Mixed Ligand Two Dimensional Cd(II)/Ni(II) Metal Organic Framework Comprising Dicarboxylate and Tripodal N-donor Ligand: Cd(II) MOF an Efficient Luminescent Sensor for Detection of Picric Acid in Aqueous Medium

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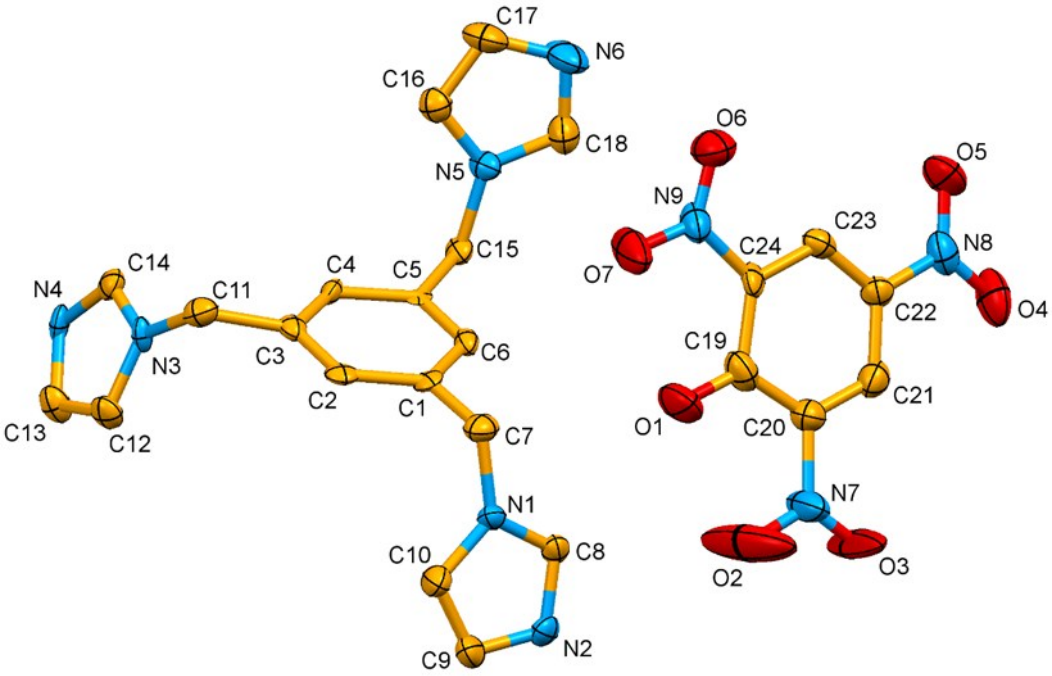


Fig. S1 ORTEP diagram of **CC1** drawn with 50% probability factor for thermal ellipsoids. All the hydrogen atoms are omitted for the sake of clarity.

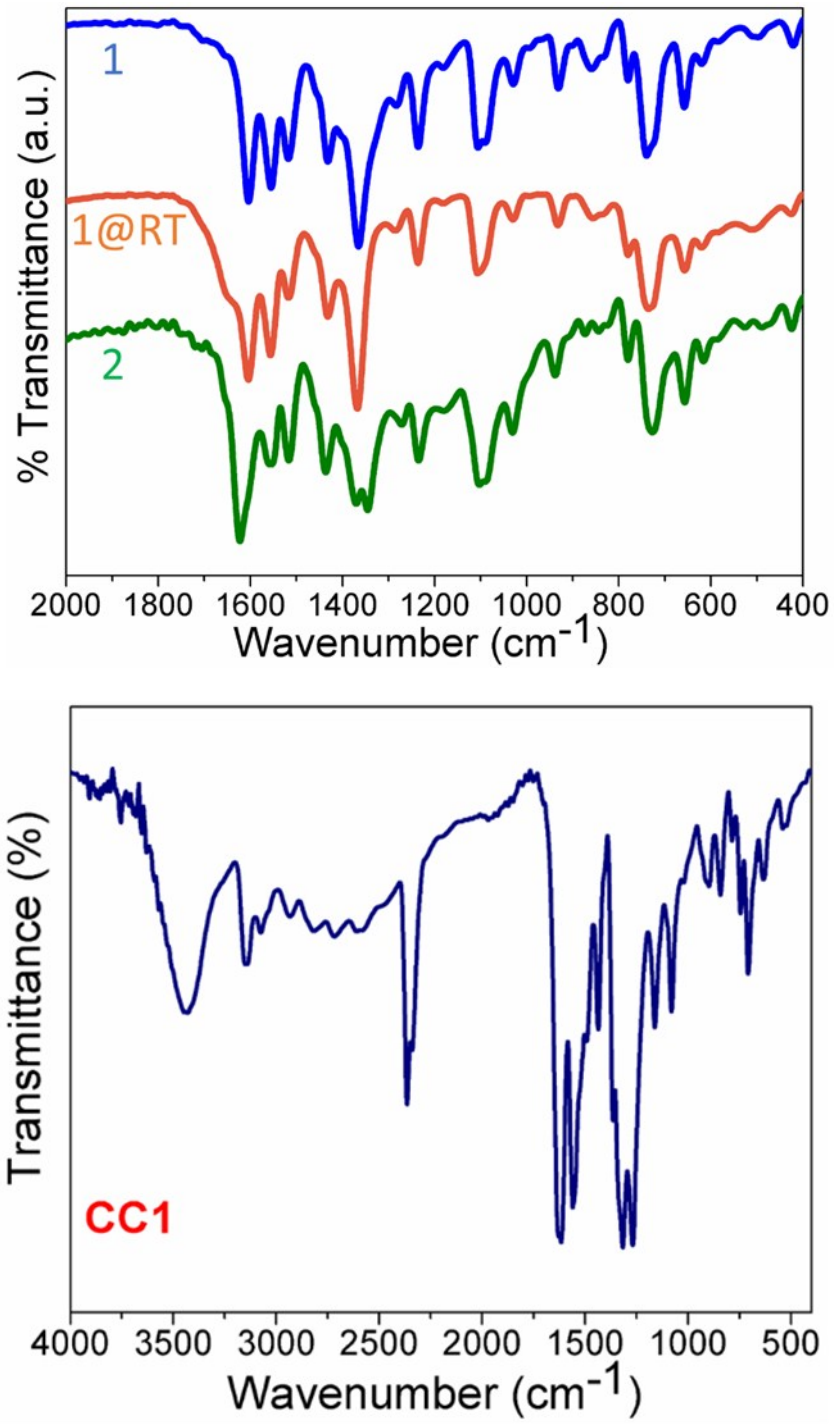


Fig. S2 FTIR recorded for compounds **1, 1@RT, 2** and **CC1** dispersed in KBr pellets.

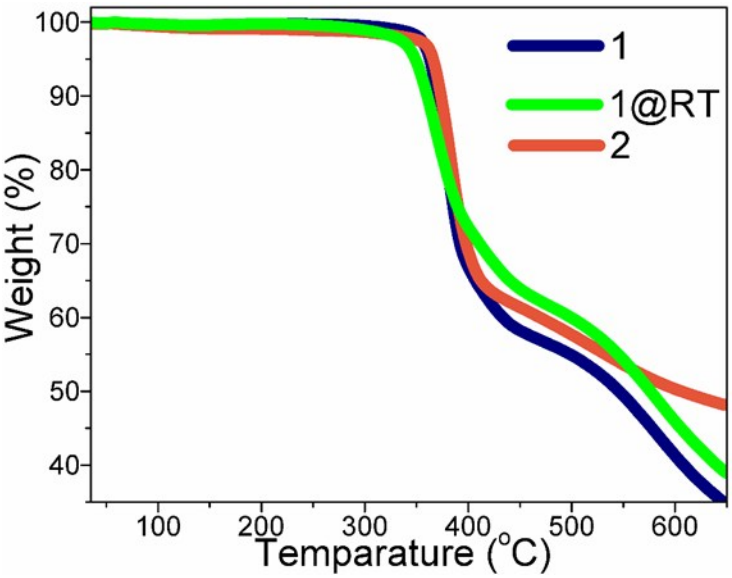


Fig. S3 TGA profiles recorded for samples **1**, **1@RT** and **2**.

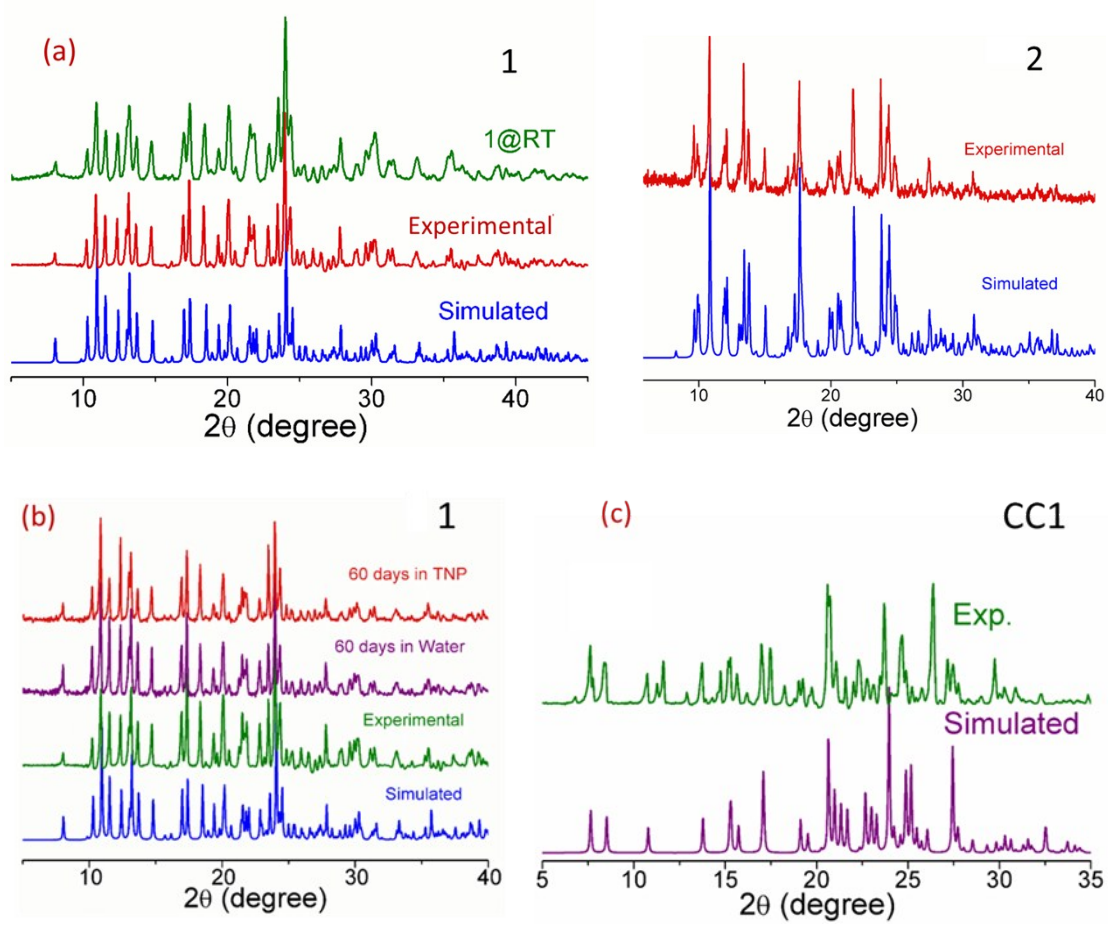


Fig. S4 (a) Simulated SCXRD for **1** and **2** experimental PXRD data for bulk **1**, **1@RT** and **2** (b) Comparison of PXRD traces of **1** was soaked in water and TNP aqueous solution for 60 days with bulk and simulated PXRD patterns of pristine samples of **1** and (c) Experimental and simulated PXRD patterns of **CC1**.

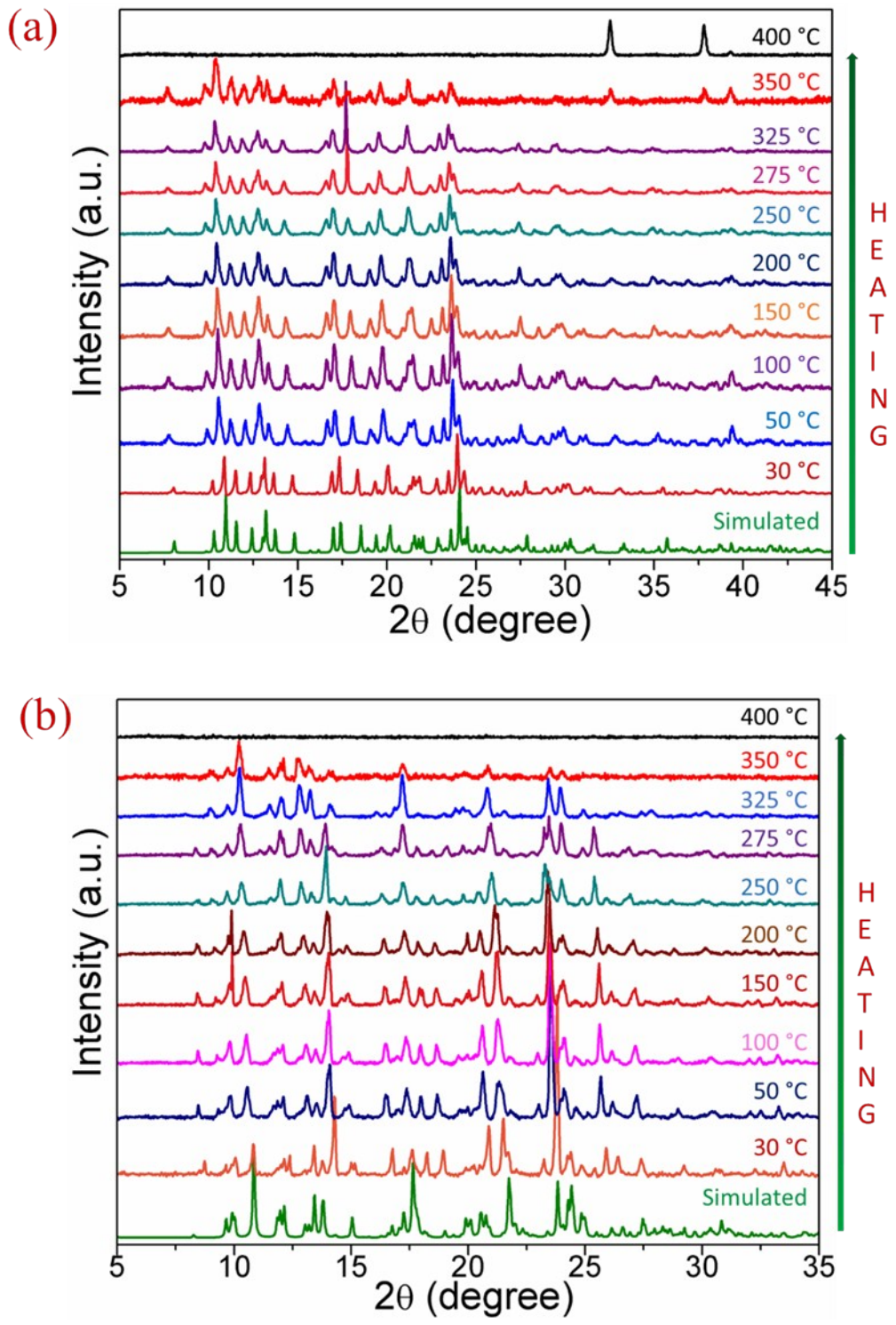


Fig. S5 VT-PXRD spectra recorded for **1** (a) and **2** (b) from room temperature to 400 ^{0}C.

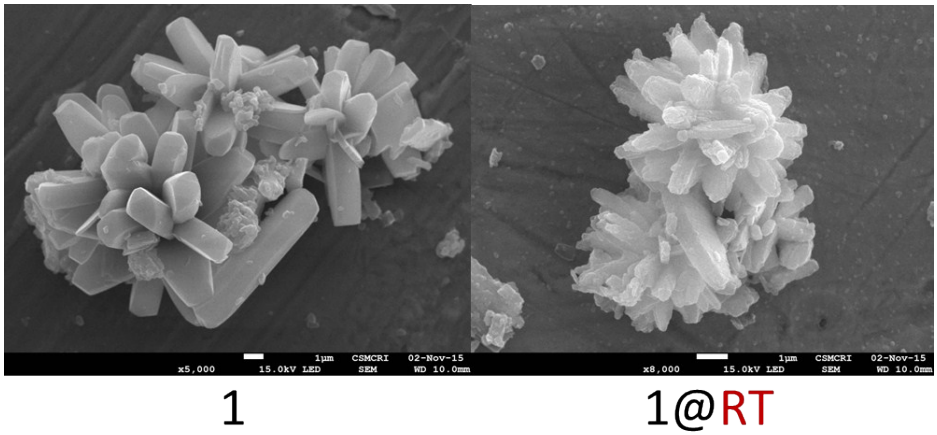


Fig. S6 SEM migrographs revealed aggregated flower like morphology of **1** (Hydrothermally sythesized) and **1@RT** (at room temperature in aqueous medium).

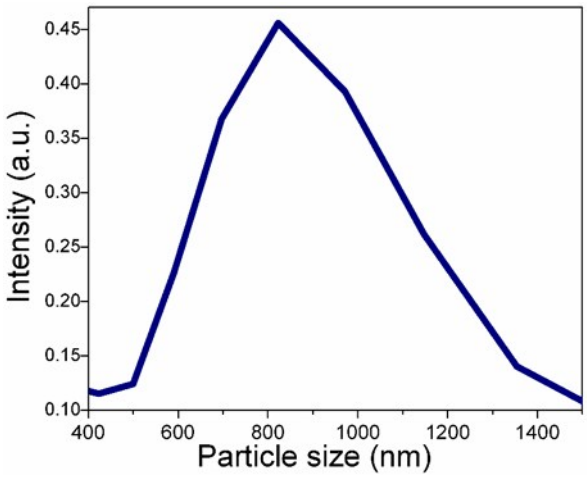


Fig S7. Particle size distribution of **1** in water studied by Dynamic Light Scattering at 25 °C.

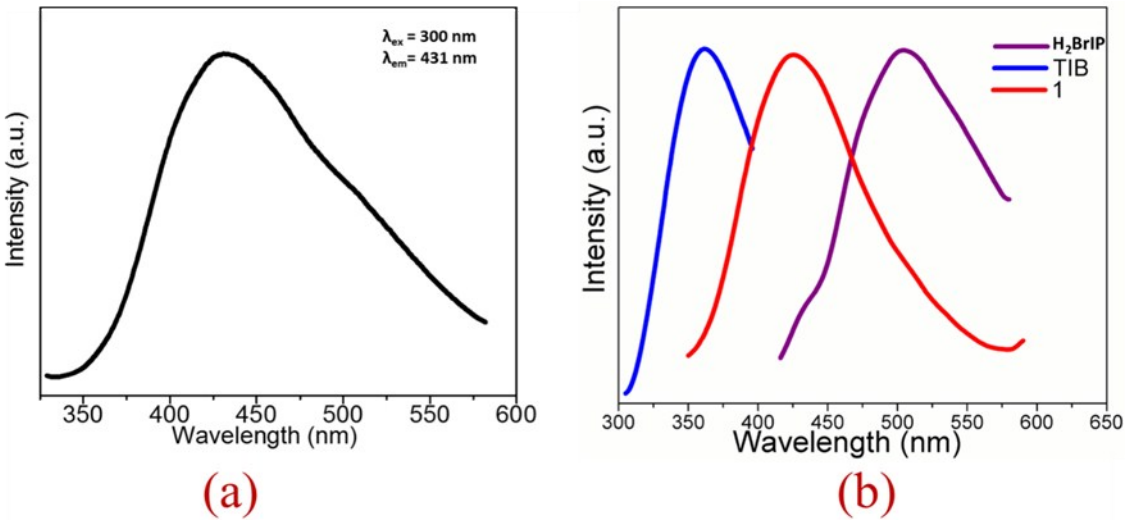


Fig. S8 (a) Photoluminescence spectra of **1** in the solid state. (b) Emission spectra of ligands and **1** recorded in the solid state.

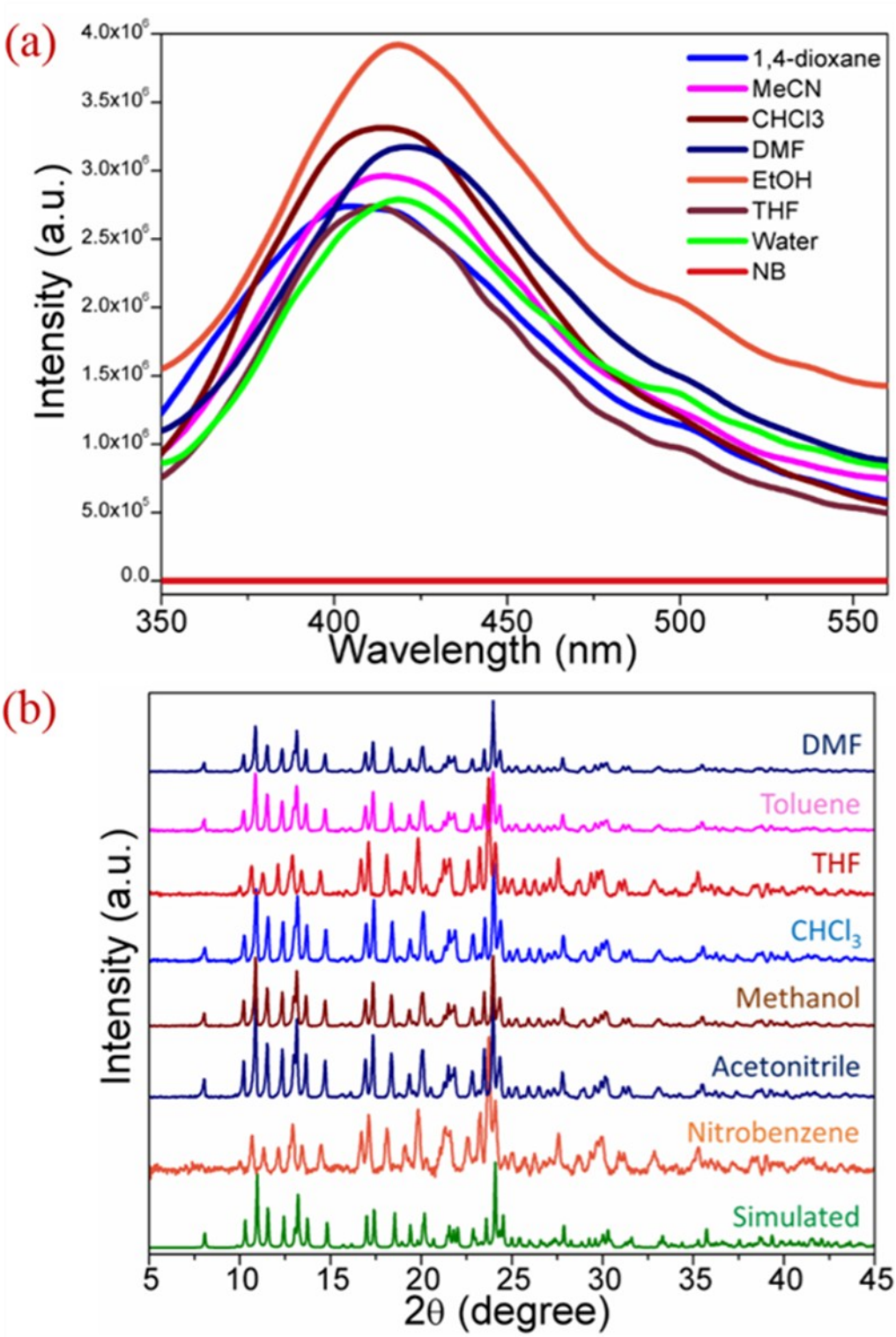


Fig. S9 (a) Fluorescence spectra of **1** in different solvents. (b) PXRD spectra recorded for samples of **1** recovered after soaking for one week in different solvents.

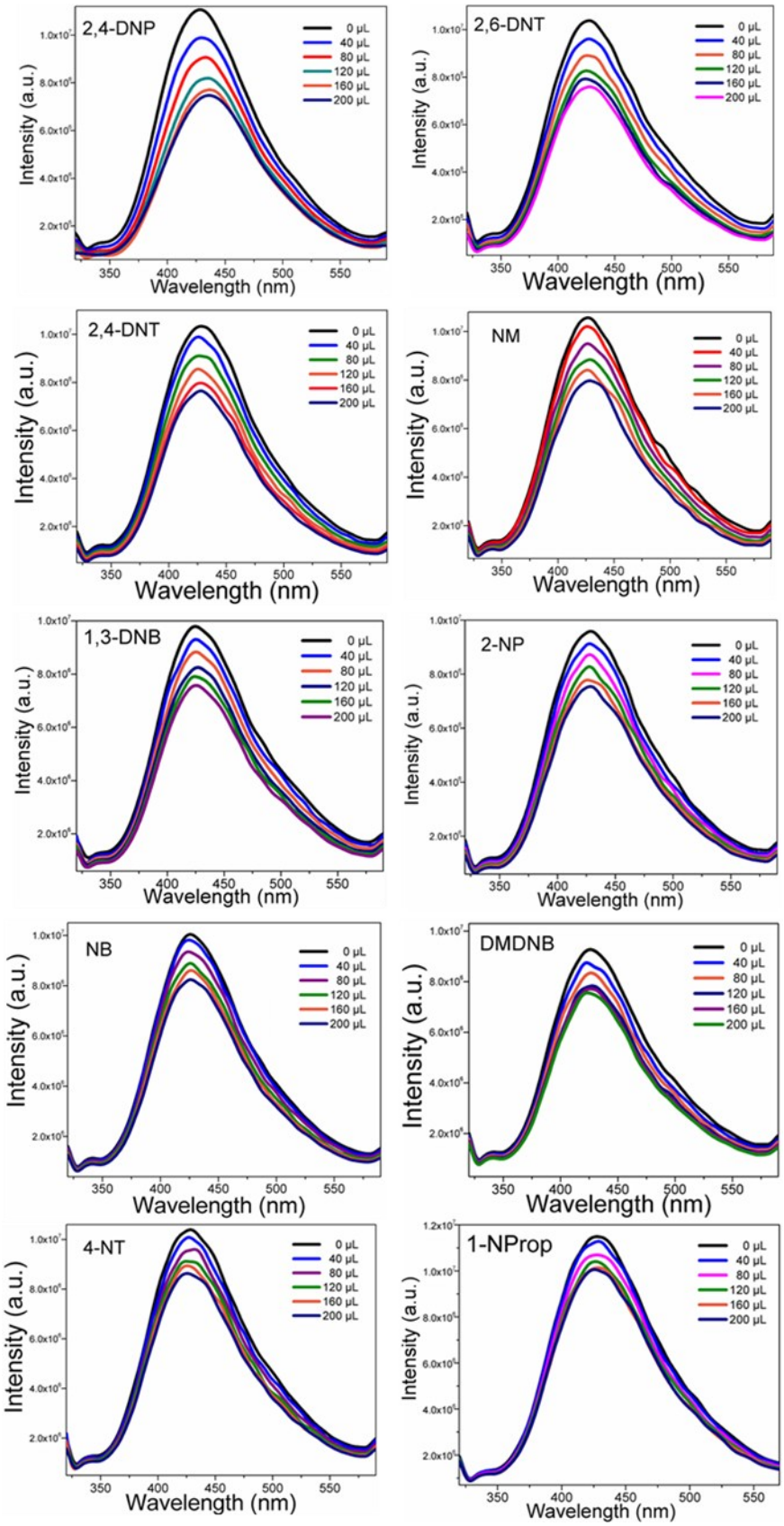


Fig. S10 PL Spectra of **1** dispersed (2 mg) in water (2 mL) upon incremental addition of different nitroanalyte (2,4-DNP, 2,6-DNT, 2,4-DNT, NM, 1,3-DNB, 2-NP, NB, DMDNB, 4-NT, 1-NProp) solution in water (2 mM).

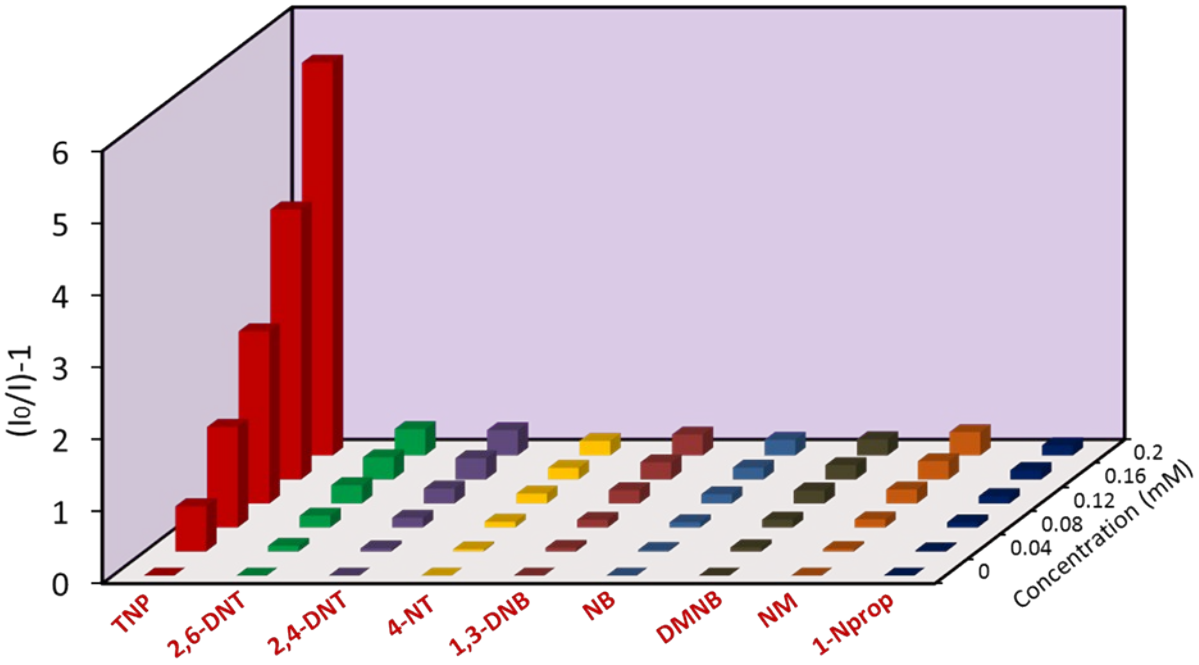
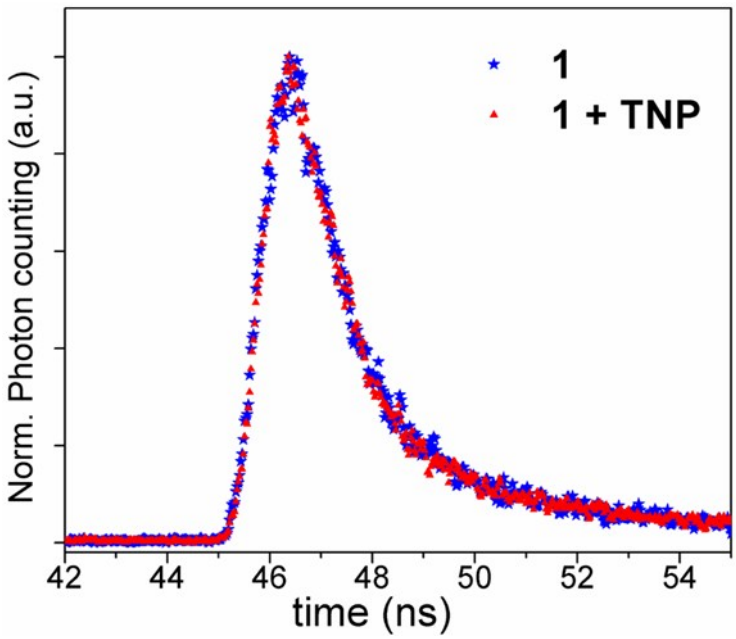


Fig. S11 Stern-Volmer plots of **1** in aqueous phase with corresponding nitro analytes from 0-200 µL.



Compound	Life time (ns)
1	1.18
1+TNP	1.13

Fig. S12 Fluorescence decay profile of **1** in the presence and absence of TNP.

Calculation of Detection Limit.

For calculating detection limit, TNP (0–200 µL, 2 µM stock solution) was added to **1** (2 mg, in 2 mL water) and fluorescent intensity was recorded. By plotting fluorescence intensity with increasing concentration of TNP, slope (m) of graph was found to be 1038970 (R^2 = 0.994). Standard deviation (σ) were calculated from five blank measurements of **1**.

Detection limit is calculated according to the formula: Detection limit= (3σ/m).

Table S1: Standard deviation for **1**.

Blank Readings	Fluorescence Intensity
1	13199698
2	13098976
3	12978659
4	13078967
5	13204589
Standard Deviation (**σ**)	93946.96643

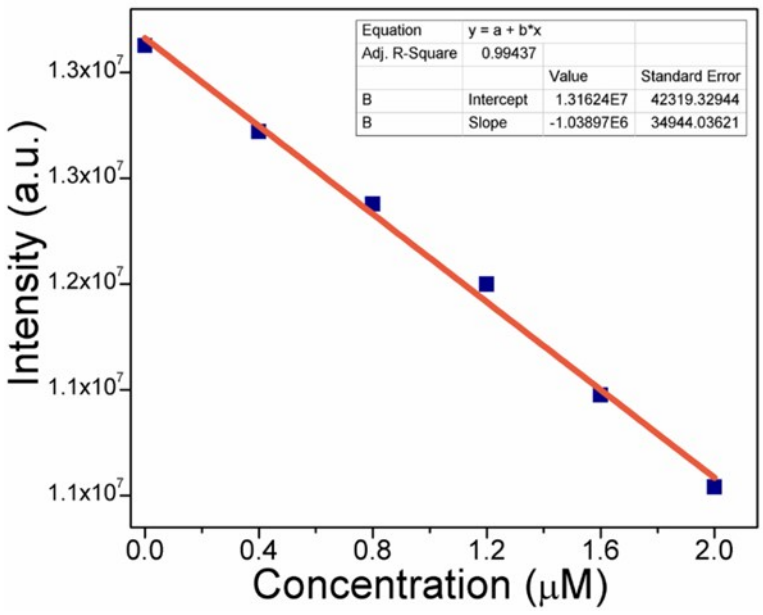


Fig. S13 Linear region of fluorescence intensity of **1** in water upon addition of TNP solution at λ_{em} = 425 nm (upon λ_{ex} = 305 nm) (R^2 = 0.994).

Table S2: Detection limit calculation for 1.

Slope (m)	1038970	
Detection limit (3σ/m)	0.271269	µM
	62	ppb

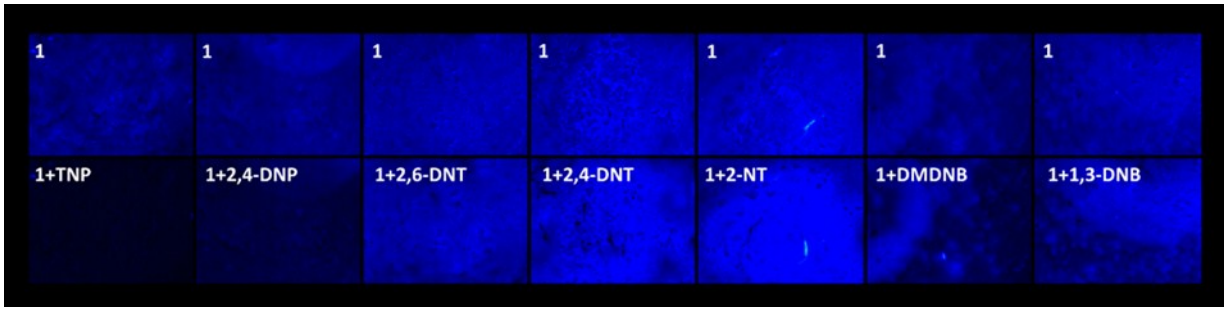


Fig. S14 Digital photographs taken under fluorescence microscope of pristine sample of **1** as well as in presence of various nitro analytes smeared over the glass plate excited at 365 nm.

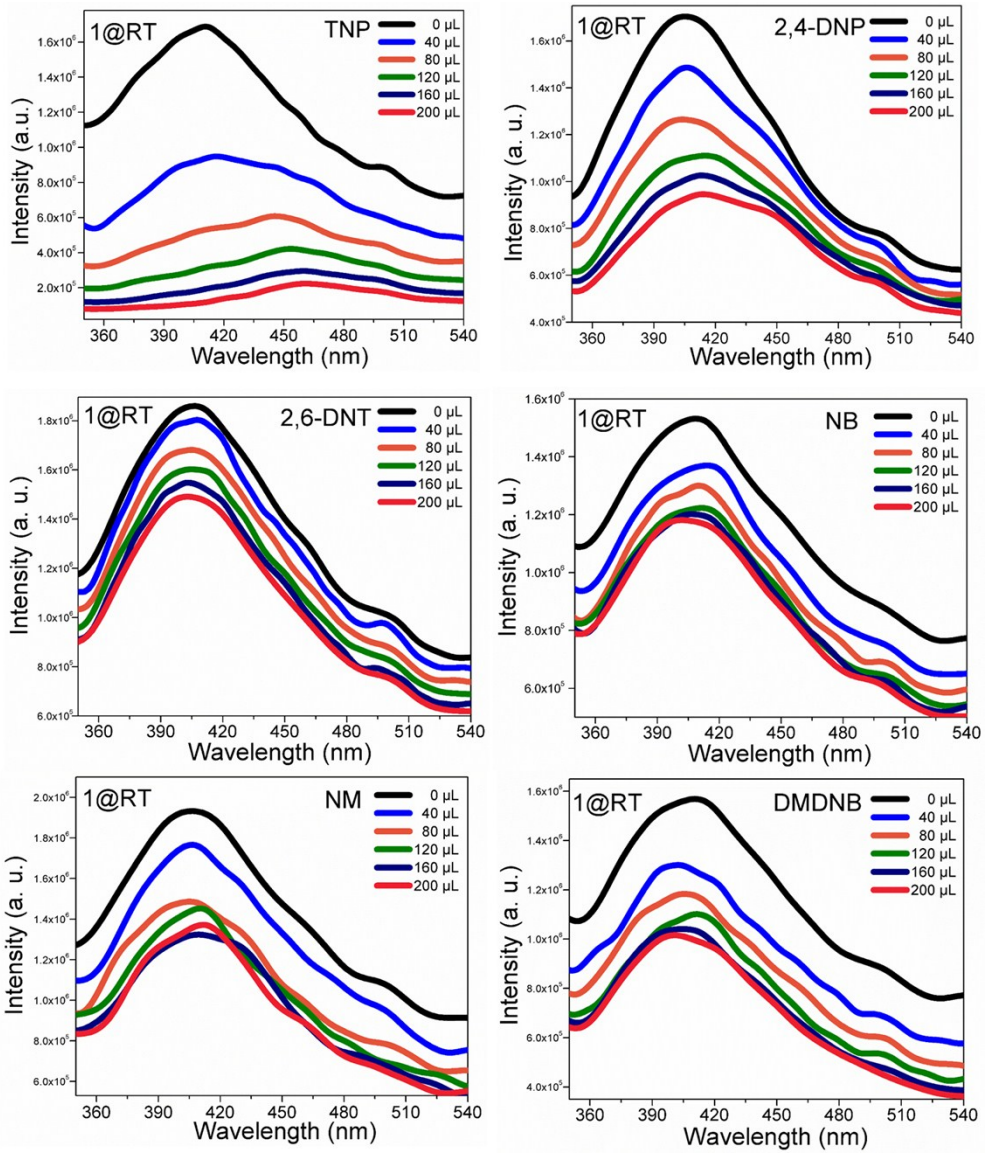


Fig. S15 PL Spectra of **1@RT** (2mg/2mL) in water upon incremental addition of different nitro analytes, TNP, 2,4-DNP, 2,6-DNT, NB, NM and DMDNB aqueous solution (2 mM) and their quenching Percentages are 86, 44, 19, 22, 29 and 35 % respectively.

Table S3. Crystal Data and Refinement Parameters for Compounds **1**, **2** and **CC1**.

Identification code	**1**	**2**	**CC1**
Chemical formula	$C_{26}H_{21}N_6O_4BrCd$	$C_{52}H_{42}N_{12}O_8Br_2Ni_2$	$C_{24}H_{21}N_9O_7$
Formula weight	673.80	1240.22	547.50
Crystal Colour	White	Green	Yellow
Crystal Size (mm)	0.28 x 0.09 x 0.03	0.12 x 0.04 x 0.02	0.14 x 0.12 x 0.07
Temperature (K)	150(2)	293(2)	150(2)
Crystal System	Monoclinic	TRICLINIC	Orthorhombic
Space Group	P21/n	P-1	Pca21
a(Å)	9.9720(10)	10.478(3)	23.224(3)
b(Å)	18.5568(18)	13.541(4)	4.5446(5)
c(Å)	13.9793(14)	17.986(5)	23.134(3)
α(°)	90	90.459(6)	90
β(°)	103.826(2)	103.389(5)	90
γ (°)	90	90.614(6)	90
Z	4	2	4
V(Å^3)	2511.9(4)	2482.1(12)	2441.6(5)
Density (Mg/m^3)	1.782	1.659	1.489
μ (mm^{-1})	2.506	2.438	0.114
F(000)	1336	1256	1136
Reflections Collected	14403	17811	11436
Independent Reflections	5452	8651	4121
$R_{(int)}$	0.0348	0.1195	0.0633
Number of parameters	423	680	362
GOF on F^2	1.027	1.048	1.140
FinalR1/wR2(I>2σ(I)	0.03410/ 0.0723	0.1058/ 0.2463	0.0853/ 0.1722
Weighted R1/wR2 (all data)	0.0430/ 0.0755	0.2100/ 0.2906	0.1036/ 0.1819
CCDC number	1444051	1444052	1444053

Table S4. Selected bond lengths and bond angles for **1, 2** and **CC1**.

1			
Cd(1)-N(1)	2.285(2)	N(6)-Cd(1)#5	2.335(2)
Cd(1)-N(4)#1	2.306(2)	O(3)-Cd(1)#6	2.452(2)
Cd(1)-N(6)#2	2.335(2)	O(4)-Cd(1)#6	2.424(2)
Cd(1)-O(4)#3	2.423(2)	O(1)-C(1)	1.262(3)
Cd(1)-O(3)#3	2.452(2)	O(2)-C(1)	1.249(4)
Cd(1)-O(2)	2.468(2)	O(3)-C(8)	1.246(4)
Cd(1)-O(1)	2.506(2)	O(4)-C(8)	1.256(3)
N(4)-Cd(1)#4	2.306(2)	N(6)#2-Cd(1)-O(1)	86.93(8)
N(1)-Cd(1)-N(4)#1	97.05(9)	O(4)#3-Cd(1)-O(1)	141.29(7)
N(1)-Cd(1)-N(6)#2	164.43(9)	O(3)#3-Cd(1)-O(1)	163.57(7)
N(4)#1-Cd(1)-N(6)#2	97.84(9)	O(2)-Cd(1)-O(1)	52.91(7)
N(1)-Cd(1)-O(4)#3	85.22(8)	C(11)-N(1)-Cd(1)	122.2(2)
N(4)#1-Cd(1)-O(4)#3	133.81(8)	C(9)-N(1)-Cd(1)	132.0(2)
N(6)#2-Cd(1)-O(4)#3	87.76(8)	C(20)-N(4)-Cd(1)#4	123.0(2)
N(1)-Cd(1)-O(3)#3	99.67(9)	C(21)-N(4)-Cd(1)#4	131.8(2)
N(4)#1-Cd(1)-O(3)#3	80.71(8)	C(24)-N(6)-Cd(1)#5	123.9(2)
N(6)#2-Cd(1)-O(3)#3	87.22(9)	C(25)-N(6)-Cd(1)#5	130.2(2)
O(4)#3-Cd(1)-O(3)#3	53.67(7)	C(1)-O(1)-Cd(1)	90.58(17)
N(1)-Cd(1)-O(2)	83.78(8)	C(1)-O(2)-Cd(1)	92.62(17)
N(4)#1-Cd(1)-O(2)	137.81(8)	C(8)-O(3)-Cd(1)#6	90.98(17)
N(6)#2-Cd(1)-O(2)	82.14(8)	C(8)-O(4)-Cd(1)#6	92.08(18)
O(4)#3-Cd(1)-O(2)	88.37(7)	O(2)-C(1)-O(1)	123.9(3)
O(3)#3-Cd(1)-O(2)	141.00(7)	O(3)-C(8)-O(4)	123.3(3)
N(1)-Cd(1)-O(1)	89.89(8)	C(24)-N(6)-Cd(1)#5	123.9(2)
N(4)#1-Cd(1)-O(1)	84.90(7)		
Symmetry transformation: #1 x+1/2,-y+1/2,z+1/2; #2 x+1,y,z+1; #3 -x+3/2,y+1/2,-z+3/2; #4 x-1/2,-y+1/2,z-1/2; #5 x-1,y,z-1; #6 -x+3/2,y-1/2,-z+3/2.			

2			
Ni(1)-O(7)#1	2.059(9)	N(6)-Ni(2)#3	2.093(11)
Ni(1)-N(1)	2.063(11)	N(10)-Ni(1)#2	2.069(12
Ni(1)-N(10)#2	2.069(12)	N(12)-Ni(1)#3	2.082(11)
Ni(1)-N(12)#3	2.082(11)	O(7)-Ni(1)#4	2.059(9)
Ni(1)-O(2)	2.103(9)	O(1)-C(1)	1.251(15)
Ni(1)-O(1)	2.370(11)	O(2)-C(1)	1.251(16)
Ni(2)-O(5)	2.017(9)	O(3)-C(8)	1.294(17)
Ni(2)-N(7)	2.045(11)	O(4)-C(8)	1.204(16)
Ni(2)-N(6)#3	2.093(11)	O(5)-C(9)	1.268(17)
Ni(2)-N(4)#2	2.123(11)	O(6)-C(9)	1.239(17)
Ni(2)-O(3)	2.159(9)	O(7)-C(16)	1.237(17)
Ni(2)-O(4)	2.292(9)	O(8)-C(16)	1.266(17)
N(4)-Ni(2)#2	2.123(11)		
O(7)#1-Ni(1)-N(1)	112.7(4)	N(7)-Ni(2)-O(4)	150.2(4)
O(7)#1-Ni(1)-N(10)#2	86.3(4)	N(6)#3-Ni(2)-O(4)	83.0(4)
N(1)-Ni(1)-N(10)#2	94.0(4)	N(4)#2-Ni(2)-O(4)	85.9(4)
O(7)#1-Ni(1)-N(12)#3	89.0(4)	O(3)-Ni(2)-O(4)	58.6(4
N(1)-Ni(1)-N(12)#3	95.8(4)	C(19)-N(1)-Ni(1)	119.7(10)
N(10)#2-Ni(1)-N(12)#3	170.1(4)	C(17)-N(1)-Ni(1)	134.7(10)
O(7)#1-Ni(1)-O(2)	158.4(4)	C(30)-N(4)-Ni(2)#2	126.8(10)
N(1)-Ni(1)-O(2)	88.8(4)	C(29)-N(4)-Ni(2)#2	131.0(10)
N(10)#2-Ni(1)-O(2)	90.7(4)	C(32)-N(6)-Ni(2)#3	125.2(9)
N(12)#3-Ni(1)-O(2)	90.5(4)	C(33)-N(6)-Ni(2)#3	129.7(10)
O(7)#1-Ni(1)-O(1)	100.5(4)	C(37)-N(7)-Ni(2)	129.7(10)
N(1)-Ni(1)-O(1)	146.7(4)	C(35)-N(7)-Ni(2)	126.9(10)
N(10)#2-Ni(1)-O(1)	85.8(4)	C(48)-N(10)-Ni(1)#2	127.1(10)
N(12)#3-Ni(1)-O(1)	86.6(4)	C(47)-N(10)-Ni(1)#2	128.8(12)
O(2)-Ni(1)-O(1)	57.9(4)	C(52)-N(12)-Ni(1)#3	125.3(10)
O(5)-Ni(2)-N(7)	107.8(4)	C(51)-N(12)-Ni(1)#3	131.3(11)
O(5)-Ni(2)-N(6)#3	87.3(4)	C(1)-O(1)-Ni(1)	84.4(9)
N(7)-Ni(2)-N(6)#3	94.0(5)	C(1)-O(2)-Ni(1)	96.7(9)
O(5)-Ni(2)-N(4)#2	90.7(4)	C(8)-O(3)-Ni(2)	91.8(8)
N(7)-Ni(2)-N(4)#2	97.8(4)	C(8)-O(4)-Ni(2)	88.0(9)
N(6)#3-Ni(2)-N(4)#2	168.1(4)	C(9)-O(5)-Ni(2)	130.5(10)
O(5)-Ni(2)-O(3)	160.2(4)	C(16)-O(7)-Ni(1)#4	129.9(9)
N(7)-Ni(2)-O(3)	91.9(4)	O(1)-C(1)-O(2)	120.9(14)

N(6)#3-Ni(2)-O(3)	89.2(4)	O(4)-C(8)-O(3)	121.5(13)
N(4)#2-Ni(2)-O(3)	88.8(4)	O(6)-C(9)-O(5)	126.1(14)
O(5)-Ni(2)-O(4)	101.7(4)	O(7)-C(16)-O(8)	125.4(12)
Symmetry transformation: #1 x,y,z-1; #2 -x+1,-y+1,-z+1; #3 -x,-y,-z+1; #4 x,y,z+1.			

CC1			
N(7)-O(3)	1.091(9)	N(7)-O(3)	1.091(9)
N(7)-O(2)	1.159(9)	N(7)-O(2)	1.159(9)
N(8)-O(4)	1.228(7)	N(8)-O(4)	1.228(7)
N(8)-O(5)	1.238(7)	N(8)-O(5)	1.238(7)
N(9)-O(6)	1.221(7)	N(9)-O(6)	1.221(7)
N(9)-O(7)	1.222(7)	N(9)-O(7)	1.222(7)
O(1)-C(19)	1.235(8)	O(1)-C(19)	1.235(8)
O(1)-H(1)	0.82	O(1)-H(1)	0.82
C(2)-H(2)	0.93	C(2)-H(2)	0.93
O(3)-N(7)-O(2)	115.0(7)	O(3)-N(7)-O(2)	115.0(7)
O(3)-N(7)-C(20)	121.7(7)	O(3)-N(7)-C(20)	121.7(7)
O(2)-N(7)-C(20)	121.7(7)	O(2)-N(7)-C(20)	121.7(7)
O(4)-N(8)-O(5)	123.9(6)	O(4)-N(8)-O(5)	123.9(6)
O(4)-N(8)-C(22)	118.8(6)	O(4)-N(8)-C(22)	118.8(6)
O(5)-N(8)-C(22)	117.4(5)	O(5)-N(8)-C(22)	117.4(5)
O(6)-N(9)-O(7)	122.1(5)	O(6)-N(9)-O(7)	122.1(5)
O(6)-N(9)-C(24)	119.1(5)	O(6)-N(9)-C(24)	119.1(5)
O(7)-N(9)-C(24)	118.8(6)	O(7)-N(9)-C(24)	118.8(6)
C(19)-O(1)-H(1)	109.5	C(19)-O(1)-H(1)	109.5

Table S5. Details of Hydrogen Bonding Interactions Observed in **1**, **2** and **CC1**.

1			
D-H···A	**d(H···A) (Å)**	**d(D···A) (Å)**	**∠ D-H···A (°)**
C(18)-H(18)···O(4)[1]	2.47(3)	3.292(4)	154(3)
C(20)-H(20)···O(3)[2]	2.33(3)	2.941(4)	122(3)
O(8)-H(8C)···O(4)[2]	2.54(4))	3.429(5)	146(3)
Symmetry code: 1. -1/2+x,-1/2-y,-1/2+z; 2. 1-x,-y,1-z			
2			
D-H···A	**d(H···A) (Å)**	**d(D···A) (Å)**	**∠ D-H···A (°)**
C(17)-H(17)···O(8)[1]	2.39	3.089(5)	132
C(22)-H(22)···Br(2)[2]	2.87	3.772(4)	164
C(27)-H(27B)···O(4)[3]	2.43	3.289(6)	148
C(29)-H(29)···O(6)[4]	2.50	3.241(7)	136
C(37)-H(37)···O(6)[3]	2.13	2.916(8)	140

C(46)-H(46)···O(6)[3]	2.30	3.201(6)	165
C(52)-H(52)···O(8)[5]	2.47	3.251(5)	142
Symmetry code: 1. x,y,-1+z; 2. -x,1-y,1-z; 3. x, y, z; 4. 1-x,1-y,1-z; 5. -x,-y,2-z.			
CC1			
D-H···A	**d(H···A) (Å)**	**d(D···A) (Å)**	**∠ D-H···A (°)**
C(7)-H(7A)···O(1)[1]	2.50	3.325(8)	143
C(8)-H(8)···O(1)[1]	2.25	3.061(7)	145
C(8)-H(8)···O(2)[1]	2.42	3.175(9)	138
C(2)-H(2)···O(5)[2]	2.54	3.445(7)	165
C(4)-H(4A)···O(3)[3]	2.57	3.429(6)	153
C(9)-H(9)···N(6)[4]	2.59	3.385(8)	145
C(12)-H(12)···O(4)[2]	2.51	3.318(7)	146
C(15)-H(15A)···O(7)[5]	2.52	3.450(8)	162
C(18)-H(18)···O(6)[5]	2.53	3.454(9)	172
Symmetry code: 1. x, y, z; 2. 1/2-x,-1+y,-1/2+z; 3. -1/2+x,1-y,z; 4. 1/2-x,y,-1/2+z; 5. x,1+y,z.			