

## Electronic supplementary information

### **A thiazoline-containing cobalt complex(II) based colorimetric fluorescent probe: “turn-on” detection of fluoride**

*Jing Wang, Hai-Bo Liu, Wei Wang\*, Il Kim and Chang-Sik Ha\**

*E-mails: csha@pusan.ac.kr (C.-S. Ha); wangweitfj@yahoo.com.cn (W. Wang)*

#### **Experimental Section**

##### **1. General Procedures and Materials**

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Flash chromatography was carried out on silica gel 60 (230–400 mesh ASTM; Merck). Melting points were measured by using a B-545 melting point apparatus. The Fourier-Transform Infrared (FTIR) spectra were recorded at room temperature on a JASCO FTIR 460 Plus operated at a resolution  $4\text{cm}^{-1}$ .  $^1\text{H}$ -NMR spectra were recorded on a Varian Gemini-2000 (300 MHz) spectrometer with tetramethylsilane as the internal reference, where chemical shifts are given in ppm. The elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer. The UV–vis spectra were measured using a Hitachi U-2010 spectrometer (1 cm quartz cell) at 25 °C. The fluorescence emission spectra were measured using a Hitachi F-4500

spectrometer (1 cm quartz cell) at 25 °C. Excitation slit size was 5.0 nm and emission slit size was also 5.0 nm. Scan speed was set at 240 nm/min.

## 2. Synthesis

### 2.1 Synthesis of thiazoline-2-thione (3)

The thiazoline-2-thione was synthesized using two steps according to the reference procedures.<sup>1</sup> First step: 18 ml H<sub>2</sub>SO<sub>4</sub> was added dropwise to ethanolamine under -5°C ~10°C, then 10 ml H<sub>2</sub>O was added to the mixture. The reaction mixture was stirred 40~60 min at room temperature, filtered, dried at 60 °C for 12 hours. NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub><sup>-</sup> was obtained, yield 47.32%, m.p 278°C. Second step: 12.3 g KOH in 20 ml 1:1 EtOH/H<sub>2</sub>O solution was added to a 1:1 EtOH/H<sub>2</sub>O solution (60 ml) of 14.21 g NH<sub>3</sub><sup>+</sup>CH<sub>2</sub>CH<sub>2</sub>OSO<sub>3</sub><sup>-</sup> and 15 ml CS<sub>2</sub>. The reaction mixture was stirred and heated at reflux for 8 h under N<sub>2</sub>, filtered, stewing, after cooling, the white needlelike crystals was separated out in the filtrate. The solvent was removed to give the corresponding thiazoline-2-thione (3) as a white solid, which was further purification by recrystallization using H<sub>2</sub>O to afford purer samples 3 (4.60 g, 38.41%), m.p 104~106°C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 25 °C, TMS): 7.92 (s,1H), 4.00 (t,2H), 3.58 (q,2H); IR: 3144 (vs), 3004 (ms, ring ν<sub>Φ-H</sub>), 1252 (ms, ring C=S), 692 (ms, ring C-S), 1298 (vs,

ring C-N ), 1040 (vs), 998 (s) and 932 (s, ring C-C ), 1512 (vs), 1452 (w) and 1434 (s, CH<sub>3</sub>-, CH<sub>2</sub>-, δ<sub>C-H</sub>), 2852 (w, CH<sub>3</sub>-, CH<sub>2</sub>-, ν<sub>C-H</sub>).

## 2.2 Synthesis of 1,4-Bis(2-thiazolin-2-ylsulfanyl)butene (2)

A solution of trans-1,4-dibromo-2-butene (0.46 g, 2.1 mmol) in ethanol (3 ml) was added dropwise to a mixture of thiazoline-2-thione (0.53 g, 4.4 mmol), KOH (0.25 g, 4.4 mmol) and ethanol (5 ml). The reaction mixture was then stirred for 16 h at room temperature. The precipitate was then filtered off, washed with water and recrystallized from ethanol and water (1:1 v/v), 2 (0.28 g, 44%) was obtained as white solid, m.p. 48~52°C. <sup>1</sup>H-NMR (300 MHz, CDCl<sub>3</sub>, 25°C, TMS): 5.81 (t, 2H, CH=CH), 4.22 (t, 4H), 3.74 (d, 4H, CH<sub>2</sub>), 3.40 (t, 4H). IR: 3444 (w), 3100 (w), 3040 (ms), 2960 (ms), 2924 (ms), 2900 (ms), 2844 (s), 1560 (vs), 1402 (vs), 1302 (s), 1236 (vs), 1190 (ms), 1016 (ms), 992 (s), 964 (vs), 920 (vs), 866 (w), 696 (s). Analysis calculated for C<sub>10</sub>H<sub>14</sub>N<sub>2</sub>S<sub>4</sub>: C : 41.38% ; H : 4.83%, N : 9.66%; Found, C : 41.34% ; H : 4.76% ; N : 9.57%.

## 2.3 Synthesis of Complex 1.

The aqueous solution of Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.018 g, 0.1 mmol) was added dropwise to 2 (0.029 g, 0.1 mmol) in 25 ml MeOH and the mixture was

stirred for 24 h at room temperature, then the precipitate was filtered and washed with cold water to give complex 1 (0.016g, 67%) as a purple powder. Anal. Calc. for  $C_{10}H_{14}CoN_4O_6S_4$ : C, 25.37; H, 2.98; N, 11.83%. Found: C, 25.41; H, 2.95; N, 11.87%. IR (KBr pellet,  $cm^{-1}$ ): 3464, 3130, 2930, 1624, 1516, 1296, 1251, 1205, 1087, 1051, 999, 932, 699, 653.

Crystals of complex 1 were grown by layer-method using three layer solutions in a slender tube with a 0.8 cm diameter. The bottom layer solution was 29 mg (0.1 mmol) of 2 in 5 ml chloroform solution. The upper layer solution was 5 ml of acetone solution containing 18 mg (0.1 mmol)  $Co(NO_3)_2 \cdot 6H_2O$  and the middle layer was 5 ml of chloroform/acetone (v/v 1:1) mixed system. After standing for 21 days, purple rod crystals were obtained.

### 3. X-ray crystallographic study of complex 1

Single-crystal X-ray diffraction measurements of complex 1 were carried out with a Bruker Smart1000 CCD diffractometer at 293(2)K. The determination of the unit cell parameters and the data collections were performed with Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) in the range of  $2.19^\circ < \theta < 25.02^\circ$ . Unit cell dimensions were obtained with least-squares refinements. The structure of the complex was solved by direct method and

successive difference Fourier syntheses (SHELXS-97), and refined by full-matrix least-squares procedure on F<sup>2</sup> with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97)<sup>2</sup>. Co<sup>II</sup> atom was located from the E-map, and the other non-hydrogen atoms were located in successive difference Fourier syntheses (SHELXS-97). The final refinement was carried out by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F<sup>2</sup> by SHELXS-97 program package. Hydrogen atoms were included in calculated positions and refined with fixed thermal factors. Crystallographic data and experimental details for structural analyses are summarized in Table 1, whereas selected bond lengths and angles are presented in Table 2.

#### **4. Photophysical evaluation**

##### **4.1 Quantum Yield Measurements**

The quantum yields for fluorescence were obtained by comparison of the integrated area of the corrected emission spectrum of the samples with that of a solution of fluorescein in 0.1 N NaOH, which has a quantum efficiency of 0.95.<sup>3</sup> The quantum efficiency was measured by using a dilute sample of 1 ( $8 \times 10^{-7}$  M) in the absence and presence of 5 equiv NaF<sub>2</sub> in 10 mM HEPES. The concentration of the reference was adjusted to match the absorbance of the test sample at the wavelength of excitation. Emission for 1 and 1-

F<sup>-</sup> was integrated from 560 to 650 nm with excitation at 520 nm. The quantum yields were calculated with the following equation:

$$\Phi_F(x) = \left( \frac{A_s}{A_x} \right) \left( \frac{F_x}{F_s} \right) \left( \frac{\eta_x}{\eta_s} \right)^2 \Phi_F(s)$$

where s is the standard, x is the unknown, A is the absorbance at the excitation wavelength, F is the integrated area under the emission curve,  $\eta$  is the refractive index of the solvent and  $\Phi_F$  is the quantum yield.

#### **4.2 Anion recognition studies: Preparation of fluorometric anion titration solutions**

The anion binding ability of 1 was determined by preparing solutions containing 100  $\mu$ M solution of 1 along with 5 equiv of a particular sodium salt in DMF/H<sub>2</sub>O (v/v, 9/1, 10 mM HEPES buffer, pH 7.5). The fluorescence spectrum of each solution was recorded with excitation at 520 nm. The anion recognition behaviour of 1 was evaluated from the changes in fluorescence spectrum upon addition of that sodium salt.

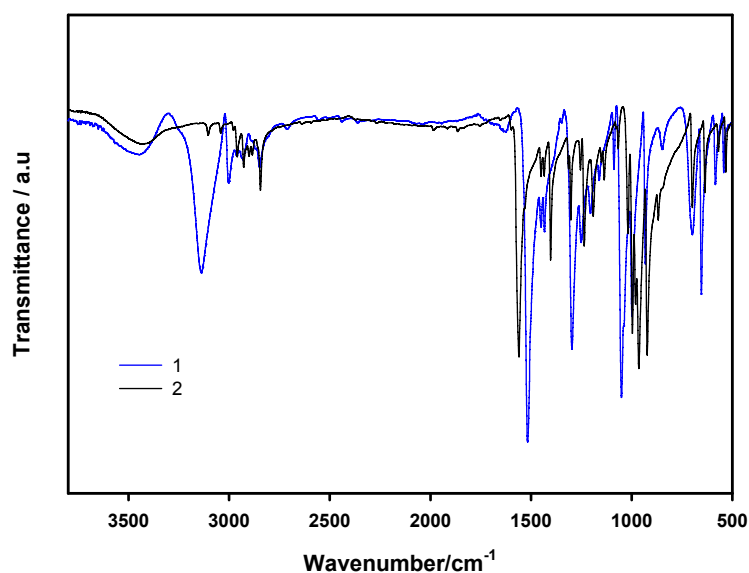
#### **4.3 Fluoride ion titration**

Volumetric flasks were taken each containing 100  $\mu$ M of 1 along with varied amounts of sodium fluoride in DMF/H<sub>2</sub>O (v/v, 9/1, 10 mM HEPES buffer, pH 7.5). The

solutions were shaken thoroughly and their fluorescence spectra were recorded with excitation at 520 nm.

#### 4.4 Competition studies

To evaluate any possible interference anions for the sensing of fluoride anion, solutions were prepared containing complex 1 (100  $\mu\text{M}$ ) along with a fixed concentration of  $\text{F}^-$  (5 equiv of 1) in the presence of competition anions in DMF/ $\text{H}_2\text{O}$  (v/v, 9/1, 10 mM HEPES buffer, pH 7.5). Their fluorescence spectra were recorded with excitation at 520 nm.



**Figure S1.** FTIR spectra of complex 1 and compound 2.

**Table S1** Crystal data and structure refinement summary for **1**

Empirical formula	C <sub>10</sub> H <sub>14</sub> CoN <sub>4</sub> O <sub>6</sub> S <sub>4</sub>
Formula weight	473.42
Crystal system	Monoclinic
Space group	P2(1)/c
<i>a</i> (Å)	9.5132(17)
<i>b</i> (Å)	17.434(3)
<i>c</i> (Å)	10.991(2)
$\alpha$ (°)	90
$\beta$ (°)	91.767(3)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	1822.0(6)
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.726
<i>F</i> (000)	964
<i>Z</i>	4
Crystal size (mm <sup>3</sup> )	0.18 x 0.14 x 0.10
$\mu$ (Mo K $\alpha$ )/mm <sup>-1</sup>	1.435
$\theta$ range(°)	2.19 to 25.02
Range of <i>h</i> , <i>k</i> , <i>l</i>	-11/9, -20/15, -13/12
Reflections collected/unique	9027 / 3218
Data/restraints/parameters	3218 / 0 / 226
<i>R</i> and <i>wR</i>	0.0457 and 0.1308
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.039
Max. res. peak and hole (e <sup>-</sup> Å <sup>-3</sup> )	0.596 and -0.417

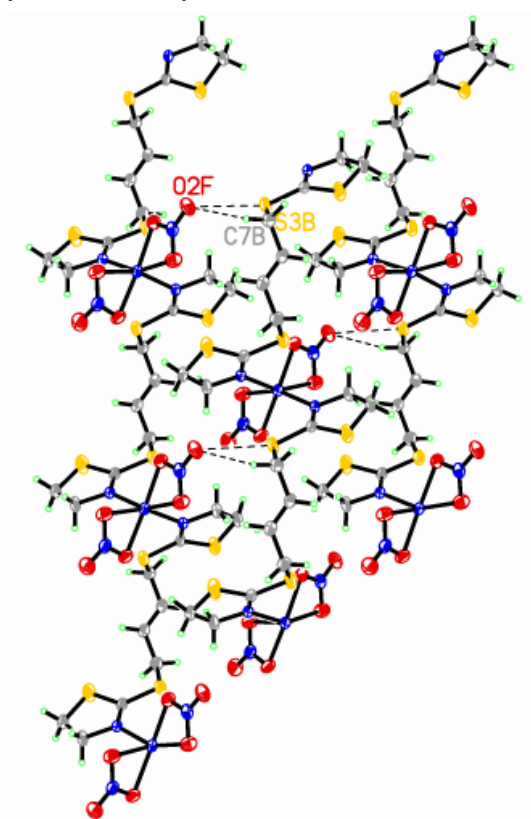


**Table S2** Selected bond lengths [Å] and angles [°] for **1**

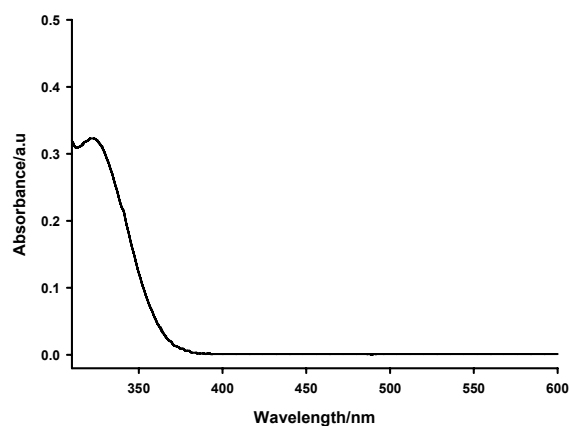
Atoms	Data	Atoms	Data
Co(1)-N(2)#1	2.057(3)	C(6)-C(7)	1.489(6)
Co(1)-N(1)	2.058(3)	C(9)-C(10)	1.492(7)
N(2)-Co(1)#2	2.051(2)	N(2)#1-Co(1)-O(1)	101.48(14)
Co(1)-O(1)	2.088(3)	N(2)#1-Co(1)-N(1)	103.28(14)
Co(1)-O(4)	2.109(3)	N(1)-Co(1)-O(1)	96.71(13)
Co(1)-O(6)	2.254(4)	N(2)#1-Co(1)-O(4)	99.15(13)
Co(1)-O(3)	2.268(4)	N(1)-Co(1)-O(4)	102.18(14)
S(1)-C(3)	1.740(4)	O(1)-Co(1)-O(4)	147.90(15)
S(1)-C(2)	1.795(5)	N(2)#1-Co(1)-O(6)	156.126(13)
S(2)-C(3)	1.741(5)	N(1)-Co(1)-O(6)	90.93(14)
S(2)-C(4)	1.814(5)	O(1)-Co(1)-O(6)	95.52(13)
S(3)-C(8)	1.736(4)	O(4)-Co(1)-O(6)	58.79(13)
S(3)-C(7)	1.826(4)	N(2)#1-Co(1)-O(3)	90.32(14)
S(4)-C(8)	1.743(4)	N(1)-Co(1)-O(3)	154.07(13)
S(4)-C(10)	1.797(5)	O(1)-Co(1)-O(3)	58.55(13)
O(1)-N(3)	1.271(5)	O(4)-Co(1)-O(3)	97.21(14)
O(2)-N(3)	1.217(5)	O(6)-Co(1)-O(3)	84.50(13)
O(3)-N(3)	1.254(5)	C(3)-S (1)-C(2)	91.0(2)
O(4)-N(4)	1.279(5)	C(3)-S (2)-C(4)	105.1(2)
O(5)-N(4)	1.211(5)	C(8)-S (3)-C(7)	105.2(2)
O(6)-N(4)	1.255(5)	C(8)-S (4)-C(10)	90.0(2)
N(1)-C(3)	1.283(6)	N(3)-O(1)-Co(1)	96.9(3)
N(1)-C(1)	1.472(5)	N(3)-O(3)-Co(1)	89.0(3)
N(2)-C(8)	1.281(5)	N(4)-O(4)-Co(1)	95.8(3)
N(2)-C(9)	1.479(5)	N(4)-O(6)-Co(1)	89.7(3)
C(1)-C(2)	1.524(7)	C(3)-N(1)-C(1)	112.7(4)
C(4)-C(5)	1.497(6)	C(3)-N(1)-Co(1)	126.8(3)
C(5)-C(6)	1.308(6)	C(1)-N(1)-Co(1)	120.5(3)
C(8)-N(2)-C(9)	111.7(4)	N(1)-C(3)-S(1)	118.1(3)
C(8)-N(2)-Co(1)#2	126.5(3)	N(1)-C(3)-S(2)	120.5(3)
C(9)-N(2)-Co(1)#2	121.5(3)	S(1)-C (3)-S(2)	121.4(3)
O(2)-N(7)-O(3)	123.2(4)	C(5)-C(4)-S(2)	115.1(3)
O(2)-N(3)-O(3)	123.2(4)	C(6)-C(5)-C(4)	123.2(4)

O(2)-N(3)-O(1)	121.3(4)	C(5)-C(6)-C(7)	123.6(4)
O(3)-N(3)-O(1)	115.5(4)	C(6)-C(7)-S(3)	114.3(3)
O(5)-N(4)-O(6)	123.6(4)	N(2)-C(8)-S(3)	120.2(3)
O(5)-N(4)-O(4)	120.8(4)	N(2)-C(8)-S(4)	118.6(3)
O(6)-N(4)-O(4)	115.7(4)	S(3)-C(8)-S(4)	121.3(3)
N(1)-C(1)-C(2)	110.9(4)	N(2)-C(9)-C(10)	111.2(4)
C(1)-C(2)-S(1)	107.2(3)	C(9)-C(10)-S(4)	107.9(3)

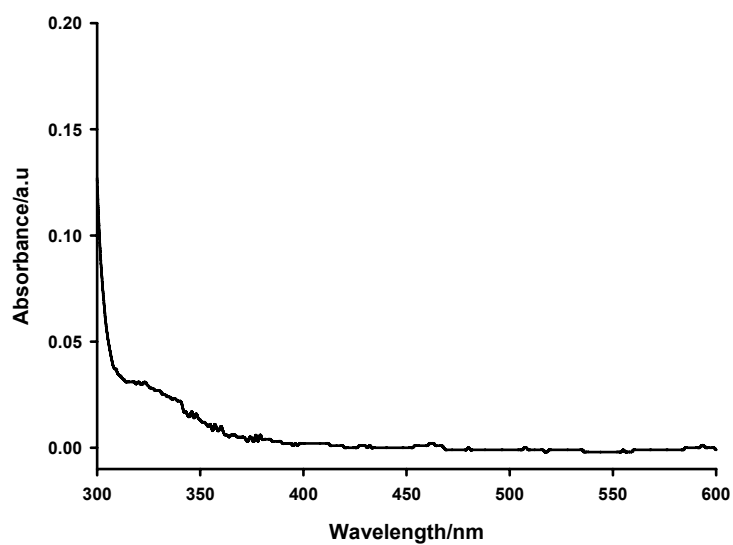
Symmetry transformations used to generate equivalent atoms: A:  $x, y, z$ ; B:  $-x+1/2, y+1/2, -z+1/2$ ; C:  $-x, -y, -z$ ; D:  $x-1/2, -y-1/2, z-1/2$ .



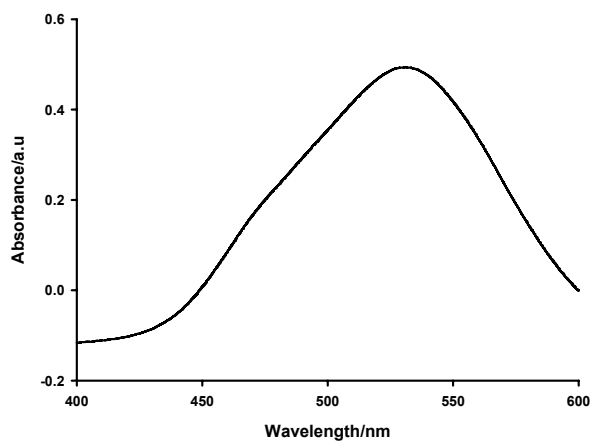
**Figure S2.** View from c-axis showing a 2D network of 1. H atoms are omitted for clarity.



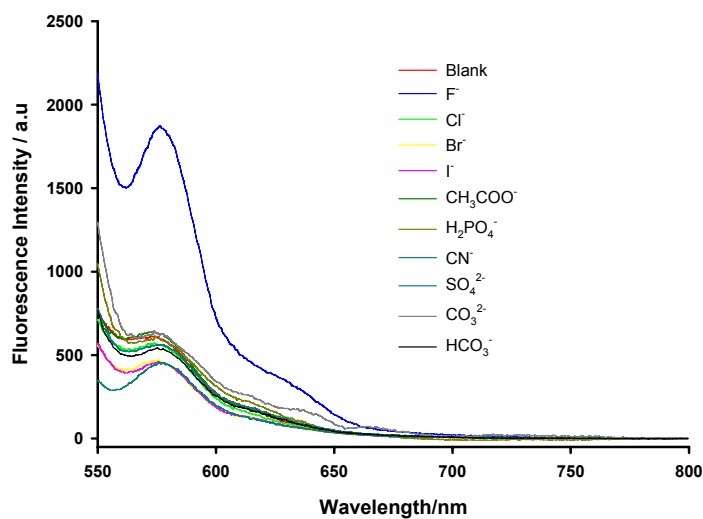
**Figure S3.** Absorption spectra of 3 ( $1 \times 10^{-4}$  M) in DMF/H<sub>2</sub>O (v/v, 9/1, 10 mM HEPES buffer, pH 7.5).



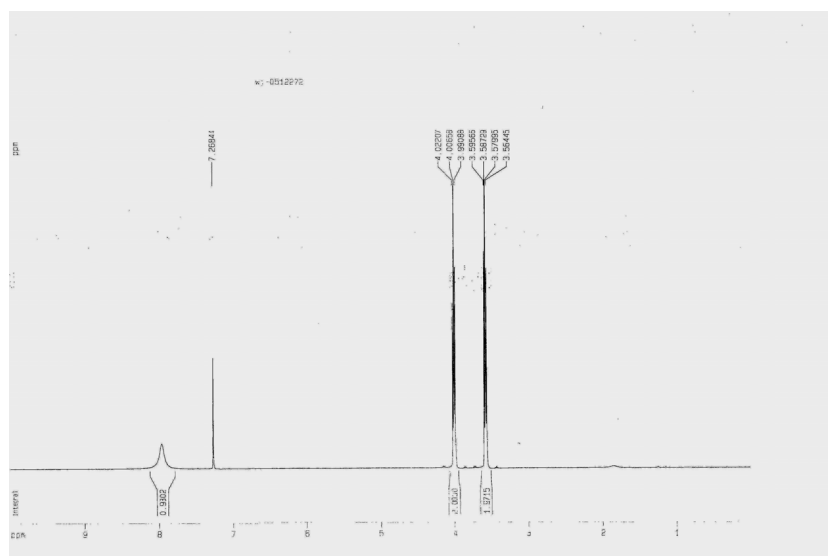
**Figure S4.** Absorption spectra of 2 ( $1 \times 10^{-4}$  M) in DMF/H<sub>2</sub>O (v/v, 9/1, 10 mM HEPES buffer, pH 7.5).



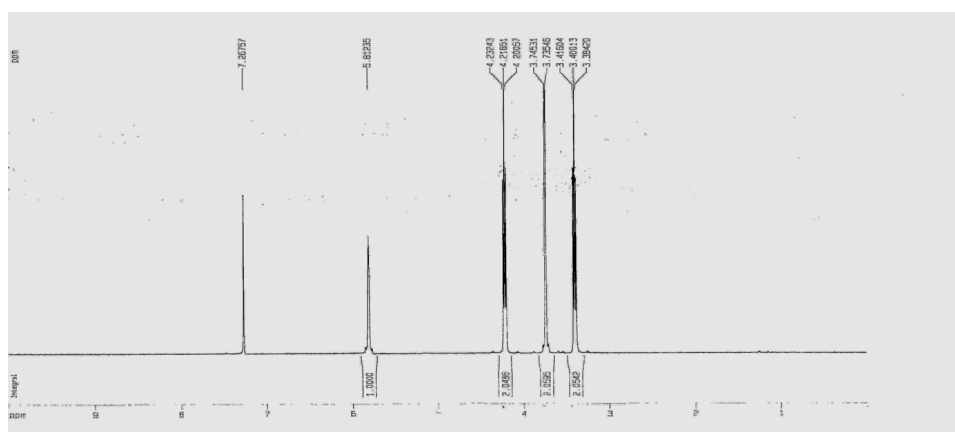
**Figure S5.** Absorption spectra of **1** ( $1 \times 10^{-4}$  M) in DMF/H<sub>2</sub>O (v/v, 9/1, 10 mM HEPES buffer, pH 7.5).



**Figure S6.** Fluorescent spectra of **1** ( $1 \times 10^{-4}$  M) in the presence of various anions ( $5 \times 10^{-4}$  M, all as sodium salt, 5.0 equiv) in DMF/H<sub>2</sub>O (v/v, 9/1, 10 mM HEPES buffer, pH 7.5).



**Figure S7.**  $^1\text{H}$  NMR spectra of 3 ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).



**Figure S8.**  $^1\text{H}$  NMR spectra of 2 ( $\text{CDCl}_3$ ,  $25^\circ\text{C}$ ).

## References

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