Supporting Information

Realizing Luminescent Cuprous Iodide Complexes with High Quantum Yields by Introducing Planar Aromatic Groups and Modification with Halogen Atoms on Ligand

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1.Preparation and ^{1}HNMR spectra of ligands: DABCO-CH_3, DABCO-F, DABCO-Cl, DABCO-Br and DABCO-I

Preparation of 1-(4-methylbenzyl)-1,4-diazabicyclo [2.2.2] octan-1-ium (DABCO-CH_3).

A 50.00ml of acetone was added to1.21g (10.80 mmol) of DABCO already weighed into a two-necked flask. The mixture was stirred thoroughly, dissolving to form a colourless solution labelled A. Solution B was formed by dissolving 2.00g (10.80mmol) of 4-methylbenzyl bromide into 40.00 ml of acetone to form a colourless solution. The colourless solution B was slowly added to A and stirred for 5 minutes, forming a white powder, filtered, and purified with ethyl acetate, and dried in the oven at 50 °C for 24 hours, obtaining a percentage yield of 97%. ^{1}HNMR (400 MHz, DMSO-d_6) δ: 7.42 – 7.36 (m, 2H), 7.34 – 7.27 (m, 2H), 4.48 (s, 2H), 3.27 (dd, J = 8.9, 6.2 Hz, 6H), 3.00 (dd, J = 8.9, 6.1 Hz, 6H), 2.35 (s, 3H). Anal. Calc. for $C_{14}H_{21}N_2^+$: C, 77.37; H, 9.74; N, 12.89 Found: C, 77.37; H,9.42; N,12.72. IR (cm $^{-1}$) 3491(s), 2965(m), (w), 1923(m), 1585(m), 1514(m), 1023(m), 816(m).

Preparation of 1-(4-fluorobenzyl)-1,4-diazabicyclo [2.2.2] octan-1-ium(DABCO-F).

A 2.80g (24.99 mmol) of DABCO was carefully weighed into a two-necked flask. A 50.00 ml of acetone was measured and added to the DABCO in the flask, stirred to dissolve, forming a colourless solution A. 4.73g 4-fluorobenzyl bromide which is equivalent to (24.99mmol) was weighed into a beaker, and 40.00ml of acetone was added to dissolve it to form solution B. Solution B was slowly transferred into solution A and stirred for 5 minutes at a temperature of 24° C. A fluffy white powder precipitated out, which was filtered and purified with ethyl acetate dried to obtain percentage yield of 92% . ^{1}HNMR (400 MHz, DMSO-d_6) δ: 7.62 – 7.54 (2H, m), 7.43 – 7.32 (2H, m), 4.54 (2H, s), 3.29 (6H, dd, J=8.8, 6.3 Hz), 3.01 (6H, dd, J=8.9, 6.1 Hz). Anal. Calc for $C_{13}H_{18}FN_2^+$: C, 70.56; H, 8.20; N, 12.66. Found: C,70.46; H,8.10; N12.53 IR (cm^{-1}) 3439(s),3065(w),2965(m), 2863(m), 1875(m), 1597(m) 1415(s), 1403(s) 809(m), 769(m).

Preparation of 1-(4-chlorobenzyl)-1,4-diazabicyclo [2.2.2]octanium (DABCO-Cl).

To a weighed amount of DABCO (1.09g, 9.73 mmol),50ml of acetone was added, stirred, and dissolved to form a colourless solution, A. 2.0g of 4-chlorobenzyl bromide was dissolved in 40ml of acetone stirred to dissolve, forming solution B. 98% yield of a fluffy white sample was obtained after a white fluffy material collected from a careful combination of solutions Band A and dried. ^{1}HNMR (400 MHz, DMSO-d_6) δ: 7.60 – 7.48 (4H, m), 4.47 (2H, s), 3.25 (7H, dd, J=8.9, 6.1 Hz), 2.99 (6H, dd, J=8.9, 6.0 Hz). Anal. Calc for $C_{13}H_{18}ClN_2^+$: C, 65.67; H, 7.63; N, 11.78. Found: C,65.57; H,7.50; N,22.77. IR (cm^{-1}) 3432(s),2953(w),2876(m), 1923 (m), 1550(m), 1206 (m), 829(m)

Preparation of 1-(4-bromobenzyl)-1,4-diazabicyclo [2.2.2] octanium (DABCO-Br).

A colourless solution made from 2g (8.00 mmol) of 4-bromobenzyl bromide and 40.00ml of acetone was gently added to another colourless solution made from DABCO (0.89g, 8.00 mmol) and acetone (50.00ml). The resulting colourless mixture was stirred for 10 minutes at room temperature hour. A shiny white powder was obtained after filtration, purification, and drying for 24 hours; a 95% sample yield was retrieved. ^{1}HNMR (400 MHz, DMSO-d_6) δ: 7.77 – 7.71 (2H, m), 7.55 – 7.29 (2H, m), 4.53 (2H, s), 3.29 (16H, t, J=7.5 Hz), 3.00 (7H, dd, J=8.8, 6.1 Hz). Anal. Calc for $C_{13}H_{18}BrN_2^+$: C, 55.33; H, 6.43; N, 9.93. Found: C,55.21; H,6.23, N,9.91 IR (cm^{-1}) 3474(s), 3038(w) 3391(s), 3071(m), 2947 (m), 2852(m), 1455(m), 846(m)

Preparation of 1-(4-iodobenzyl)-1,4-diazabicyclo [2.2.2] octanium (DABCO-I).

Solution A, prepared by dissolving 0.75g of DABCO (6.73 mmol) in 50.00 ml of acetone, was stirred to dissolve, appearing as a colourless mixture. Dropping solution B, which was formed by dissolving 2.00g of 4-iodobenzyl bromide in 40.00ml acetone slowly into A and stirring for 5. minutes, a white precipitate sample powdery in nature representing 98% yield based on the mass of the DABCO was formed after filtration, purification, and vacuum dried for 24 hours. ^{1}HNMR (400 MHz, DMSO-d_6) δ: 7.92 – 7.87 (2H, m), 7.32 – 7.28 (2H, m), 4.48 (2H, s), 3.27 (6H, t, J=7.5 Hz), 3.00 (6H, dd, J=8.8, 6.1 Hz). Anal. Calc for $C_{13}H_{18}IN_2^+$: C, 47.43; H, 5.51; N, 8.51. Found: C,47.41; H,5.51; N.8.50. IR (cm $^{-1}$) 3402(s),3026(m) 2940(m) 2864(m), 1599(m) 1415(m) 1380(m), 828(m),600(m).

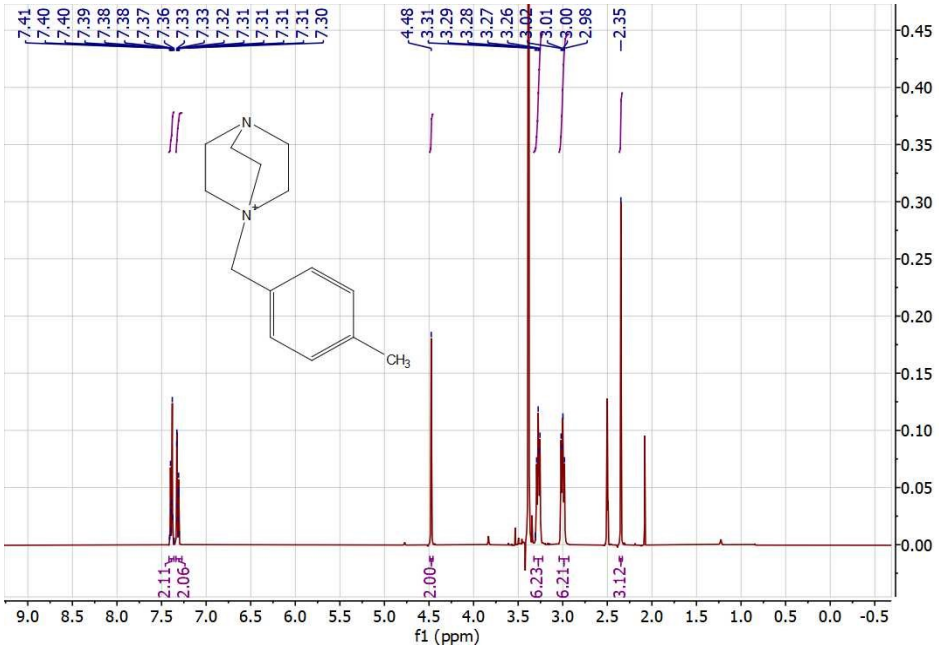

Figure S1 ^{1}HNMR Spectrum of DABCO-CH_3

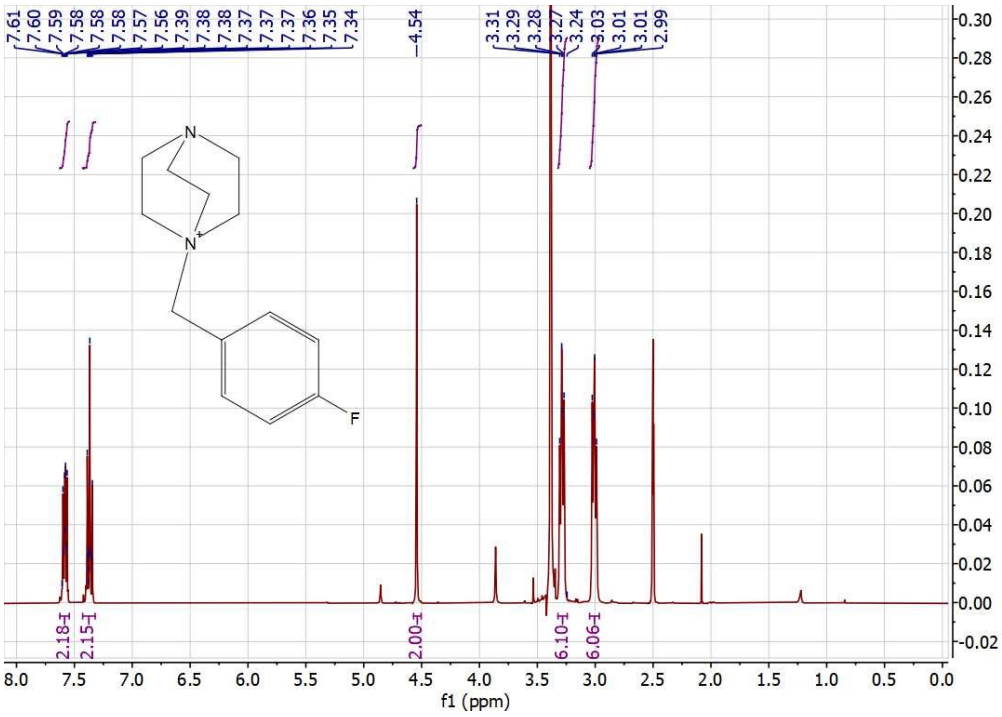

Figure S2 ^{1}H NMR Spectrum of DABCO-F

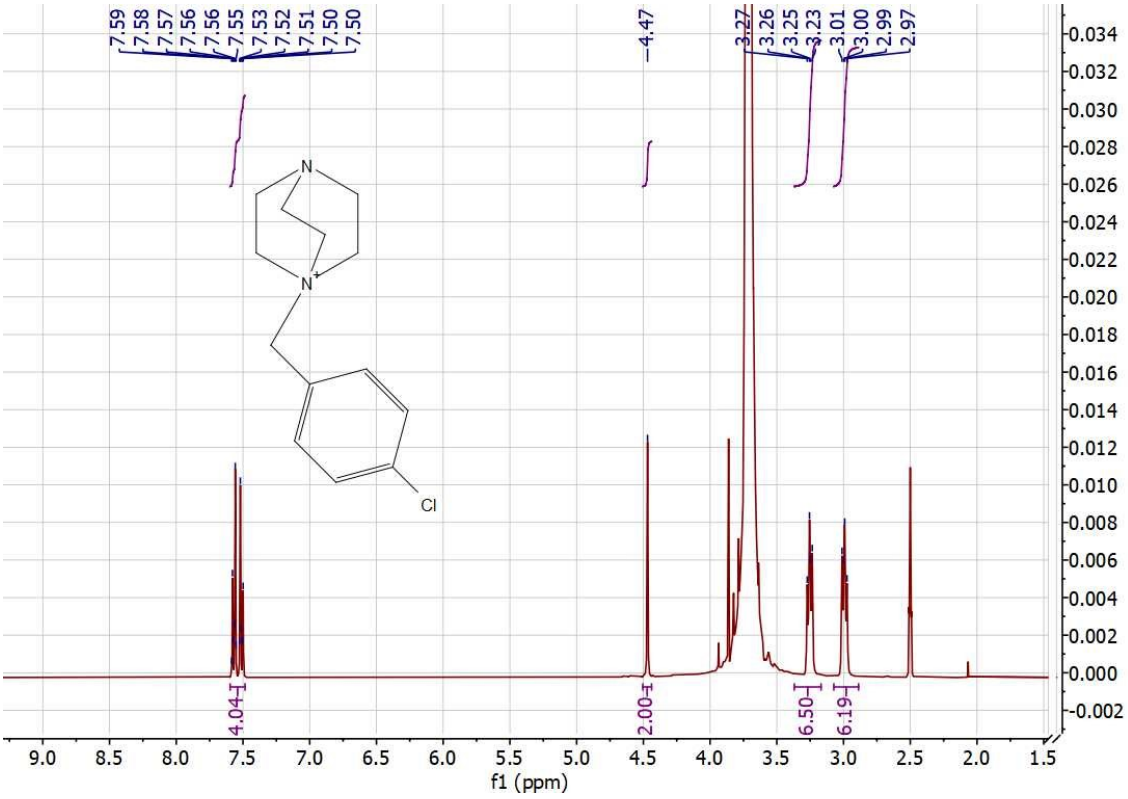

Figure S3 ^{1}H NMR Spectrum of DABCO-Cl

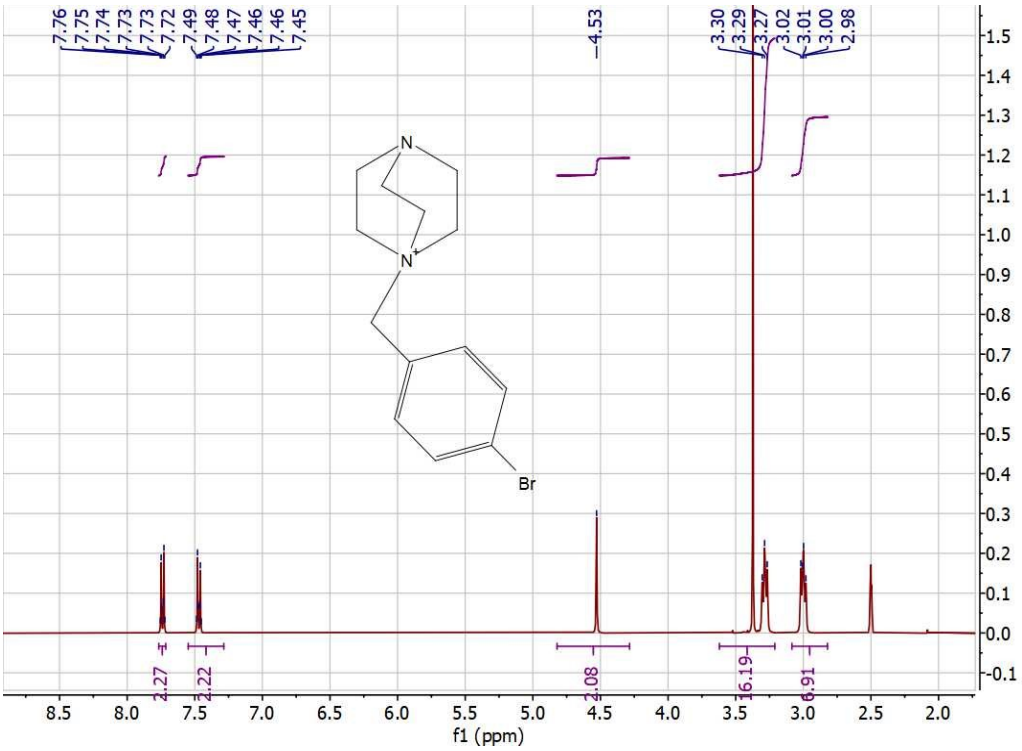

Figure S4 [1]H NMR Spectrum of DABCO-Br

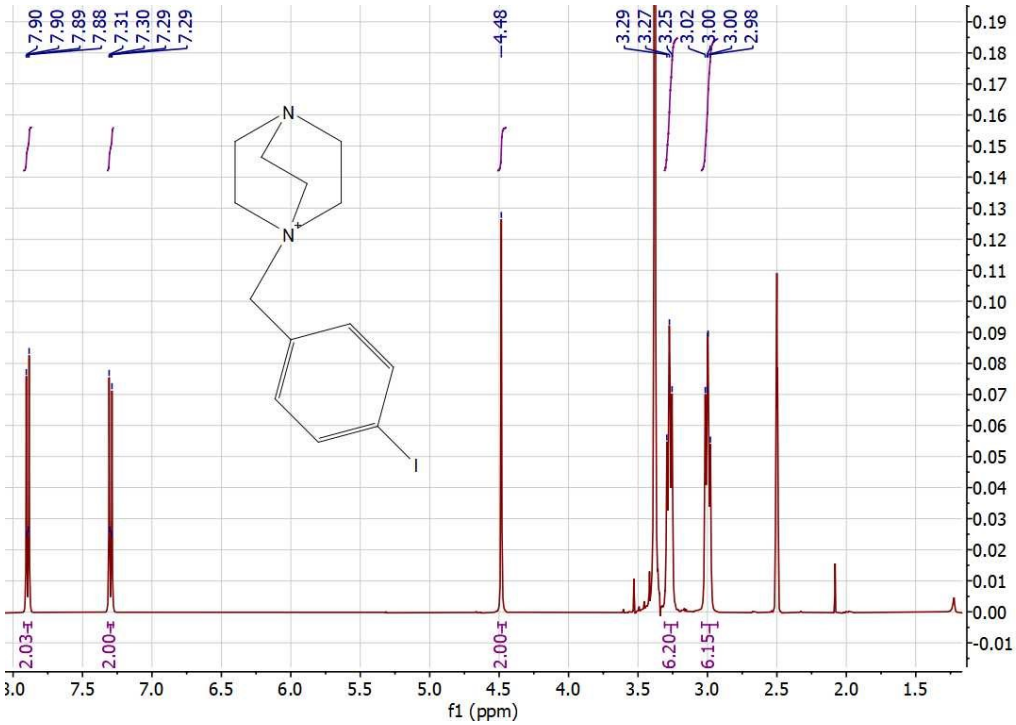

Figure S5 [1]H NMR Spectrum of DABCO-I

2. IR of Ligands: DABCO-CH_3, DABCO-F, DABCO-Cl, DABCO-Br and DABCO-I

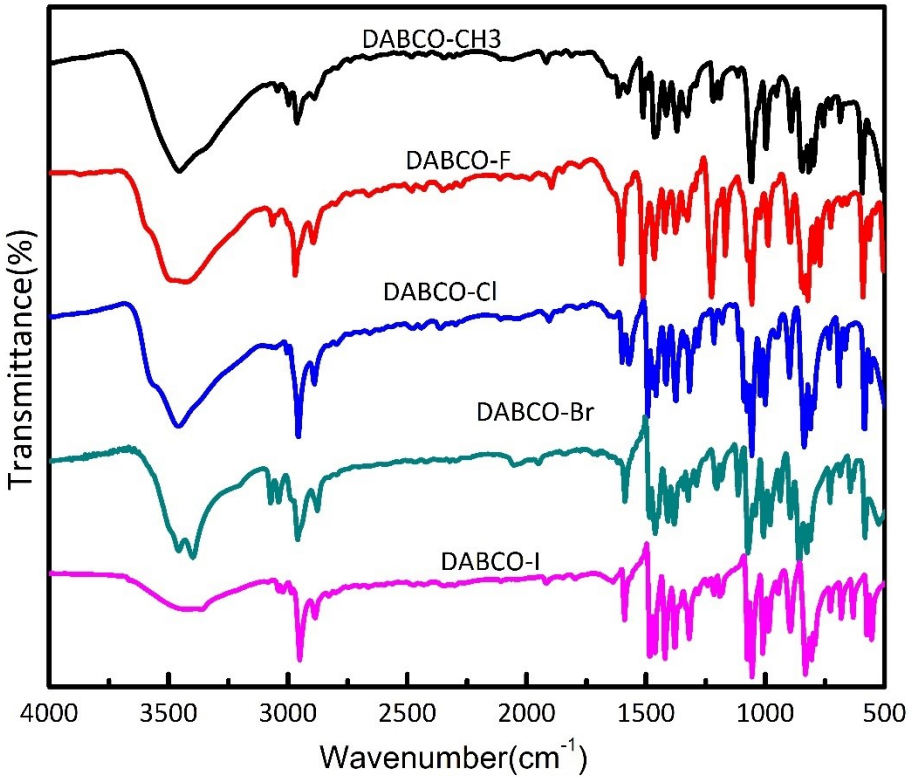

Figure S6 IR spectra of Ligands

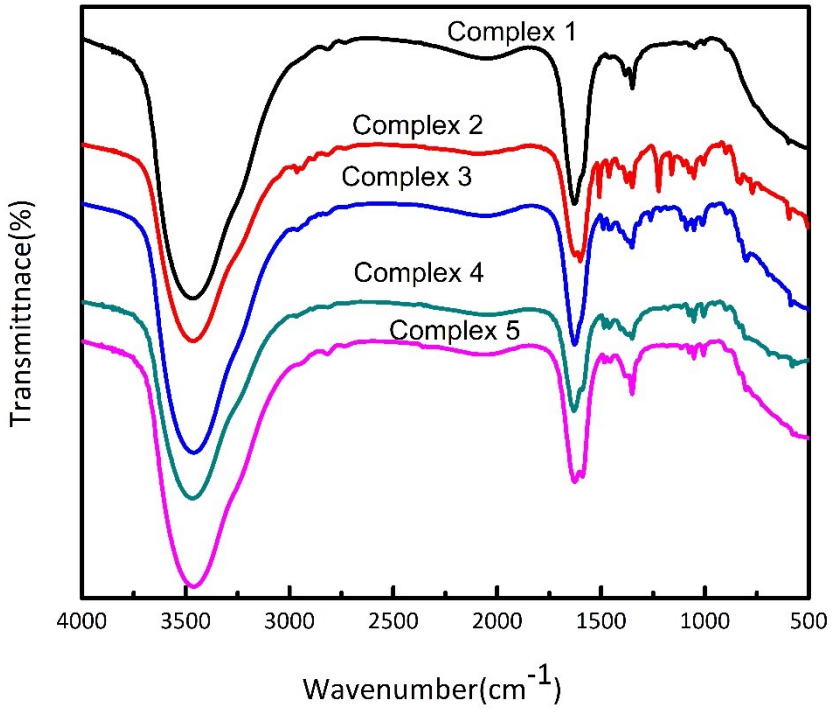

Figure S7 FT IR spectra of Complexes **1-5**

3. Slected bond length and angles of complexes 1~5

Table S1 Bond length and Angles of Complex 1

Bond	Dist/Å	Bond	Dist/Å	Bond	Dist/Å	Bond	Dist/Å
I1-Cu7	2.6481(14)	I2-Cu9	3.024(2)	I2-Cu1	2.738(2)	I5-Cu9	2.5968(18)
I1-Cu8	2.6685(15)	I3-Cu7	2.6200(15)	I5-Cu8	2.6111(15)	I6-Cu9	2.6536(18)
I2-Cu7	2.6582(14)	I3-Cu9	2.688(2)	I6-Cu1	2.539(2)	Cu7-Cu8	2.6380(18)
I2-Cu8	2.6593(14)	I4-Cu1	2.481(2)	Cu7-Cu9	2.838(2)	Cu7-N8	2.146(8)
Cu8-Cu9	2.768(2)	Cu8-N6	2.166(8)	Cu9-Cu1	2.578(2)		
Angle	**(°)**	**Angle**	**(°)**	**Angle**	**(°)**	**Angle**	**(°)**
Cu7-I-Cu8	59.49(4)	Cu7-I2-Cu8	59.49(4)	Cu7-I2-Cu9	59.51(5)	Cu7-I2-Cu1	75.89(7)
Cu8-I2 -Cu9	57.87(4)	Cu8-I2-Cu1	109.55(6)	Cu1-I2-Cu9	52.87(5)	Cu7-I3-Cu9	64.62(5)
Cu9-I5-Cu8	64.22(5)	Cu1-I6-Cu9	59.48(6)	I1-Cu7-I2	115.20(5)	I1-Cu7-Cu9	104.04(5)
I2-Cu7-Cu9	66.67(6)	I3-Cu7-I1	106.70(5)	I3-Cu7-I2	117.03(5)	I3-Cu7-Cu8	110.95(6)
I3-Cu7-Cu9	58.85(6)	Cu8-Cu7-I1	60.64(4)	Cu8-Cu7-I2	60.28(4)	Cu8-Cu7-Cu9	60.60(5)
N8-Cu7-I1	100.7(2)	I1-Cu8-Cu9	105.42(6)	I2-Cu8-I1	114.48(5)	I5-Cu8-I1	109.73(5)
Cu1-Cu9-Cu8	111.07(9)	N6-Cu8-I1	100.22(19)	I3-Cu9-I2	103.85(6)	Cu7-Cu8-I1	59.87(4)
Cu1-Cu9-Cu7	75.41(7)	I2-Cu8-Cu9	67.68(5)	I5-Cu9-I3	121.52(8)	I6-Cu9-Cu7	132.78(7)

Bond	Dist/Å	Bond	Dist/Å	Bond	Dist/Å	Bond	Dist/Å
I(0AA)-Cu(7)	2.6470(15)	I(0AA)-Cu(8)	2.6678(16)	I(2)-Cu(7)	2.6576(15)	I(2)-Cu(8)	2.6592(15)
I(2)-Cu(9)	3.025(2)	I(2)-Cu(1)	2.735(3)	I(3)-Cu(7)	2.6219(16)	I(3)-Cu(9)	2.682(2)
I(5)-Cu(8)	2.6120(17)	I(5)-Cu(9)	2.6012(19)	I(6)-Cu(9)	2.6553(19)	I(6)-Cu(1)	2.535(2)
Cu(7)-Cu(8)	2.6361(19)	Cu(7)-Cu(9)	2.834(2)	Cu(8)-Cu(9)	2.770(2)	Cu(9)-Cu(1)	2.575(3)
Angle	**(°)**	**Angle**	**(°)**	**Angle**	**(°)**	**Angle**	**(°)**
Cu(7)-I(0AA)-Cu(8)	59.47(4)	Cu(7)-I(2)-Cu(8)	59.44(4)	Cu(7)-I(2)-Cu(9)	59.41(5)	Cu(7)-I(2)-Cu(1)	76.03(7)
Cu(8)-I(2)-Cu(9)	57.90(5)	Cu(8)-I(2)-Cu(1)	109.58(7)	Cu(1)-I(2)-Cu(9)	52.81(6)	Cu(7)-I(3)-Cu(9)	64.58(6)
Cu(9)-I(5)-Cu(8)	64.19(6)	Cu(1)-I(6)-Cu(9)	59.42(7)	I(0AA)-Cu(7)-I(2)	115.26(6)	I(3)-Cu(7)-I(2)	117.00(6)
I(3)-Cu(7)-Cu(8)	110.97(6)	I(3)-Cu(7)-Cu(9)	58.73(6)	Cu(8)-Cu(7)-I(2)	60.31(5)	Cu(8)-Cu(7)Cu(9)	60.72(6)
I(2)-Cu(7)-Cu(9)	66.76(6)	I(3)-Cu(7)-I(0AA)	106.71(5)	Cu(8)-Cu(7)-I(0AA)	60.66(5)	I(0AA)-Cu(7)-Cu(9)	104.11(6)

Table 2 Selected Bond and Angles of Complex 2

Bond	Dist//Å	Bond	Dist/Å	Bond	Dist/Å
I1- Cu6	2.6314(10)	I1- Cu5	2.7758(9)	Cu6- N3	2.198(4)
I2- Cu5	2.5860(9)	Cu5-N8	2.155(5)	I4-Cu6	2.6243(9)
I3 Cu6	2.6599(8)	I3-Cu5[1]	2.6392(9)		
Angle	(°)	Angle	(°)	Angle	(°)
Cu6-I1-Cu5	124.18(3)	Cu51-I3-Cu6	130.74(3)	I2-Cu5-I1	101.06(3)
N3-Cu6-I4	102.14(13)	I31-Cu5-I1	119.95(3)	N8-Cu5-I1	97.08(13)
N8-Cu5-I2	119.64(12)	N3-Cu6-I1	98.56(14)	N3-Cu6-I3	106.36(12)

Table S3 Selected Bond Length and Angles of Complex 3

Bond	Dist/Å	Bond	Dist/Å	Bond	Dist/Å
I(1)-Cu(5)	2.7590(7)	I(1)-Cu(6)	2.6330(7)	I(2)-Cu(5)	2.6310(7)
I(2)-Cu(6)	2.6564(6)	I(3)-Cu(5)	2.6009(6)	I(4)-Cu(6)	2.6197(7)
Cu(5)-N(22)	2.170(3)	Cu(6)-N(11)	2.207(3)		
Angle	**(°)**	**Angle**	**(°)**	**Angle**	**(°)**
Cu(6)-I(1)-Cu(5)	125.180(19)	Cu(5)-I(2)-Cu(6)[1]	129.25(2)	I(2)-Cu(5)-I(1)	120.18(2)
I(3)-Cu(5)-I(1)	100.46(2)	I(3)-Cu(5)-I(2)	117.06(3)	I(4)-Cu(6)-I(1)	121.29(2)
I(4)-Cu(6)-I(2)1	110.41(2)	N(22)-Cu(5)-I(1)	97.91(9)	N(22)-Cu(5)-I(2)	101.53(9)

Table S4 Selected Bond Length and Angles of Complex 4

Bond	Dist/Å	Bond	Dist/Å	Bond	Dist/Å
I(1)-Cu(5)	2.7547(12)	I(1)-Cu(6)	2.6320(11)	I(2)-Cu(5)	2.6020(11)
I(3)-Cu(5)	2.6304(12)	I(3)-Cu(6)[1]	2.6515(11)	I(4)-Cu(6)	2.6224(11)
Cu(5)-N(11)	2.174(6)	Cu(6)-N(38)	2.196(6)		
Angle	(°)	Angle	(°)	Angle	(°)
Cu(6)-I(1)Cu(5)	125.43(4)	Cu(5)-I(3)-Cu(6)[1]	129.29(4)	I(2)-Cu(5)-I(1)	100.08(4)
I(2)-Cu(5)-I(3)	116.76(4)	I(3)-Cu(5)-I(1)	120.78(4)	I(1)-Cu(6)-I(3)[1]	115.65(4)
I(4)-Cu(6)-I(1)	121.07(4)	N(38)-Cu(6)-I(1)	98.63(16)	N(38)-Cu(6)-I(4)	101.96(16)

Table 5 Selected Bond Length and Angles of Complex 5

Bond	Dist/Å	Bond	Dist/Å	Bond	Dist/Å
I(2)- Cu(1)	2.6934(12)	I(2)- Cu(1)^{1}	2.6683(11)	I(2)- Cu(2)	2.5831(14)
I(3)- Cu(1)	2.6209(11)	I(3)-Cu(2)	2.5420(14)	I(4)-Cu(2)	2.5094(13)
Cu(1)-Cu(1	2.711(2)	Cu(1)-Cu(2)	2.7525(14)	Cu(1)-N(2)	2.143(6)
Angle	(°)	Angle	(°)	Angle	(°)
Cu(1)^{1}-I(2)-Cu(1)	60.76(4)	Cu(2)-I(2)-Cu(1)	62.85(4	Cu(2)-I(2)-Cu(1)1	91.28(4)
I(3)-Cu(1)-I(2)	110.03(4)	N(2)-Cu(1)-I(2)	104.84(17)	I(2)-Cu(2)-Cu(1)	60.54(3)
I(4)-Cu(2)-Cu(1)	156.20(6)	I(4)-Cu(2)-I(3)	118.96(5)	I(4)-Cu(2)-I(2)	124.35(6)

4.Stacking modules of complexes 1~5

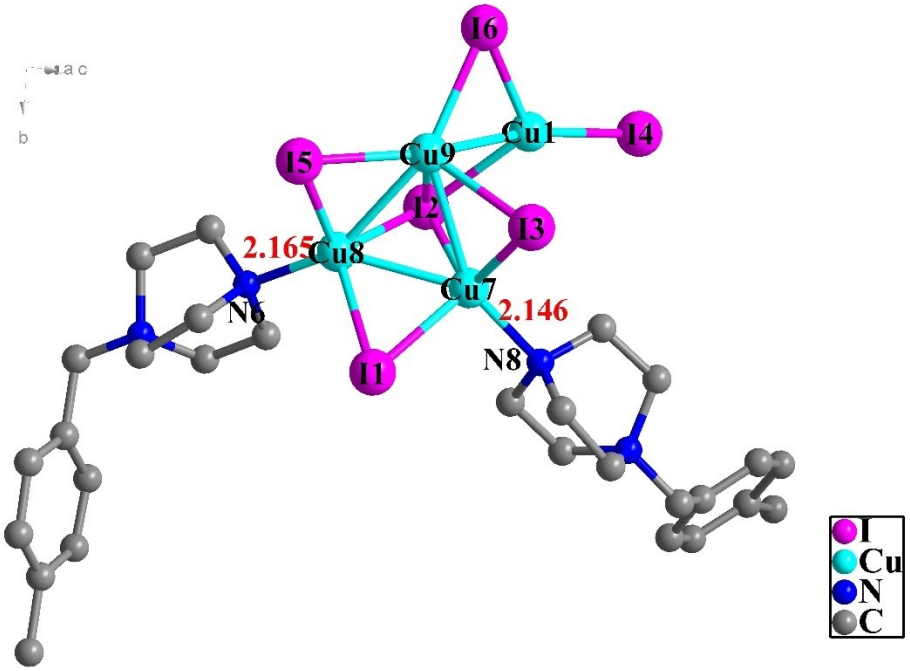

Figure S8 labeled CuI unit showing coordination in Complex **1**

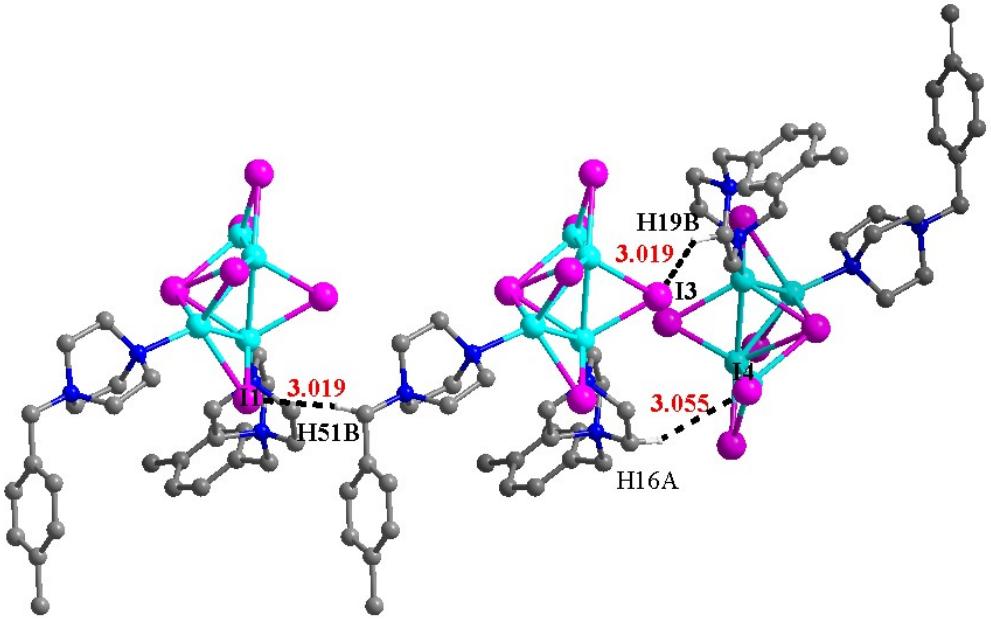

Figure S9 Different halogen bonds connections in Complex **1**

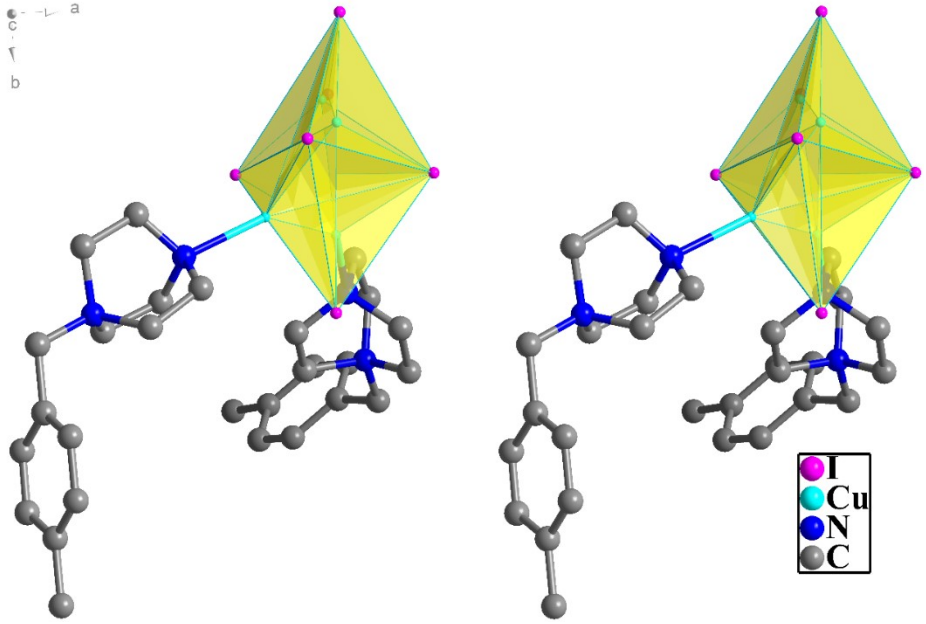

Figure S10 Packing of Complex **1** along b-axis

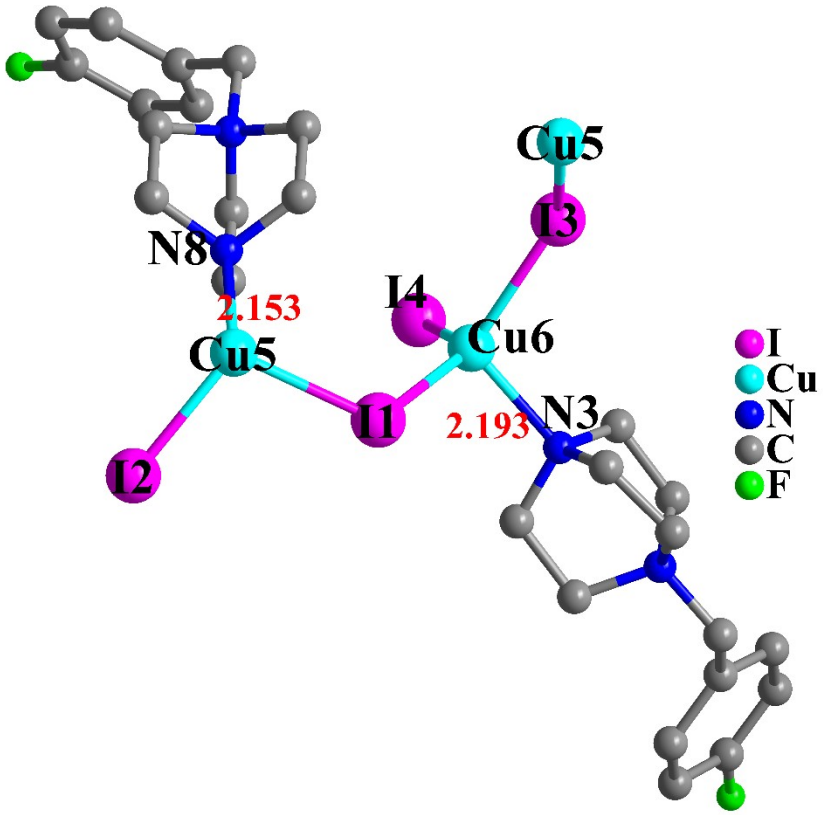

Figure S11 Labelled coordination portion in Complex **2** in the asymmetric unit

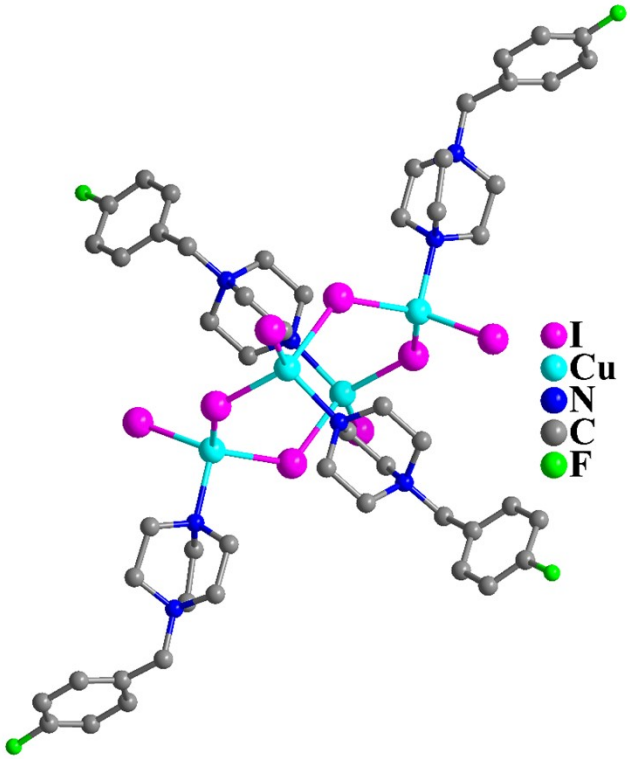

Figure S12 Structural view of Complex **2** in the symmetric unit.

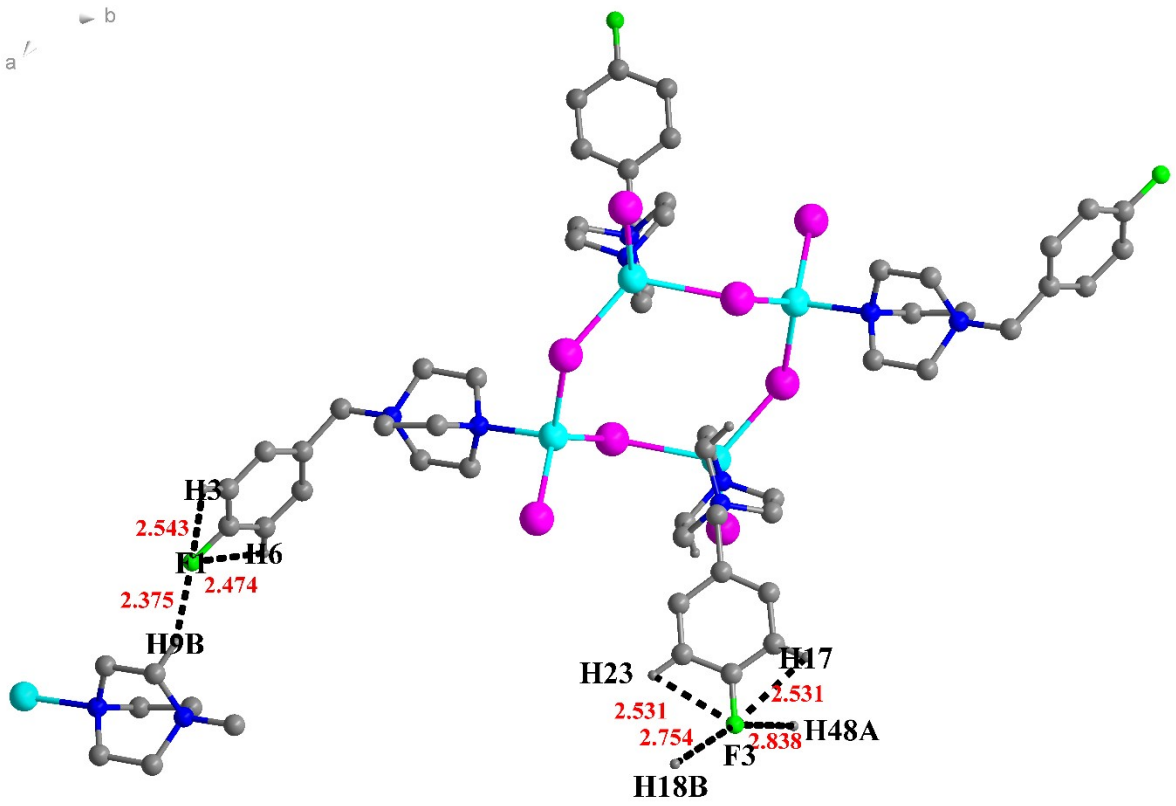

Figure S13 Different halogen bonds connections in Complex **2**

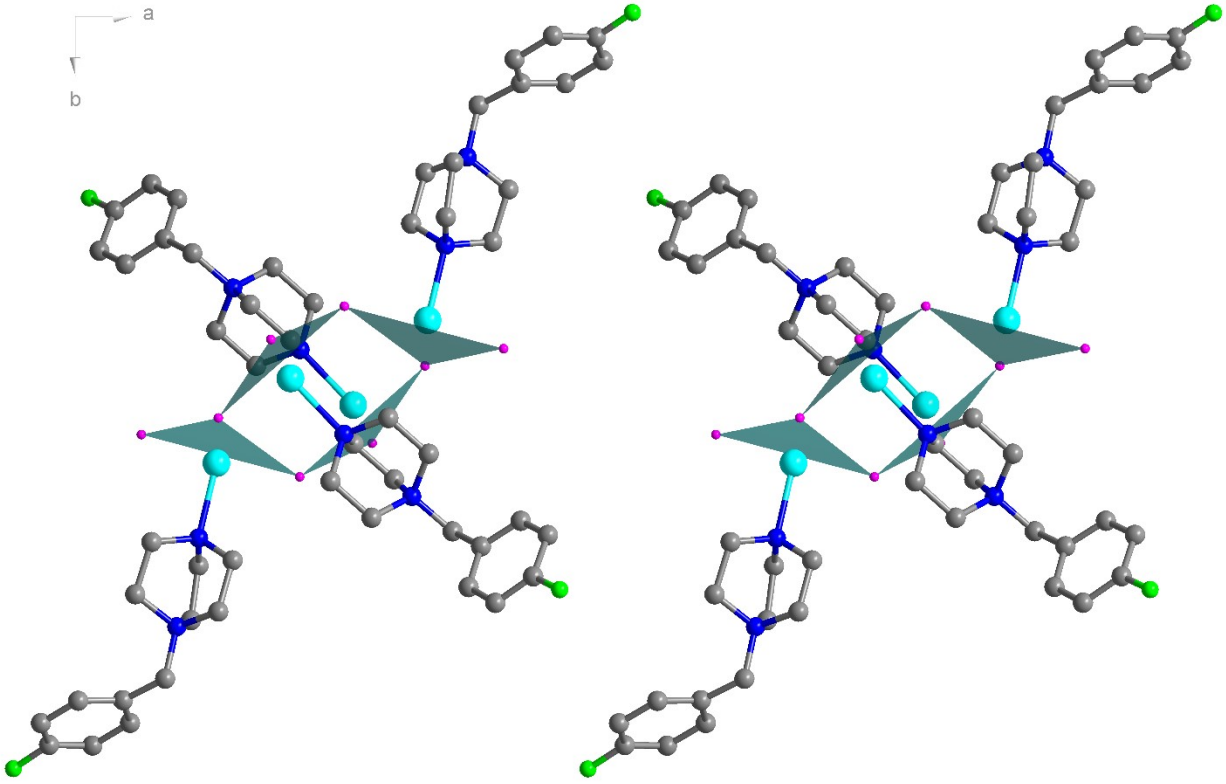

Figure S14 Packing of Complex **2**

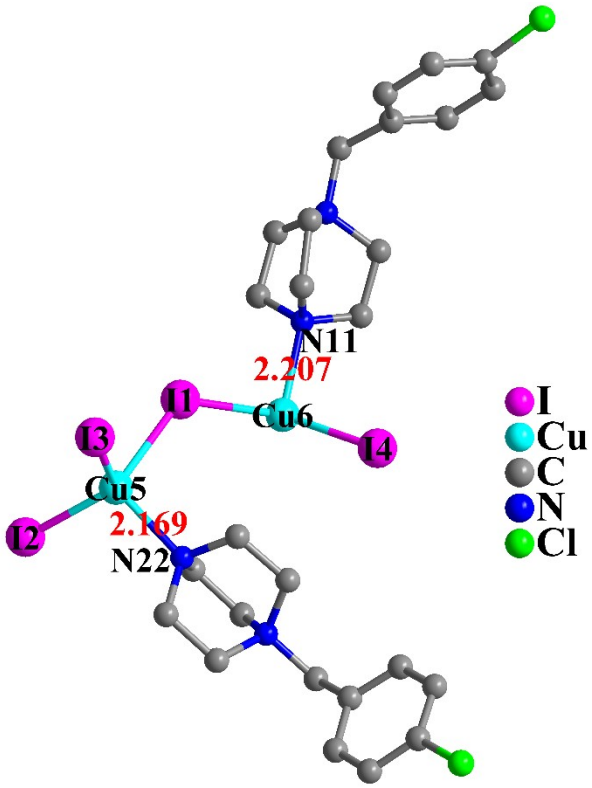

Figure S15 Labelled coordination portion in Complex **3** in the asymmetric unit.

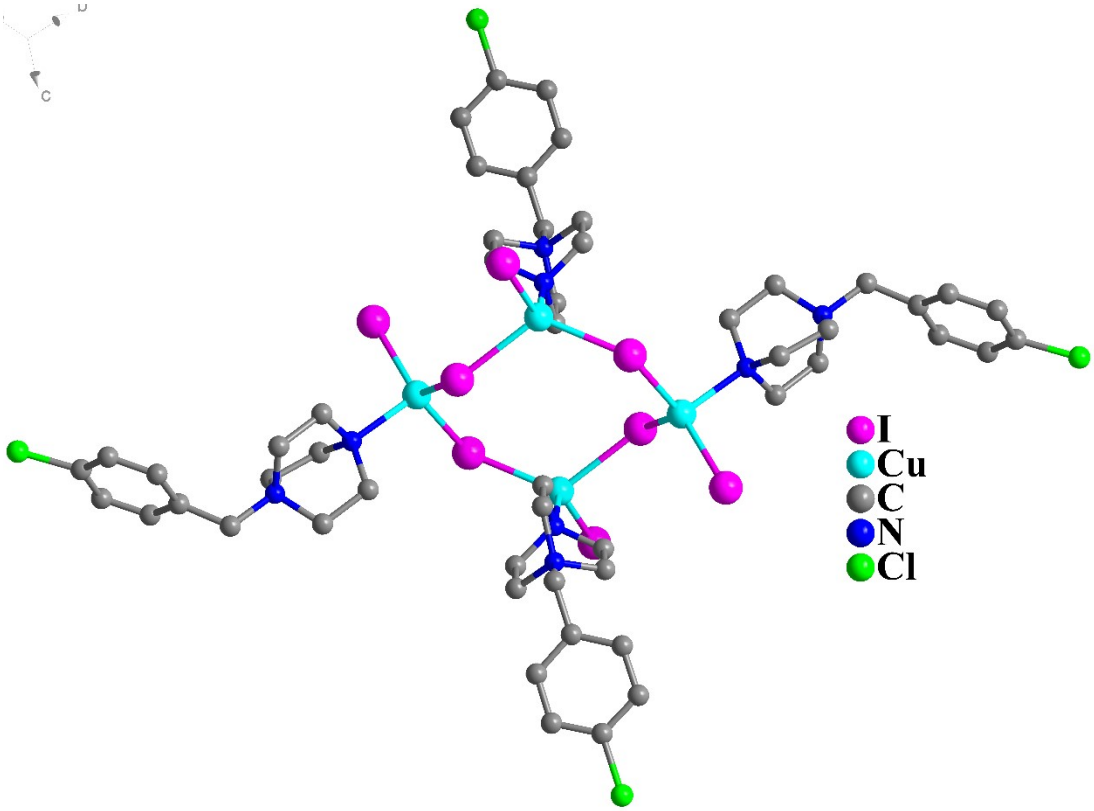

Figure 16 Structure of Complex **3** symmetric unit

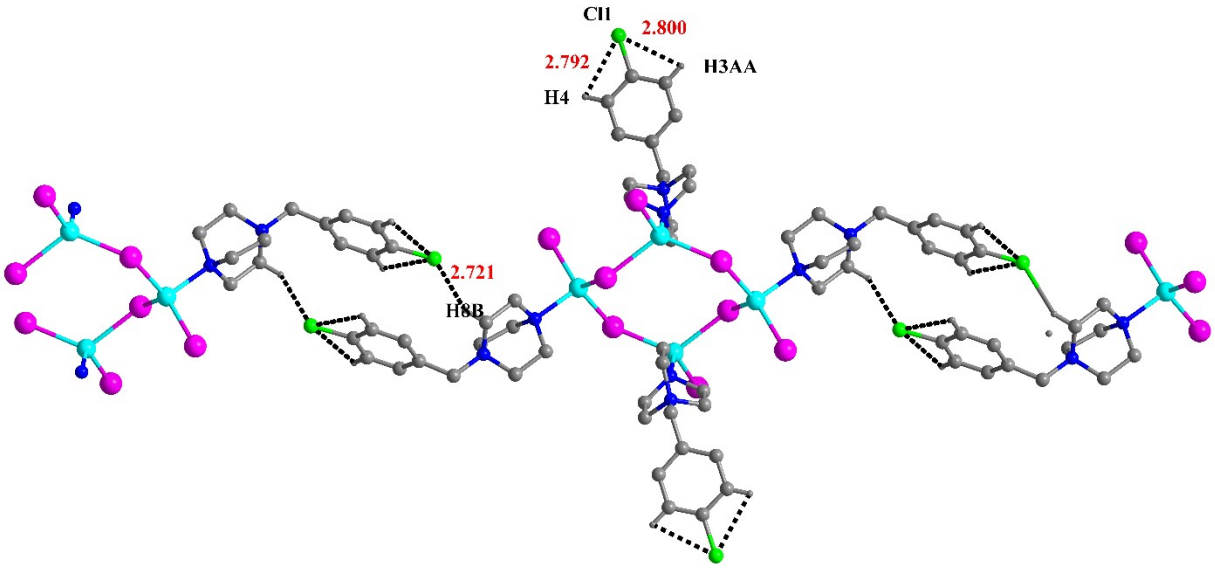

Figure S17 Different halogen bonds connections in Complex **3**

Figure S18 Packing of Complex **3**

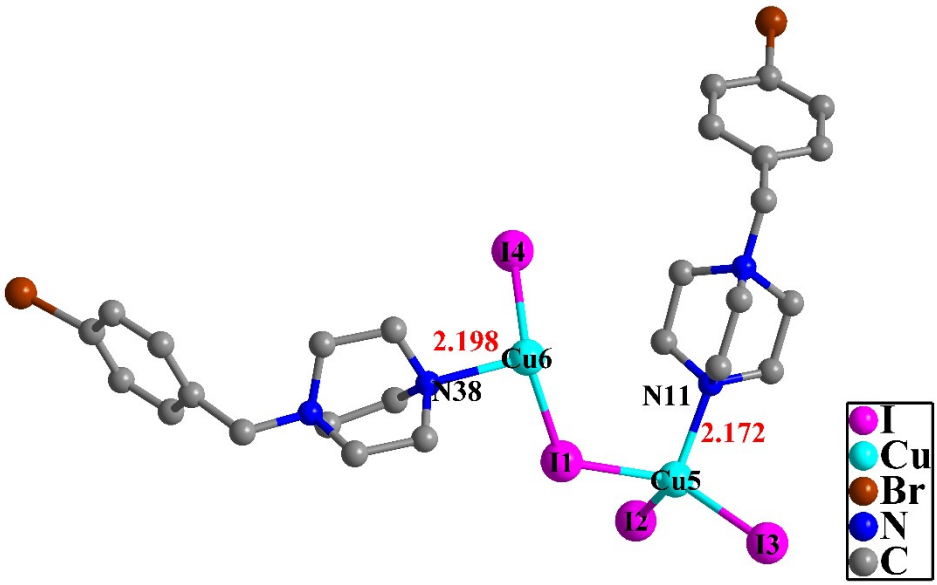

Figure S19 Labelled coordination portion in Complex **4** in the asymmetric unit

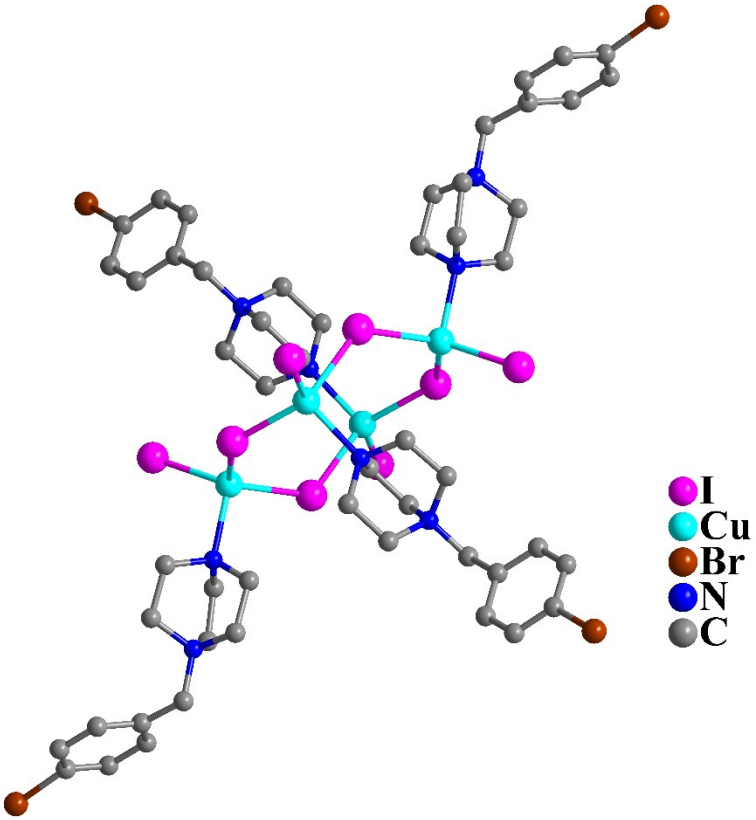

Figure S20 Structure of Complex **4** symmetric unit.

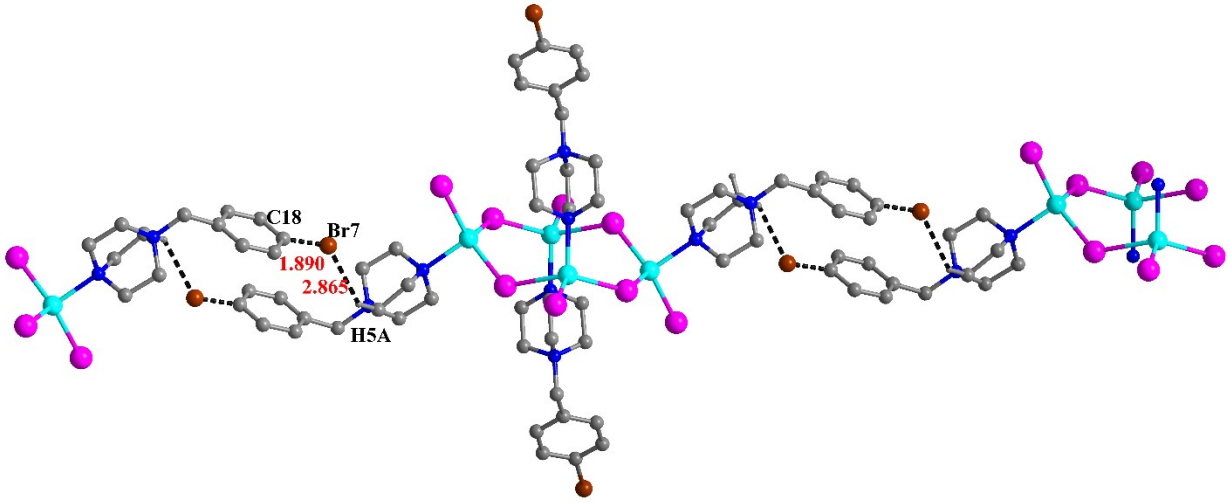

Figure S21 Different halogen bonds connections in Complex **4**

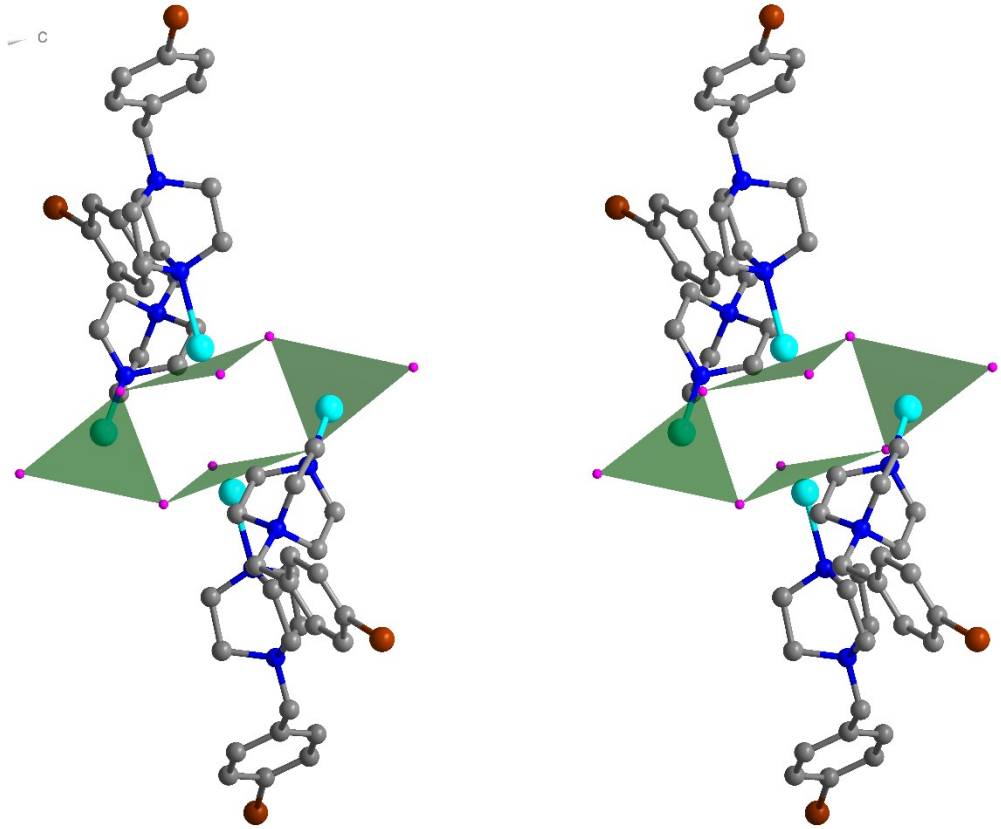

Figure S22 Packing of Complex **4**

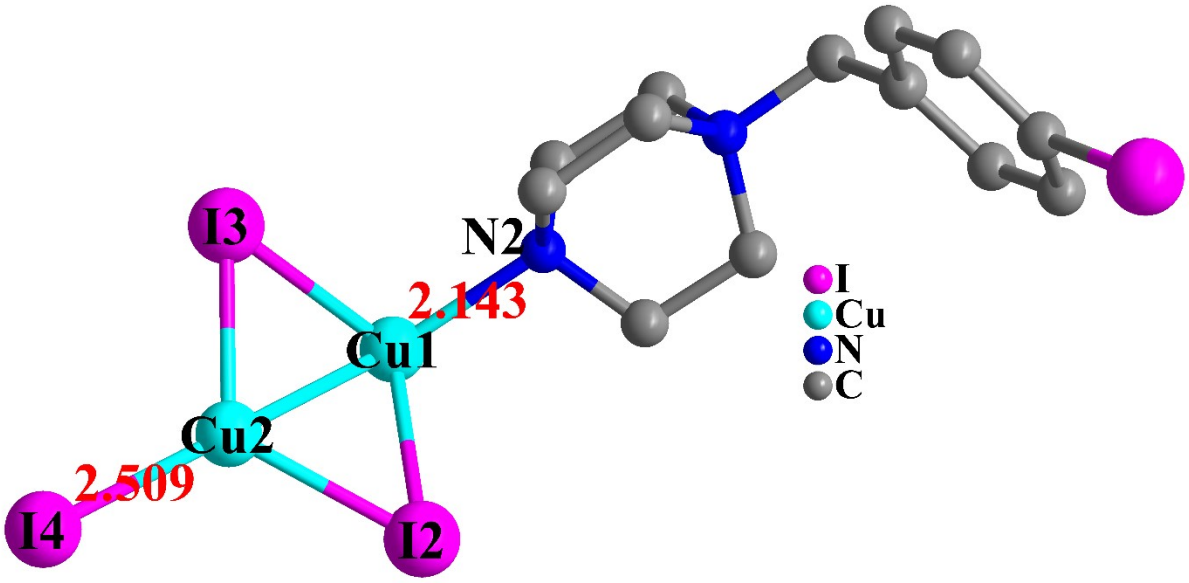

Figure S23 Labelled coordination portion in Complex **5** in the asymmetric unit

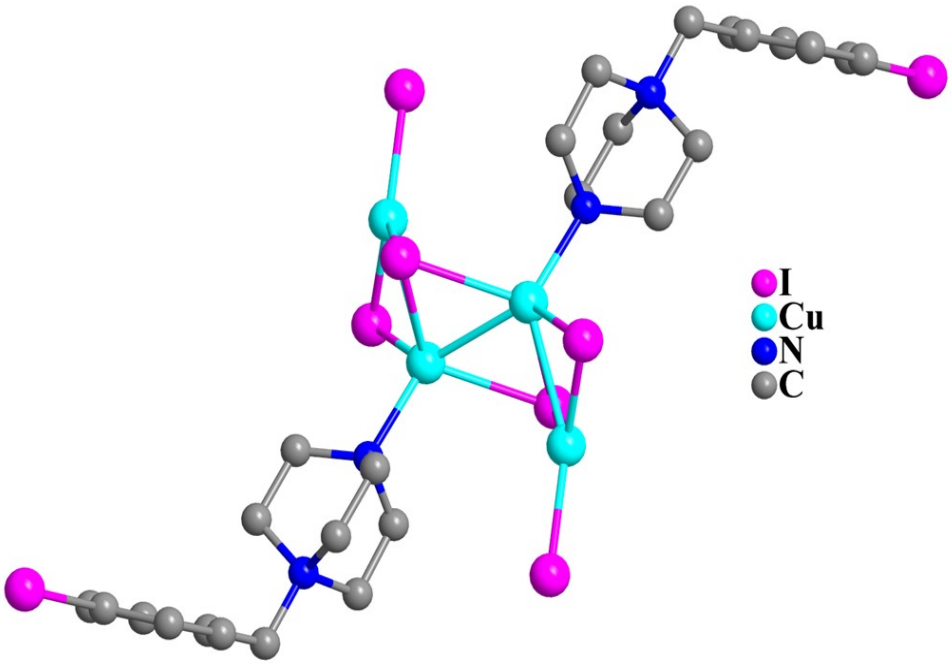

Figure S24 Structure of Complex **5** symmetric unit

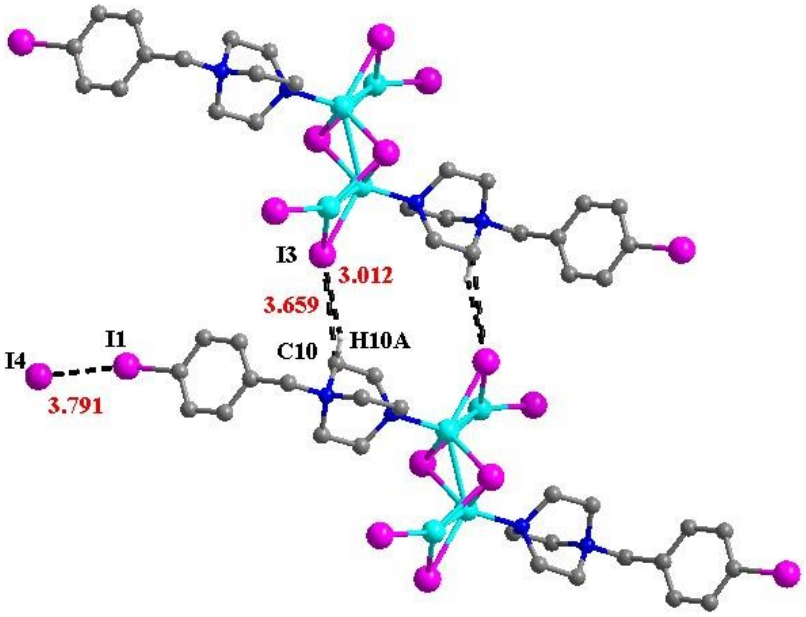

Figure S25 Different halogen bonds connections in Complex **5**

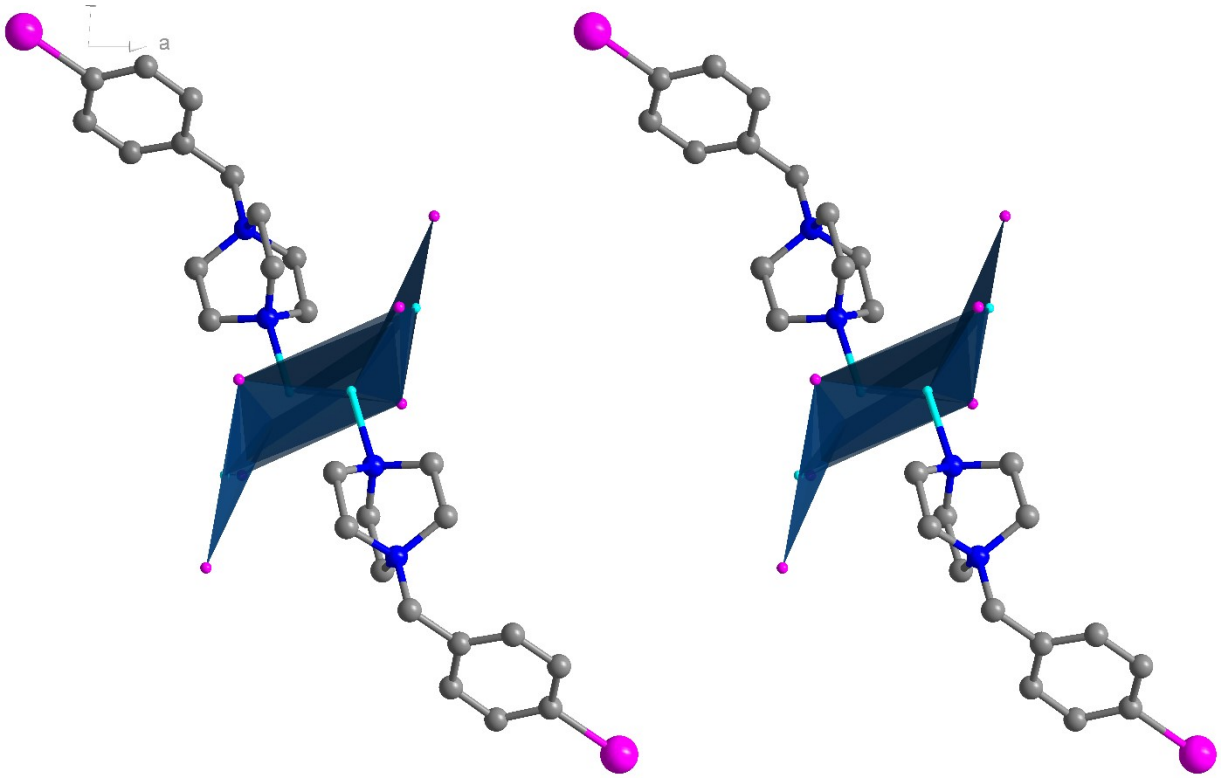

Figure S26 Stacking arrangement of **5**

5. PXRD of complexes 1~5.

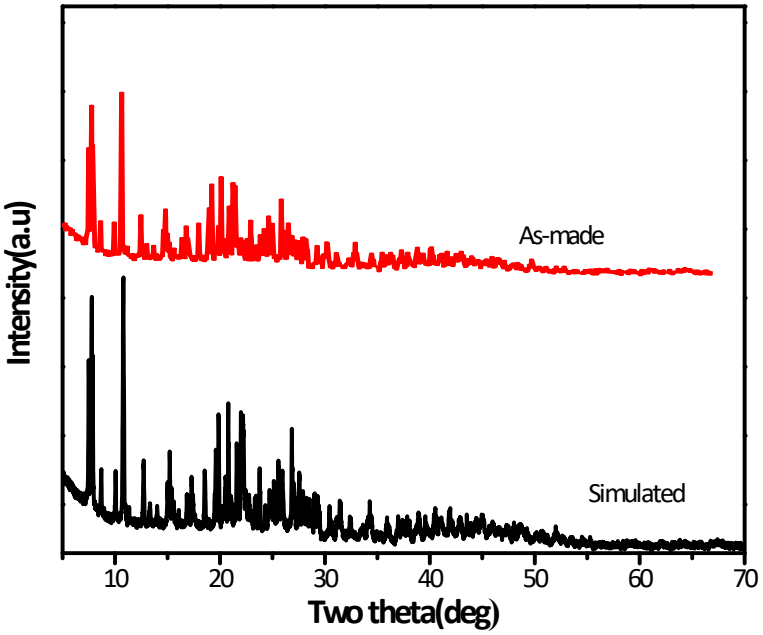

Figure S27 PXRD plot of Complex **1**

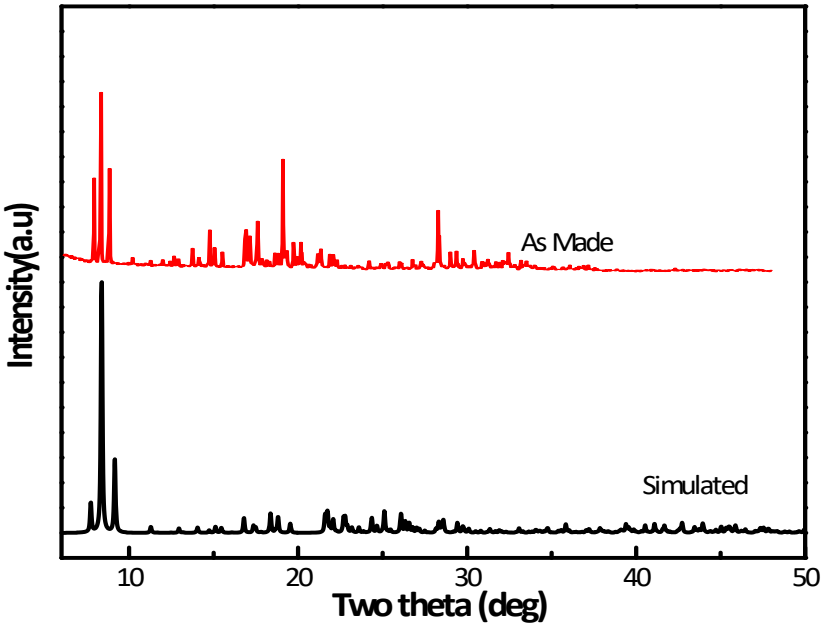

Figure S28 PXRD of complex **2**

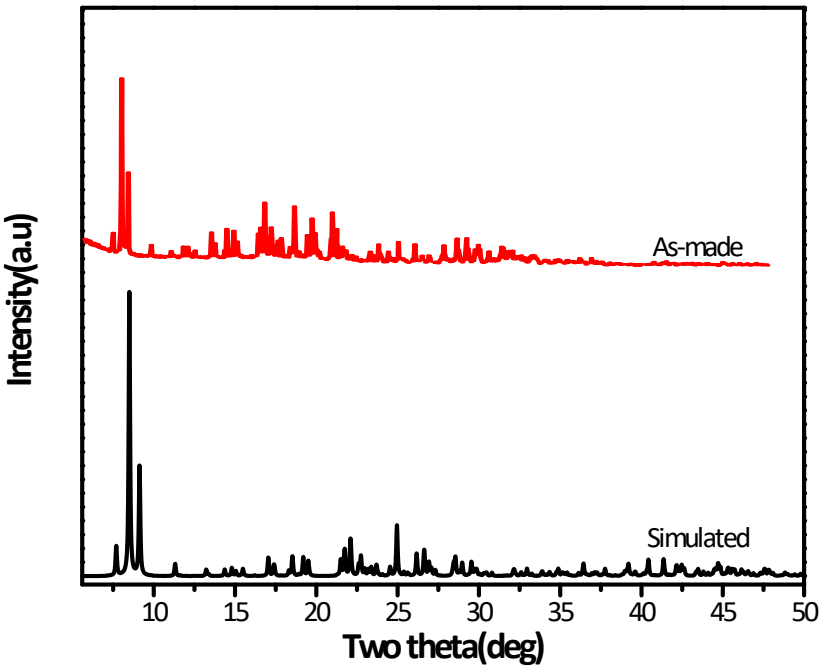

Figure S29 PXRD of complex **3**

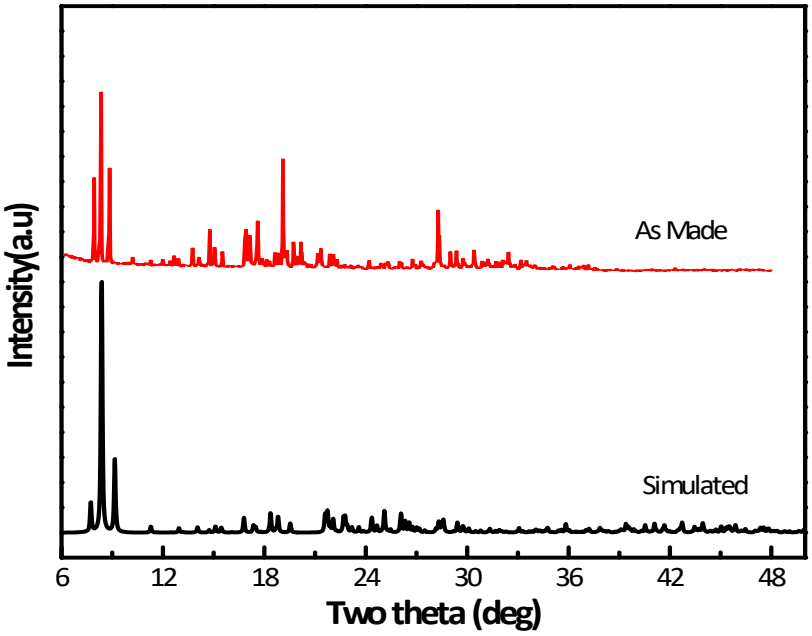

Figure S30. PXRD of Complex **4**

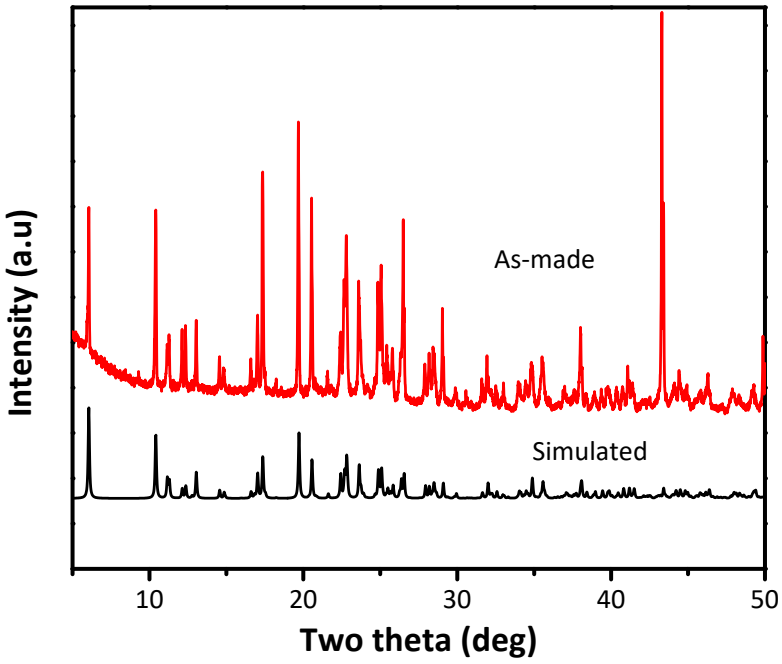

Figure S31 PXRD of Complex **5**

6 Thermogravimetric plots of complexes 1~5

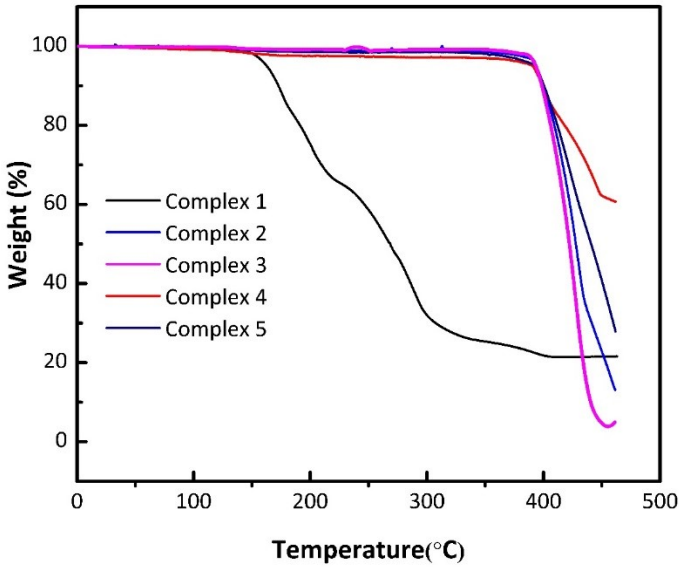

Figure S32 TG plots of Complexes **1-5**

7.UV Absorption Graphes of Complexes 1~5

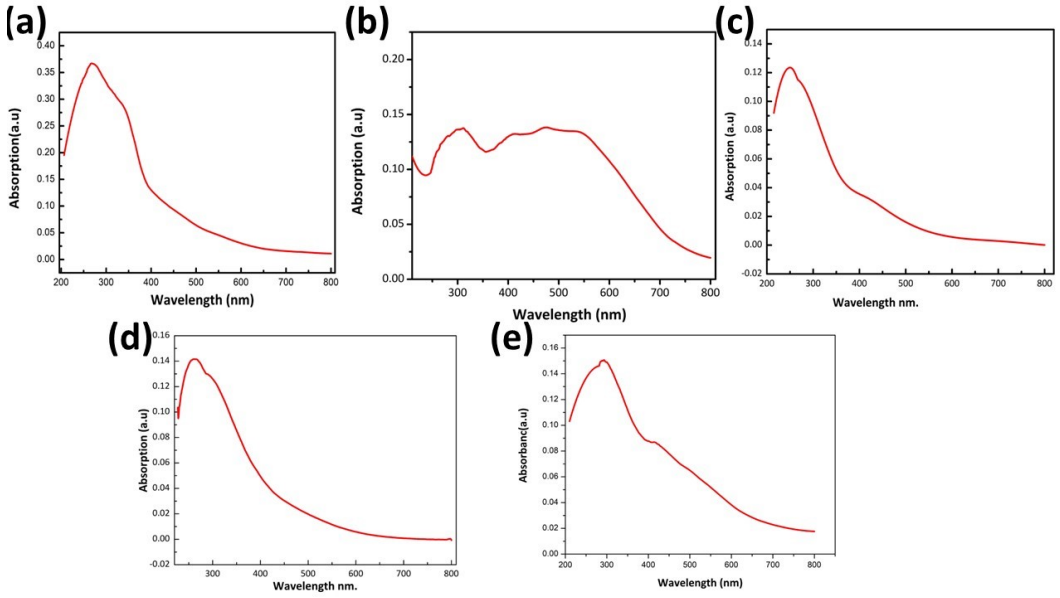

Figure S 33 UV absorbance of complexes **1-5** (a)-(e)

8. Experimatal Band Gaps of complexes 1~5

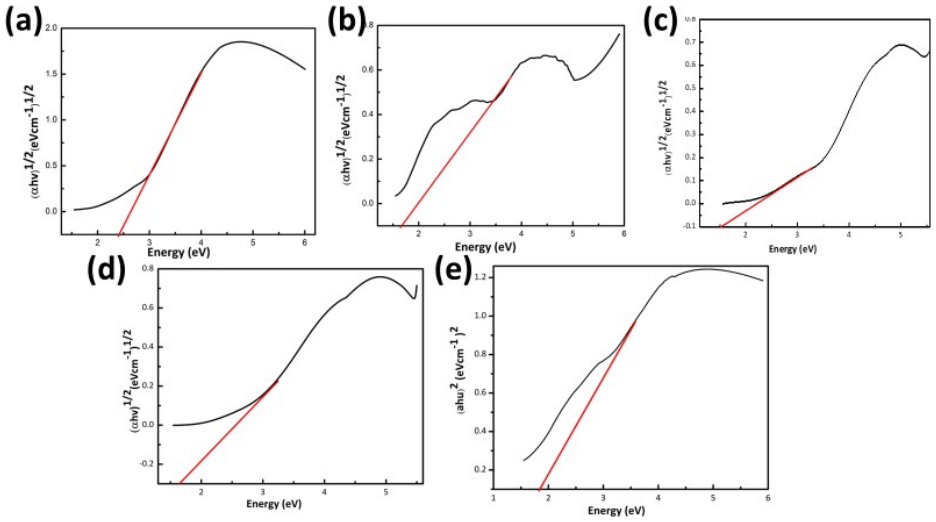

Figure S34 Experimental Band Gaps of **1-5** (a)-(e)

9. Excitation spectra of complexes 1~5

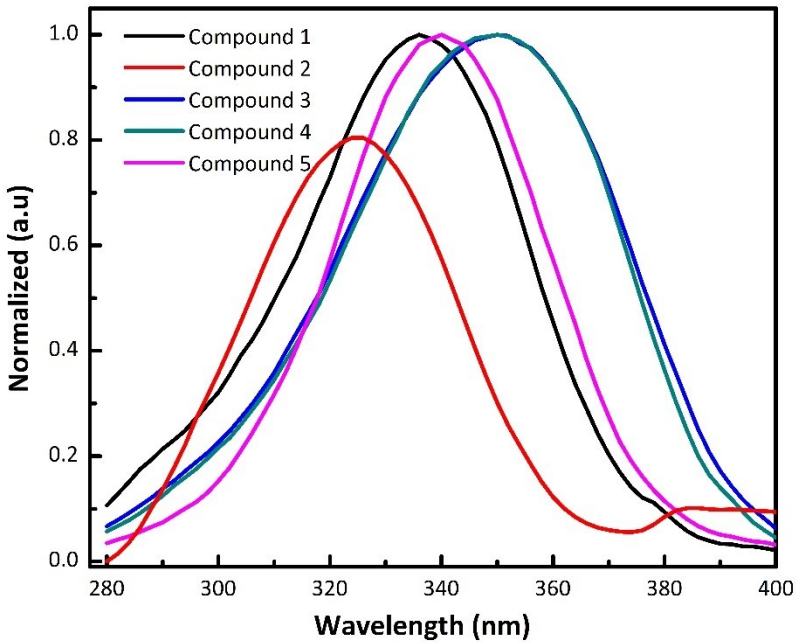

Figure S35 Excitation spectrum of complexes **1~5**

10. Luminescence Decay plots of complexes 1~5

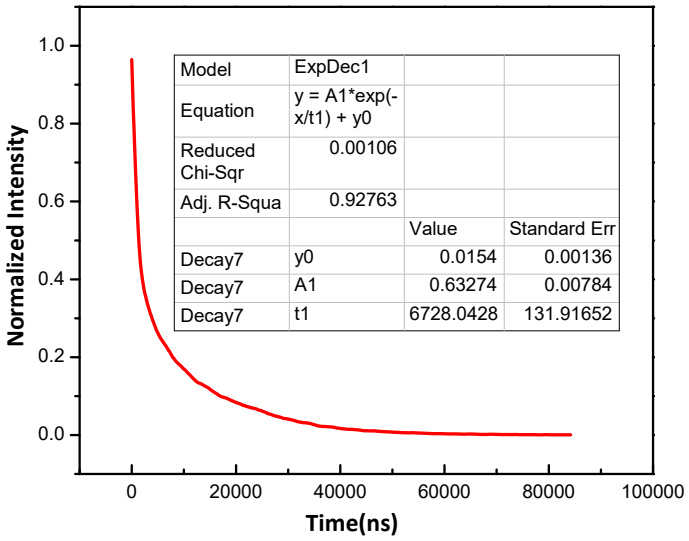

Figure S36 Half-time of Complex **1**

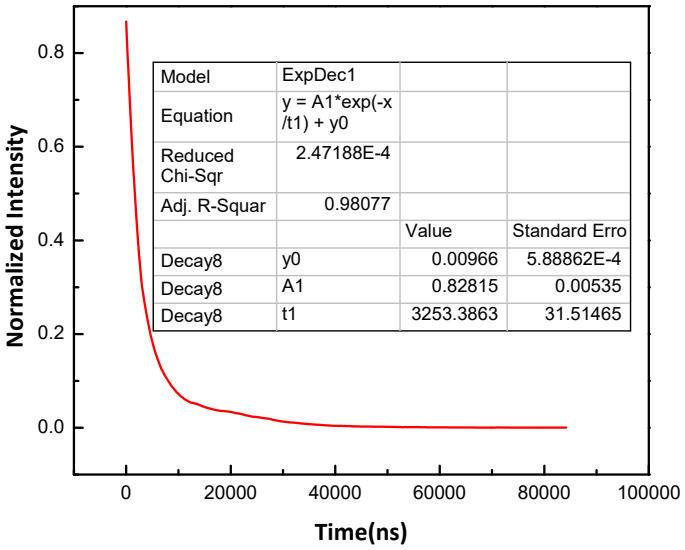

Figure S37 Half time of Complex **2**

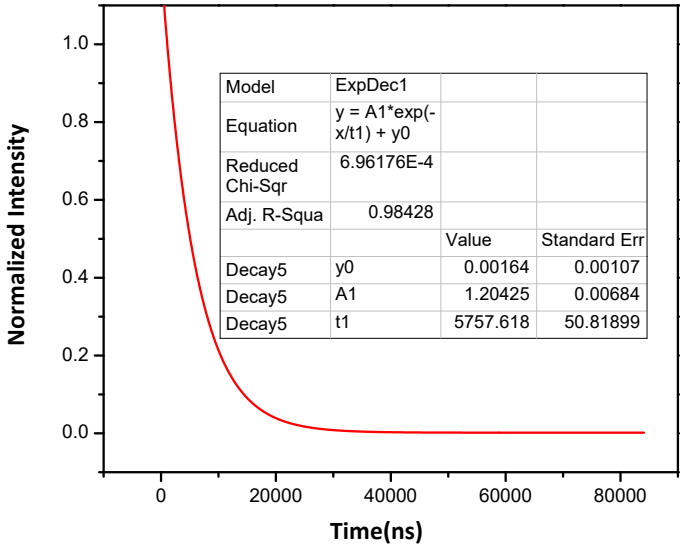

Figure S38 Half-time of Complex **3**

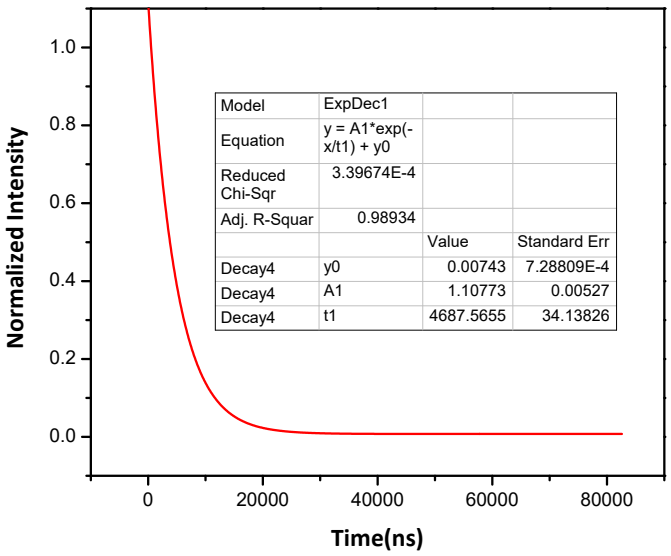

Figure S39 Half-time of Complex **4**

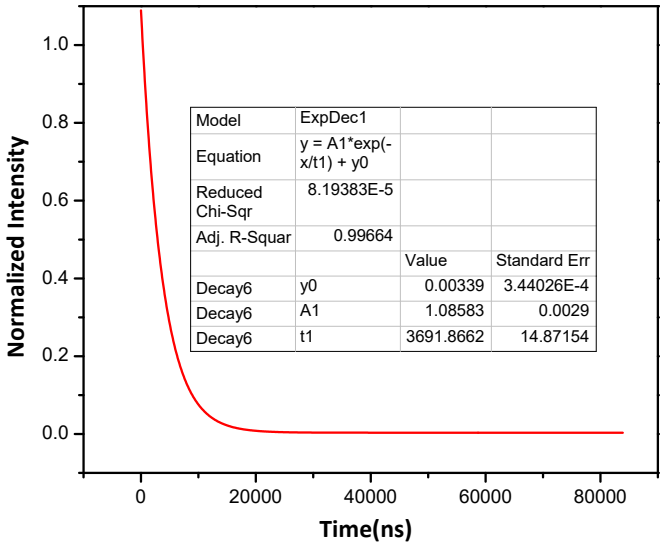

Figure S40 Half-time of Complex **5**

11. Theoretical Band Gap plots of complexes 2~5

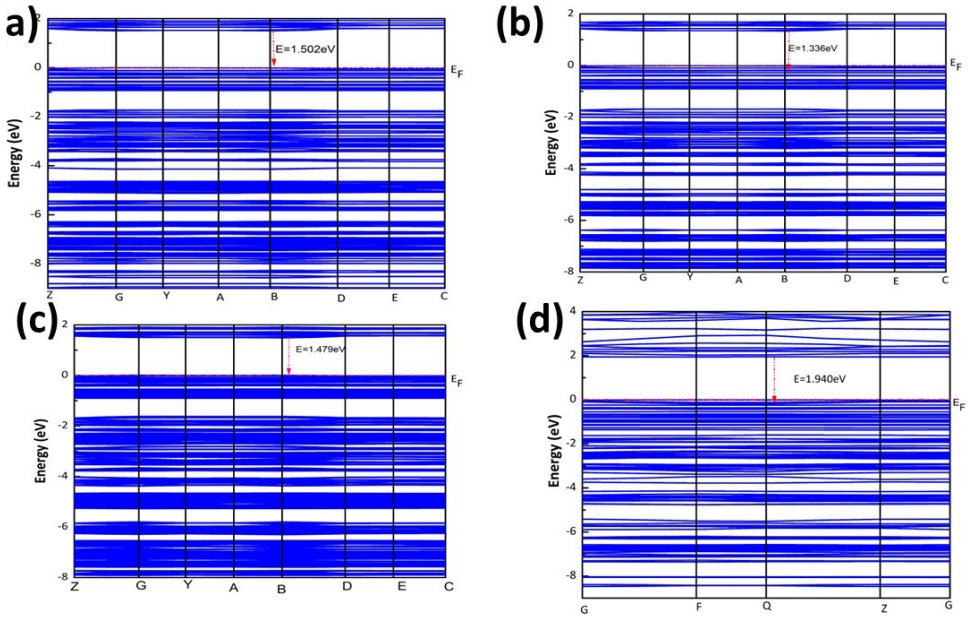

Figure S41 Theoretical Band gap of complexes **2-5** (a)-(d)

Reference

1. V. Satinder Kessar, Paramjit Singh, K. N. Singh, and S. K. Singh, *Chem. Commun.*, 1999, 1927–1928.
2. M. Szostak and J. Aubé, *Chem. Rev.*, 2013, **113**, 5701–5765.
3. G. S. Wilkinson, R. D. Gillard and J. A. McCleverty, 1987.
4. P. Boden, P. Di Martino-Fumo, J. M. Busch, F. R. Rehak, S. Steiger, O. Fuhr, M. Nieger, D. Volz, W. Klopper, S. Brase and M. Gerhards, *Chemistry*, 2021, **27**, 5439-5452.
5. S. L. Li and X. M. Zhang, *Inorg Chem*, 2014, **53**, 8376-8383.
6. P. Boden, P. Di Martino-Fumo, J. M. Busch, F. R. Rehak, S. Steiger, O. Fuhr, M. Nieger, D. Volz, W. Klopper, S. Brase and M. Gerhards, *Chem European J*, 2021, **27**, 5439-5452.
7. T. Nishi, M. Nishikawa, and T. Tsubomura, *European Journal of Inorganic Chemistry*, 2017, DOI: 10.1002/ejic.201601293, 1054-1059.
8. A. Yadav, M. S. Deshmukh and R. Boomishankar, *Journal of Chemical Sciences*, 2017, **129**, 1093-1103.
9 S. S. Devkule and S. S. Chavan, *Transit Met Chem*, 2017, **42**, 347–356.