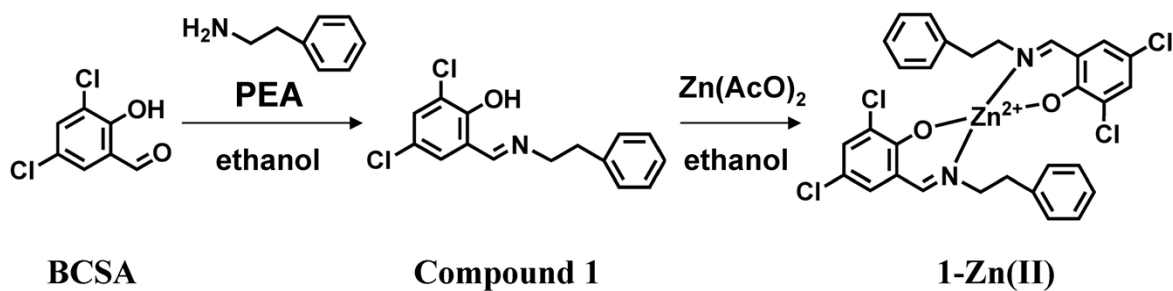
stored in a vacuum dryer overnight, UV-Vis/fluorescence spectra were measured at room temperature.

### Synthesis of compound 1

Compound 1 was prepared according to our previous works.<sup>5</sup> <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 14.558 (s, 1H), 8.471 (s, 1H), 7.568 (d, *J* = 2.65 Hz, 1H), 7.368 (d, *J* = 2.65 Hz, 1H), 7.313 (t, *J* = 7.30 Hz, 2H), 7.261 (d, *J* = 6.95 Hz, 2H), 7.222 (t, *J* = 7.15 Hz, 1H), 3.897 (t, *J* = 7.00 Hz, 2H), 2.995 (t, *J* = 7.05 Hz, 2H). MS: *m/z* calculated for C<sub>15</sub>H<sub>13</sub>Cl<sub>2</sub>NO [M<sup>+</sup>]: 293.04, found 293.15. Elemental analysis calculated for C<sub>15</sub>H<sub>13</sub>Cl<sub>2</sub>NO: C, 61.24; H, 4.45; N, 4.76%. Found: C, 61.43; H, 4.350; N, 4.73%.

### Synthesis of complexes 1-Zn(II)

0.29 g (1 mmol) compound 1 was dissolved in 30 ml of anhydrous ethanol and treated with 0.09 g (0.5 mmol) of zinc acetate and 0.08 g (1 mmol) sodium bicarbonate, and the mixture was refluxed for 2 h. After the reaction, the mixture was cooled in the ice bath. The precipitate was filtered and washed with 15 ml of ethanol for three times. Recrystallization of the crude products from THF for about one week afforded complex 1-Zn(II) as yellow powder, which was subjected to the following NMR, mass, elemental analysis and the single-crystal X-ray diffraction measurement. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>): δ 8.289 (s, 2H), 7.489 (d, *J* = 2.78 Hz, 2H), 7.211-7.241 (m, 6H), 7.164 (t, *J* = 7.22 Hz, 2H), 7.097 (d, *J* = 7.23 Hz, 4H), 3.935 (t, *J* = 7.45 Hz, 4H), 2.857 (t, *J* = 7.49 Hz, 4H). <sup>13</sup>C NMR (500 MHz, CDCl<sub>3</sub>): δ 170.769, 164.093, 139.153, 133.290, 132.412, 129.270, 128.683, 126.632, 126.599, 120.102, 114.880, 62.201, 37.512. MS: *m/z* calculated for C<sub>30</sub>H<sub>24</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Zn [M<sup>+</sup>]: 651.74, found 651.28. Elemental analysis calculated for C<sub>30</sub>H<sub>24</sub>Cl<sub>4</sub>N<sub>2</sub>O<sub>2</sub>Zn: C, 55.29; H, 3.71; N, 4.30%. Found: C, 55.37; H, 3.64; N, 4.13%.



Scheme S1. Synthetic route to 1-Zn(II).

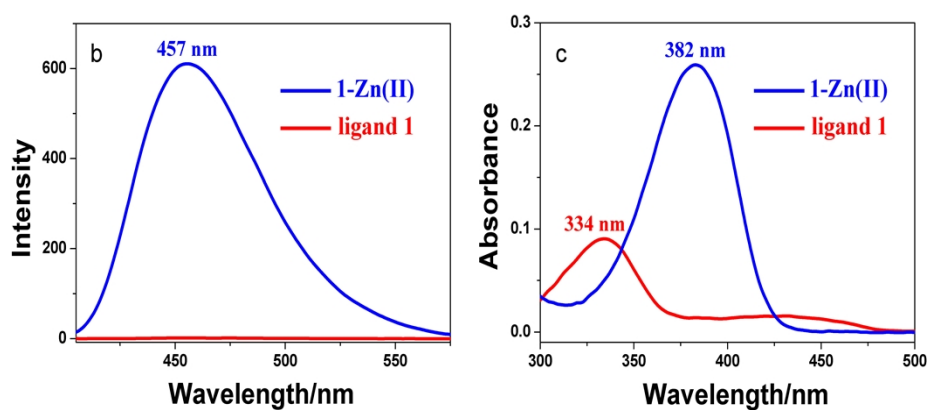


Fig. S1 (a) Fluorescence and (b) absorption spectra of 1-Zn(II) and 1 in THF ( $\lambda_{\text{ex}} = 400 \text{ nm}$ ,  $[1\text{-Zn(II)}] = 20 \mu\text{M}$ .)

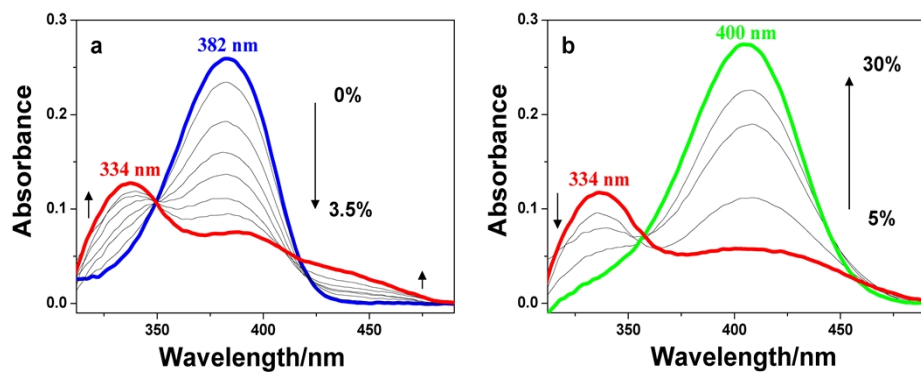
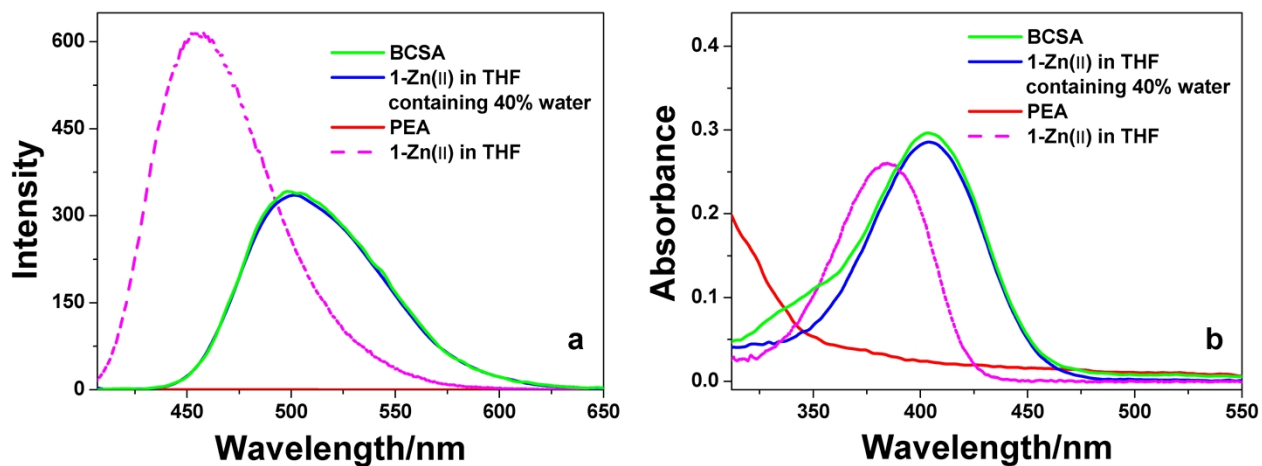
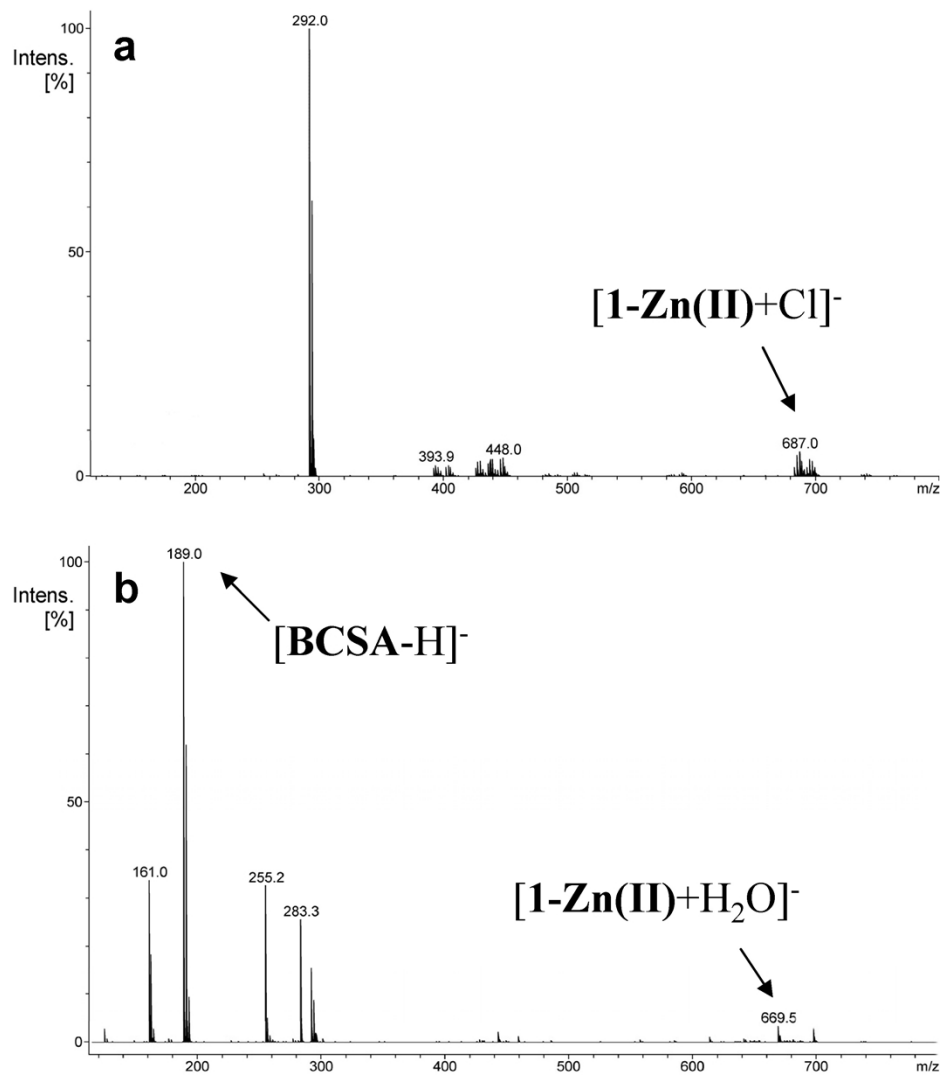


Fig. S2 (a) Absorption spectra of 1-Zn(II) in THF containing water (0, 0.1, 0.4, 0.6, 0.8, 1, 2,

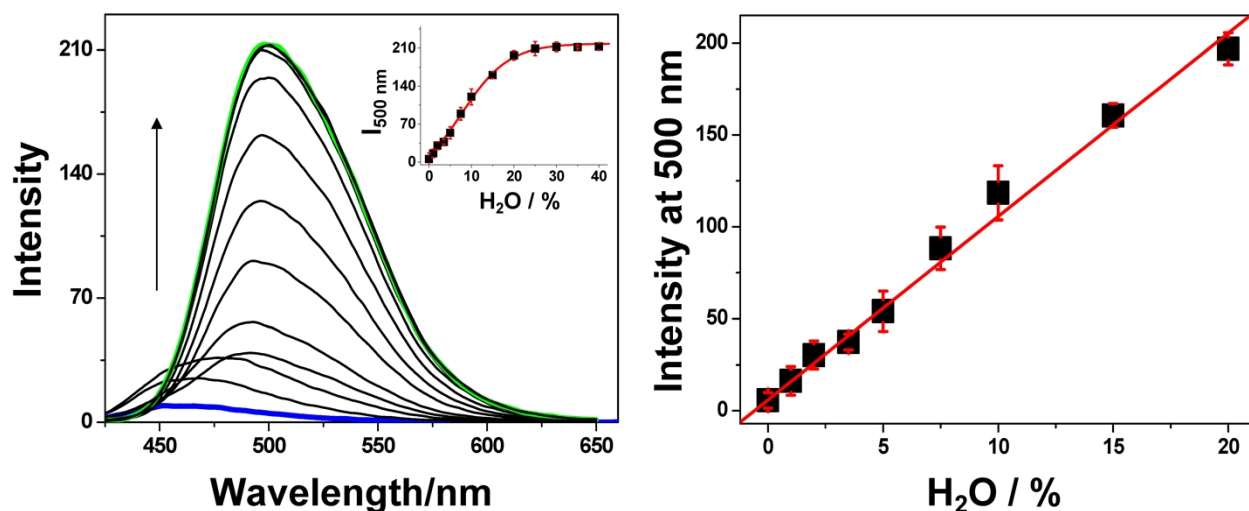
3.5% v/v). (b) Absorption spectra of **1-Zn(II)** in THF containing water (5, 10, 20, 30, 40% v/v). ( $\lambda_{\text{ex}} = 400 \text{ nm}$ ,  $[\mathbf{1-Zn(II)}] = 20 \mu\text{M}$ ).



**Fig. S3** (a) Fluorescence and (b) absorption spectra of  $20 \mu\text{M}$  of **1-Zn(II)** and  $40 \mu\text{M}$  of **BCSA** and **PEA** in THF- $\text{H}_2\text{O}$  (6:4, v/v, pH = 7.0) solution as well as  $20 \mu\text{M}$  of **1-Zn(II)** in THF, respectively.



**Fig. S4** ESI mass spectrum of **1-Zn(II)** in (a) THF and (b) THF-H<sub>2</sub>O (9:1, v:v) under negative ion mode.

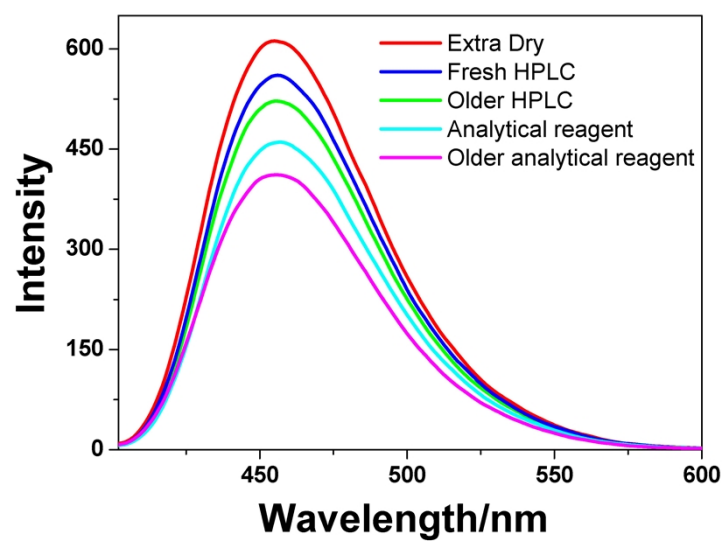


**Fig. S5** (a) Fluorescence spectra of **1** in THF containing water (0, 1, 2, 3.5, 5, 7.5, 10, 15, 20, 25, 30, 35, 40% v/v). ( $\lambda_{\text{ex}}=400$  nm,  $[1] = 20$   $\mu\text{M}$ ). Inset: The fluorescence intensity changes at 500 nm of **1** in THF with increasing water contents. (b) The fluorescence intensity at 500 nm of **1** in THF with increasing water contents (below 20% v/v). The calibration curve for water detection of **1** in THF was obtained:  $F = 9.85 [\text{H}_2\text{O}] + 8.44$  ( $R = 0.9960$ ,  $[\text{H}_2\text{O}] = 0\text{-}20\%$ ).  $F$  stands for the fluorescence intensity at 500 nm. The detection limit and quantitation limit were estimated to be 0.0734 (949 ppm) and 0.2223, respectively.

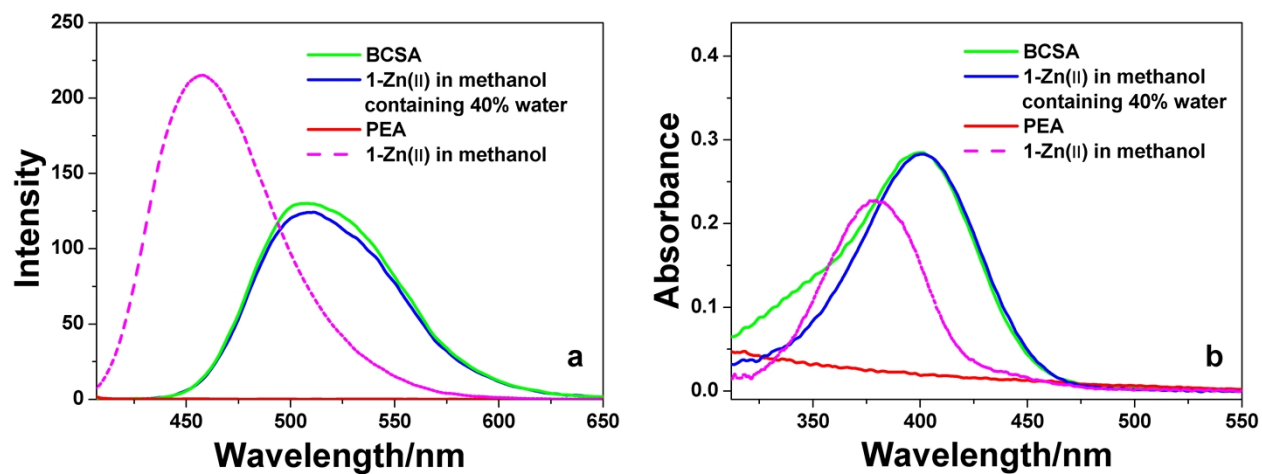
**Table S1.** Comparison of previously developed fluorescence water sensor with the proposed sensor.

<b>Detection limit</b>	<b>Quantitation limit</b>	<b>Ref.</b>
0.1 wt% (acetonitrile)	0.4 wt% (acetonitrile)	3a
0.2 wt% (THF)	0.5 wt% (THF)	3b
0.04 wt% (acetonitrile)	0.1 wt% (acetonitrile)	
0.038 v/v% (acetonitrile)	—	1b
0.0035 v/v% (THF)	—	2a
0.0063 v/v% (acetonitrile)	—	
0.02 v/v% (THF)	—	1c
0.021 v/v% (acetonitrile)	—	
0.291 v/v% (methanol)	—	
0.006 v/v% (acetonitrile)	—	1d
0.002 v/v% (acetonitrile)	—	1e
0.02 wt% (acetonitrile)	0.07 wt% (acetonitrile)	4
0.0068 v/v% (THF)	0.0206 v/v% (THF)	This work
0.0075 v/v% (methanol)	0.0227 v/v% (methanol)	

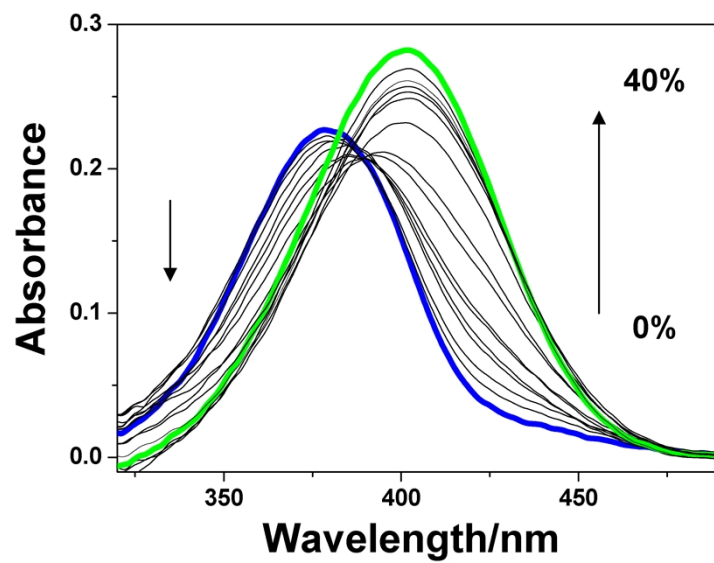




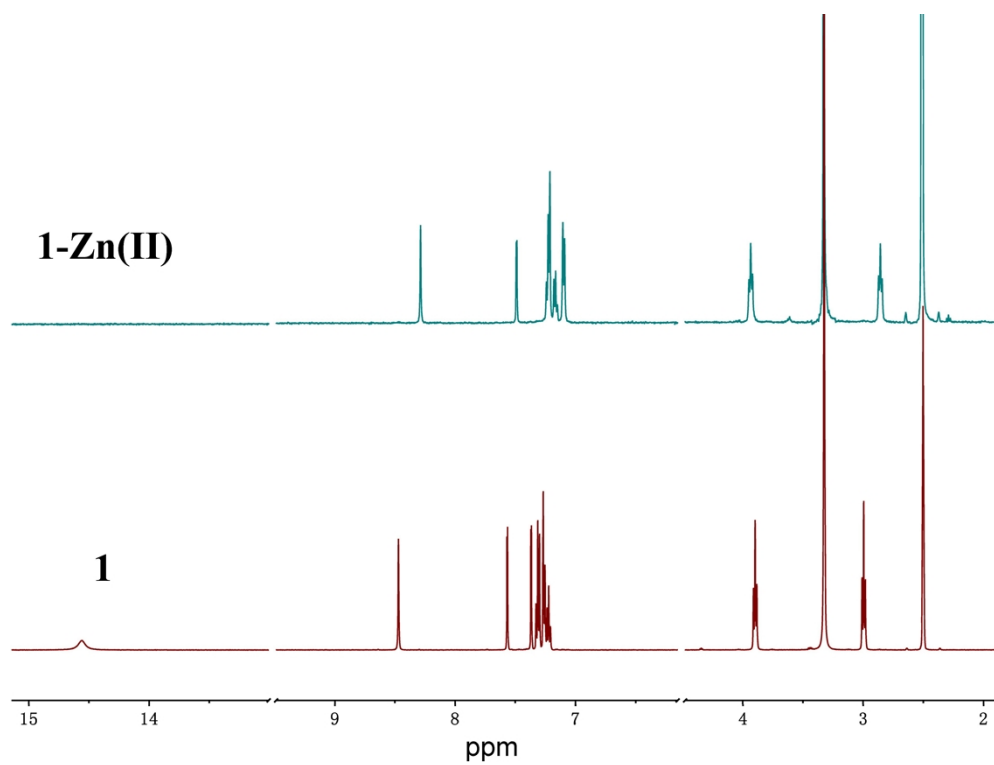
**Fig. S6** Fluorescence spectra of **1-Zn(II)** in various grades of commercial THF. ( $\lambda_{\text{ex}}=400$  nm,  $[1\text{-Zn(II)}] = 20 \mu\text{M}$ ).



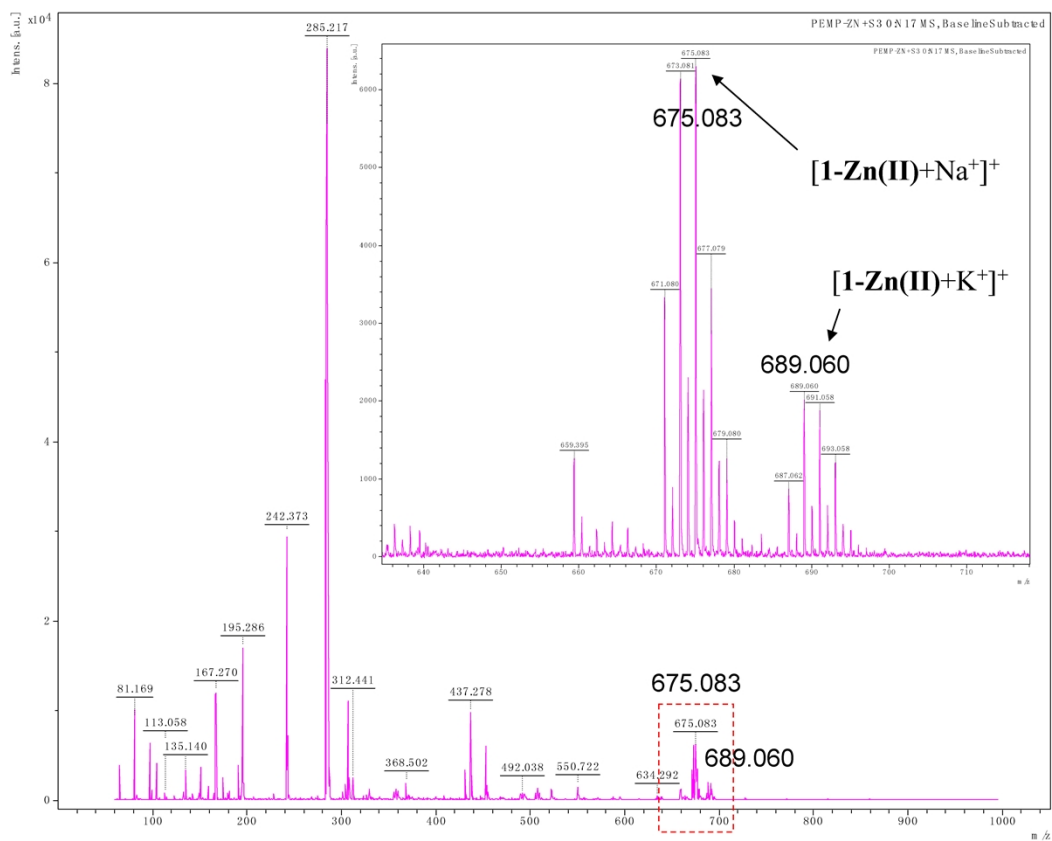
**Fig. S7** (a) Fluorescence and (b) absorption spectra of 20  $\mu\text{M}$  of **1-Zn(II)** and 40  $\mu\text{M}$  of **BCSA** and **PEA** in methanol- $\text{H}_2\text{O}$  (6:4, v/v, pH = 7.0) solution as well as 20  $\mu\text{M}$  of **1-Zn(II)** in methanol, respectively.



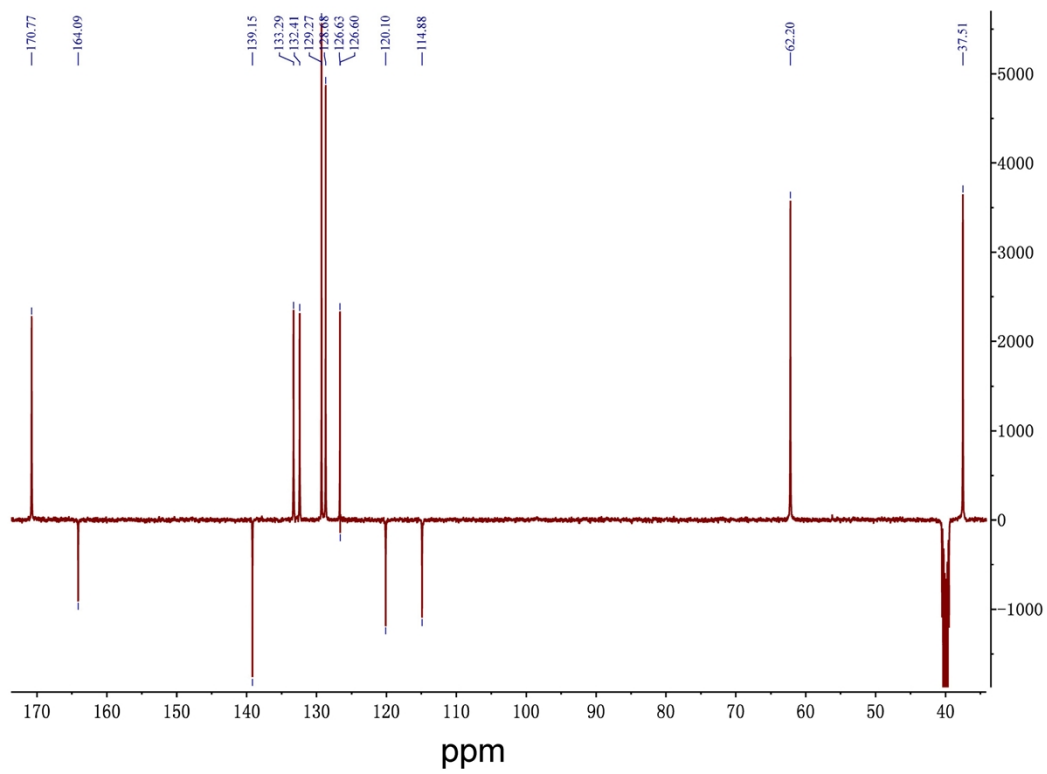
**Fig. S8** Absorption spectra of **1-Zn(II)** in methanol containing water (0, 0.025, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1, 1.5, 2, 4, 6, 9, 10, 15, 20, 30, 40% v/v). ( $\lambda_{\text{ex}} = 400 \text{ nm}$ ,  $[\mathbf{1-Zn(II)}] = 20 \mu\text{M}$ ).



**Fig. S9** <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz) spectrum of **1** and **1-Zn(II)** .



**Fig. S10** MALDI-TOF mass spectrum of **1-Zn(II)**. Inset: The magnification of the region between 635 and 718 m/z.



**Fig. S11** DEPTQ <sup>13</sup>C NMR(CDCl<sub>3</sub>, 500 MHz) spectrum of **1-Zn(II)**.

**Table S2.** Crystal data and structure refinement for **1-Zn(II)**.

	<b>1-Zn(II)</b>
Identification code	<b>1-Zn(II)</b>
Empirical formula	C <sub>30</sub> H <sub>24</sub> Cl <sub>4</sub> N <sub>2</sub> O <sub>2</sub> Zn
Formula weight	651.68
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	a = 21.692(8) Å alpha = 90 deg. b = 4.868(16) Å beta = 111.442(16) deg. c = 28.611(10) Å gamma = 90 deg.
Volume	2799.9(17) Å <sup>3</sup>
Z, Calculated density	4, 1.546 mg/m <sup>3</sup>
Absorption coefficient	1.291 mm <sup>-1</sup>
F(000)	1328
Theta range for data collection	1.53 to 27.96 deg.
Limiting indices	-28<=h<=23, -6<=k<=6, -35<=l<=37
Reflections collected / unique	10474 / 3305 [R(int) = 0.0266]
Completeness to theta = 27.96	97.6 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3305 / 0 / 177
Goodness-of-fit on F <sup>2</sup>	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0781
R indices (all data)	R1 = 0.0374, wR2 = 0.0825
Largest diff. peak and hole	0.288 and -0.292 e.Å <sup>-3</sup>