Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Structural Studies and Detection of Nitro Aromatics by Luminescent 2D Coordination Polymers with Angular Dicarboxylate Ligand

Yadagiri Rachuri,[a][b] Bhavesh Parmar,[a][b] Kamal Kumar Bisht[a][b][c] and Eringathodi Suresh*[a][b]

[a] Analytical Discipline and Centralized Instrument Facility, CSIR–Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, G. B. Marg, Bhavnagar–364 002, Gujarat, India
E-mail: esuresh@csmcri.org; sureshe123@rediffmail.com

[b] Academy of Scientific and Innovative Research (AcSIR), CSIR–Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research, G. B. Marg, Bhavnagar –364 002, Gujarat, India

[c] Department of Chemistry, University of Petroleum and Energy Studies (UPES), P.O. Bidholi Via-Prem Nagar, Dehradun 248007, Uttarakhand, India

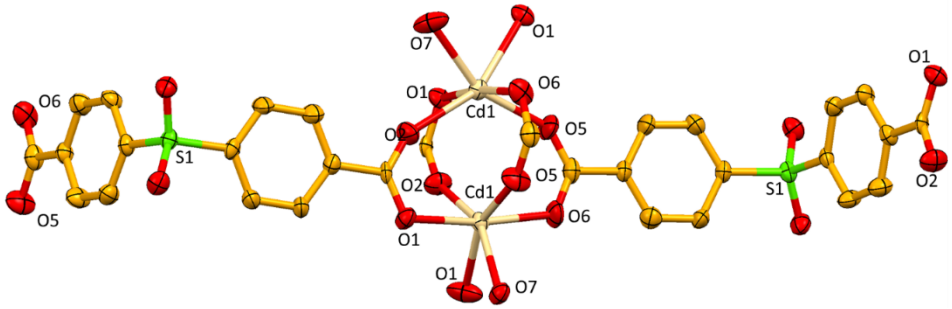

Fig. S1.ORTEP diagram of**1** depicting the coordination environment around the metal center.

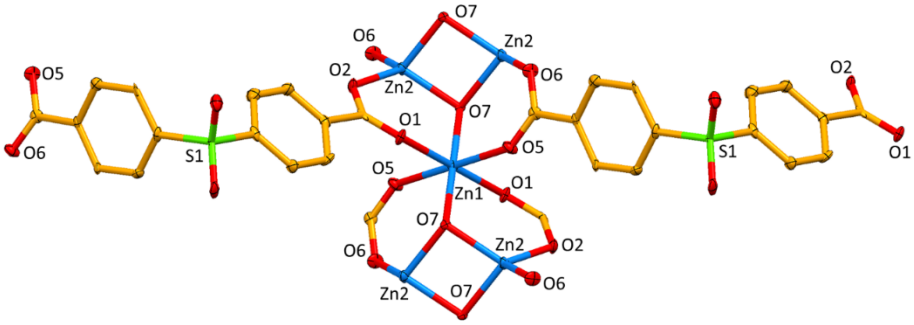

Fig. S2.ORTEP diagram of CP **2** depicting the coordination environment around the metal center.

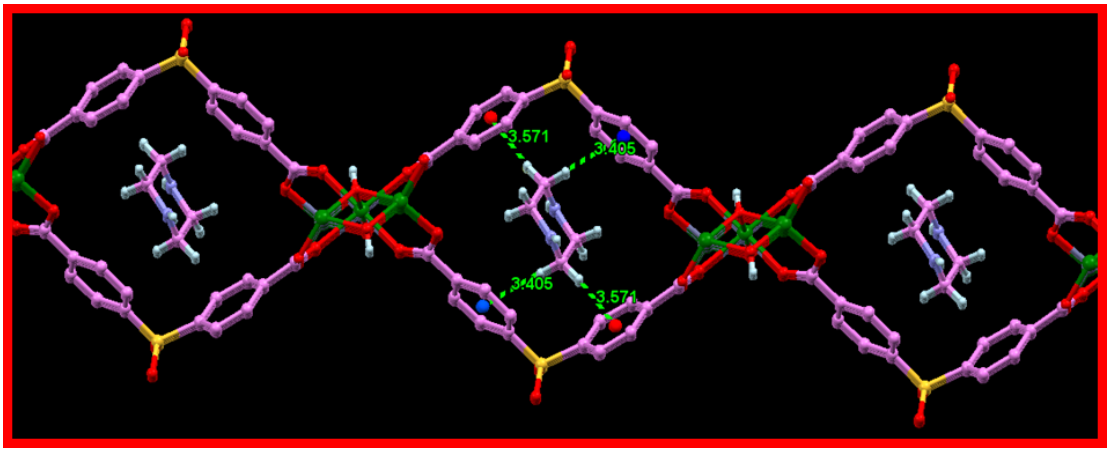

Fig. S3. Weak C-H···π interaction between the piperazine moiety and the centroid of the phenyl rings of the SDB ligand of the two dimensional network.

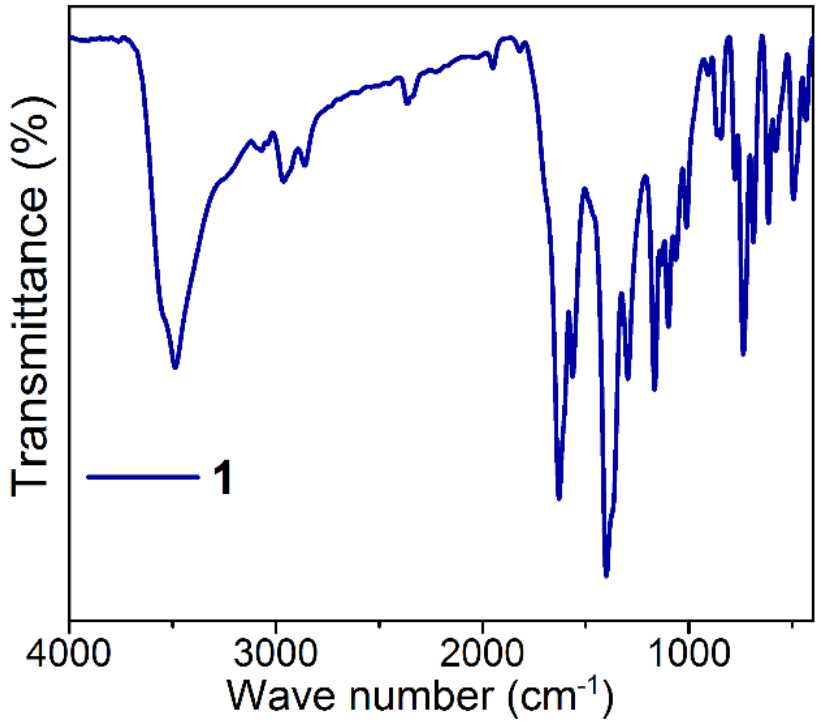

Fig. S4. FTIR of **1** recorded for compound dispersed in KBr pellets.

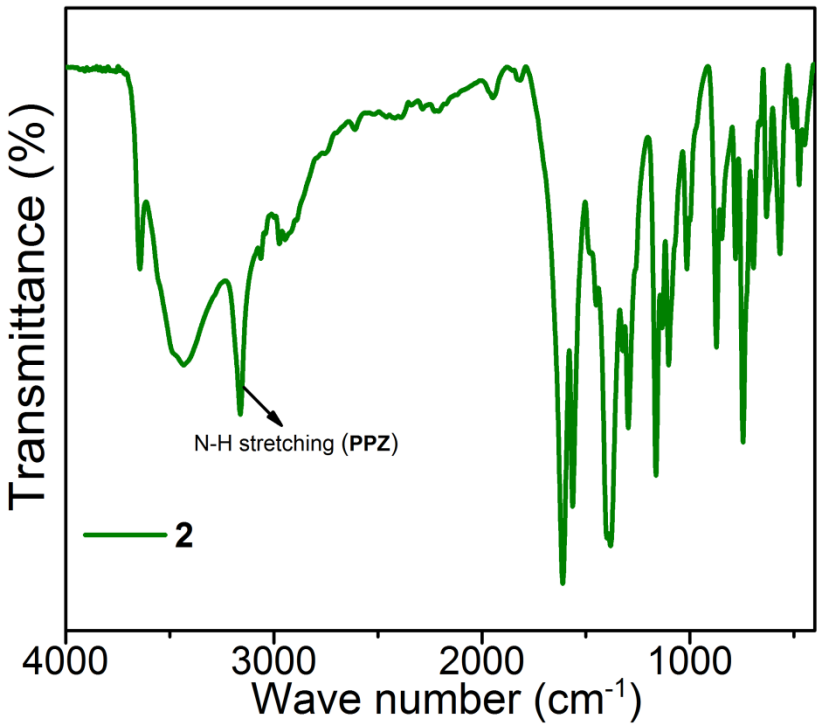

Fig. S5. FTIR of **2** recorded for compound dispersed in KBr pellets.

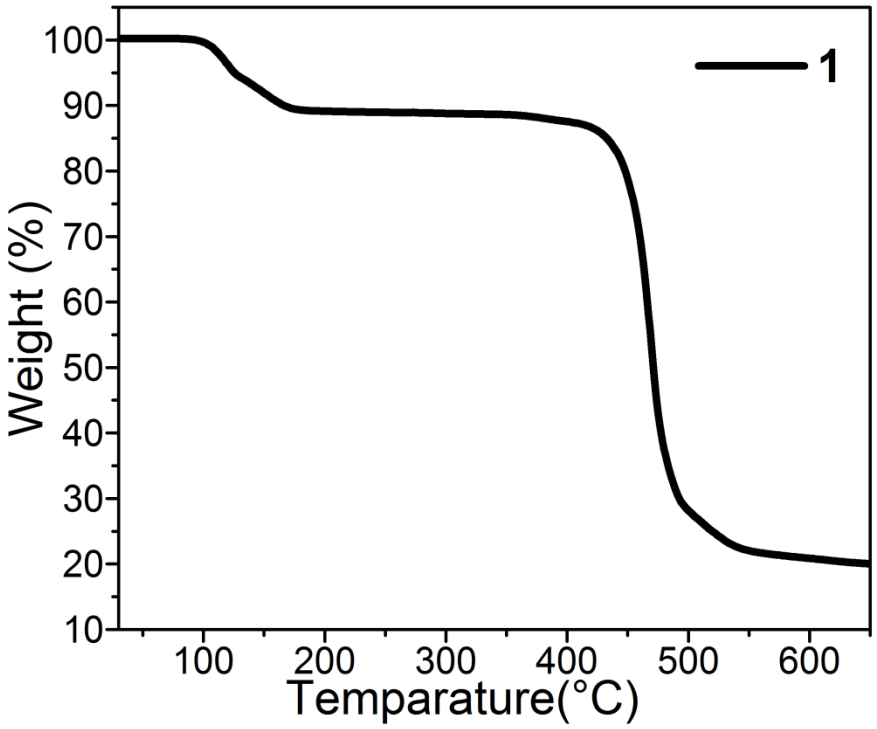

Fig. S6. TGA plot for compound **1**.

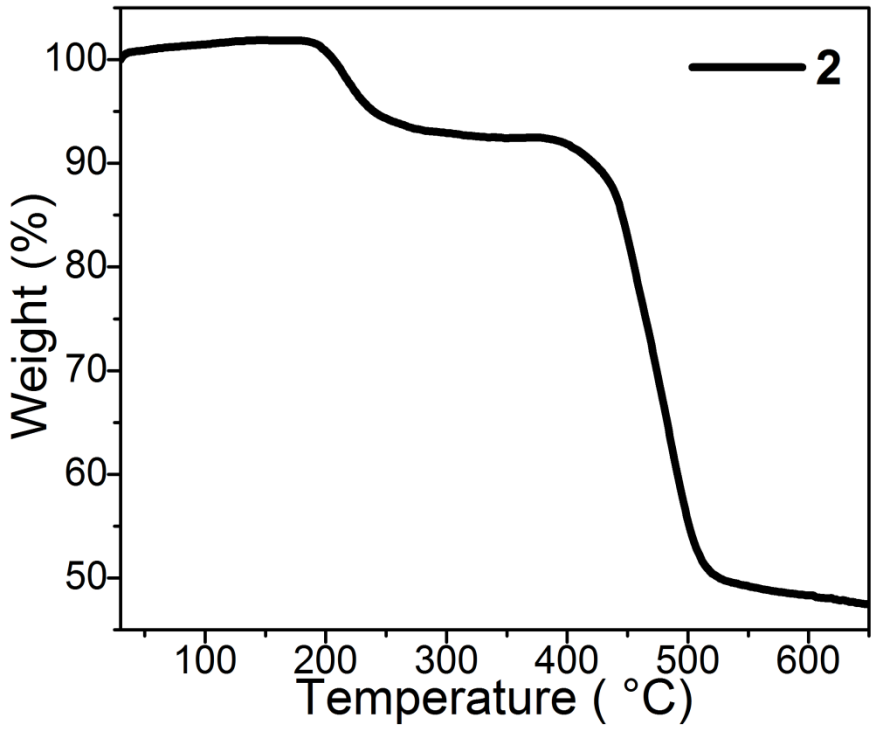

Fig. S7. TGA plot for compound **2.**

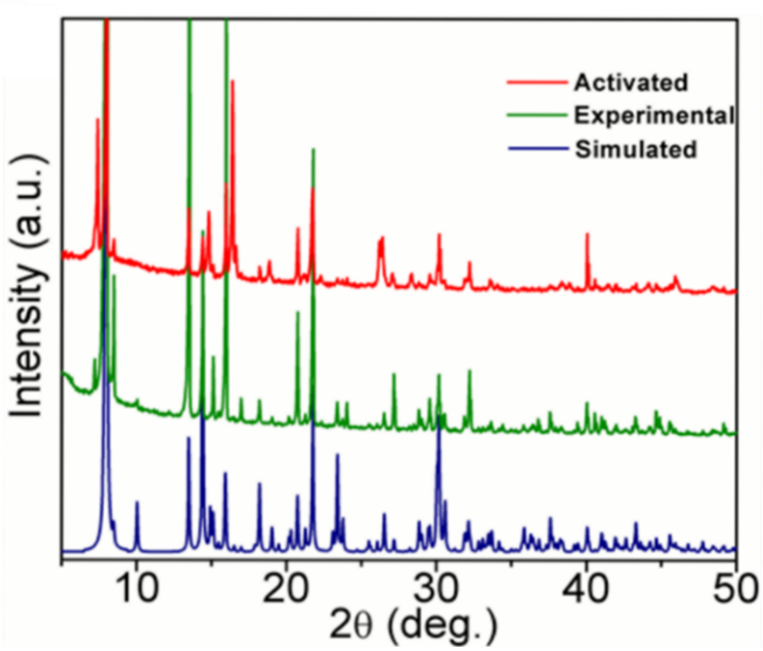

Fig. S8.PXRD patterns of **2**, comparison of bulk and **2′** with simulated of single crystal data.

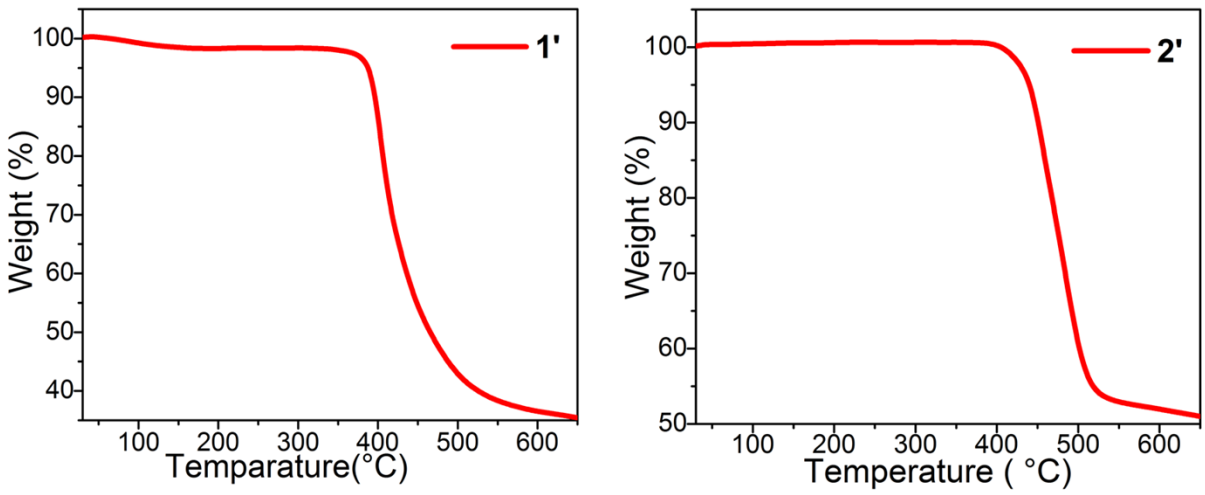

Fig. S9. TGA plots for activated compounds **1′&2′.**

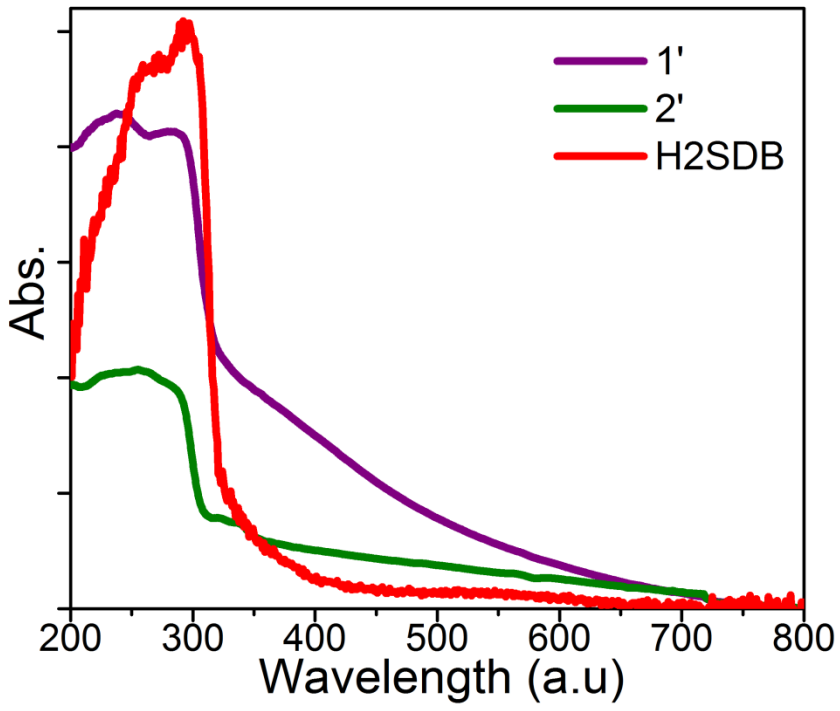

Fig. S10. Solid state absorption spectra of **1′**, **2′** and H_2**SDB**

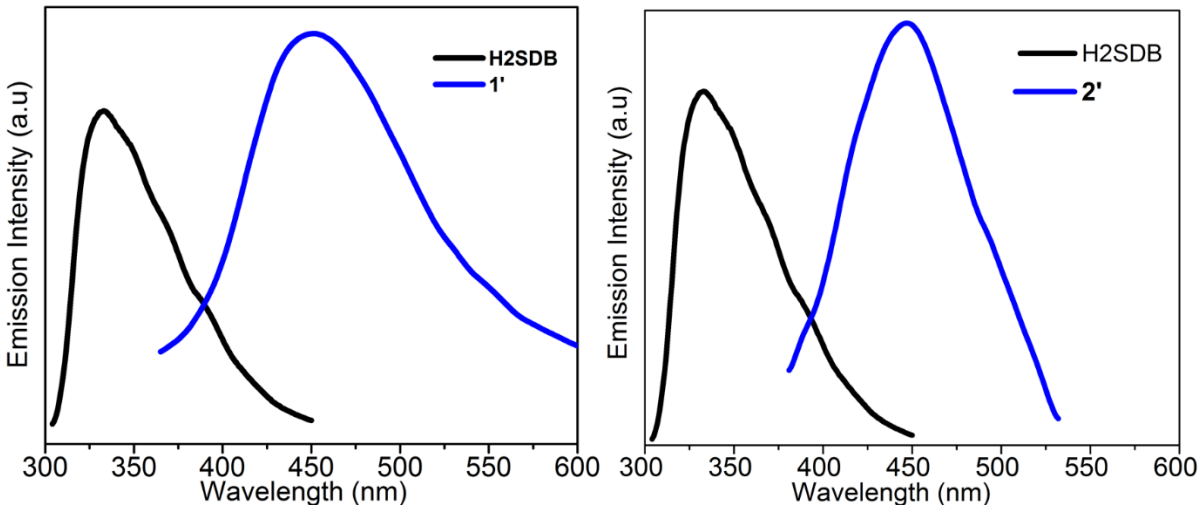

Fig. S11. Fluorescence spectra of**1′**(λ_{em} 451 nm, λ_{ex} 330 nm),**2′** (λ_{em} 447 nm, λ_{ex} 330 nm) and H_2**SDB** (λ_{em} 333 nm, λ_{ex} 270 nm) in the solid state at room temperature.

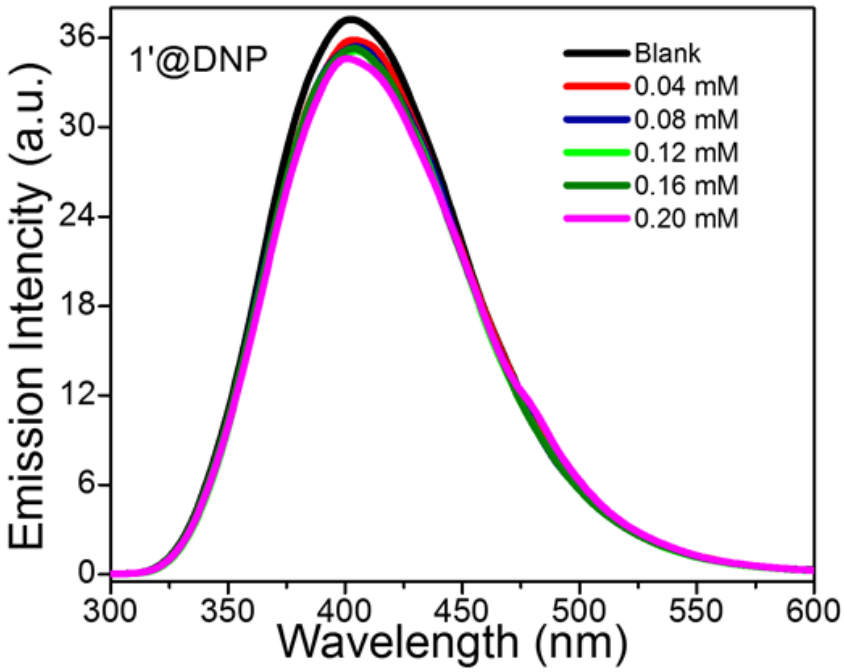

Fig. S12. Fluorescence spectra of **1′**dispersed in acetone with the incremental addition of DNP (2 mM) solution in acetone

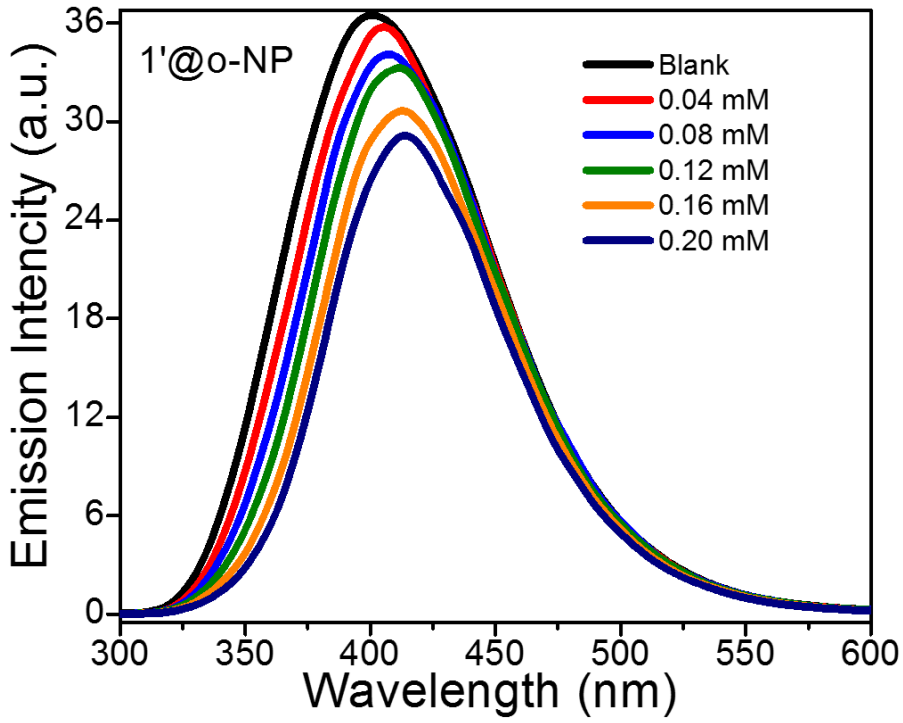

Fig. S13. Fluorescence spectra of **1′** dispersed in acetone with the incremental addition of o-NP (2 mM) solution in acetone

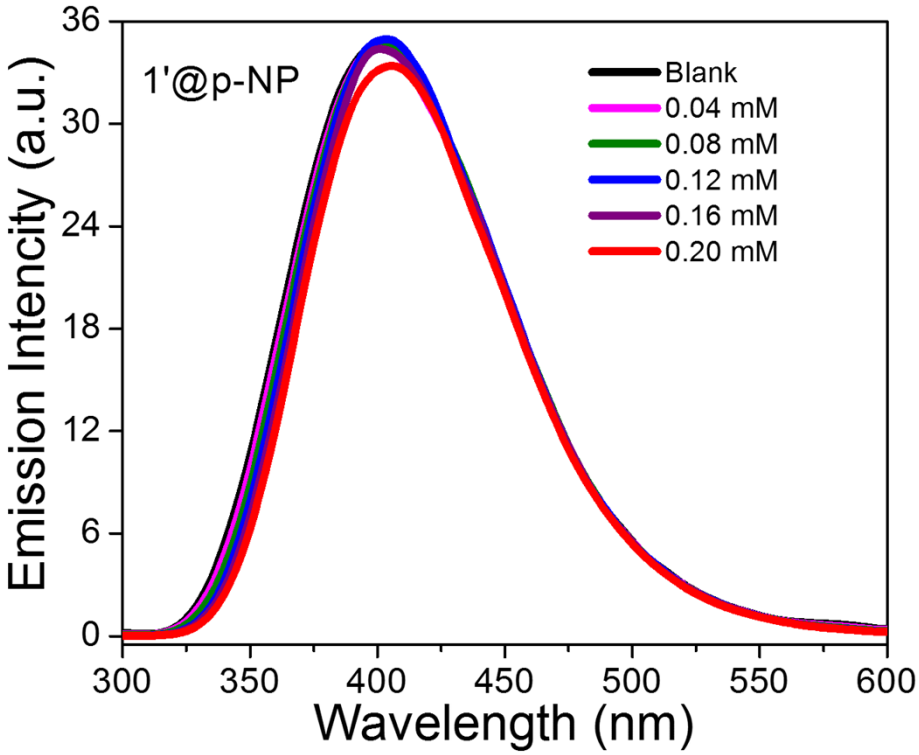

Fig. S14. Fluorescence spectra of **1′** dispersed in acetone with the incremental addition of p-NP (2 mM) solution in acetone

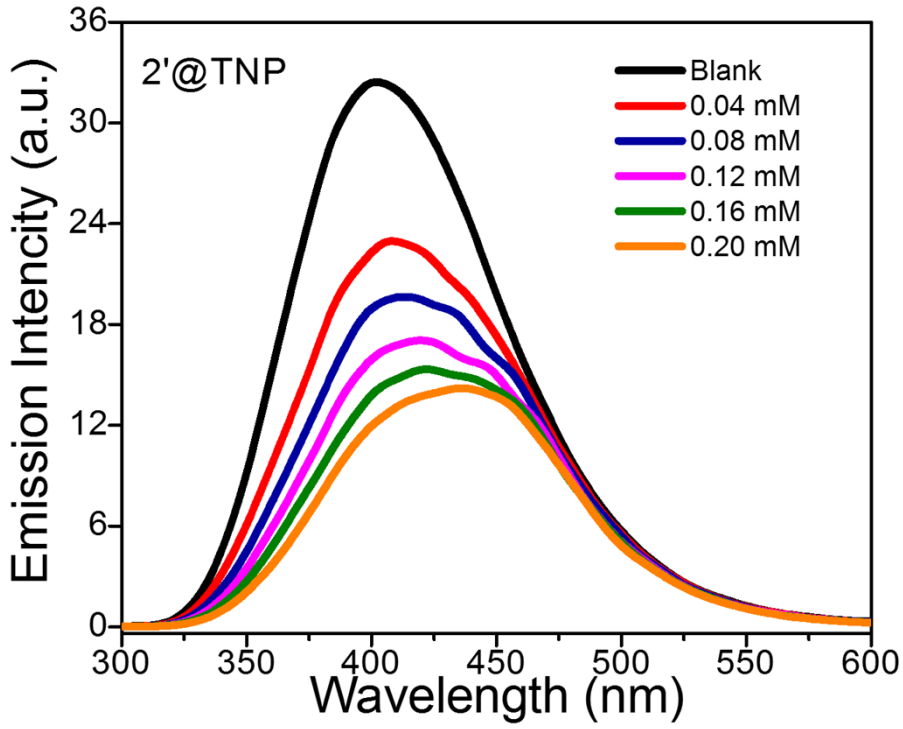

Fig. S15. Fluorescence spectra of **2′** dispersed in acetone with the incremental addition of TNP (2 mM) solution in acetone. Emission wavelength 404 nm was upon excitation by 292 nm.

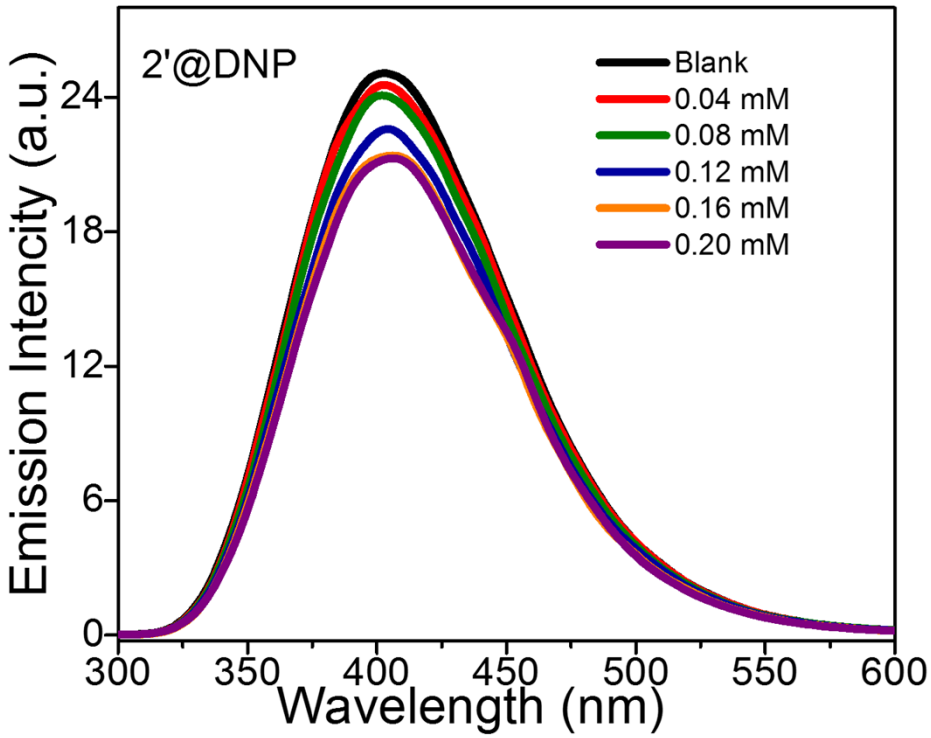

Fig. S16. Fluorescence spectra of **2′** dispersed in acetone with the incremental addition of DNP (2 mM) solution in acetone

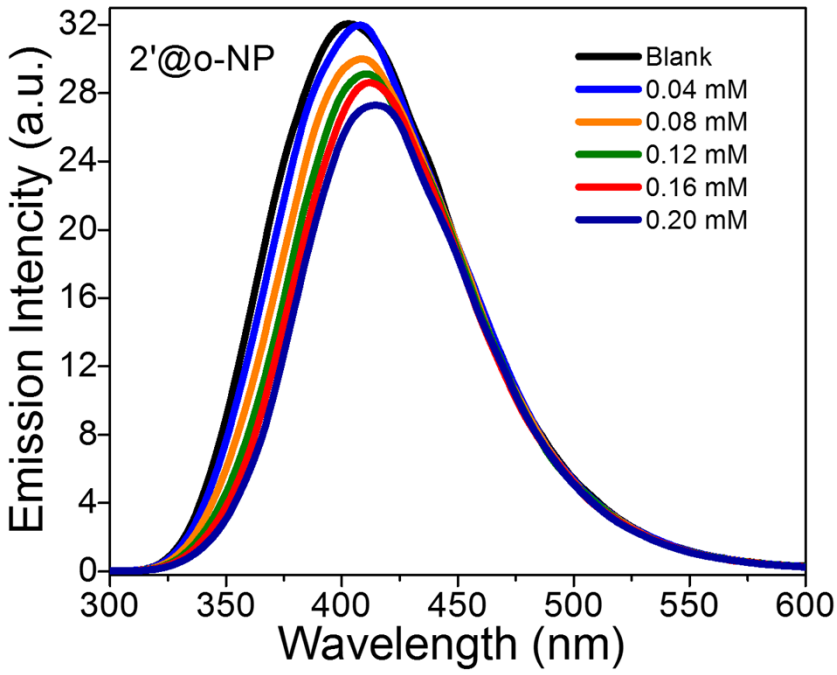

Fig. S17. Fluorescence spectra of **2′** dispersed in acetone with the incremental addition of o-NP (2 mM) solution in acetone

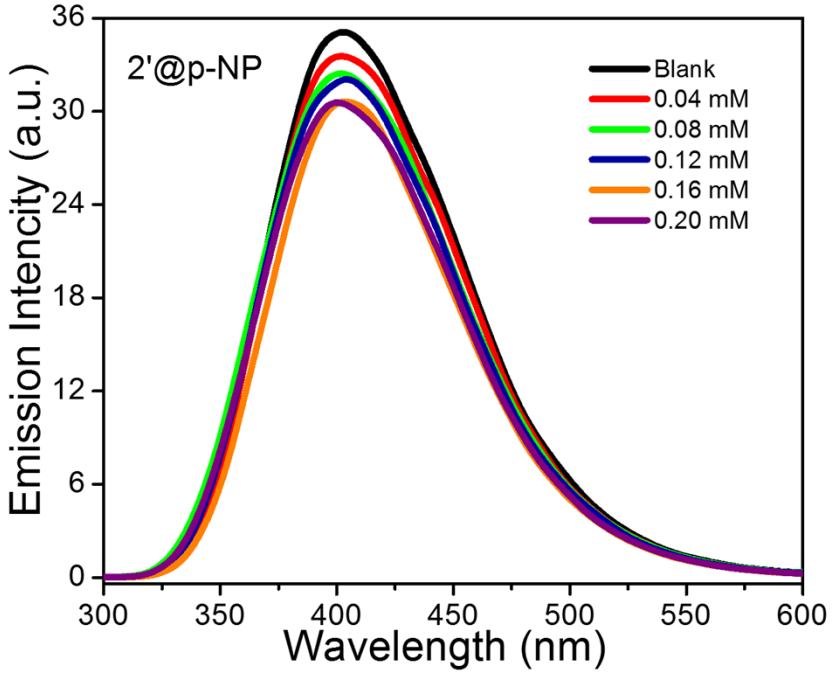

Fig. S18. Fluorescence spectra of **2′** dispersed in acetone with the incremental addition of p-NP (2 mM) solution in acetone

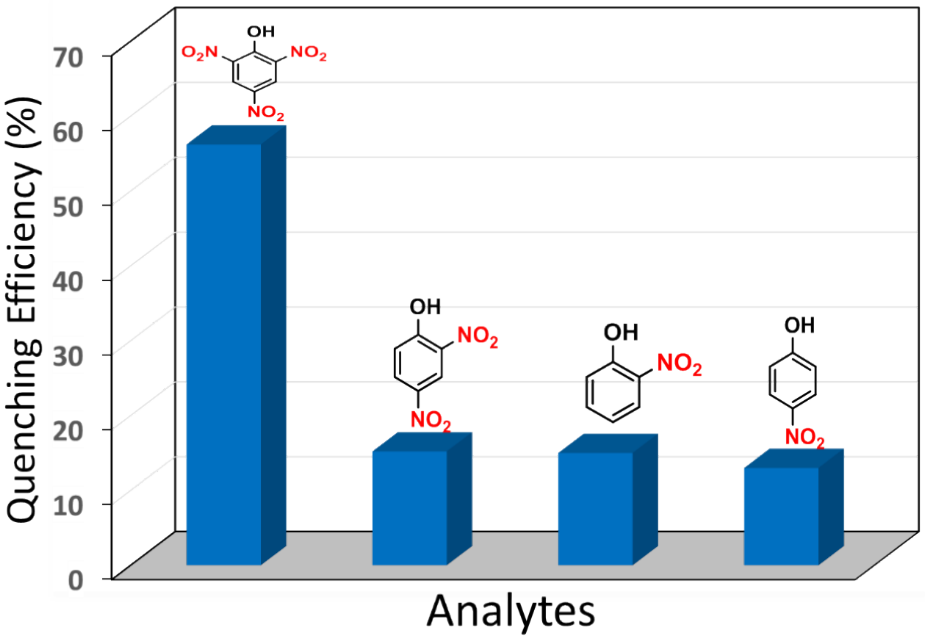

Fig. S19. Quenching percentage of **2′** by different nitro compounds.

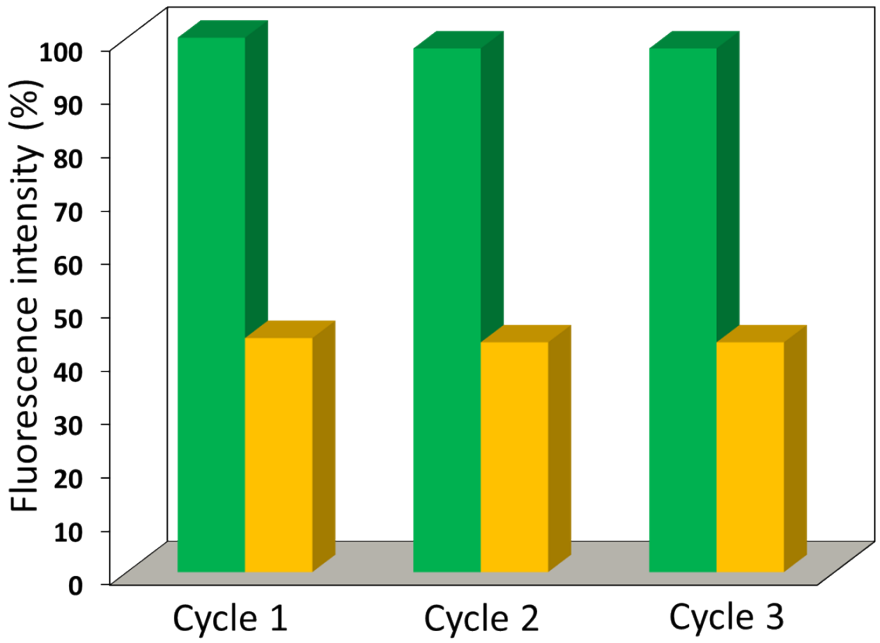

Fig. S20. Reproducibility of the quenching capacity of **2′**dispersed in acetone with titration of TNP in acetone. The material was recovered by centrifuging after each cycle experiment and washed several times with acetone. Fluorescence quenching efficiency of **2′**effectively up to 3 cycles [green bars = initial intensity, orange bars = after addition of 200 µL (2 mM) TNP solution].

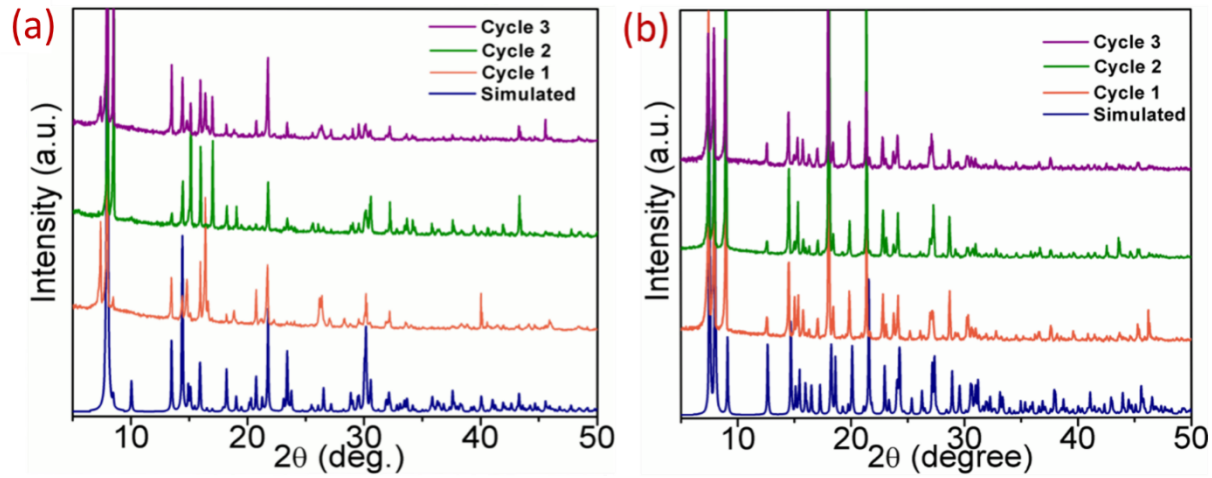

Fig. S21.(a) Recovered material **1′**from titration with TNP up to 3 cycles are also presented for compare with simulated pattern of **1**, (b) Recovered material **2′**from titration with TNP up to 3 cycles are also presented for compare with simulated pattern of **2.**

Experimental Section:

Preparation of Activated Compounds $[Cd(SDB)]_n$ 1′ and $\{[Zn_3(\mu\text{-}OH)_2(SDB)_2]_n$ 2′

Activated compounds **1′** and **2′** were prepared by heating CPs **1** and **2** at 200°C in a temperature controlled oven for 8 hours in order to expel the lattice guest molecule. The material thus obtained is designated as **1′**, **2′** and stored in the vacuum desiccator. **1′** and **2′** thus obtained was characterized by Elemental analysis and IR data which clearly indicate the expulsion of the encapsulated molecules from the CPs **1** and **2**. Details of the elemental analysis, peak positions from the FTIR data for **1′**and **2′** along with the FTIR spectra for the pristine CPs **1**,**2** and the activated ones **1′** and **2′**is given below:

$[Cd(SDB)]_n$ 1′ : Elemental analysis (%) $C_{14}H_8O_6SCd$, Calc: C, 40.36; H, 1.94; S, 7.69. Found: C, 40.57; H, 2.12; S, 7.26. FTIR cm^{-1} (KBr): 3432 (br), 2367 (w), 1603 (m), 1546 (m), 1402 (s), 1294 (s), 1157 (s), 1100 (m), 1013 (w), 869 (m), 746 (s), 616 (w), 472 (m).

$\{[Zn_3(\mu\text{-}OH)_2(SDB)_2]\}_n$ (2′): Elemental analysis (%) $C_{28}H_{18}O_{14}S_2Zn_3$ Calc.: C, 40.10; H, 2.16; S, 7.65; found: C, 39.44, H, 1.96, S, 7.4. FTIR cm^{-1} (KBr): 3510 (br), 3044 (w), 1952 (w), 1612 (s), 1570 (s), 1409 (s), 1295 (s),1171 (m), 1099(m), 1015(m), 847 (w), 741 (s), 619 (m), 497 (w).

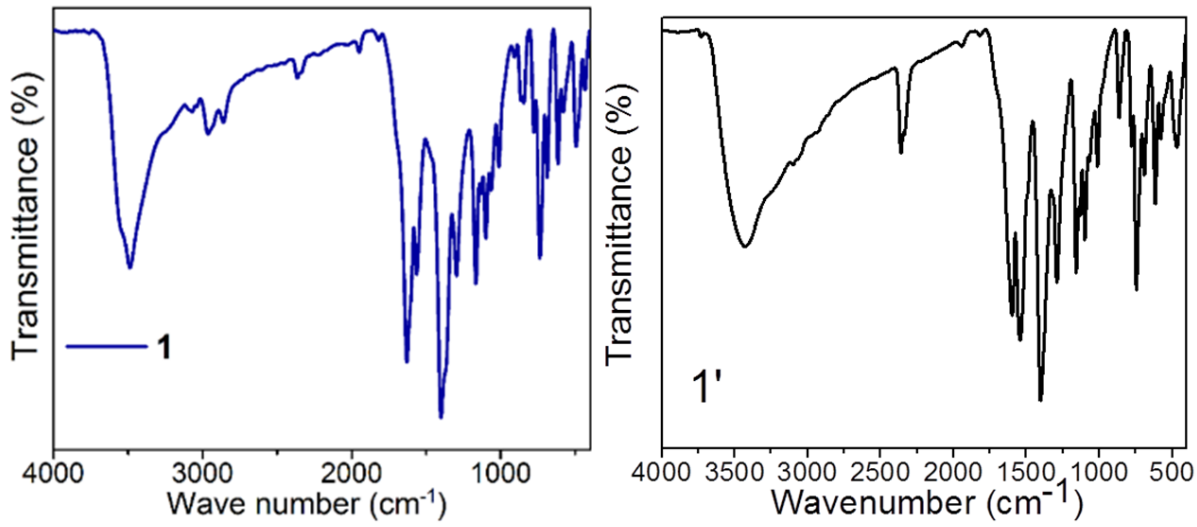

Fig. S22. FTIR spectra for the pristine **1** and the activated compound **1′**

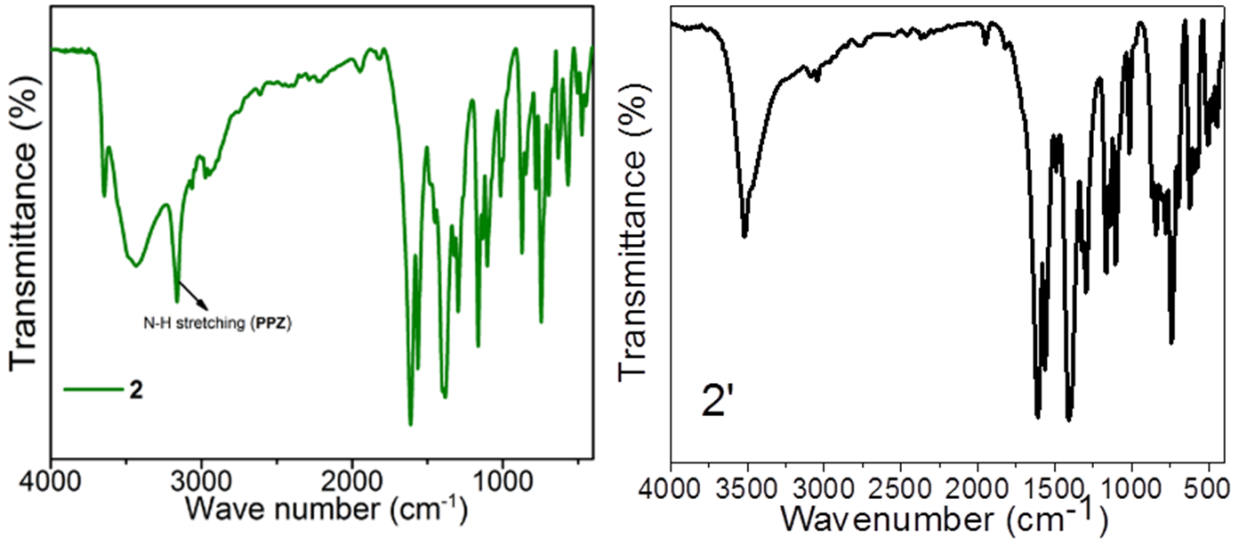

Fig. S23. FTIR spectra for the pristine **2** and the activated compound **2′**

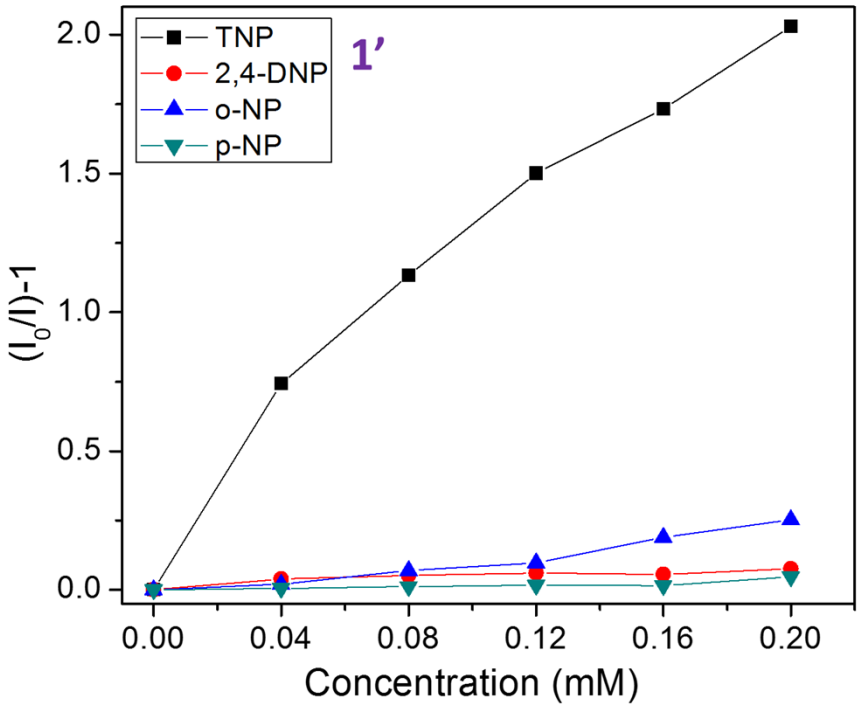

Fig. S24. Stern-Volmer (SV) plots for various analytes in acetone with **1′**

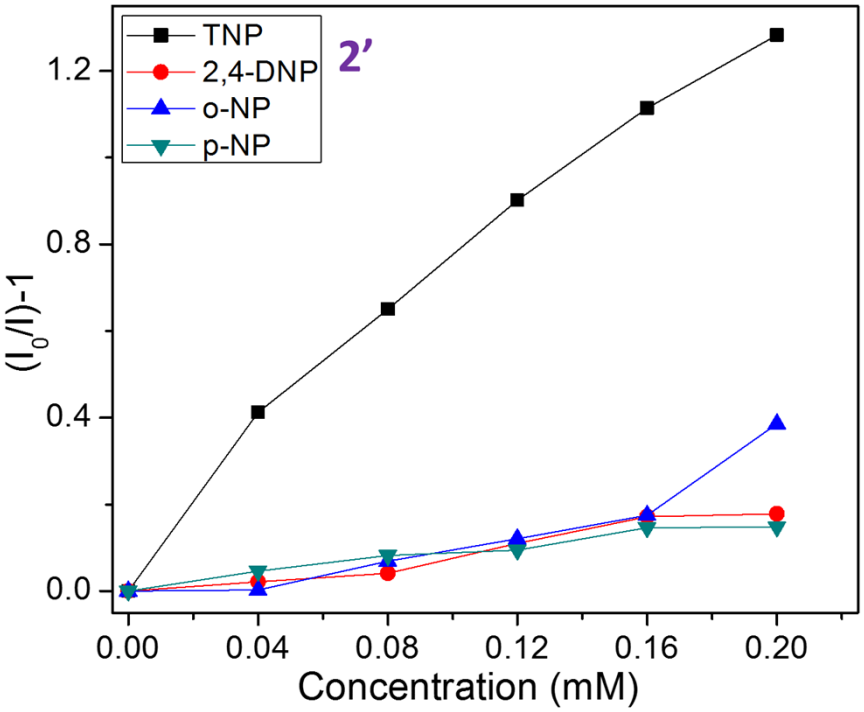

Fig. S25. Stern-Volmer (SV) plots for various analytes in acetone with **2′**

Identification code	**1**	**2**
Chemical formula	$C_{14}H_{10}O_7SCd$	$C_{32}H_{28}N_2O_4S_2Zn_3$
Formula weight	434.68	924.79
Crystal Color	Colorless	Pale yellow
Crystal Size (mm)	0.32 x 0.24 x 0.14	0.23 x 0.06 x 0.02
Temperature (K)	150(2)	150(2)
Crystal System	Monoclinic	Monoclinic
Space Group	C2/c	P21/n
a(Å)	21.896(3)	14.0167(19)
b(Å)	13.1180(14)	6.0416(8)
c(Å)	12.3002(14)	19.452(3)
α(°)	90	90
β(°)	107.635(2)	93.811(2)
γ (°)	90	90
Z	8	2
V(Å^3)	3367.0(7)	1643.6(4)
Density (Mg/m^3)	1.715	1.869
μ (mm^{-1})	1.451	2.376
F(000)	1712	936
Reflections Collected	7566	8454
Independent Reflections	3149	3235
R_{int}	0.0290	0.0503
Number of parameters	214	244
GOF on F^2	1.115	1.212
FinalR_1/wR_2 ($I \geq 2\sigma(I)$)	0.0404/ 0.0955	0.0768/ 0.1494
Weighted R_1/wR_2 (all data)	0.0482/0.0989	0.0947/0.1565
CCDC number	1024317	1024318

$R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$; $wR = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w(Fo^2)^2]^{1/2}$

Table S1: Crystal Data and Refinement Parameters for **1** and **2**

1			
Cd(1)-O(6)#1	2.189(3)	Cd(1)-O(1)#2	2.236(3)
Cd(1)-O(5)#3	2.258(3)	Cd(1)-O(7)	2.286(4)
Cd(1)-O(2)#4	2.353(3)	Cd(1)-O(1)	2.502(3)
Cd(1)-Cd(1)#5	3.389(7)	O(1)-C(1)	1.269(5)
O(2)-C(1)	1.249(5)	O(5)-C(14)	1.248(6)
O(6)-C(14)	1.259(6)	O(6)#1-Cd(1)-O(1)#2	171.71(13)
O(6)#1-Cd(1)-O(5)#3	88.69(15)	O(1)#2-Cd(1)-O(5)#3	84.84(14)
O(6)#1-Cd(1)-O(7)	85.87(15)	O(1)#2-Cd(1)-O(7)	102.13(14)
O(5)#3-Cd(1)-O(7)	155.79(15)	O(6)#1-Cd(1)-O(2)#4	88.69(14)
O(1)#2-Cd(1)-O(2)#4	91.03(12)	O(5)#3-Cd(1)-O(2)#4	126.72(12)
O(7)-Cd(1)-O(2)#4	76.77(13)	O(6)#1-Cd(1)-O(1)	102.22(12)
O(1)#2-Cd(1)-O(1)	81.23(11)	O(5)#3-Cd(1)-O(1)	75.80(12)
O(7)-Cd(1)-O(1)	82.33(13)	O(2)#4-Cd(1)-O(1)	155.66(12)
Symmetry transformation: #1. x,-y+1,z+1/2;#2. -x+1,-y,-z+1; #3. -x+1,-y+1,-z+1;#4. x,-y,z+1/2; #5. -x+1,y,-z+3/2			
2			
Zn(1)-O(7)#1	2.030(5)	Zn(1)-O(7)	2.030(5)
Zn(1)-O(1)#1	2.076(4)	Zn(1)-O(1)	2.076(4)
Zn(1)-O(5)#2	2.169(4)	Zn(1)-O(5)#3	2.169(4)
Zn(2)-O(6)#4	1.914(4)	Zn(2)-O(2)	1.929(5)
Zn(2)-O(7)	1.965(4)	Zn(2)-O(7)#5	2.009(4)
Zn(2)-Zn(2)#5	2.901(5)	O(7)#1-Zn(1)-O(7)	179.996(2)
O(7)#1-Zn(1)-O(1)#1	95.05(18)	O(7)-Zn(1)-O(1)#1	84.95(18)
O(7)#1-Zn(1)-O(1)	84.95(18)	O(7)-Zn(1)-O(1)	95.05(18)
O(1)#1-Zn(1)-O(1)	179.998(1)	O(7)#1-Zn(1)-O(5)#2	84.95(17)
O(7)-Zn(1)-O(5)#2	95.05(17)	O(1)#1-Zn(1)-O(5)#2	86.32(18)
O(1)-Zn(1)-O(5)#2	93.68(18)	O(7)#1-Zn(1)-O(5)#3	95.05(17)
O(7)-Zn(1)-O(5)#3	84.95(17)	O(1)#1-Zn(1)-O(5)#3	93.68(18)
O(1)-Zn(1)-O(5)#3	86.32(18)	O(5)#2-Zn(1)-O(5)#3	180.00(19)
O(6)#4-Zn(2)-O(2)	108.5(2)	O(6)#4-Zn(2)-O(7)	116.2(2)
O(2)-Zn(2)-O(7)	119.45(19)	O(6)#4-Zn(2)-O(7)#5	113.8(2)
O(2)-Zn(2)-O(7)#5	111.02(19)	O(1)-C(1)-O(2)	126.0(6)
O(5)-C(14)-O(6)	126.2(6)		
Symmetry transformation: #1. -x+1,-y+1,-z+1; #2.x-1,y,z; #3. -x+2,-y+1,-z+1; #4. -x+2,-y+2,-z+1; #5. -x+1,-y+2,-z+1			

Table S2. Selected bond lengths and bond angles for **1** and **2.**