Electronic Supplementary Material (ESI) for *CrystEngComm*

Supporting Information

Four new metal-organic frameworks constructed from H_2DBTDC-O_2 (H_2DBTDC-O_2 = Dibenzothiophene-5,5'-dioxide-3,7-dicarboxylic acid) ligand with guest-responsive photoluminescence

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Table S1. Crystal Data and structure Refinement Parameters for Complexes **1**-**4**.

	1	2	3	4
Formula	$C_{24}H_{16}Cd\ N_2O_6S$	$C_{38}H_{20}N_2O_{12}S_2Zn_2$	$C_{24}H_{20}N_4O_6SZn$	$C_{24}H_{14}CoN_2O_6S$
Mr	572.85	891.42	557.87	517.36
T (K)	180	180	180	180
Radiation, wavelength (Å)	Cu Kα, 1.54184	Cu Kα, 1.54184	Mo Kα, 0.71073	Mo Kα, 0.71073
crystal System	monoclinic	monoclinic	orthorhombic	triclinic
space group	*C*2/c	$P2_1/c$	*P*bcm	*P*-1
a [Å]	18.5317(8)	13.9610(7)	10.1489(7)	7.2086(4)
b [Å]	16.6605(6)	22.649(2)	22.0518(12)	12.3243(7)
c [Å]	22.9353(7)	19.601(3)	14.1837(9)	13.8591(9)
V [$Å^3$]	7061.4(5)	6076.2(11)	3171.2(3)	1138.89(12)
Z	8	4	4	2
ρ_{calcd} [g cm^{-3}]	1.078	0.974	1.168	1.509
F(000)	2288	1800	1144	526
θ range /°	3.57-62.63	3.02-62.93	2.64-26.02	2.76-26.02
Reflns collected	15212	43382	21639	8446
Independent reflns	5547	9633	3262	4464
Goodness-of-fit	1.011	0.979	1.011	0.996
R_1[a] (I > 2σ (I))	0.0459	0.0661	0.0523	0.0405
wR_2[b] (I > 2σ (I))	0.1147	0.1138	0.1463	0.0875

aR1 = Σ||F□| − |Fc||/Σ|F□|. bwR2 = [Σ[w(F□2 − Fc2)2]/Σw(F□2)2]1/2.

Table S2.Selected bond lengths (Å) and bond angles (°) of compounds 1-4

1

Cd1 – O1	2.420 (3)	Cd1 – O6B	2.638 (3)
Cd1 – O2	2.386 (3)	Cd1 – N1	2.301 (4)
Cd1 – O5A	2.338 (3)	Cd1 – N2	2.278 (5)
Cd1 – O6A	2.637 (3)		
O5A Cd1 O6A	51.891 (17)	N2 Cd1 O2	92.849 (16)
O5A Cd1 O2	85.325 (12)	N1 Cd1 O5A	94.078 (14)
O6B Cd1 O1	92.420 (12)	N2 Cd1 O5A	88.622 (17)
O6B Cd1 O6A	75.851 (12)	N1 Cd1 O6B	88.639 (15)
O2 Cd1 O1	54.775 (12)	N1 Cd1 O6A	88.193 (12)
N1 Cd1 O1	87.539 (13)	N2 Cd1 O6B	87.876 (18)
N2 Cd1 O1	91.881 (15)	N2 Cd1 O6A	91.659 (15)
N1 Cd1 O2	89.687 (14)		

2

Zn1 – O8	2.258 (5)	Zn2 – O12A	2.054 (9)
Zn1 – O2	2.044 (1)	Zn2 – O7	1.991 (4)
Zn1 – O6A	2.022 (1)	Zn2 – O1	2.030 (4)
Zn1 – O11A	2.005 (7)	Zn2 – O5A	1.998 (1)
Zn1 – N2	2.047 (4)	Zn2 – N1	2.026 (2)
N1 Zn2 O1	105.903 (22)	O1 Zn2 O7	88.986 (19)
N1 Zn2 O5A	98.881 (24)	O1 Zn2 O5A	88.707 (21)
N1 Zn2 O7	100.154 (22)	O12A Zn2 O7	85.549 (19)
N1 Zn2 O12A	97.149 (24)	O12A Zn2 O5A	88.082 (21)
N2 Zn1 O2	93.696 (22)	O2 Zn1 O8	88.020 (21)
N2 Zn1 O6A	102.528 (21)	O2 Zn1 O6A	86.435 (21)
N2 Zn1 O11A	103.884 (22)	O11 Zn1 O6A	89.788 (21)
N2 Zn1 O8	98.997 (21)	O11A Zn1 O8	89.129 (21)

3

Zn1 – O1	1.937 (1)	Zn1 – N1	1.967 (2)
Zn1 – O3B	1.941 (1)	Zn1 – N1B	1.957 (2)
O1 Zn1 O3B	93.355 (90)	O3B Zn1 N1	110.582 (59)
O1 Zn1 N1D	113.402 (59)	O3B Zn1 N1D	110.582 (59)
O1 Zn1 N1	113.402 (59)	N1 Zn1 N1D	113.741 (87)

4

O2 – Co1	2.038 (4)	N1 – Co1	2.108 (2)
O1 – Co1	2.108 (2)	O4A – Co1	2.202 (8)
N2 – Co1	2.104 (2)	O3A – Co1	2.193 (5)
O1A Co1 O3A	90.424 (80)	N1 Co1 O3A	98.916 (83)
O1A Co1 O4A	97.362 (81)	N1 Co1 O2	84.326 (86)
O1A Co1 N2	93.646 (87)	O3A Co1 O4A	59.478 (75)
O1A Co1 O2	94.449 (83)	O4A Co1 N2	88.408 (87)
N1 Co1 N2	77.295 (92)	O2 Co1 O3A	110.614 (79)
N1 Co1 O4A	85. 645 (84)	O2 Co1 N2	100.815 (95)

Symmetry transformations used to generate equivalent atoms: for **1**: A) 1/2+x, 1/2–y, 1/2+z; B) 1/2–x, 1/2+y, 1/2–z; for **2**: A) x,1/2–y, 1/2+z; for **3**: A) –x, –y, 1/2+z; B) –x, 1/2+y, 1/2–z; C) –x, –y, –z; D) x, y, 1/2–z; E) –x, 1/2+y, z; for **4**: A) –x, –y, –z.

Supplementary description of the structure for compound 1 and 4.

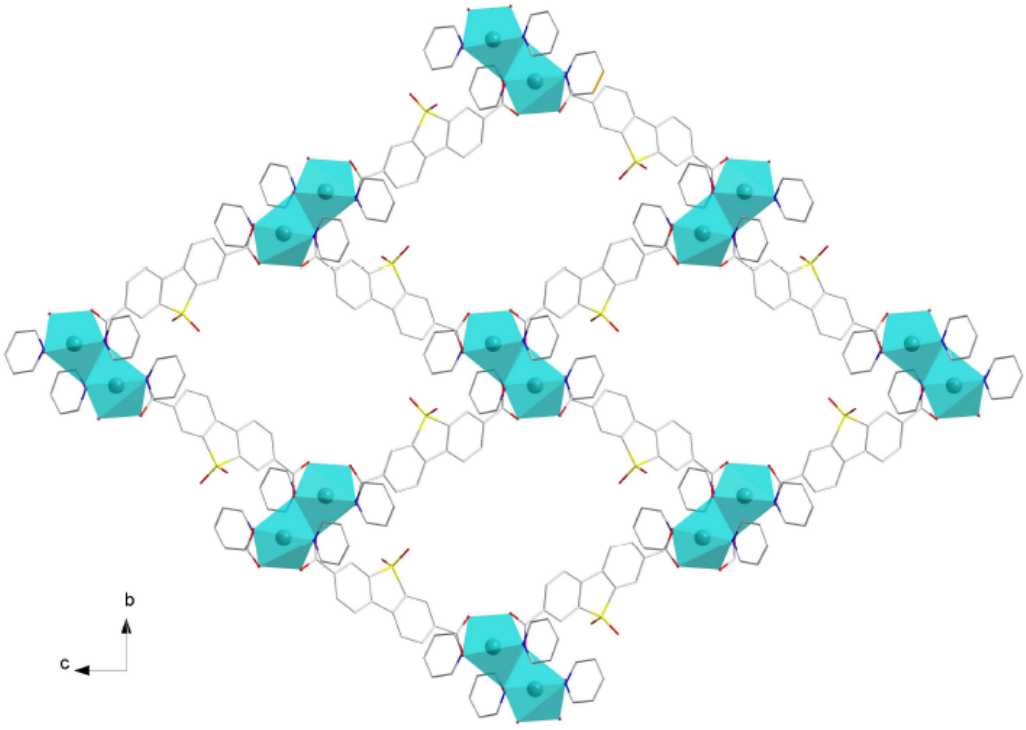

Figure S1. The four-connected dinuclear SBUs in compound **1** interlink each other to afford 2D single layer, which exhibits large rhombic grids viewed along the c-axis.

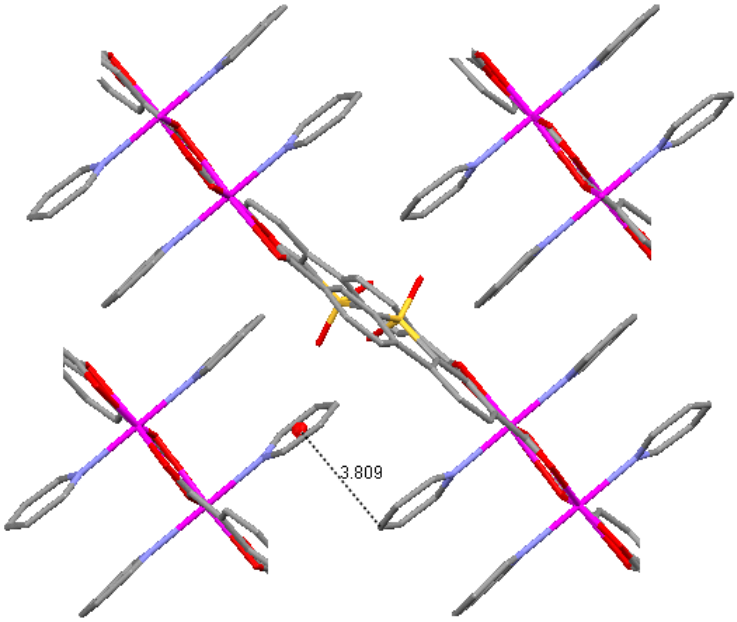

Figure S2. The 2D sheets of compound **1** accumulate in ABAB type and exhibit π–π stacking interaction between the pyridine moieties.

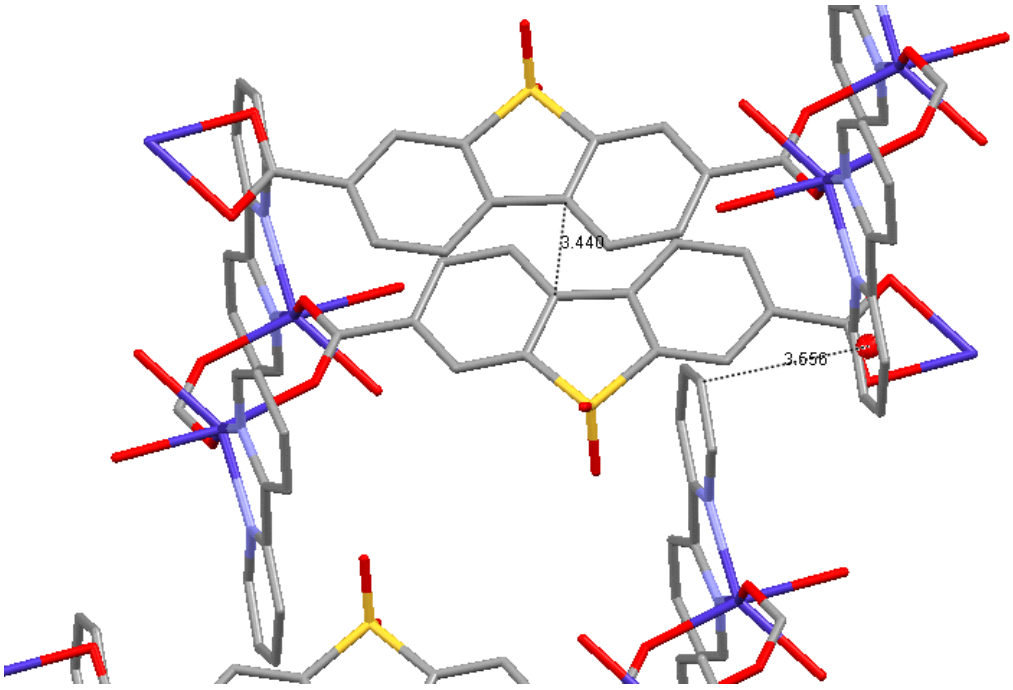

Figure S3. Intermolecular π-π stacking interactions of both L^{2-} - L^{2-} and 2,2'-bipy - 2,2'-bipy molecules in compound **4**.

Powder X-ray Diffraction (PXRD) for compound 2, 3and 4.

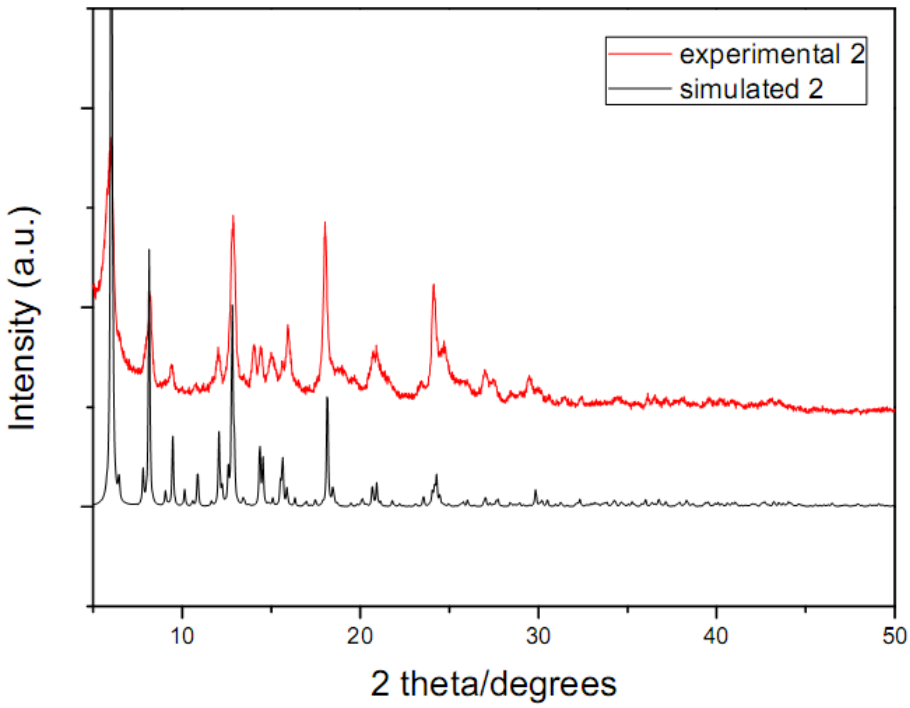

Figure S4. PXRD analysis for compound **2**

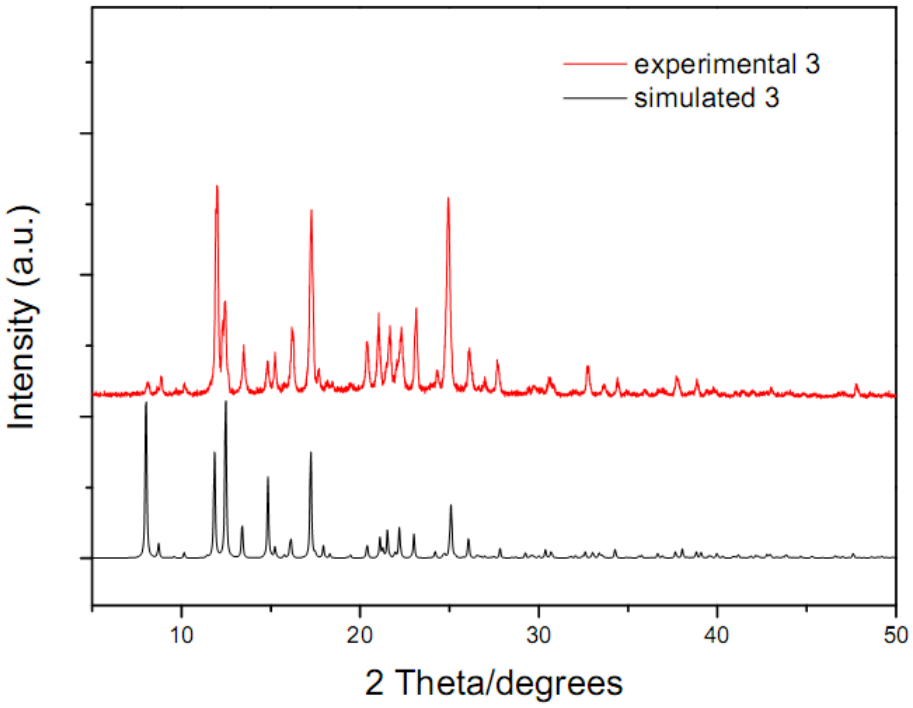

Figure S5. PXRD analysis for compound **3**

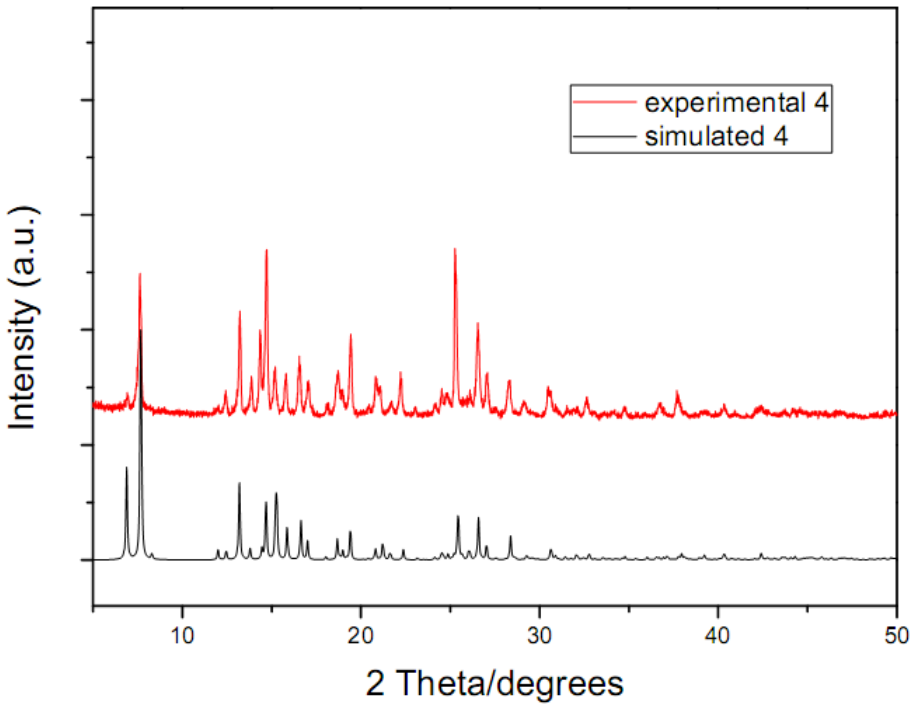

Figure S6. PXRD analysis for compound **4**

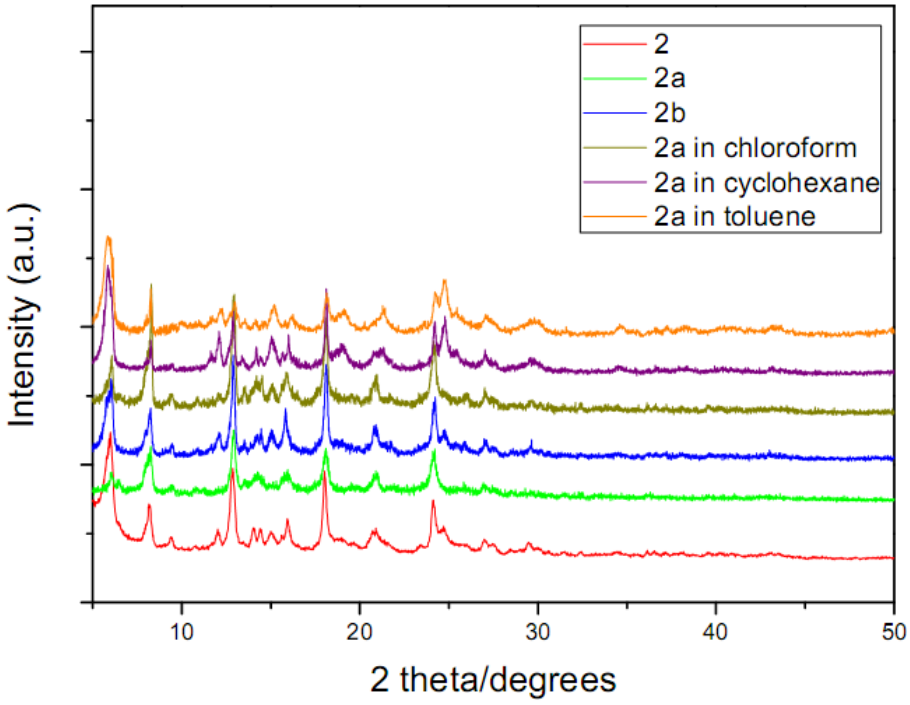

Figure S7. PXRD analyses for **2**, **2a**, **2b**, **2a** samples soaked in chloroform, cyclohexane, and toluene.

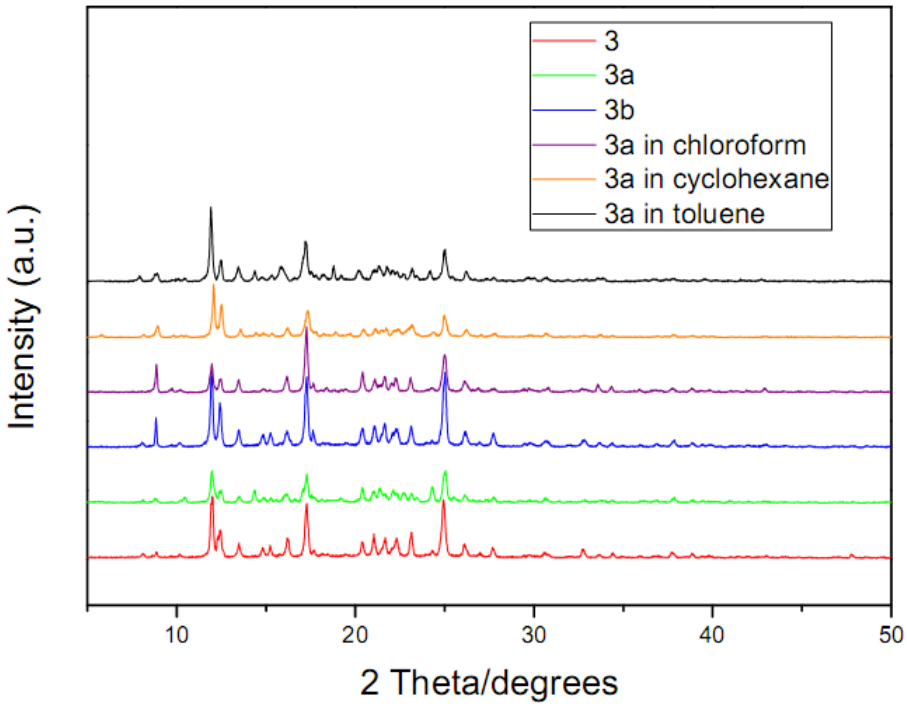

Figure S8. PXRD analyses for **3**, **3a**, **3b**, **3a** samples soaked in chloroform, cyclohexane, and toluene.

Optical Microscope Images of Compound 1 Crystals

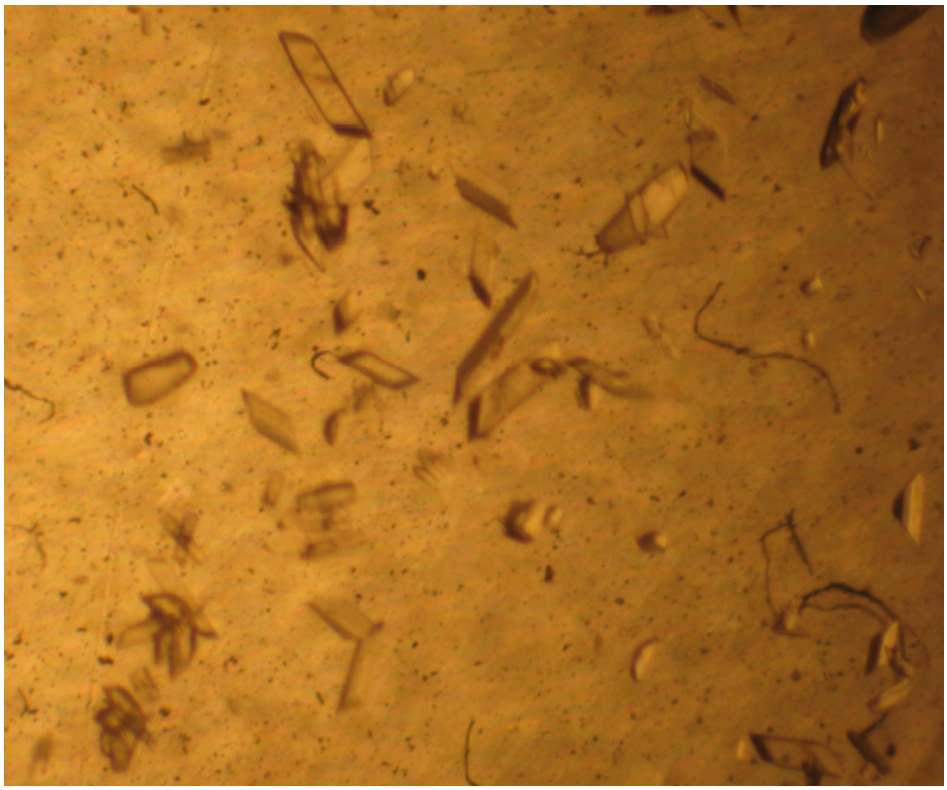

Figure S9. Optical image of compound **1**

The crystals of Compound 1 are stable inside their mother liquor. They are moisture sensitive and

decompose within few minutes. We could not get their accurate PXRD patterns.

Semilogarithmic emission decay plots of the free H_2L ligand and compound 1-4

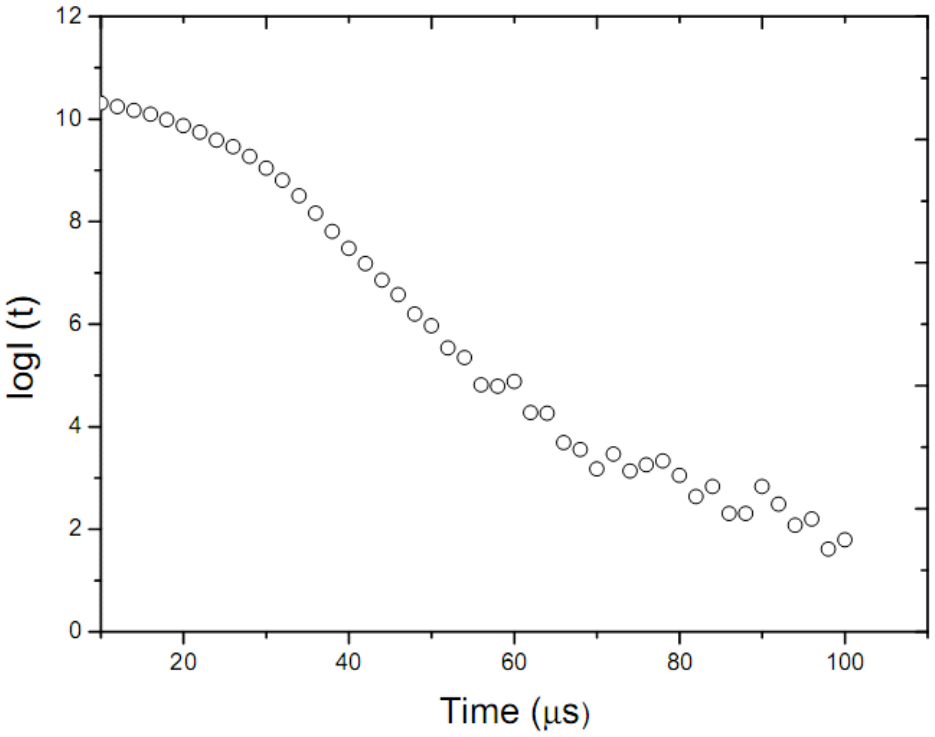

Figure S10. Semilogarithmic emission decay plots of free H_2L ligand.

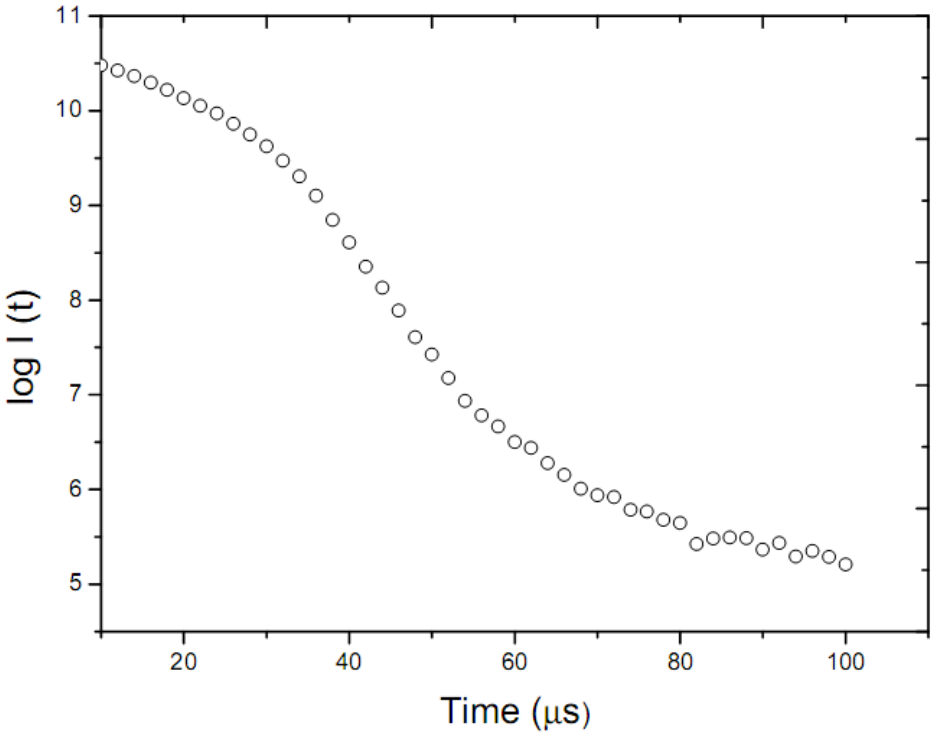

Figure S11. Semilogarithmic emission decay plots of compound **1**.

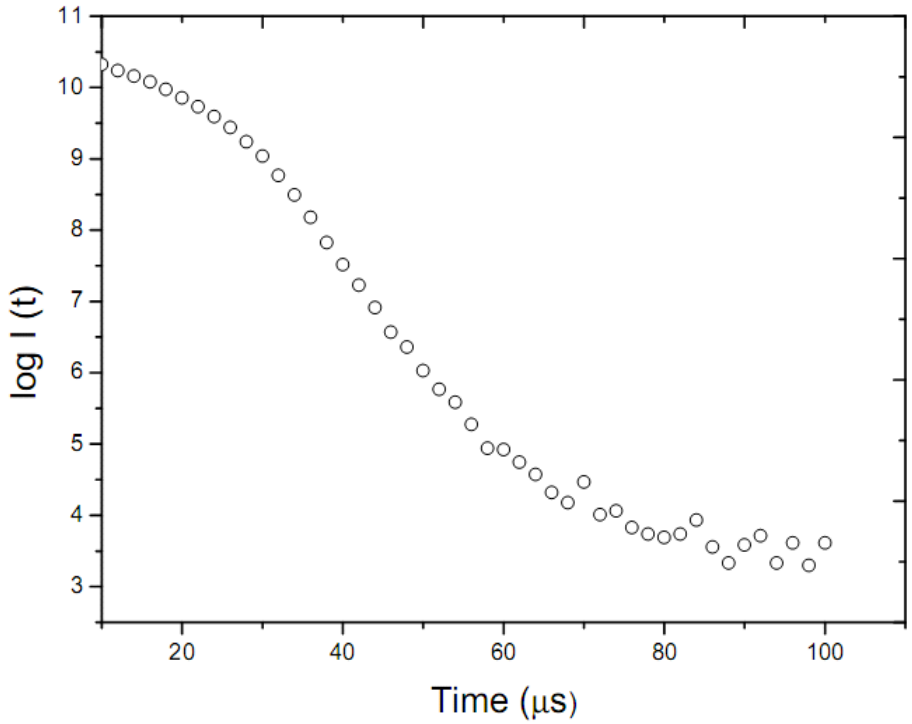

Figure S12. Semilogarithmic emission decay plots of compound **2**.

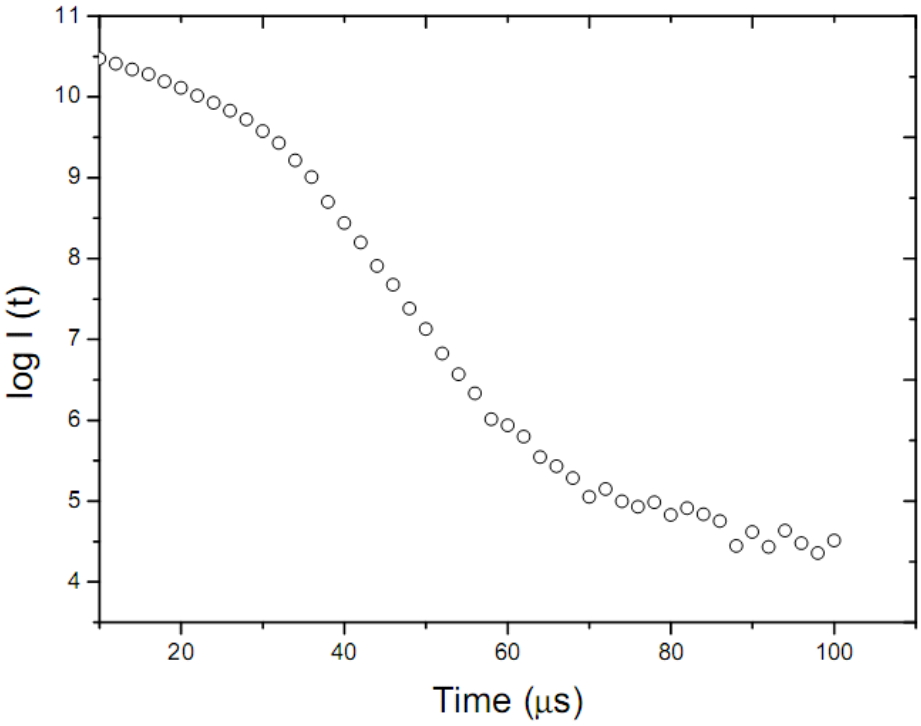

Figure S13. Semilogarithmic emission decay plots of compound **3**.

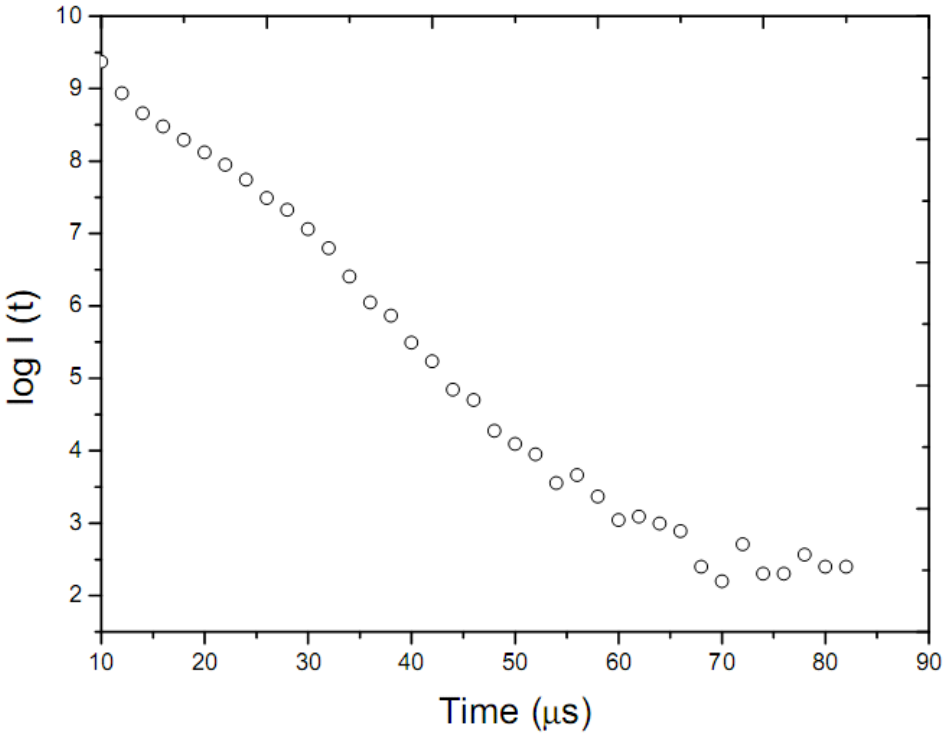

Figure S14. Semilogarithmic emission decay plots of compound **4**.