Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Symmetrical and unsymmetrical thiazole based ESIPT derivatives: Highly selective fluorescence sensing of Cu^{2+} and structure controlled reversible mechanofluorochromism

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1. NMR studies

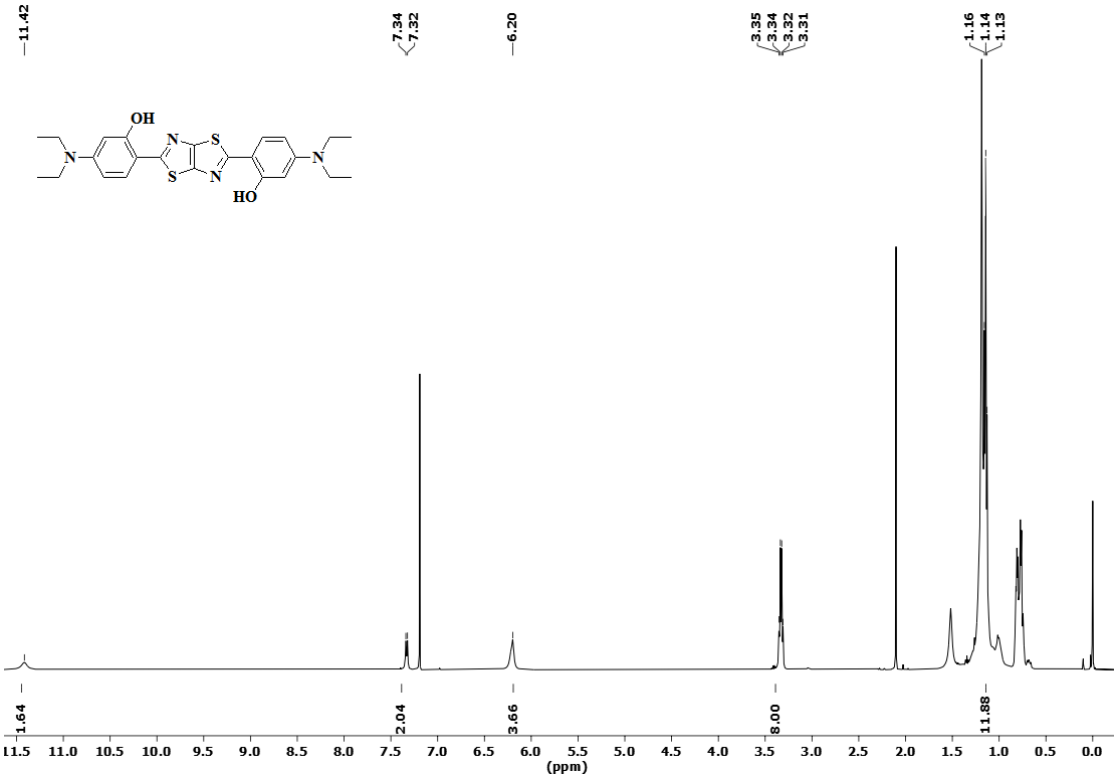

Fig. S1 ^{1}H NMR spectrum of compound **1**

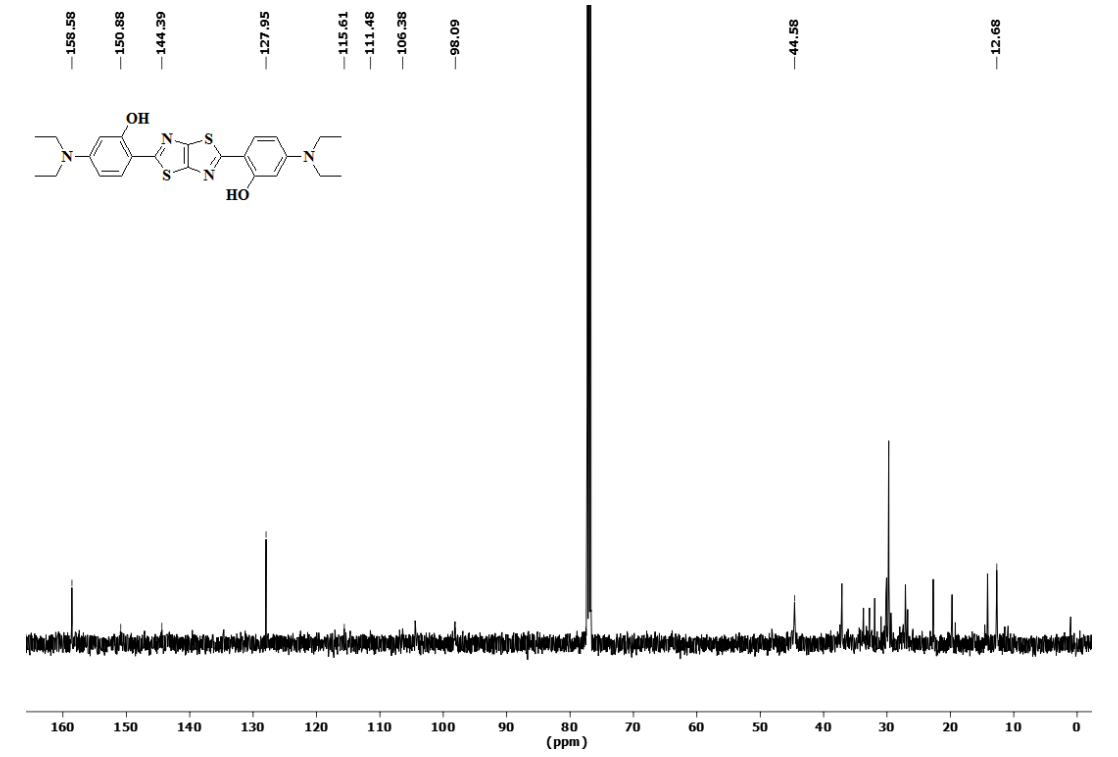

Fig. S2 ^{13}C NMR spectrum of compound **1**

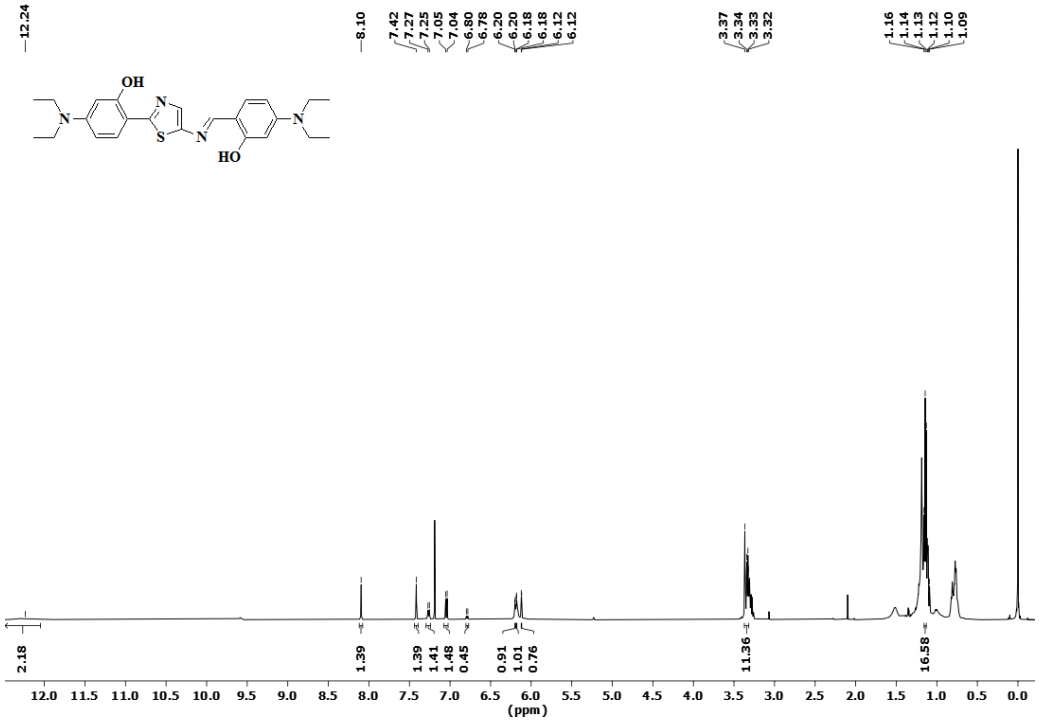

Fig. S3 ^{1}H NMR spectrum of compound **2**

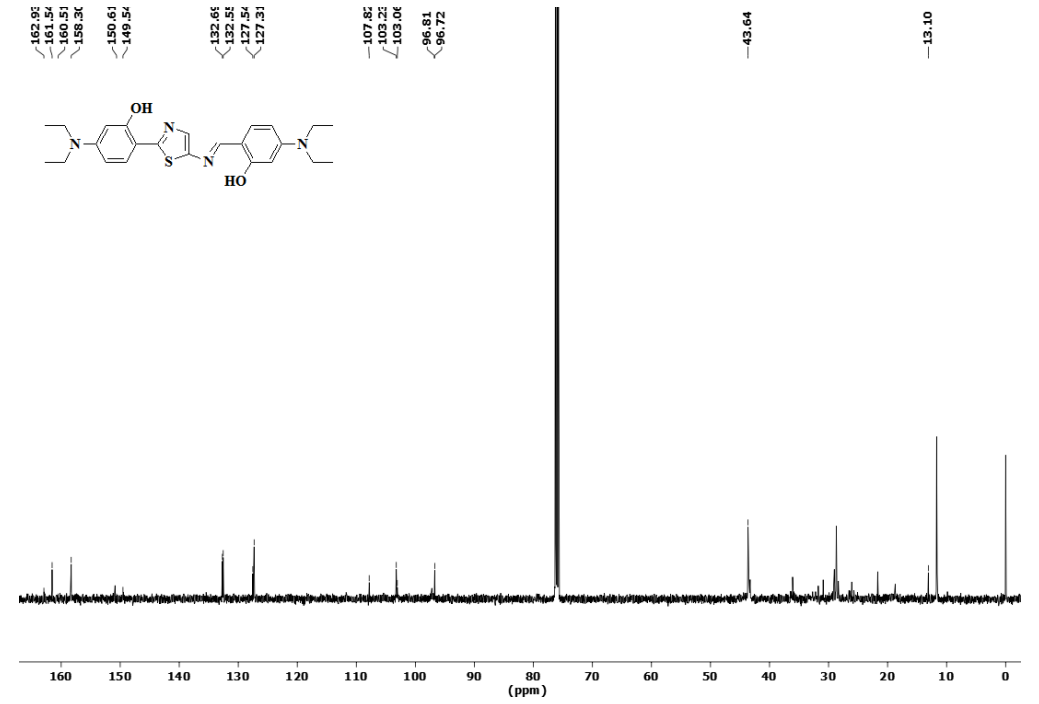

Fig. S4 ^{13}C NMR spectrum of compound **2**

2. FT-IR analysis

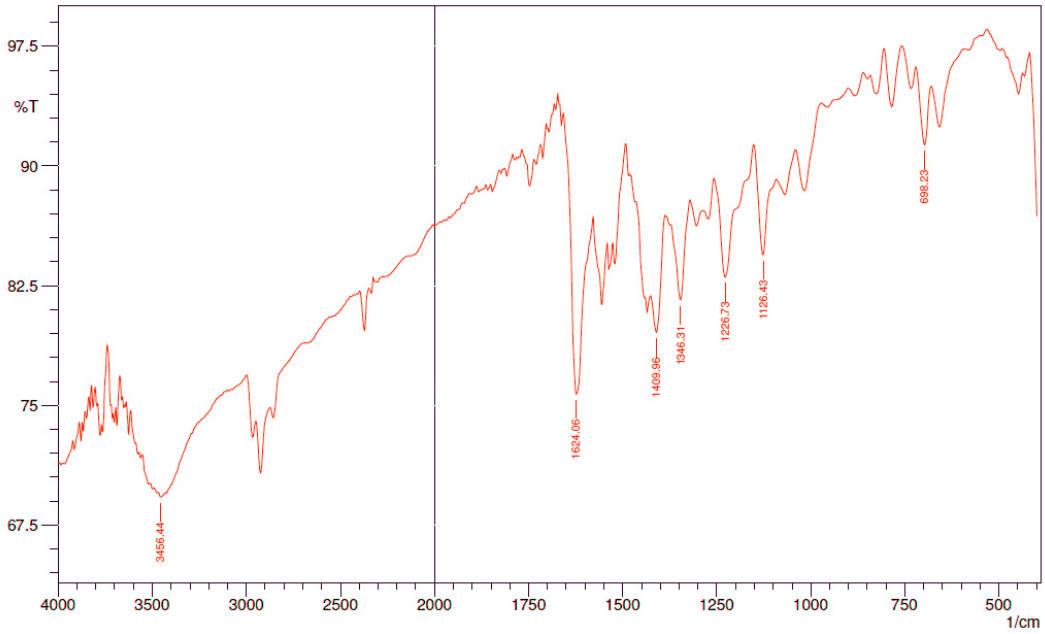

Fig. S5 FT-IR spectrum of compound **1.**

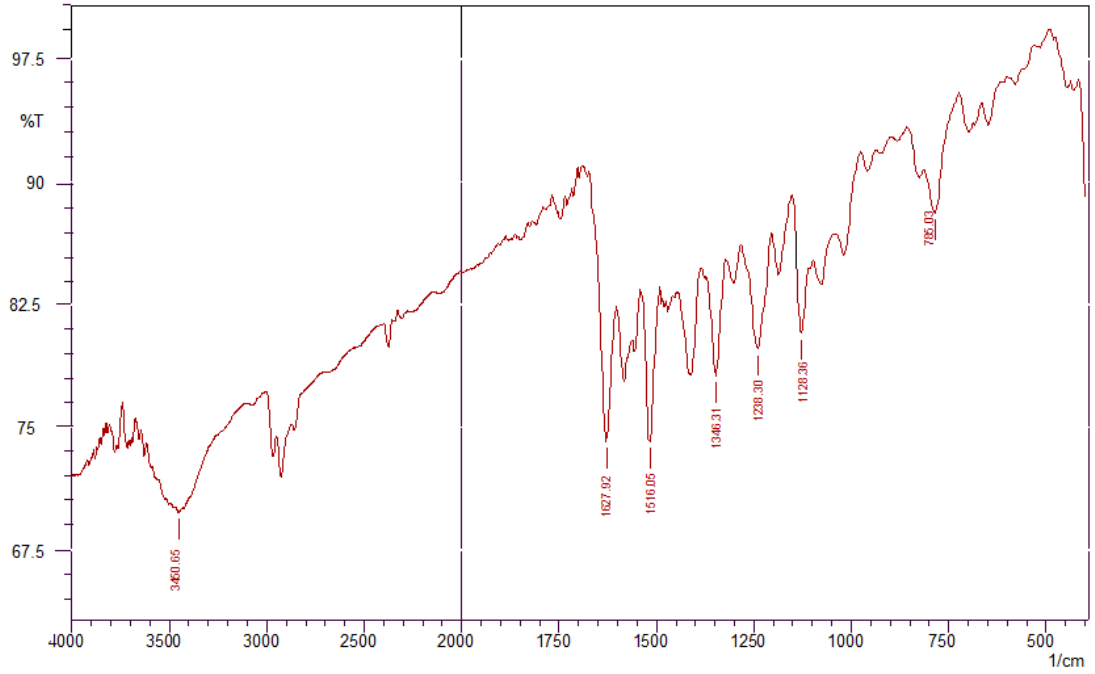

Fig. S6 FT-IR spectrum of compound **2.**

3. Single crystal X-ray crystallography studies

Table S1. Crystal data and structure refinement for **1** (CCDC 2073010)

Identification code	SPA532	
Empirical formula	$C_{24}H_{28}N_4O_2S_2$	
Formula weight	468.62	
Temperature	220(2) K	
Wavelength	0.630 Å	
Crystal system	Triclinic	
Space group	*Pī*	
Unit cell dimensions	a = 7.1770(14) Å	α= 105.64(3)°.
	b = 7.4550(15) Å	β= 97.57(3)°.
	c = 11.030(2) Å	γ = 90.80(3)°.
Volume	562.6(2) $Å^3$	
Z	1	
Density (calculated)	1.383 Mg/m^3	
Absorption coefficient	0.192 mm^{-1}	
F(000)	248	
Crystal size	0.101 x 0.004 x 0.003 mm^3	
Theta range for data collection	1.717 to 26.499°.	
Index ranges	-10≤.h≤10, -10≤k≤10, -15≤l≤15	
Reflections collected	6355	
Independent reflections	3280 [R(int) = 0.0455]	
Completeness to theta = 22.210°	99.1 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.766	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3280 / 0 / 166	
Goodness-of-fit on F^2	1.115	
Final R indices [I>2sigma(I)]	R1 = 0.0943, wR2 = 0.2936	
R indices (all data)	R1 = 0.1284, wR2 = 0.3170	
Largest diff. peak and hole	0.896 and -0.791 $e.Å^{-3}$	

Table S2. Crystal data and structure refinement for **2** (CCDC 2073011)

Identification code	SPA447	
Empirical formula	$C_{24}H_{30}N_4O_2S$	
Formula weight	438.58	
Temperature	220(2) K	
Wavelength	0.610 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 6.6330(13) Å	α= 90°.
	b = 8.5300(17) Å	β= 94.24(3)°.
	c = 19.929(4) Å	γ = 90°.
Volume	1124.5(4) $Å^3$	
Z	2	
Density (calculated)	1.295 Mg/m^3	
Absorption coefficient	0.117 mm^{-1}	
F(000)	468	
Crystal size	0.135 x 0.094 x 0.084 mm^3	
Theta range for data collection	1.759 to 25.000°.	
Index ranges	-9≤h≤9, -11≤k≤11, -27≤l≤27	
Reflections collected	11469	
Independent reflections	6002 [R(int) = 0.0420]	
Completeness to theta = 21.469°	97.6 %	
Absorption correction	Empirical	
Max. and min. transmission	1.000 and 0.849	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6002 / 1 / 286	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0545, wR2 = 0.1556	
R indices (all data)	R1 = 0.0583, wR2 = 0.1585	
Absolute structure parameter	0.06(3)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.982 and -0.459 e.$Å^{-3}$	

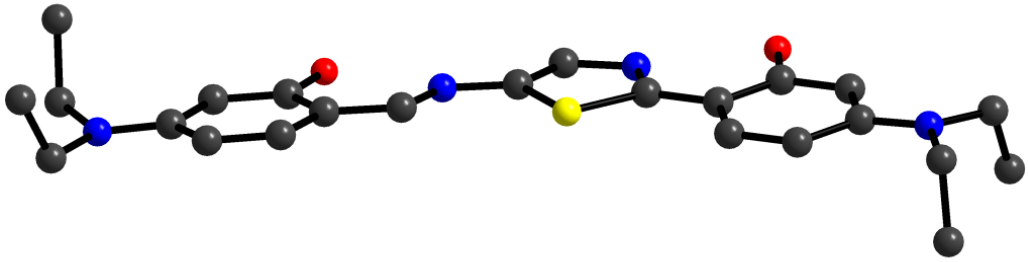

Fig. S7 Orientation of terminal diethyl moiety in **2**.

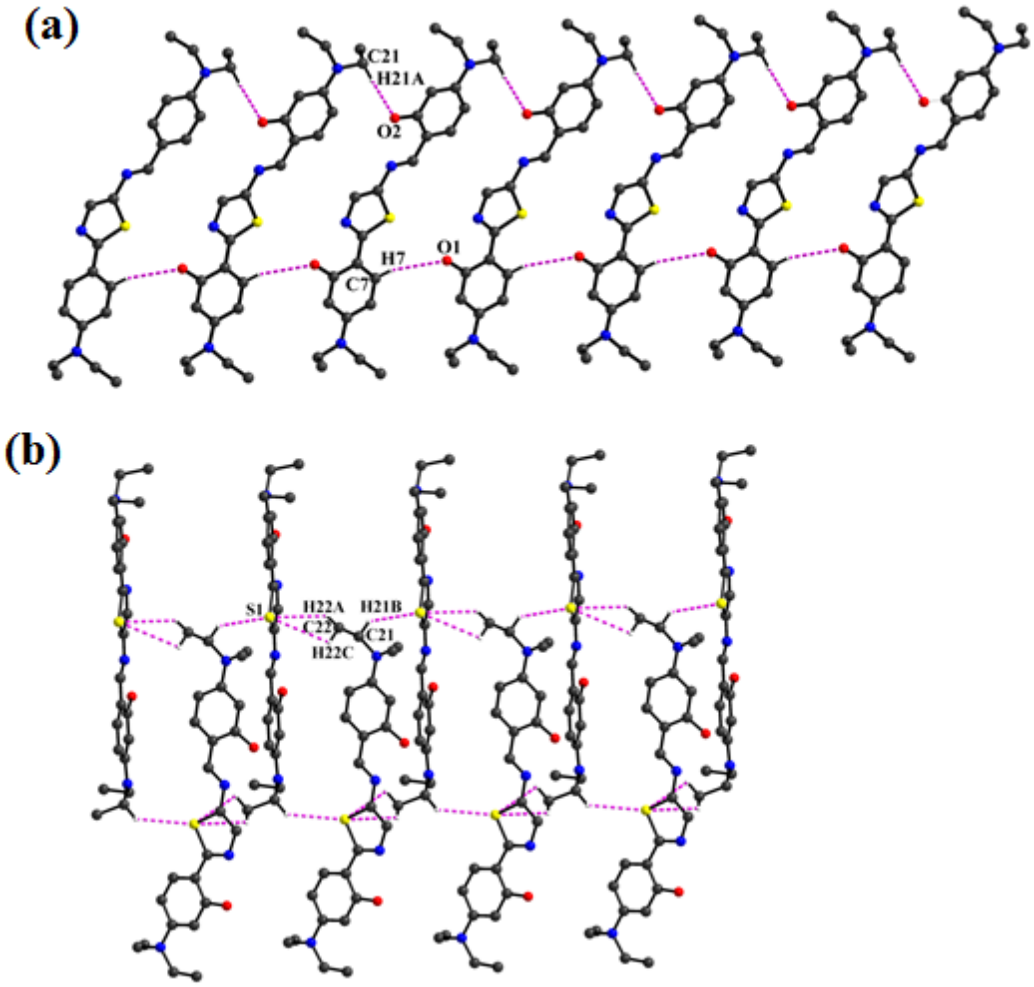

Fig. S8 Intermolecular C−H···O and C−H···S hydrogen bonding interactions in **2**.

4. UV-Visible and fluorescence studies

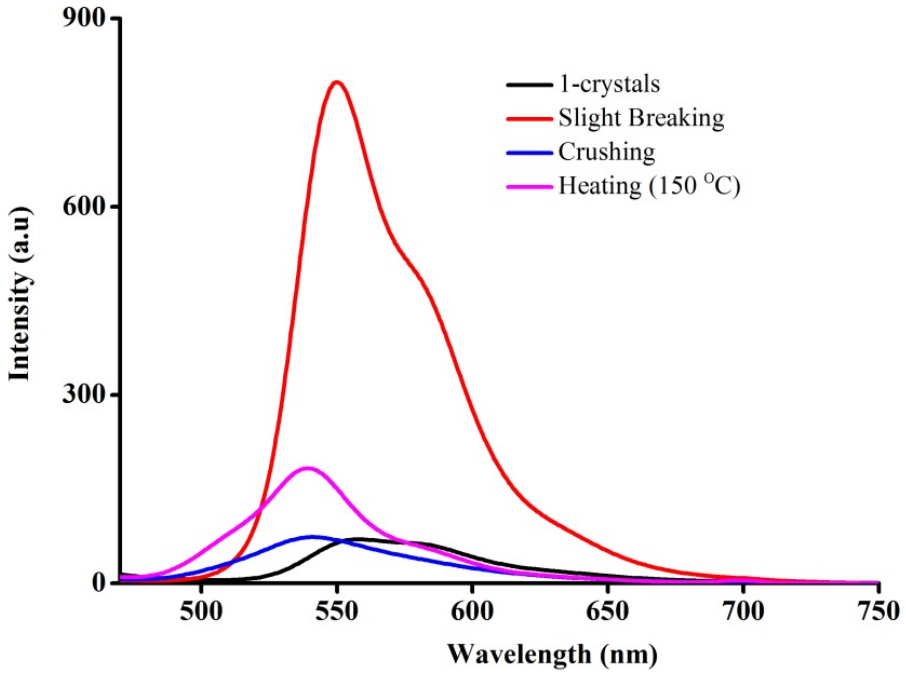

Fig. S9 Fluorescence spectra of **1**. Original crystals (black), after slight breaking (red), after crushing (blue) and after heating (purple).

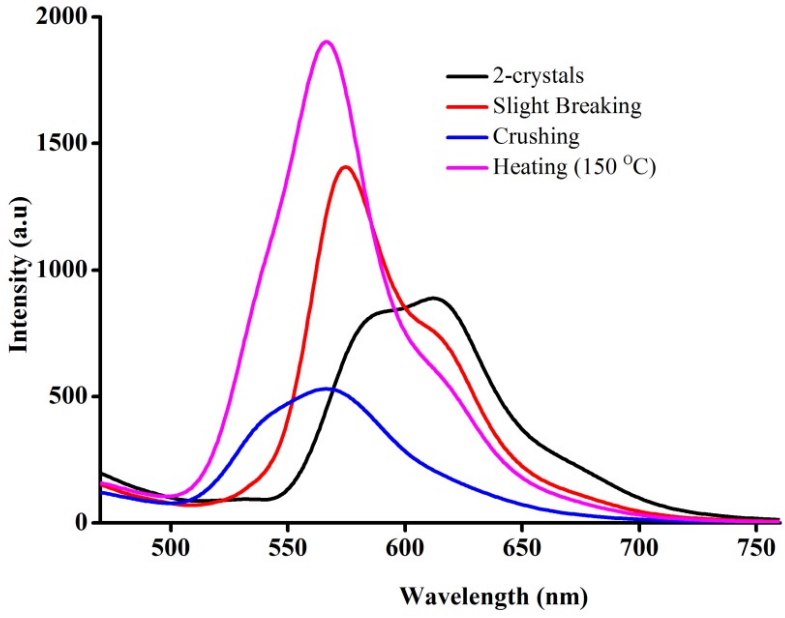

Fig. S10 Fluorescence spectra of **2**. Original crystals (black), after slight breaking (red), after crushing (blue) and after heating (purple).

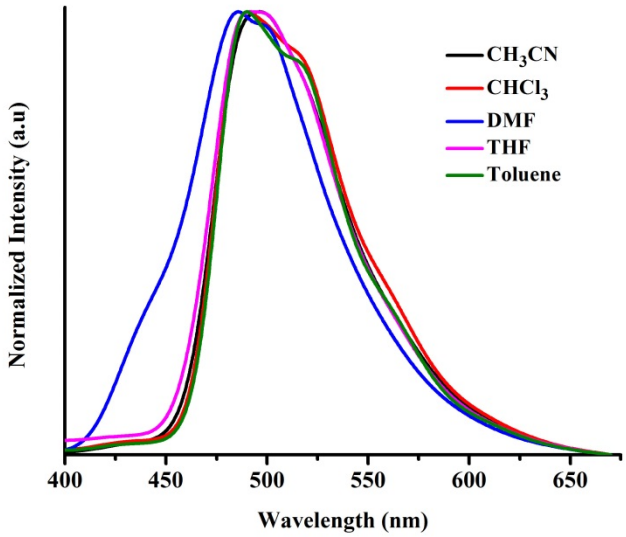

Fig. S11 Fluorescence spectra of **1** with different solvents (10^{-3} M).

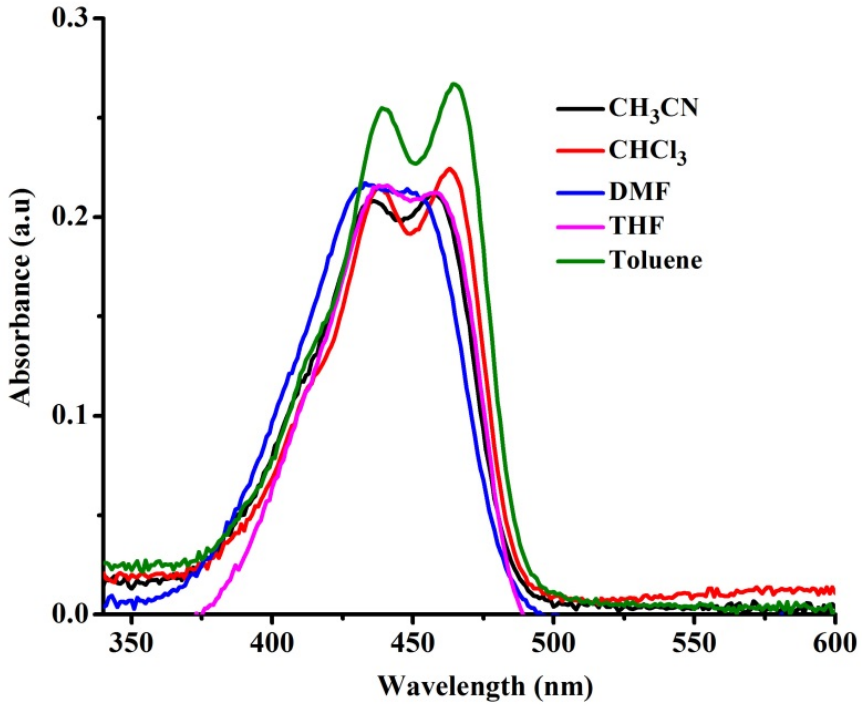

Fig. S12 Absorption spectra of **1** with different solvents (10^{-3} M).

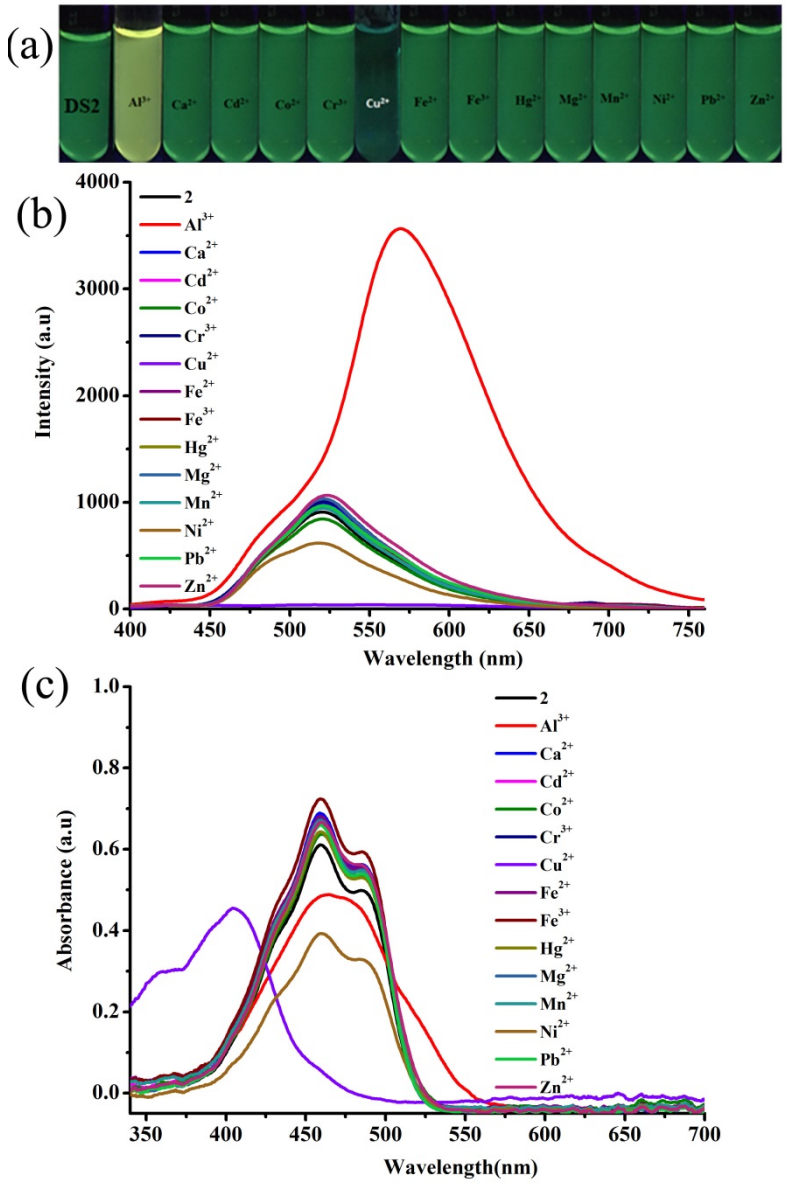

Fig. S13 (a) Digital images (b) fluorescence and (c) absorption spectra of **2** with different metal ions. (10^{-3} M of **2**; 10^{-3} M of metal ions).

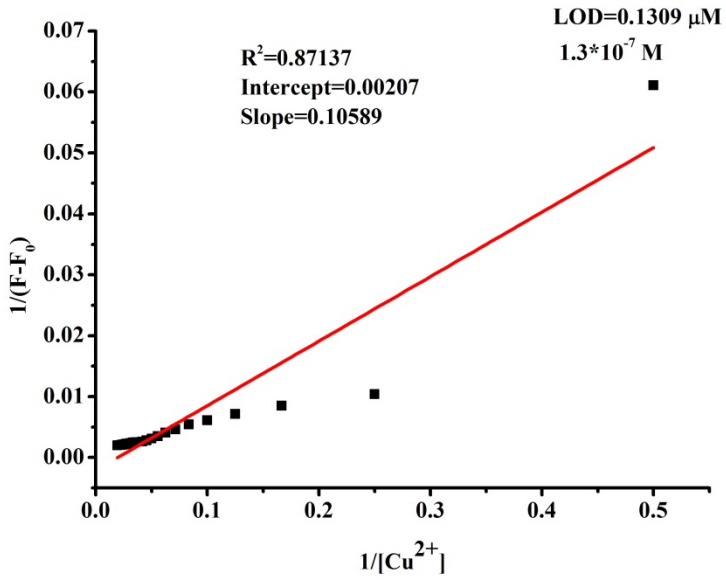

Fig. S14 Limit of detection (LOD) calculation

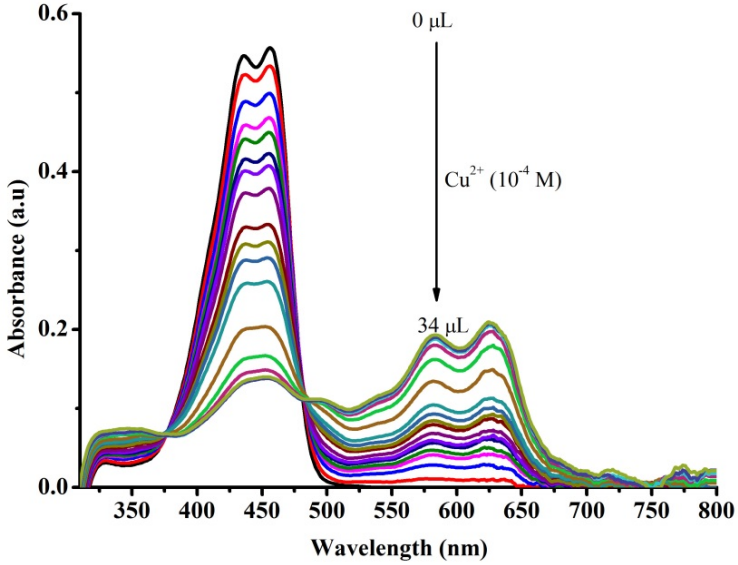

Fig. S15 Cu^{2+} concentration dependent absorption changes of 1 in CH_3CN.

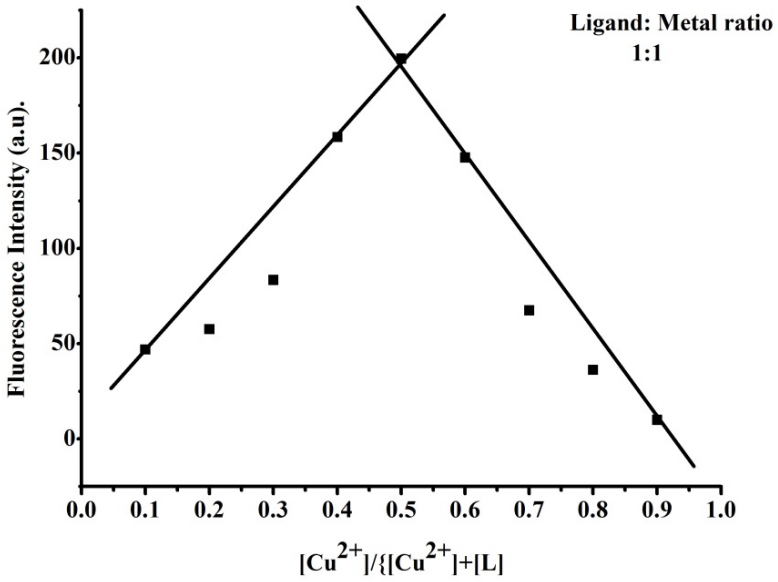

Fig. S16 Jobs plot for **1**.

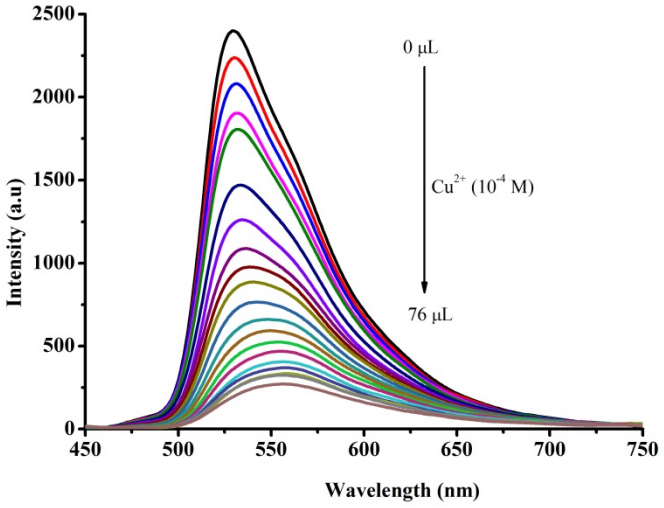

Fig. S17 The Cu^{2+} ions concentration dependent fluorescence studies of **2**

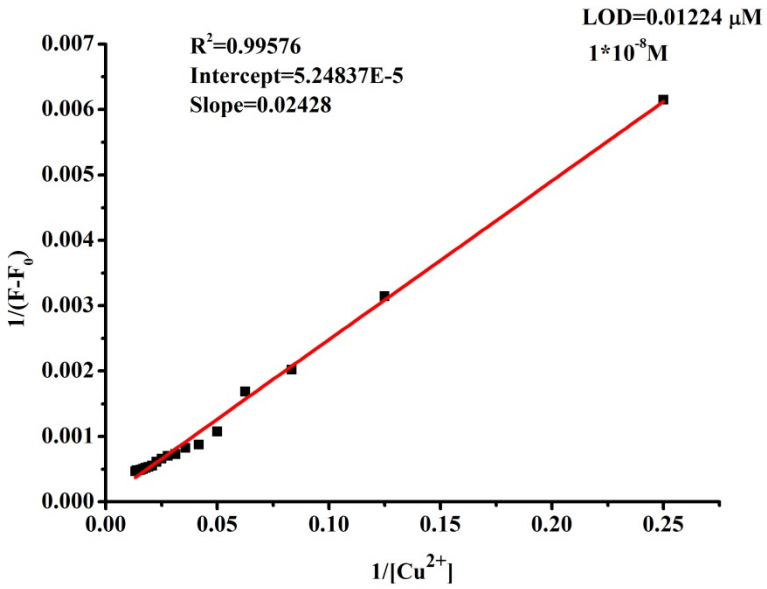

Fig. S18 Limit of detection (LOD) calculation.

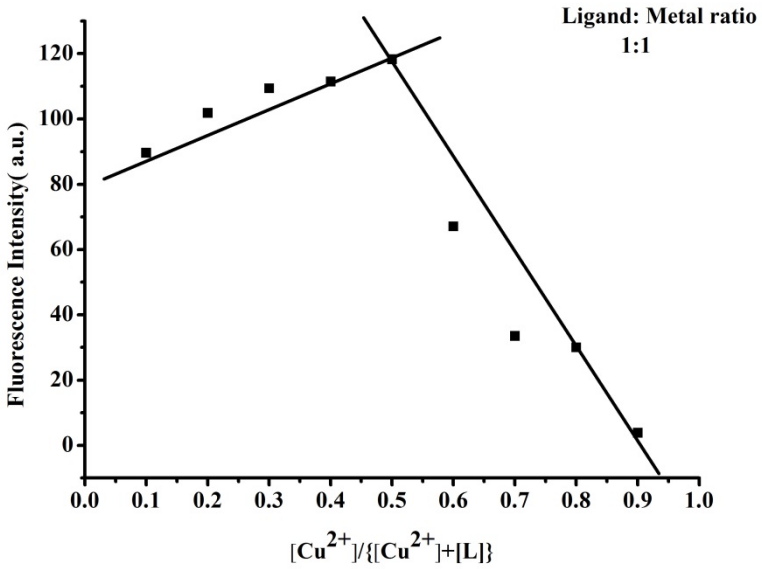

Fig. S19 Jobs plot for **2**.

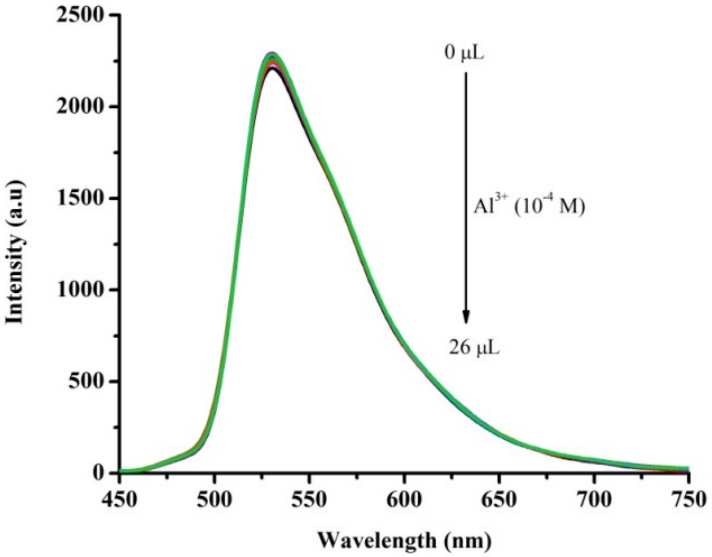

Fig. S20 Fluorescence spectra of **2** with 10^{-4} M concentration of Al^{3+}

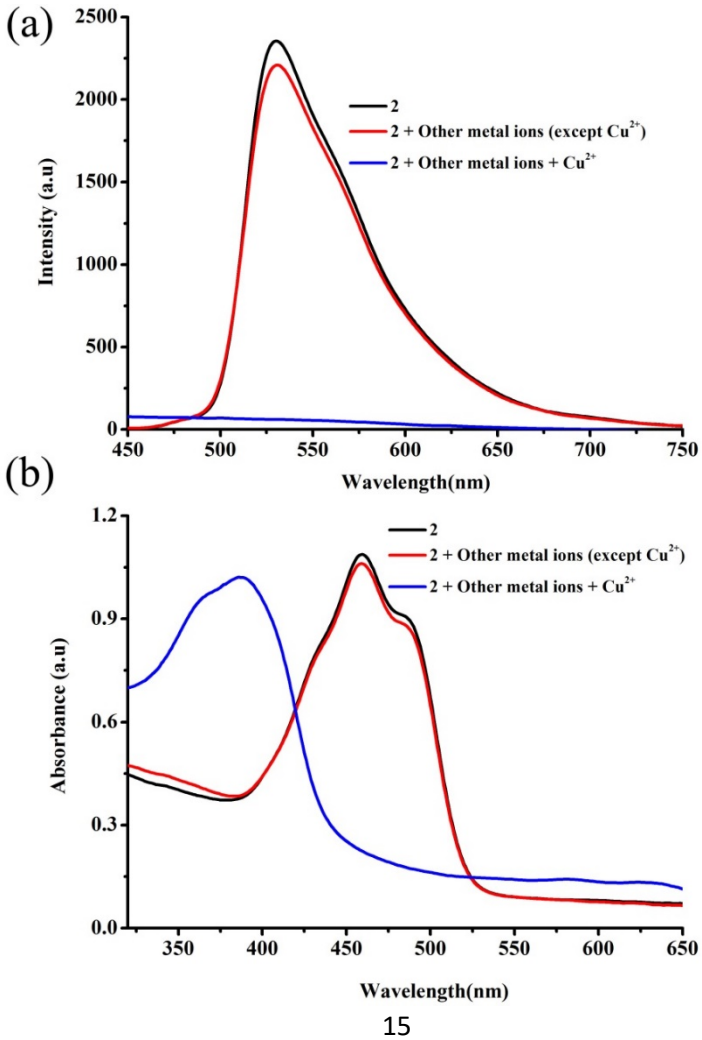

Fig. S21 Interference studies of **2** in presence of other metal cation (a) fluorescence and (b) absorption spectra.