Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information for

Colorimetric Selective Cu^{2+} Detection by Lanthanide based Hybrid Complexes Associated with a Single Crystal Growth Mediated Transformation

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Table S1: Selected bond lengths [Å] of the compounds **1** and **2** with estimated standard deviations in parentheses.

1: $H_2[Dy_2(PABA)_4(bpy)_2(NO_3)_2].(bpy)_2(EtOH)_2(NO_3)_2$			
Bond Label	**Distances (Å)**	**Bond Label**	**Distances (Å)**
O1-Dy1	2.386(7)	N4-Dy1	2.543(8)
O2-Dy1	2.709(7)	O2-Dy1 A	2.320(7)
O3-Dy1	2.335(7)	O4-Dy1 A	2.302(7)
O5-Dy1	2.462(8)	Dy1-O2 A	2.320(7)
O6-Dy1	2.522(7)	Dy1-O4 A	2.302(7)
N7-Dy1	2.925(10)	Dy1-Dy1 A	3.9241(9)
N3-Dy1	2.594(8)		
2: $H_2[Nd_2(3\text{-nba})_2(DMF)_2(CH_3CO_2)_4(H_2O)_2].(CH_3CO_2)_2$			
O1-Nd1	2.422(4)	O8-Nd1A	2.427(3)
O2-Nd1A	2.433(4)	O8-Nd1	2.653(4)
O1W-Nd1	2.455(4)	O11-Nd1	2.466(4)
O3-Nd1	2.566(4)	Nd1-O8A	2.427(4)
O4-Nd1	2.511(4)	Nd1-O2A	2.433(4)
O7-Nd1	2.520(4)	Nd1-Nd1A	4.0767(8)

Table S2. Important stretching frequency peaks oberved in the IR spectrum of compound **1**

Compound	ν(OH) + ν(N-H)	ν(C-H)	ν^1	$\nu(N\text{-}H)_{def}$	ν (C=C)	ν(N=O)
1	3469 3364	3072	1677	1602	1602 1513	1470_{asym} 1308_{sym}

	3209				1524	$1036_{bidentate}$

Table S3. The bands observed in the solid state UV spectra of the compounds **1** and **2.**

Compound	**UV bands (nm)**	**Assignments**
1	290-305	π - π* of ligand
	370	n- π* of ligand
	760	$^6H_{15/2} \rightarrow {}^6F_{3/2}$
	810	$^6H_{15/2} \rightarrow {}^6F_{5/2}$
	912	$^6H_{15/2} \rightarrow {}^6F_{7/2}$
2	250-300	π - π* of ligand
	348	n- π* of ligand
	470	$^4I_{9/2} \rightarrow {}^4G_{11/2,}\ {}^2G_{9/2,}\ {}^2K_{15/2}$
	520	$^4I_{9/2} \rightarrow {}^4G_{7/2,}\ {}^3K_{13/2}$
	583	$^4I_{9/2} \rightarrow {}^4G_{5/2}$
	683	$^4I_{9/2} \rightarrow {}^4F_{9/2}$
	745	$^4I_{9/2} \rightarrow {}^4F_{7/2,}\ {}^4S_{3/2}$
	801	$^4I_{9/2} \rightarrow {}^4F_{5/2,}\ {}^2H_{9/2}$
	870	$^4I_{9/2} \rightarrow {}^4F_{5/2}$

Table S4: Assignment of PL bands in the solid/ solution state photoluminiscence spectra of **1** and **2.**

Compound	**PL bands (nm)**		**Assignments**
	Solid	EtOH solution	
1	350-450 (centred at 394)	300-400 (centred at 350)	L→M charge transfer band, Ligand radiative relaxation
	479	479	$^4F_{9/2} \rightarrow {}^6H_{15/2}$
	572	571	$^4F_{9/2} \rightarrow {}^6H_{13/2}$
	750	703	$^4F_{9/2} \rightarrow {}^6H_{9/2}$ / $^4I_{15/2} \rightarrow {}^6H_{9/2}$
2	350-450		L→M charge transfer band, Ligand radiative relaxation

Table S5: ICP-OES analysis of metal exchange studies of **1** and **2.**

No	Sample	Salt	Conc	Analyte	Cation 1 (ppm)	Cation 2 (ppm)	Cation 3 (ppm)
A	**1-Dy**	$Cu(NO_3)_2$	0.5 M	Supernatant	Cu - Saturated	Dy- 54	None
B				Crystals	Cu - 19	Dy- 4	None
C		$CuSO_4$	0.5 M	Crystals	Cu - 57	Dy-6	None
D				Supernatant	Cu - Saturated	Dy-69	None
E		$AgNO_3$	0.5 M	Crystals	Dy - 1	Ag-6	None
F				Supernatant	Dy - 30	Ag-3000	None
G		$CuCl_2$	0.5 M	Crystals	Cu - 47	Dy-0.6	None
H				Supernatant	Cu - Saturated	Dy-48	None
I	**2-Nd**	$Cu(NO_3)_2$	0.5 M	Crystals	Cu - 90	Nd-8	None
J				Supernatant	Cu - Saturated	Nd-170	None
K		$CuSO_4$	0.5 M	Crystals	Cu - 49	Nd-4	None
L				Supernatant	Cu - Saturated	Nd-91	None
M		$CuCl_2$	0.5 M	Crystals	Cu - 87	Nd-5	None
N				Supernatant	Cu - Saturated	Nd-145	None
Mixed Solvent Study							
P	**2-Nd**	Cu, Ni, Co, Zn, Au, Cd	~ 0.1 M each	Crystals	Cu -18	Nd-44	None
Q				Supernatant-a	Nd -72	All other cations present	
R				Supernatant-b	Nd -54	All other cations present	
T	**1-Dy**	Cu, Ni, Co, Zn, Au, Cd	~ 0.1 M each	Crystals	Cu -4	Dy-13	Au-5
U				Supernatant-a	Dy -12	All other cations present	
V				Supernatant-b	Dy -3	All other cations present	

Table S6. Crystal data and structure refinement for **2_Cu exchanged**: $C_{28}H_{32}Cu_2N_4O_{24}$ at 100 K.

Empirical formula	$C_{28}H_{32}Cu_2N_4O_{24}$
Formula weight	935.65
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P*21/*c*
Unit cell dimensions	a = 17.3672(15) Å, α = 90° b = 7.1242(6) Å, β = 101.285(5)° c = 14.5591(13) Å, γ = 90°
Volume	1766.5(3) $Å^3$
Z	2
Density (calculated)	1.759 g/cm^3
Absorption coefficient	1.309 mm^{-1}
F(000)	956
Crystal size	0.140 x 0.050 x 0.040 mm^3
θ range for data collection	2.853 to 24.997°
Index ranges	-20<=h<=20, 0<=k<=8, 0<=l<=17
Reflections collected	3011
Independent reflections	3011
Completeness to θ = 24.997°	97.2%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3011 / 277 / 288
Goodness-of-fit	1.073
Final R indices [I > 2σ(I)]	R_{obs} = 0.0623, wR_{obs} = 0.1544
R indices [all data]	R_{all} = 0.1013, wR_{all} = 0.1795
Extinction coefficient	0.0039(11)
Largest diff. peak and hole	1.511 and -0.709 e·$Å^{-3}$

$R = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$, $wR = \{\Sigma[w(|F_o|^2 - |F_c|^2)^2] / \Sigma[w(|F_o|^4)]\}^{1/2}$ and
$w=1/[\sigma^2(Fo^2)+(0.0729P)^2+15.6912P]$ where $P=(Fo^2+2Fc^2)/3$

Table S7: Study of the detection limit of Cu2+ ($CuCl_2$) detection by **2**

Sample	Salt	Concentration	Ananlyte	Cu (ppm)	Nd (ppm)
2 (Nd crystal)	CuCl2	10-1 M	Crystal	Saturated	150
			Solution	Saturated	Saturated
		10-2 M	Crystal	40	Saturated
			Solution	Saturated	250
		10-3 M	Crystal	5	Saturated
			Solution	106	200
		10-4 M	Crystal	3	Saturated
			Solution	10	140
		10-5 M	Crystal	1.9	Saturated
			Solution	2	150

Figures

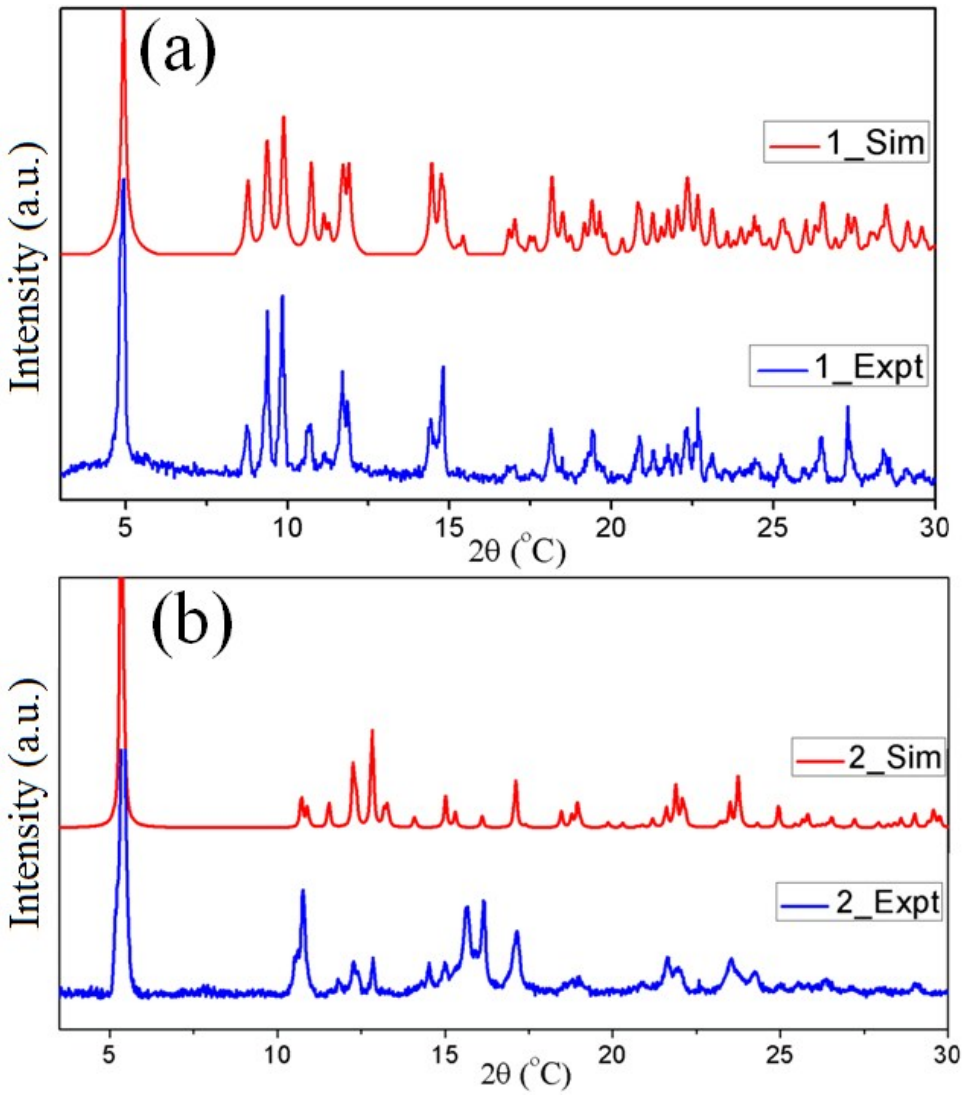


Figure S1. Comparison of experimental and simulated PXRD patterns of the bulk samples of (a) **1** and (b) **2**

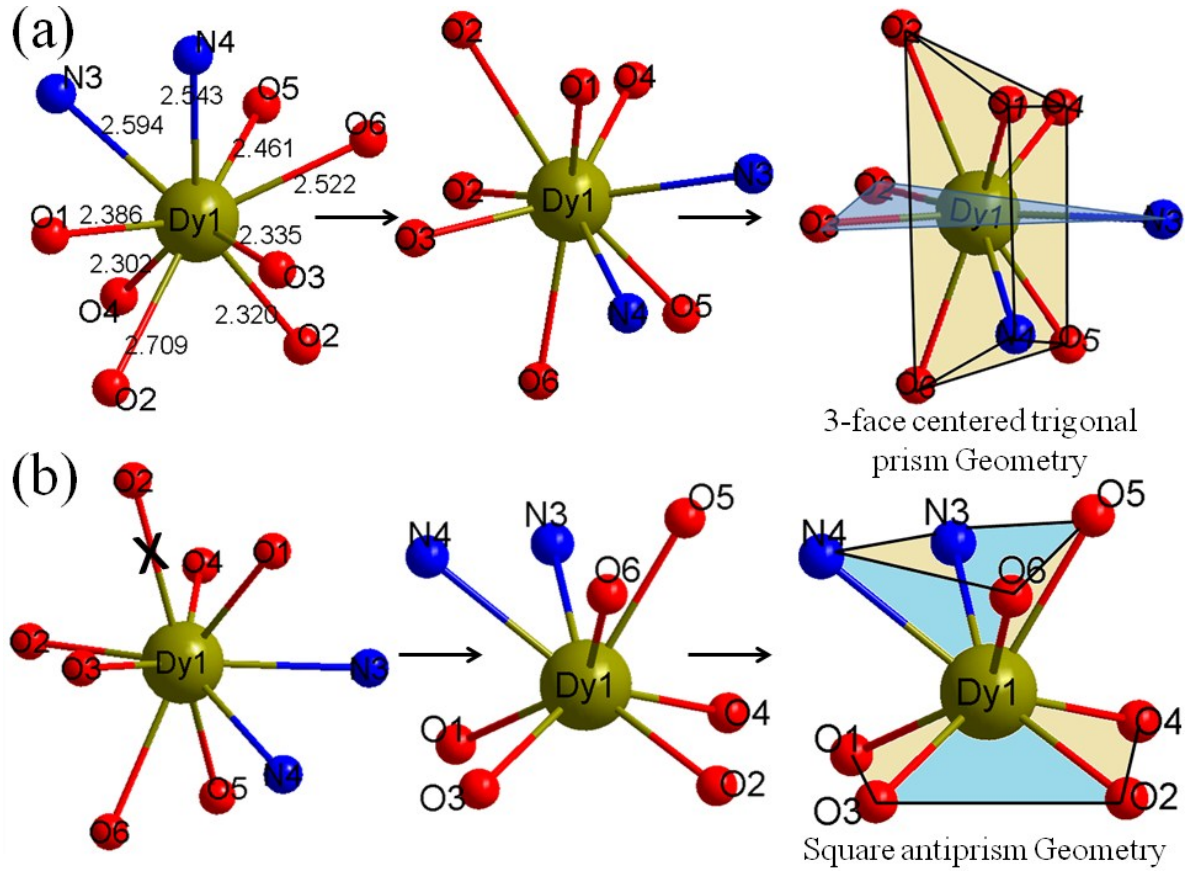


Figure S2. Coordination geometry of Dy in the compound **1.** (a) 3-face centred Trigonal prism geometry when 9 coordinating oxygens are considered and (b) Square antiprism geometry of **1** considering 8 coordinating oxygens (removing O2: bond distance 2.71 Å)

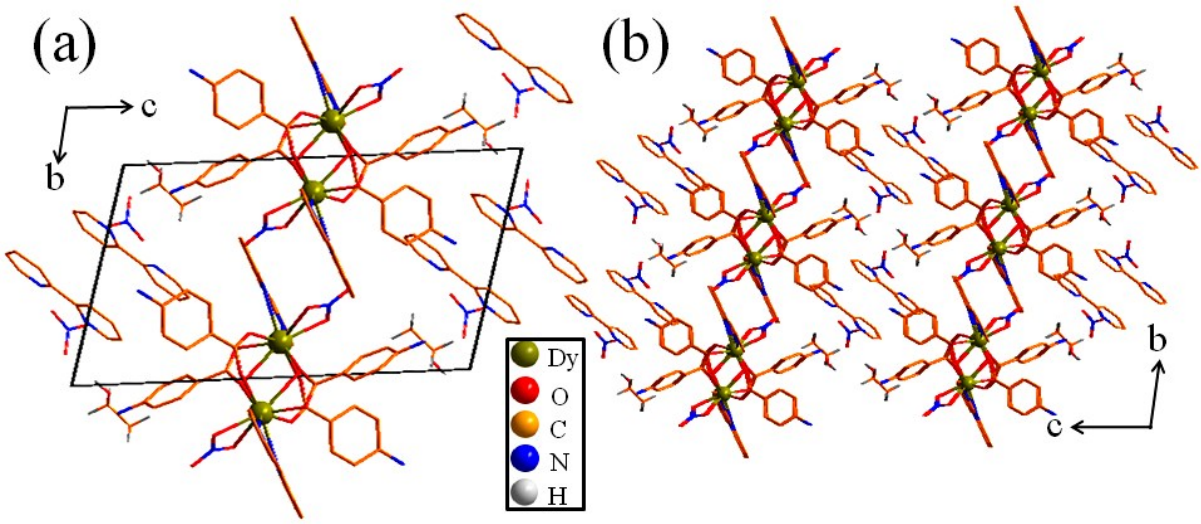


Figure S3. (a) Unit cell and (b) super cell of **1.**

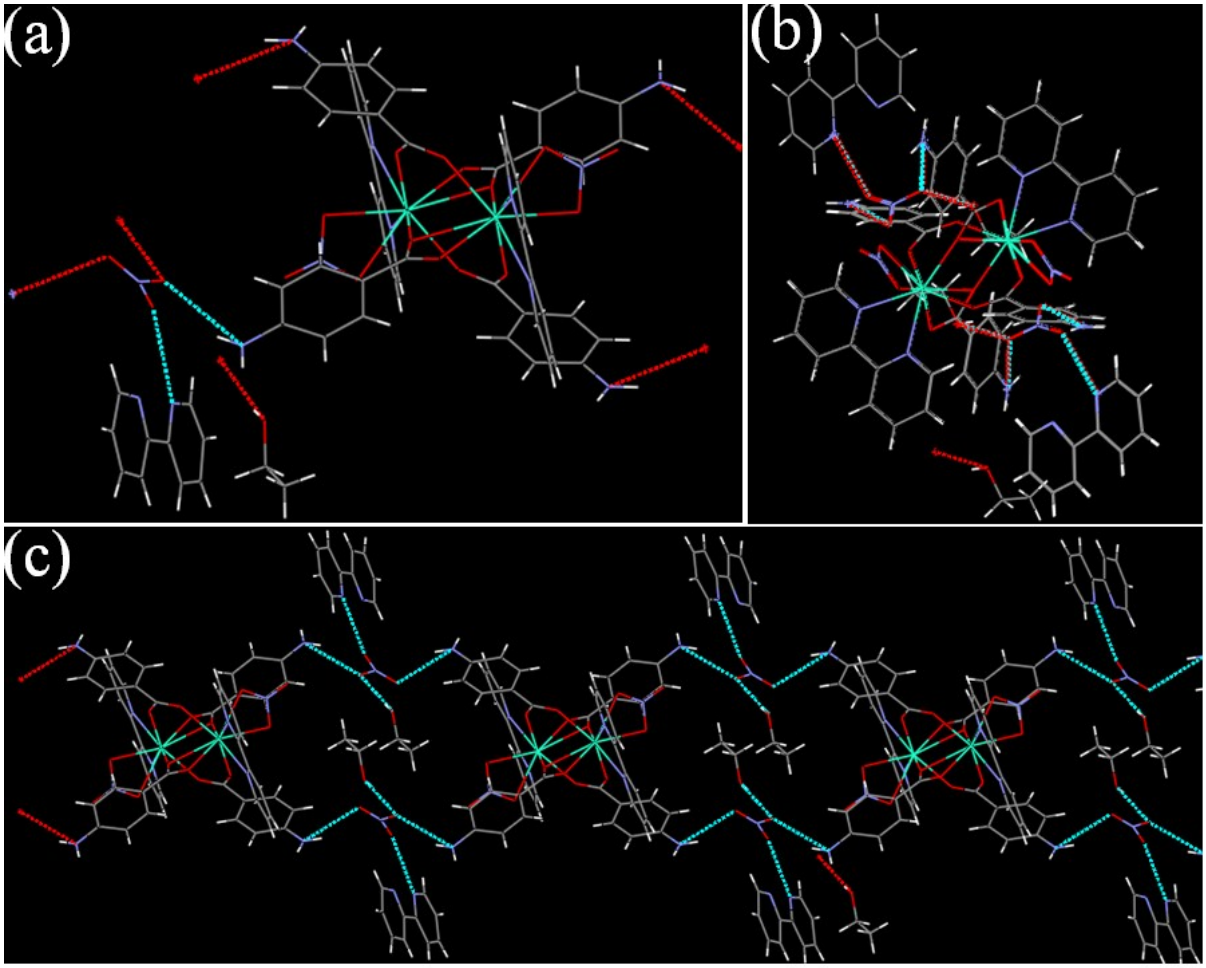


Figure S4. Hydrogen bonding in compound **1.**(a) and (b) H-bonding/ C-H O interactions shown as red dashed lines in the dinuclear unit of **1** and (c) 2D crystal growth due to H-bonding/ C-H O interactions in **1.**

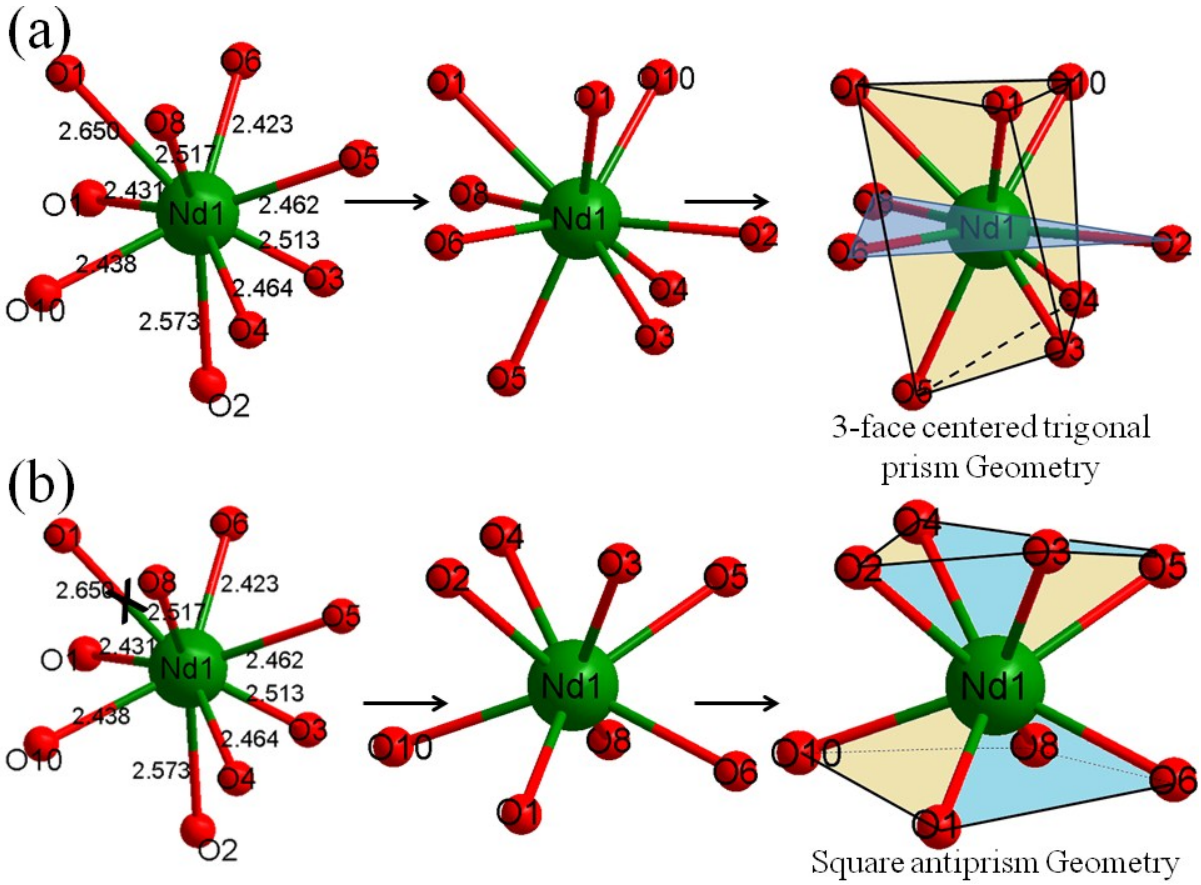


Figure S5. Coordination geometry of Nd in **2.** (a) 3-face centred Trigonal prism geometry of Nd centre when 9 coordinating oxygens are considered and (b) Square antiprism geometry of Nd centre considering 8 coordinating oxygens (removing O1: bond distance 2.66 Å)

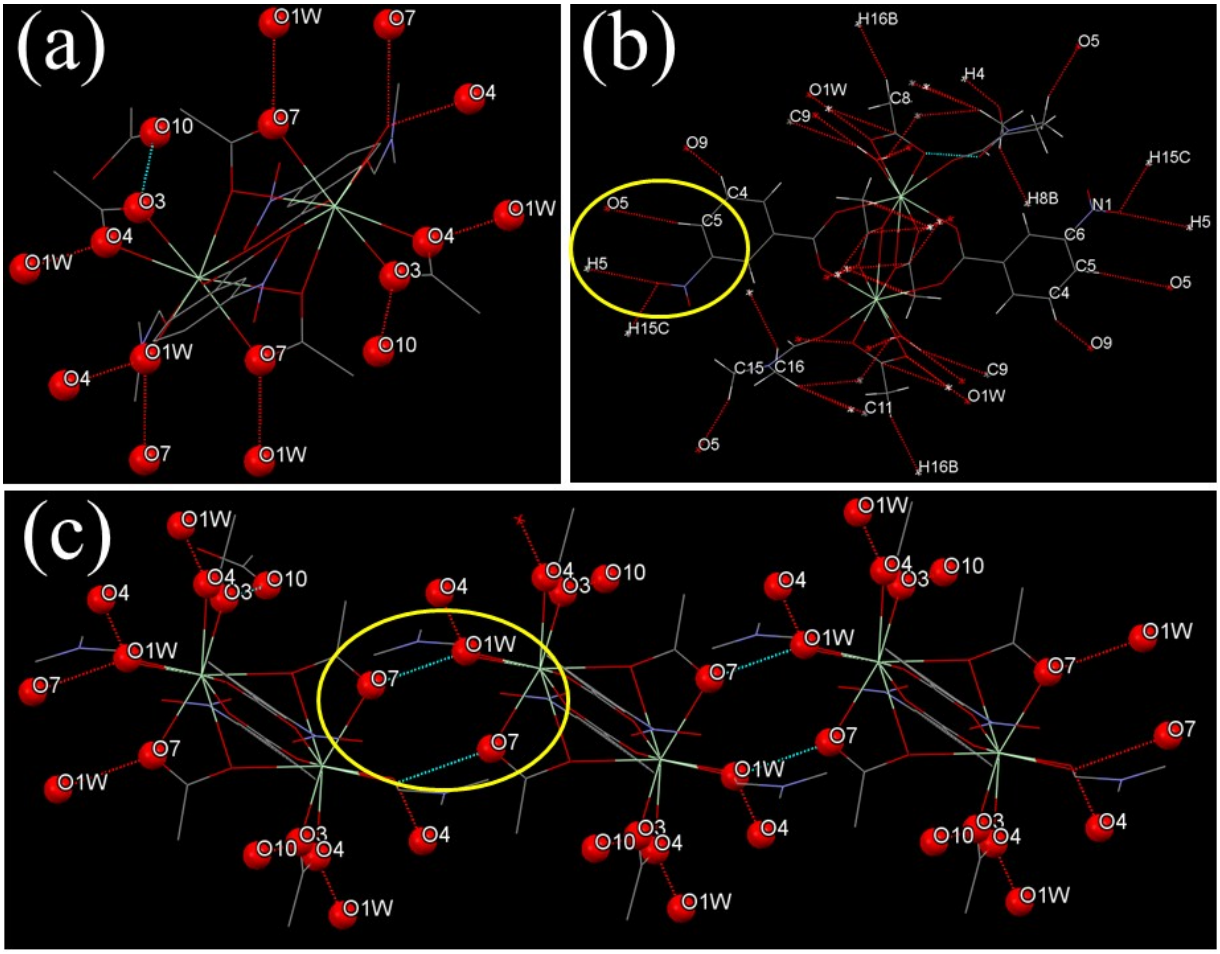


Figure S6. Hydrogen bonding and C-H O interactions in compound **2** (a) H-bonding shown as red dashed lines in dinulear unit of 2, (b) C-H O interactions in 2. (c) H-bonding shown as dashed red line (also highlighted in yellow circle) in a chain of dinuclear units of 2 .

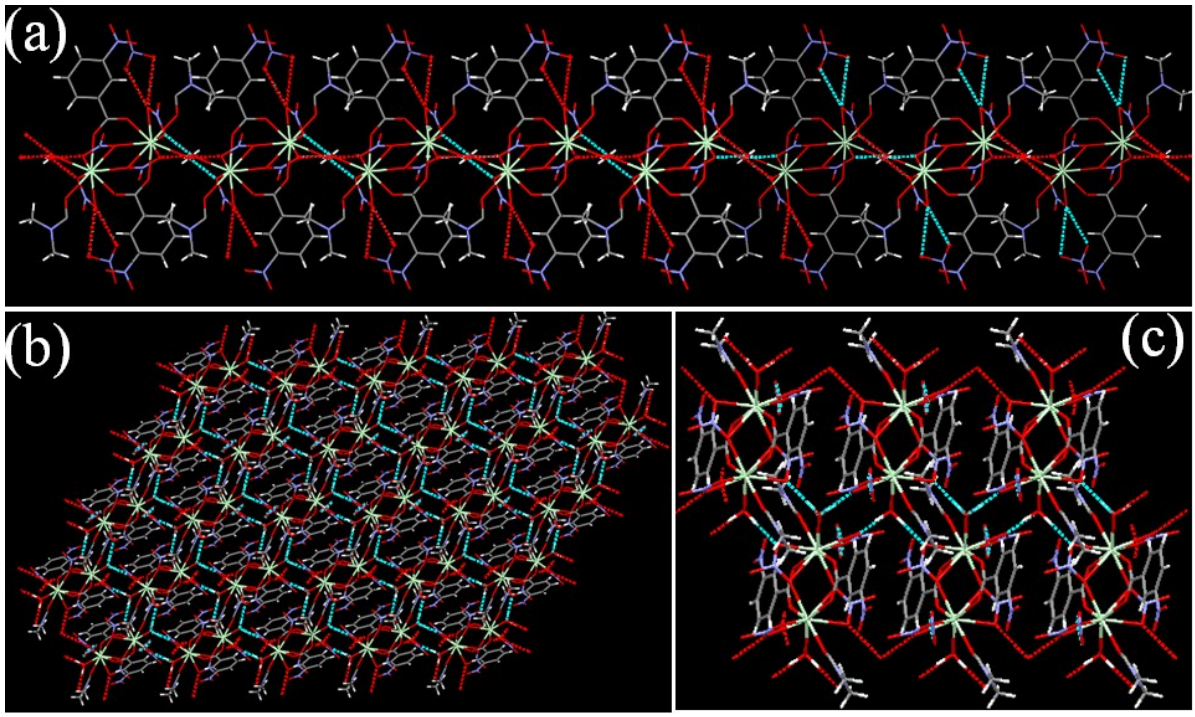


Figure S7. Hydrogen bonding and C-H-O interactions in the crystal packing of compound **2** (a), (b) and (c) showing growth of the crystal structure along various directions arising from H-bonding and C-H O interactions.

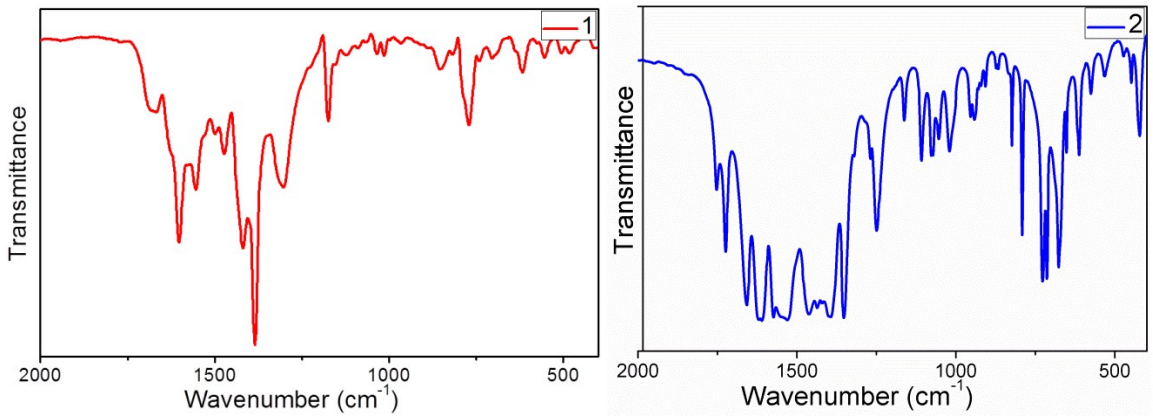


Figure S8. IR spectra of 1 (left) and 2 (right). The spectra shows all the stretching frequencies in the two compounds corresponding to the organic moieties present in the respective structures.

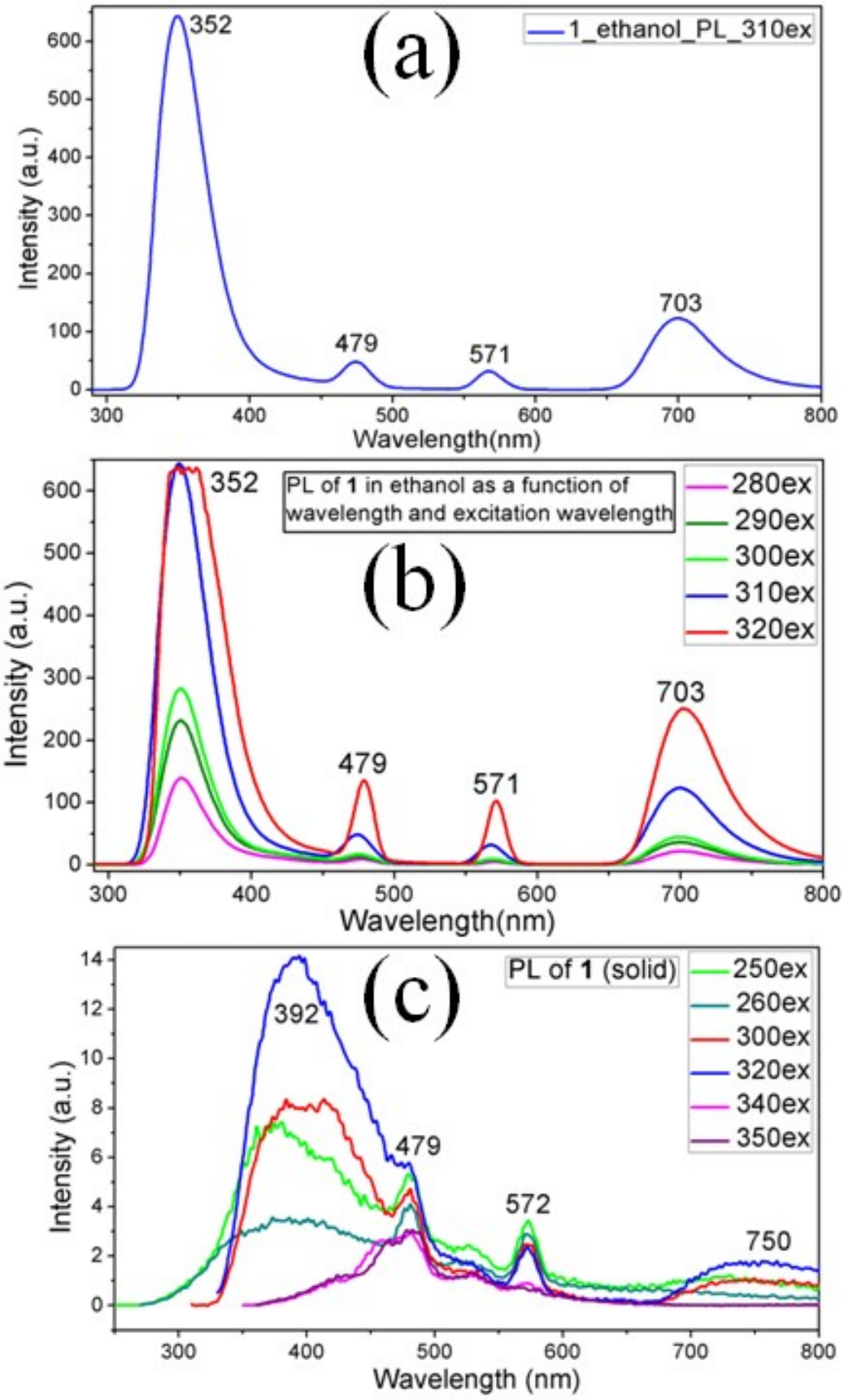


Figure S9. PL of **1.** (a) PL in ethanol, (b) PL of **1** in ethanol as a function of wavelength and (c) PL of **1** (solid).

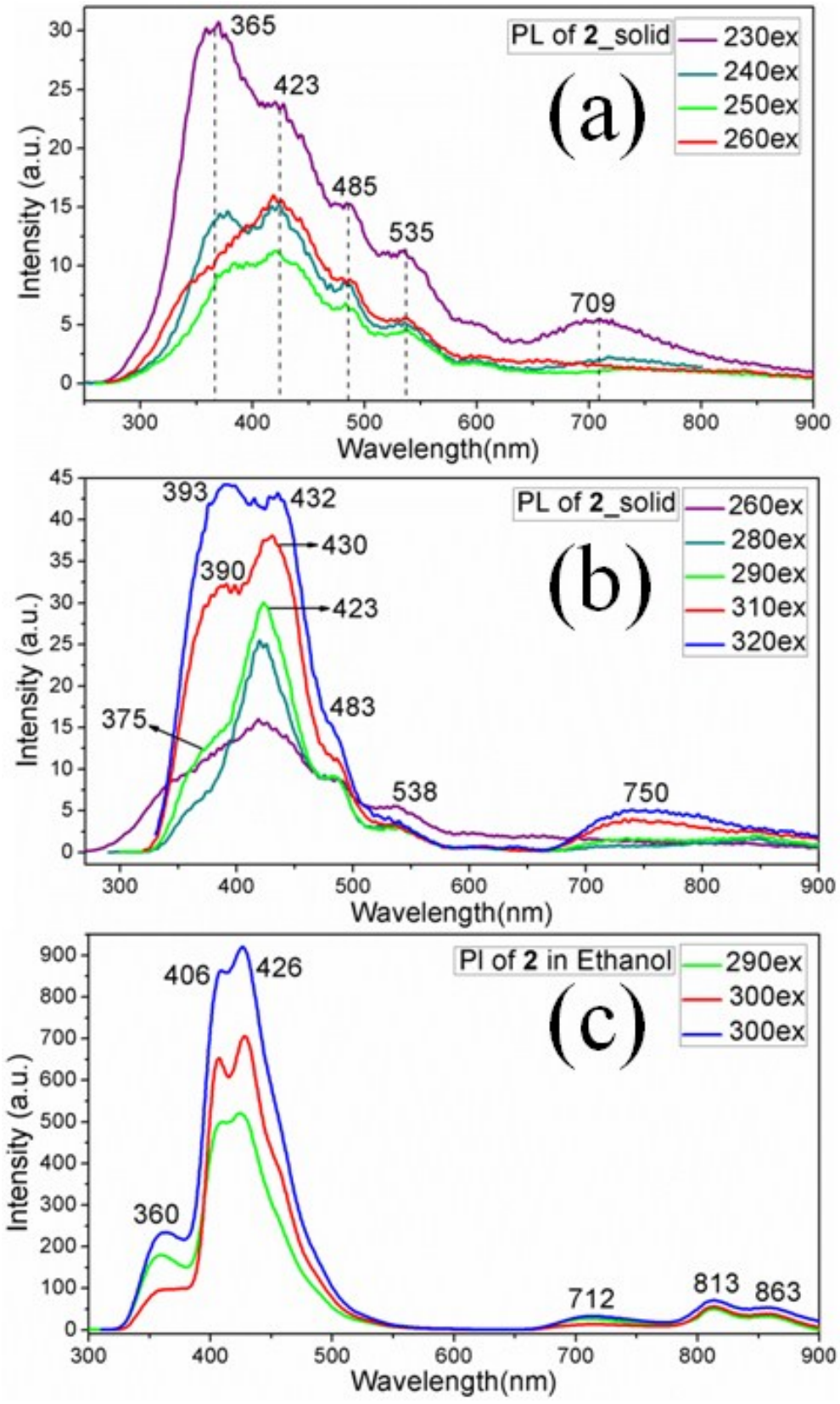


Figure S10. PL of **2.** (a) PL of 2 (solid) as a function of wavelength, (b) PL of 2 (solid) as a function of wavelength and (c) PL of **2** in ethanol as a function of wavelength.

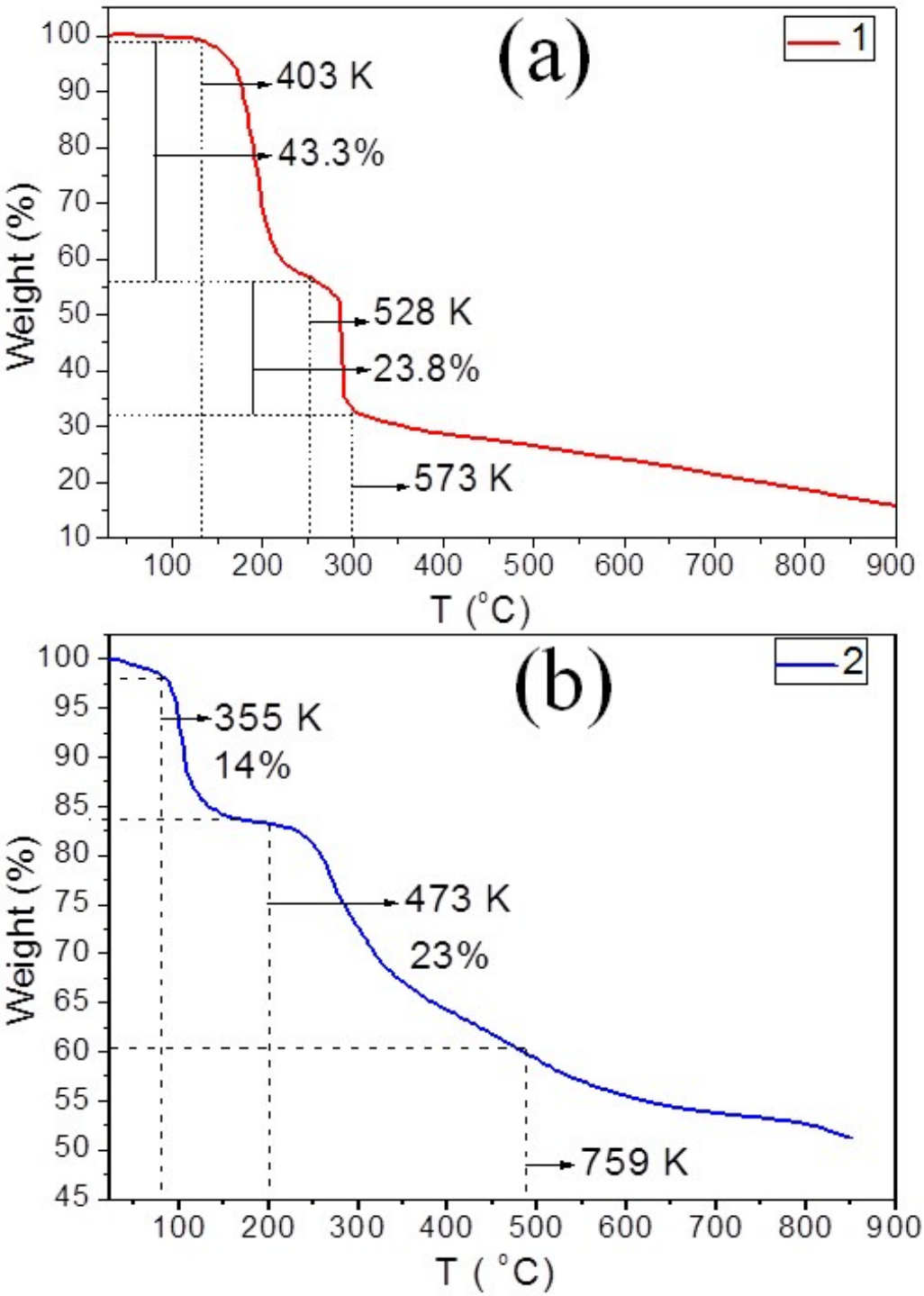


Figure S11. Thermogravimetric plot of the compounds **1** (a) and **2** (b). The weight loss percentages at various temperatures are marked.

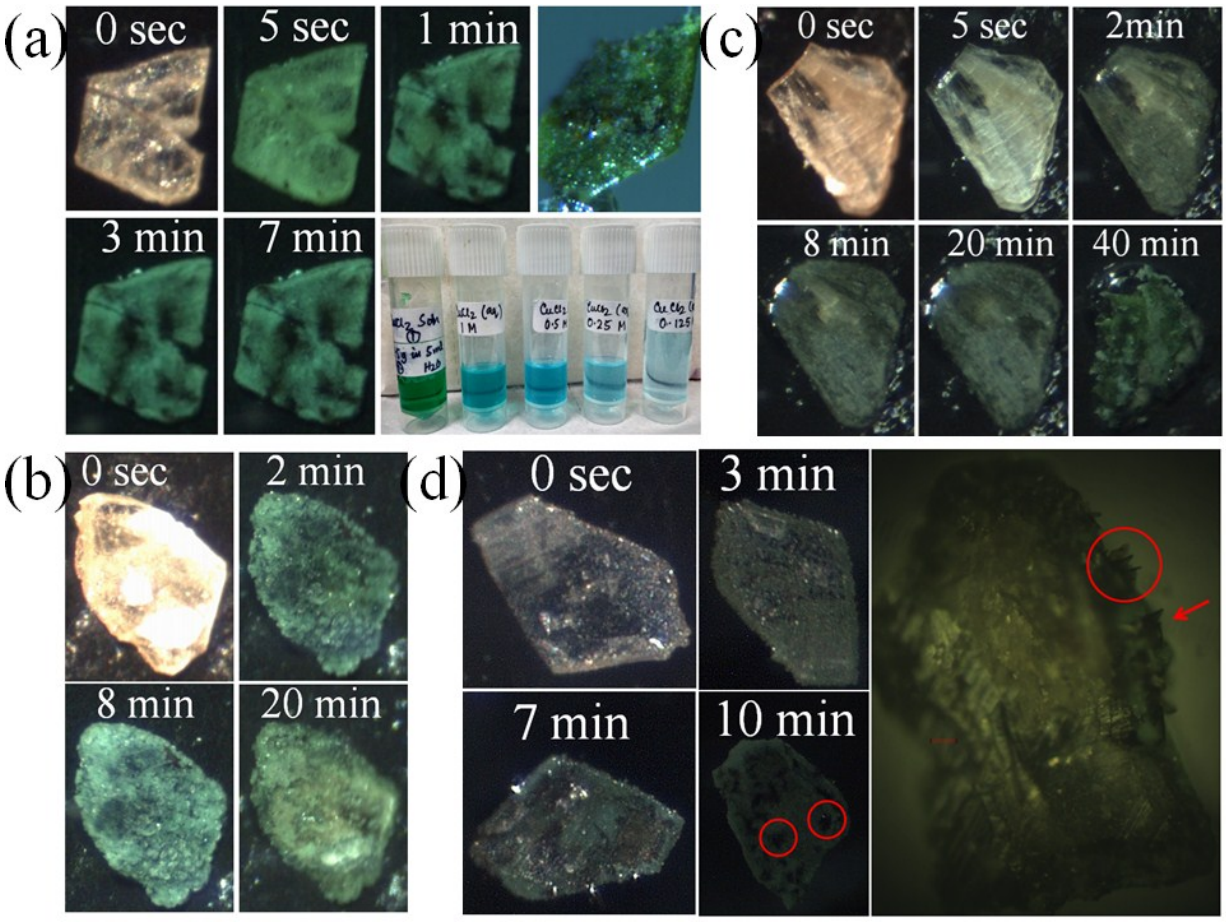


Figure S12. $Cu2^{+}$ sensing study on single crystals of Compound **1** at different concentrations of $CuCl_2$. (a) In 2 M $CuCl_2$, (b) Compound **1** in 1 M $CuCl_2$, (c) Compound **1** in 0.5 M and (d) Compound **1** in 0.25 M $CuCl_2$.

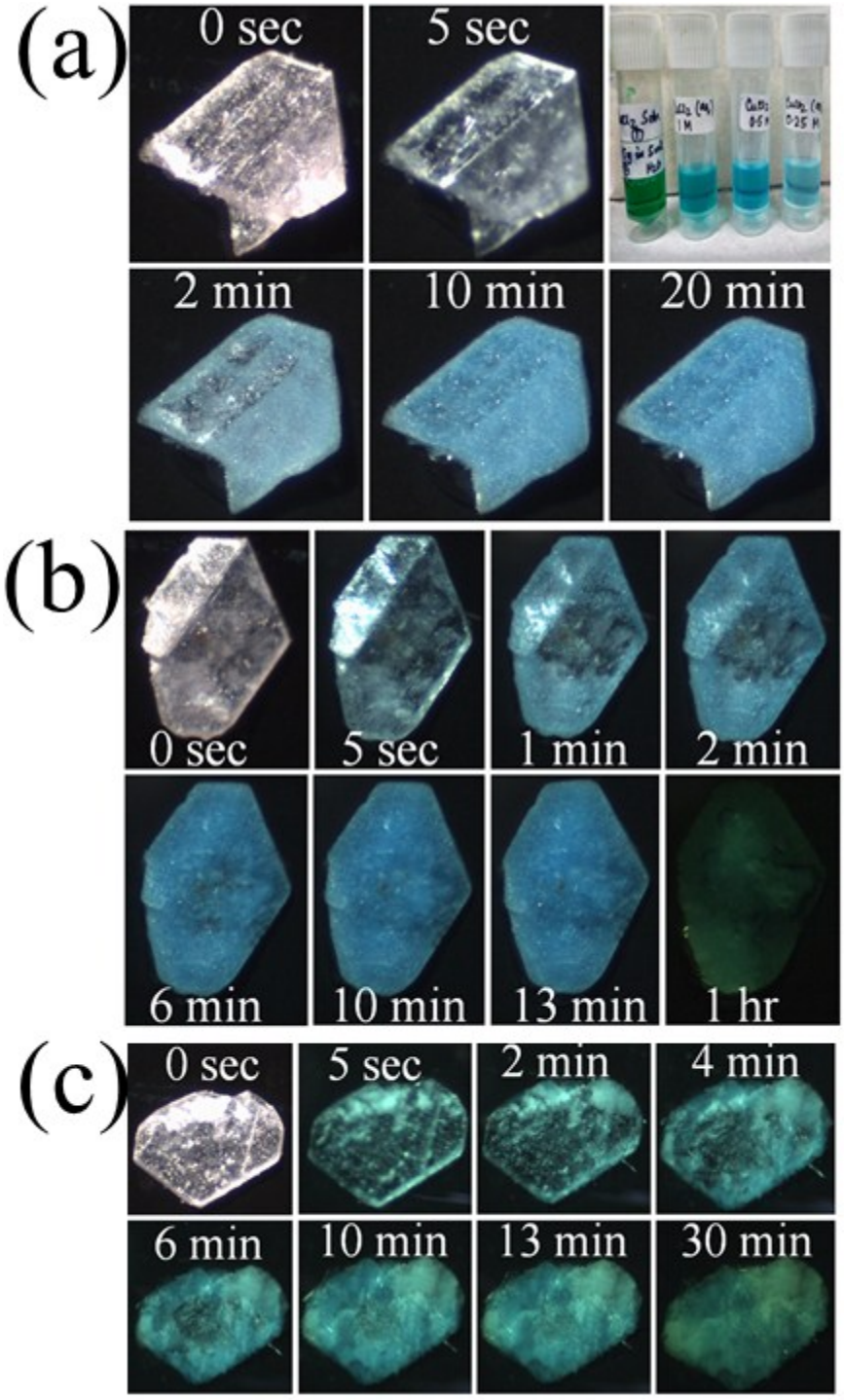
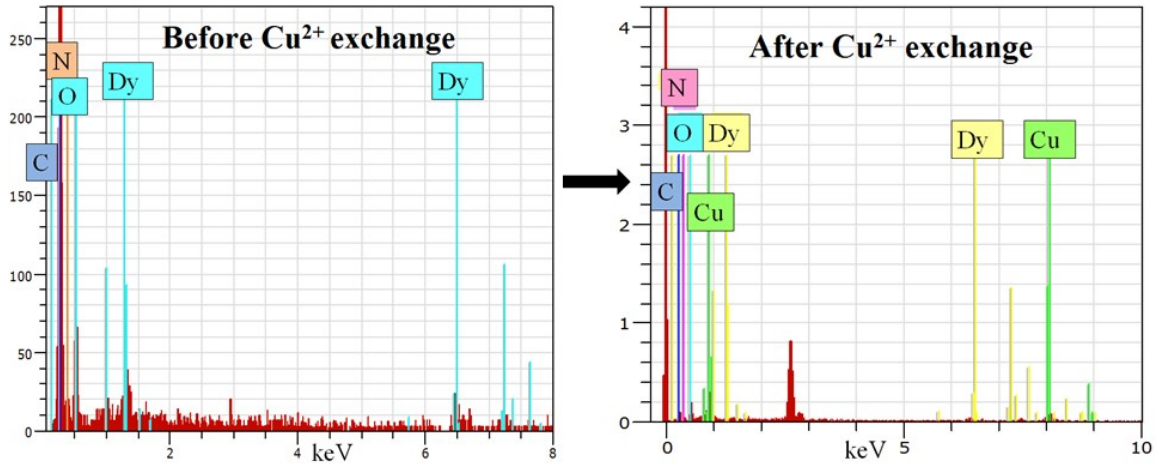


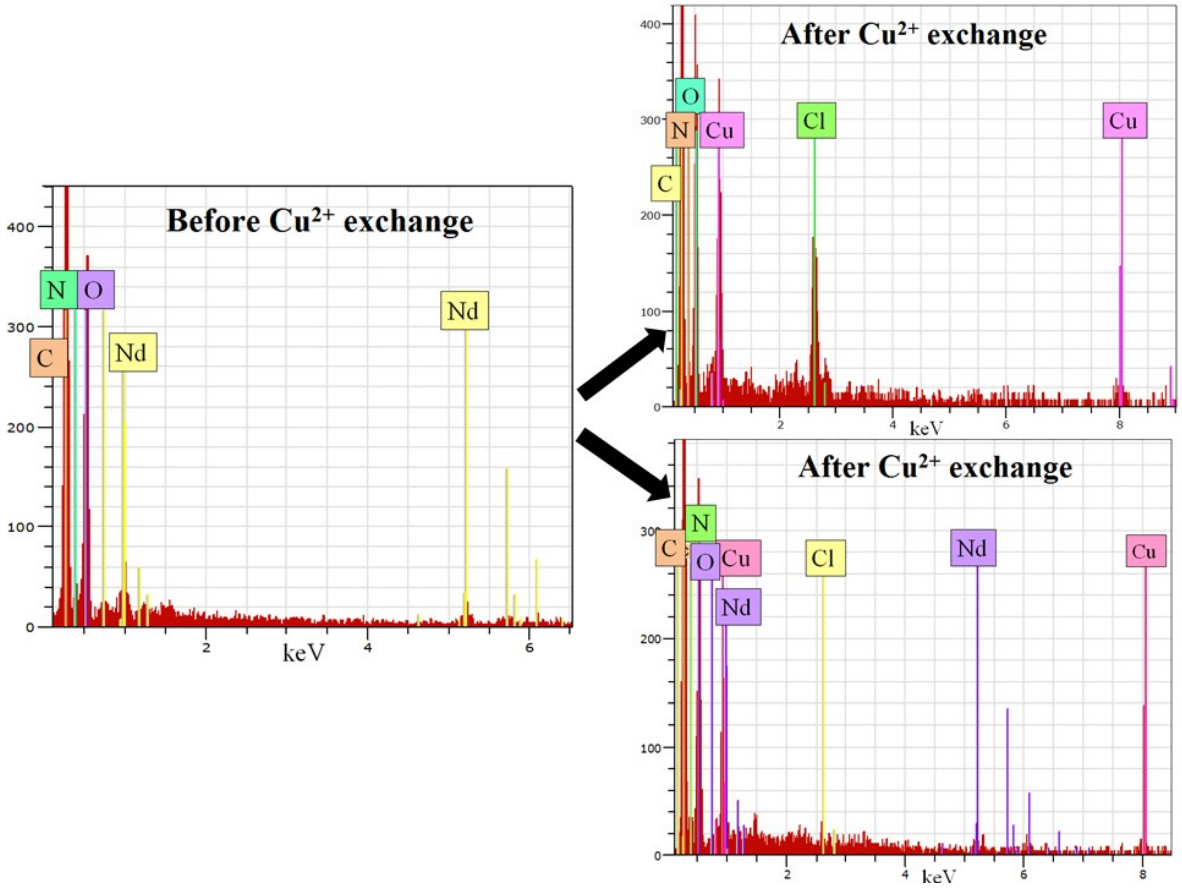
Figure S13. $Cu2^{+}$ sensing study on single crystals of Compound **2** at different concentrations of $CuCl_2$. (a) Compound **2** in 0.5 M $CuCl_2$, (b) Compound **2** in 1 M $CuCl_2$ and (c) Compound **2** in 2 M $CuCl_2$.



Elements	Before Cu2+ exchange (At %)	After Cu2+ exchange (At %)
C	65.35	52.54
Dy	2.48	0.89
O	20.82	17.67
N	11.34	7.24
Cu	0.00	21.65
Cl	0.00	0.00

Elements	Before Cu2+ exchange (At %)	After Cu2+ exchange (At %)
Dy	100.0	1.07
Cu	0.00	98.93

Figure S14. EDS of **1** before (left) and after (right) Cu^{2+} exchange along the compositions obtained shown in tables below.



Elements	Before Cu2+ exchange (At %)	After Cu2+ exchange (At %)
C	49.50	61.49
Nd	1.97	0.00
O	37.66	18.44
N	10.86	4.00
Cu	0.00	16.00
Cl	0.00	0.07

Elements	Before Cu2+ exchange (At %)	After Cu2+ exchange (At %)
Nd	100.0	0
Cu	0.00	100.0

Figure S15. EDS of **2** before (left) and after (right) Cu^{2+} exchange along the compositions obtained shown in tables below.

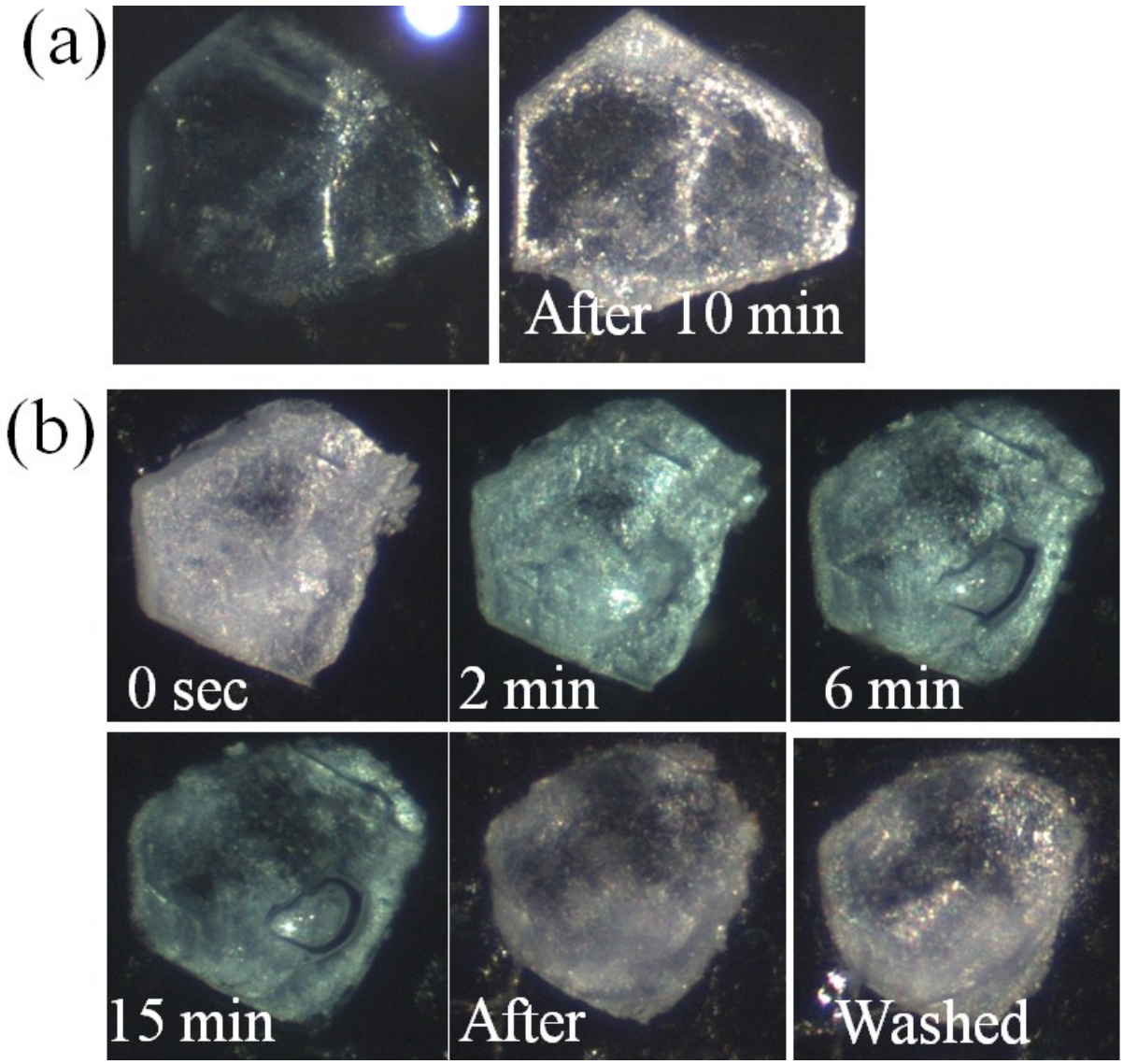


Figure S16. Ni^{2+} exchange studies on **2.** (a) Compound **2** in 0.5 M $NiCl_2$ at different intervals of time and (b) Compound **2** in 1 M $NiCl_2$ at different intervals of time.

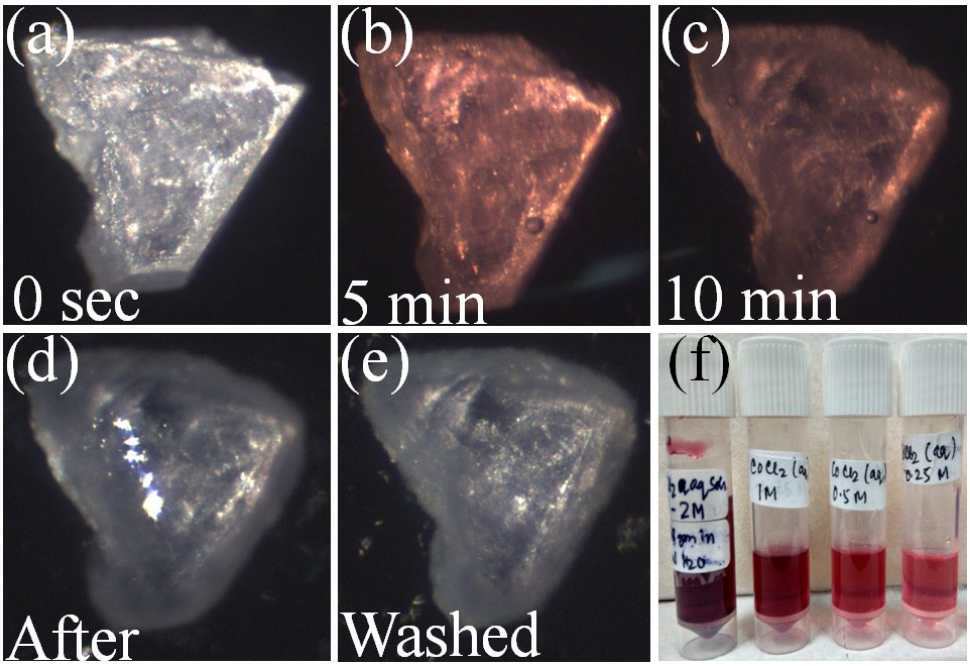


Figure S17. Compound **2** in 1 M $CoCl_2$ after various intervals of time. (a) Pristine crystal of **2**. The red colour that is seen in (b) and (c) are of the solution, as the crystals are inside the red solution of $CoCl_2$, (d) Crystal after being taken out of the solution and (e) Crystal after being thoroughly washed with water.

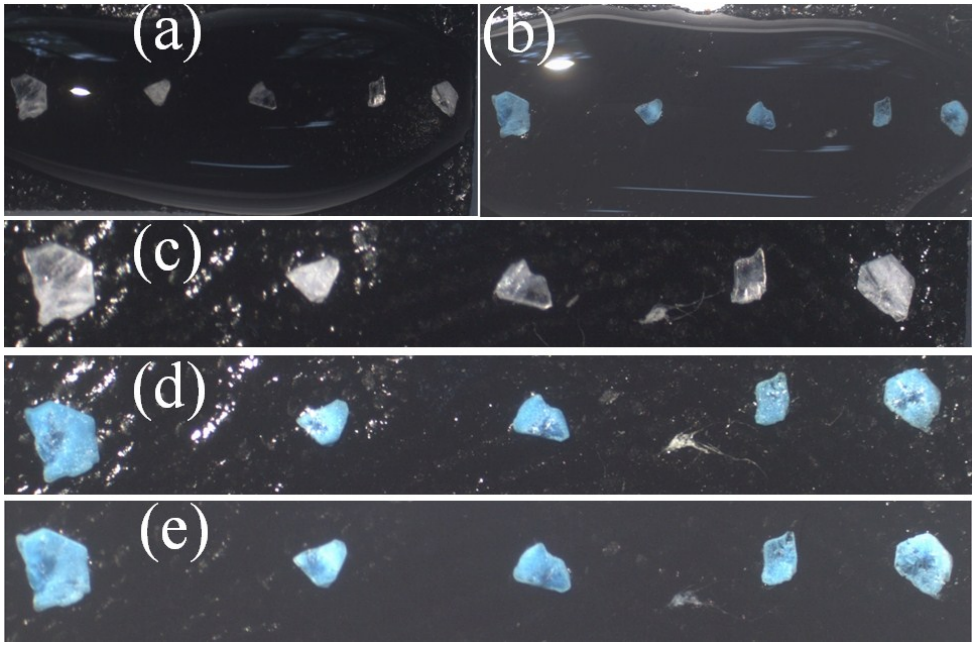


Figure S18. Compound **2** in Solution of mixed salts (0.5 m of each of $CuCl_2$, $CoCl_2$, $NiCl_2$). (a) Immediately after addition of the solution, (b) After 5 mins, (c) Pristine crystals of **2,** (d) After 10 mins, (e) After washing thoroughly with deionized water.

Reference

1. X.-W. Lei, G.-H. Zhong, L.-H. Li, C.-L. Hu, M.-J. Li and J.-G. Mao, *Inorg. Chem.*, 2009, **48**, 2526-2533.