Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Thiazolothiazole Based Cu^{2+} Selective Colorimetric and Fluorescent Sensor via Unique Radical Formation

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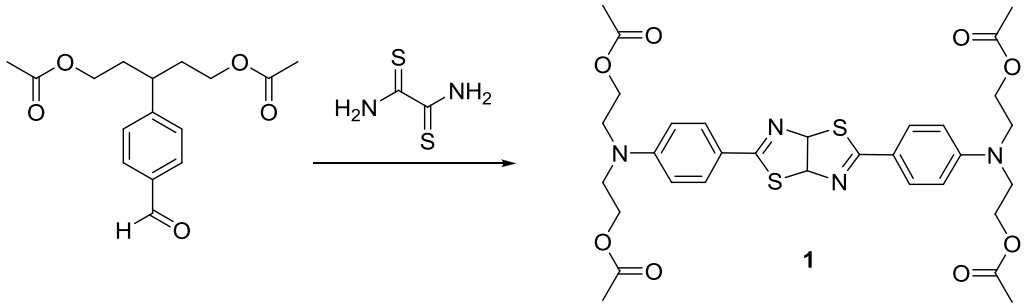
Experimental

1. Synthesis



Synthesis of 1

A mixture of 4-(bis(2-(acethyloxy)ethyl)amino)benzaldehyde (1.3 g, 4.43 mmol) and dithiooxamide (0.15 g, 1.25 mmol) in DMF (5 ml) was heated at 160°C. The reaction was refluxed under the N_2 for 60h, then the solvent was evaporated. The crude product was purified by column chromatography using hexane:ethyl acetate (9:1) as eluent to give compound **1** as yellow powder (0.54 g, 64 %). Mp 280 ^{o}C dec. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.78 (d, 4H, *J* = 11.3Hz), 6.74 (d, 4H, *J* = 11.3Hz) 4.21 (t, 8H, *J* = 7.1Hz), 3.63 (t, 8H, *J* = 7.08Hz), 2.00 (s, 12H); ^{13}C NMR ($CDCl_3$, 250 MHz) δ 170.9, 168.5, 148.9, 141.1, 127.8, 123.1, 112.3,61.2, 49.6, 20.9; HRMS (FAB) calcd for $C_{32}H_{36}N_4O_8S_2$ 668.1975; found 669.2953 $(M + H)^+$.

UV and fluorescent study

Stock solutions (10 mM) of the perchlorate salts of Al^{3+}, Cr^{3+}, Ag^{+}, Fe^{2+}, Fe^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, K^{+}, Li^{+}, Cs^{+}, Mg^{2+}, Mn^{2+}, Na^{+}, Ni^{2+}, Pb^{2+}, Zn^{2+}, Cu^{+} ions in CH_3CN were prepared. Stock solutions of **1** (0.1 mM) was also prepared in CH_3CN, respectively. Test solutions were prepared by placing 300 μL of the probe stock solution into a test tube, adding an appropriate aliquot of each metal stock, and diluting the solution to 3mL with CH_3CN and DW. The absorption and fluorescence properties of **1** was tested in CH_3CN:DW (95:5, v/v).

X-ray Crystallography

The X-ray diffraction data for two compounds were collected on a Bruker SMART APEX diffractometer equipped with a monochromater in the Mo Ka (k = 0.71073 A) incident beam. Each crystal was mounted on a glass fiber. The CCD data (CCDC number: 900345) were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12. All hydrogen atoms were placed in the calculated positions.

The crystallographic data were listed in Table S1. The bond lengths and angles were listed in Table S2.

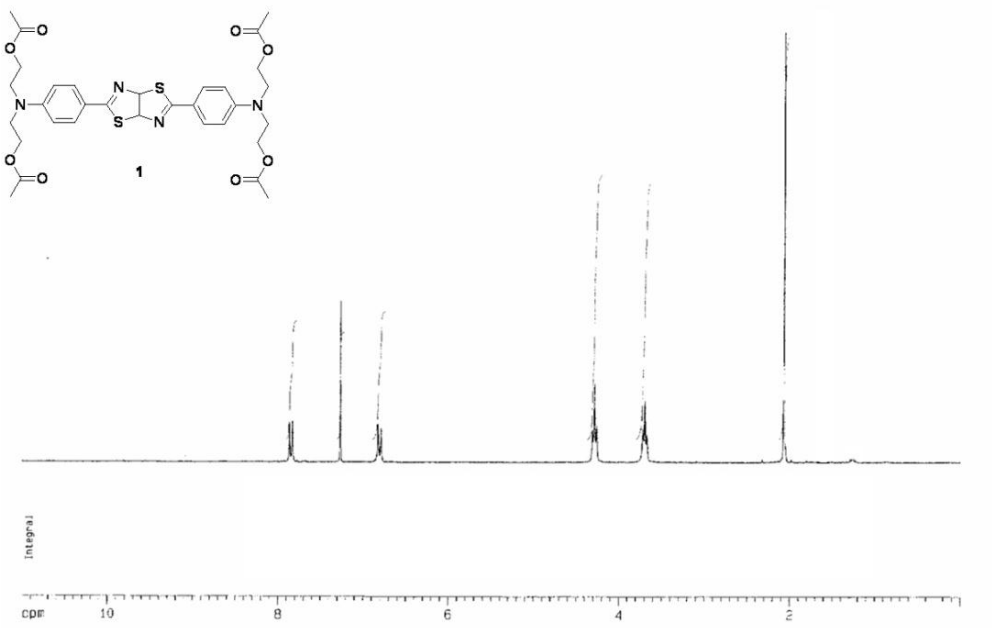


Fig. S1. ^{1}H NMR (250 MHz) of compound **4** in $CDCl_3$

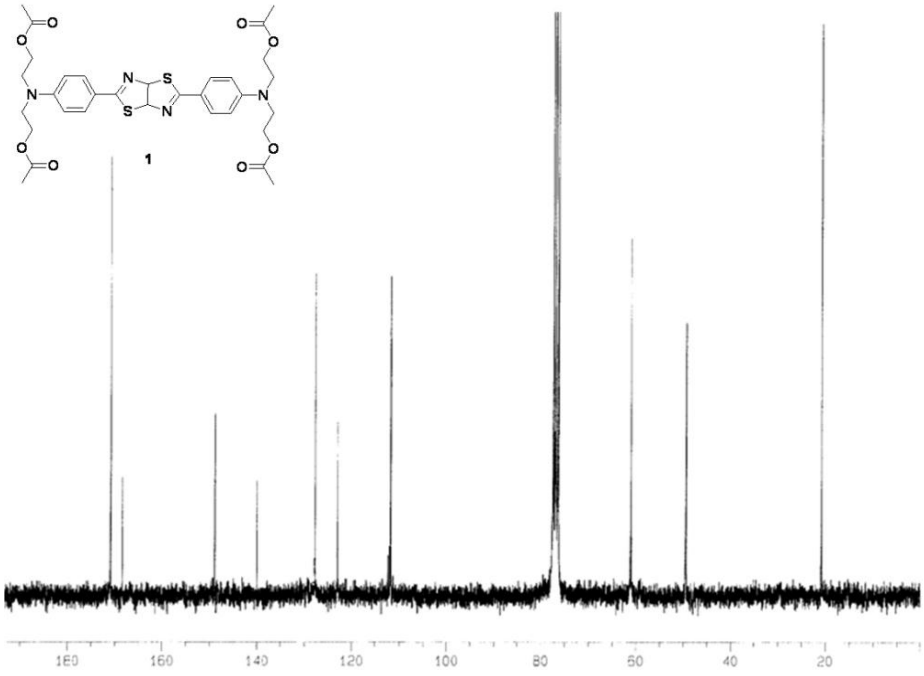


Fig. S2. ^{13}C NMR (125 MHz) spectrum of compound **4** in $CDCl_3$.

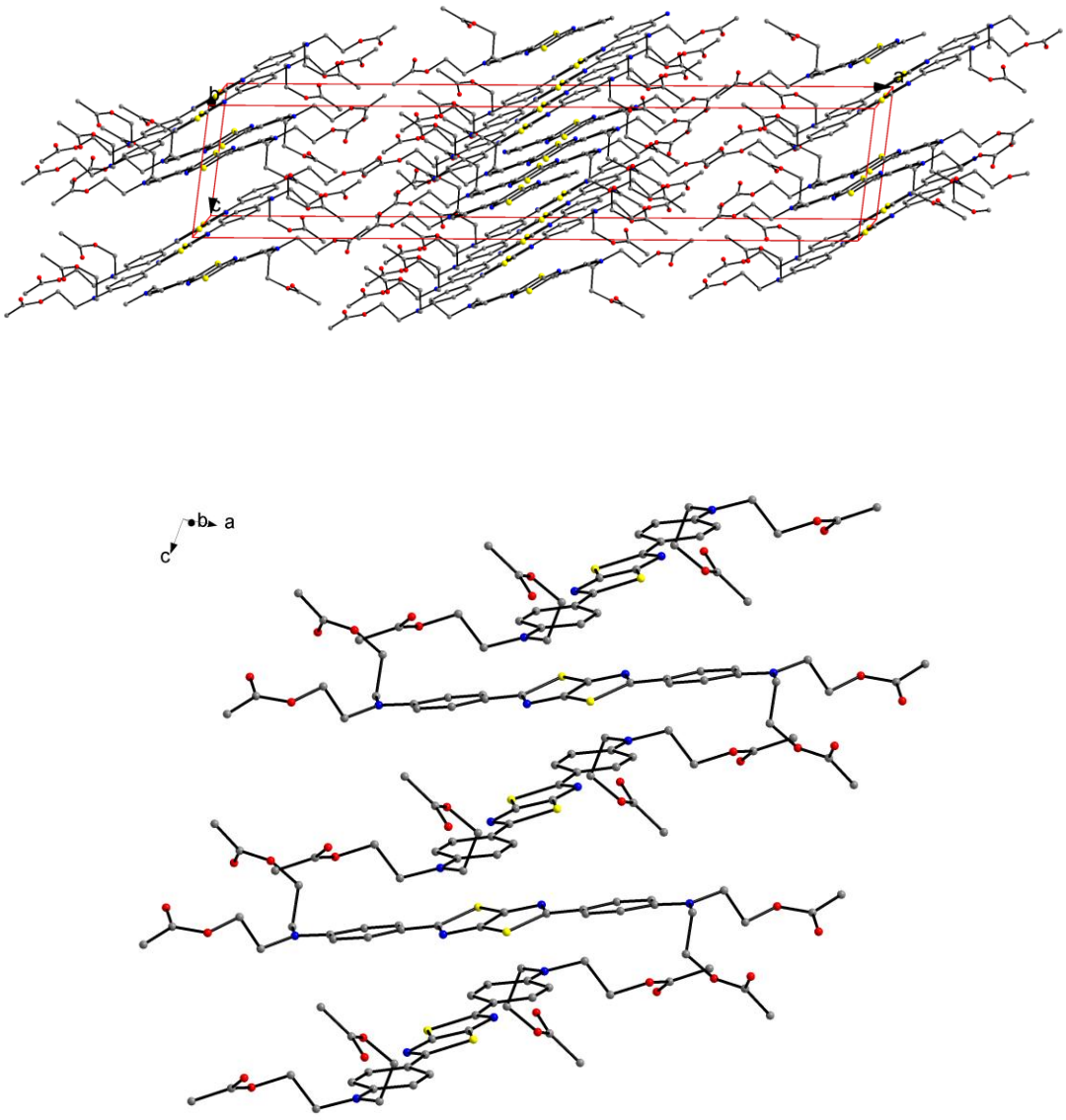


Fig. S3. The packing pattern of the unit cell for compound **1**.

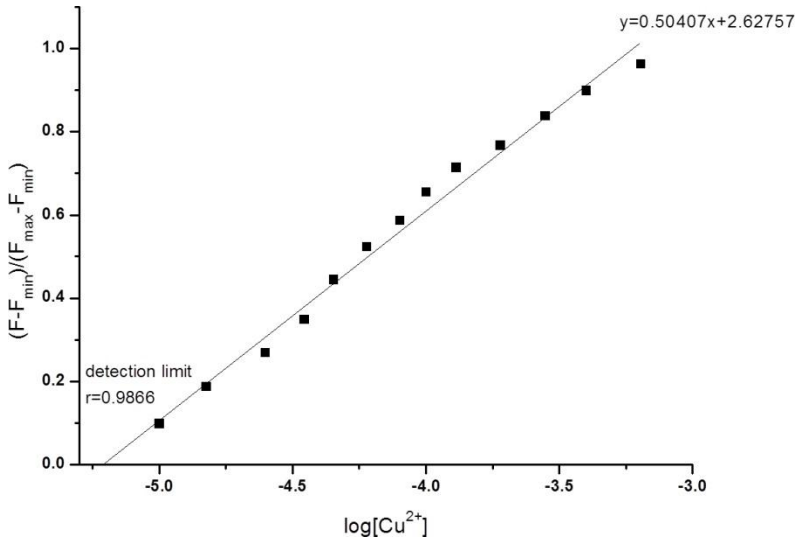


Fig. S4. Normalized fluorescence responses of 1 (1×10^{-5} M) to changing Cu^{2+} concentrations in CH_3CN:H_2O (95:5, v/v).

Table S1. Crystallographic data for **I**.

	I
Empirical formula	$C_{32}H_{36}N_4O_8S_2$
Formula weight	668.77
Temperature	293 K
Wavelength	0.71073 Å
Space group	C2/c
a	42.455(9) Å
b	9.0245(18) Å
c	8.5542(17) Å
α	90.00°
β	97.96(3)°
γ	90.00°
Volume	3245.8(11) $Å^3$
Z	4
Calculated density	1.369 Mg/m^3
Absorp.coefficient	0.221 mm^{-1}
F(000)	1408
Crystal size	0.08 x 0.05 x 0.05 mm^3
Reflections collected	8847
Independent reflections	3186 [R(int) = 0.0578]
Data/restraints/parameters	3186 / 0 / 210
Goodness-of-fit[a] on F^2	1.004
Final R indices [I>2σ(I)]	R_1 = 0.0549, wR_2 = 0.1113
R indices (all data)	R_1 = 0.1402, wR_2 = 0.1359
Largest diff. peak and hole	0.200 and -0.186 $e.Å^{-3}$
CCDC number	CCDC 900345

Table S2. The bond lengths and angles for **I**.

S(1)-C(1)	1.713(3)
S(1)-C(2)	1.751(3)
N(1)-C(2)	1.310(4)
N(1)-C(1)#1	1.371(4)
N(2)-C(6)	1.389(4)
N(2)-C(13)	1.456(4)
N(2)-C(9)	1.457(4)
O(1)-C(15)	1.338(4)
O(1)-C(14)	1.444(4)
O(2)-C(15)	1.197(4)
O(3)-C(11)	1.324(5)
O(3)-C(10)	1.440(4)
O(4)-C(11)	1.172(4)
C(1)-C(1)#1	1.371(5)
C(1)-N(1)#1	1.371(4)
C(2)-C(3)	1.471(4)
C(3)-C(8)	1.385(4)
C(3)-C(4)	1.386(4)
C(4)-C(5)	1.378(4)
C(4)-H(4)	0.9300
C(5)-C(6)	1.402(4)
C(5)-H(5)	0.9300
C(6)-C(7)	1.396(4)
C(7)-C(8)	1.371(4)
C(7)-H(7)	0.9300
C(8)-H(8)	0.9300
C(9)-C(10)	1.492(5)
C(9)-H(9A)	0.9700
C(9)-H(9B)	0.9700
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-C(12)	1.479(6)
C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600

C(12)-H(12C)	0.9600
C(13)-C(14)	1.507(4)
C(13)-H(13A)	0.9700
C(13)-H(13B)	0.9700
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-C(16)	1.493(5)
C(16)-H(16A)	0.9600
C(16)-H(16B)	0.9600
C(16)-H(16C)	0.9600

C(1)-S(1)-C(2)	88.84(15)
C(2)-N(1)-C(1)#1	108.0(2)
C(6)-N(2)-C(13)	120.7(3)
C(6)-N(2)-C(9)	120.7(3)
C(13)-N(2)-C(9)	118.4(3)
C(15)-O(1)-C(14)	118.0(3)
C(11)-O(3)-C(10)	119.3(3)
C(1)#1-C(1)-N(1)#1	118.2(3)
C(1)#1-C(1)-S(1)	108.9(3)
N(1)#1-C(1)-S(1)	132.9(2)
N(1)-C(2)-C(3)	123.9(3)
N(1)-C(2)-S(1)	116.0(2)
C(3)-C(2)-S(1)	120.1(2)
C(8)-C(3)-C(4)	117.1(3)
C(8)-C(3)-C(2)	121.4(3)
C(4)-C(3)-C(2)	121.5(3)
C(5)-C(4)-C(3)	121.9(3)
C(5)-C(4)-H(4)	119.0
C(3)-C(4)-H(4)	119.0
C(4)-C(5)-C(6)	121.1(3)
C(4)-C(5)-H(5)	119.5
C(6)-C(5)-H(5)	119.5
N(2)-C(6)-C(7)	122.2(3)
N(2)-C(6)-C(5)	121.5(3)
C(7)-C(6)-C(5)	116.3(3)

C(8)-C(7)-C(6)	122.2(3)
C(8)-C(7)-H(7)	118.9
C(6)-C(7)-H(7)	118.9
C(7)-C(8)-C(3)	121.3(3)
C(7)-C(8)-H(8)	119.3
C(3)-C(8)-H(8)	119.3
N(2)-C(9)-C(10)	112.9(3)
N(2)-C(9)-H(9A)	109.0
C(10)-C(9)-H(9A)	109.0
N(2)-C(9)-H(9B)	109.0
C(10)-C(9)-H(9B)	109.0
H(9A)-C(9)-H(9B)	107.8
O(3)-C(10)-C(9)	109.0(3)
O(3)-C(10)-H(10A)	109.9
C(9)-C(10)-H(10A)	109.9
O(3)-C(10)-H(10B)	109.9
C(9)-C(10)-H(10B)	109.9
H(10A)-C(10)-H(10B)	108.3
O(4)-C(11)-O(3)	121.9(4)
O(4)-C(11)-C(12)	126.4(5)
O(3)-C(11)-C(12)	111.7(4)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(2)-C(13)-C(14)	114.3(3)
N(2)-C(13)-H(13A)	108.7
C(14)-C(13)-H(13A)	108.7
N(2)-C(13)-H(13B)	108.7
C(14)-C(13)-H(13B)	108.7
H(13A)-C(13)-H(13B)	107.6
O(1)-C(14)-C(13)	111.8(3)
O(1)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14A)	109.3

O(1)-C(14)-H(14B)	109.3
C(13)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	107.9
O(2)-C(15)-O(1)	121.8(4)
O(2)-C(15)-C(16)	126.7(4)
O(1)-C(15)-C(16)	111.5(4)
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+3,-z+1