Four coordination polymers derived from a one-pot reaction and their controlled synthesis

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Experimental section

Materials and methods.

Reagents and solvents were commercially available and used as received without further purification. Elemental analyses of C, H, N were performed on a Perkin-Elmer model 240C Elemental Analyzer. Fourier Transform Infrared (FT-IR) spectra of these complexes and ligands were obtained on a Bruker Vector 22 FT-IR spectrophotometer by using KBr pellets. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer thermal analyzer under nitrogen with a heating rate of 10 °C min^{-1}. Powder X-ray diffraction (PXRD) patterns were collected in the 2θ = 5-50 ° range with a scan speed of 0.1 s deg^{-1} on a Bruker D8 Advance instrument using Cu Kα radiation at room temperature. Solid-state UV-vis diffuse reflectance spectra were obtained at room temperature using Shimadzu UV-3600 double monochromator spectrophotometer, and $BaSO_4$ was used as a 100% reflectance standard for all materials.

Crystal structure determination.

Single crystals of complexes **1-3** were tested on a Bruker SMART APEX CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at

296 K. From the data reduction to the structure determination, the follow procedures were used: the International Tables for X-ray Crystallography,[1] SAINT,[2] SADABS,[3] XPREP,[4] SHELXTL-97 program[5] package. Squeeze refinement was performed for complex **2** using PLATON[6] for its serious disorder, which shows two water molecules in it. The contribution of the solvent molecules has been incorporated in both the empirical formula and formula weight of complex **2**. The crystal and refinement data are collected in Table 1. Selective bond distances and angles are given in Table S1 (Supporting Information).

Synthesis of complex 1-4: 4,4'-dicarboxydiphenyl sulfone (4,4'-sdb) (9 mg, 0.03 mmol) and 1,4-bis((1H-imidazol-1-yl)methyl)benzene (BMB) (7 mg, 0.03 mmol) $Co(NO_3)_2 \cdot 6H_2O$ (9 mg, 0.03 mmol) were dissolved in 2 mL / 2 mL / 2 mL DMF / CH_3CN / H_2O by ultrasonication. The solution was placed in a teflon lined with stainless steel reaction kettle (15 mL) and kept at 95 °C for three days. Until it cooled down to ambient temperature.

The black crystals of **1** were collected in 30% yield (based on BMB ligand). Elemental analysis calcd. for $C_{26}H_{20}CoN_6O_6S$ (**1**): C, 51.70%; H, 3.31%; N, 13.92%. Found: C, 51.75%; H, 3.34%; N, 13.88%. IR(KBr): 3436(w), 3135(w), 1685(s), 1625(s), 1564(w), 1530(w), 1407(s), 1313(w), 1295(m), 1252(s), 1162(m), 1136(w), 1101(m), 1013(w), 853(w), 781(w), 740(m), 695(w), 660(w), 623(m), 503(w), 445(w) (Fig. S6).

The red crystals of **2** were collected in 12% yield (based on BMB ligand). Elemental analysis calcd. for $C_{21}H_{19}CoN_2O_8S$ (**2**): C, 48.60%; H, 3.67%; N, 5.40%. Found: C, 48.49%; H, 3.64%; N, 5.43%. IR(KBr): 3452(m), 3114(w), 2364(w), 1676(m), 1594(m), 1547(s), 1419(s), 1296(w), 1162(m), 1133(w), 1015(m), 1015(w), 947(w), 858(w), 743(s), 695(w), 661(w), 624(m), 578(w), 476(w) (Fig. S7).

The pink crystals of **3** were collected in 19% yield (based on 4,4'-sdb ligand). Elemental analysis calcd. for $C_{63}H_{50}Co_6N_3O_{42}S_4$ (**3**): C, 37.75%; H, 2.50%; N, 2.10%. Found: C, 37.72%; H, 2.53%; N, 2.14%. IR(KBr,): 2357(w), 2334(w), 1671(m), 1607(s), 1562(m), 1401(s), 1289(w), 1162(m), 1135(w), 1103(w), 1013(w), 795(w),

745(m), 693(w), 629(w), 491(w), 449(w) (Fig. S8).

The purple crystals of **4** were collected in 25% yield (based on BMB ligand). Elemental analysis calcd. for $C_{42}H_{42}CoN_{12}$(**4**): C, 65.2%; H, 5.43%; N, 21.73%, Found: C, 65.23%; H, 5.47%; N, 21.72%. IR(KBr): 3446(m), 3139(w), 2359(w), 2338(w), 1629(s), 1604(s), 1562(m), 1397(s), 1379(s), 1354(s), 1316(m), 1294(s), 1242(m), 1155(m), 1099(s), 1013(w), 950(w), 854(w), 744(s), 694(m), 657(w), 621(w), 568(w), 502(w), 474(w), 430(w) (Fig. S9).

Table S1. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1-2**.

Complex **1**			
Co(1)-N(1)	2.055(2)	Co(1)-O(2)	2.153(2)
Co(1)-N(1)#1	2.055(2)	Co(1)-O(1)	2.2009(17)
Co(1)-O(2)#1	2.153(2)	Co(1)-O(1)#1	2.2009(17)
N(1)-Co(1)-N(1)#1	100.03(11)	O(2)#1-Co(1)-O(1)	105.90(7)
N(1)-Co(1)-O(2)#1	151.06(7)	O(2)-Co(1)-O(1)	59.81(6)
N(1)#1-Co(1)-O(2)#1	93.46(8)	N(1)-Co(1)-O(1)#1	92.65(7)
N(1)#1-Co(1)-O(2)	151.06(7)	N(1)#1-Co(1)-O(1)#1	98.97(7)
O(2)#1-Co(1)-O(2)	86.58(11)	O(2)#1-Co(1)-O(1)#1	59.81(6)
N(1)-Co(1)-O(1)	98.97(7)	O(2)-Co(1)-O(1)#1	105.90(7)
N(1)#1-Co(1)-O(1)	92.65(7)	O(1)-Co(1)-O(1)#1	161.91(10)
N(1)-Co(1)-O(2)	93.46(8)		
Complex **2**			
Co(1)-O(5)#1	2.0330(13)	Co(1)-O(6)#3	2.0507(13)
Co(1)-O(7)#2	2.0330(13)	Co(1)-O(4)	2.1001(13)
Co(1)-N(1)	2.0337(15)	Co(1)-Co(1)#1	2.8706(5)
O(5)-Co(1)#1	2.0330(13)	O(6)-Co(1)#4	2.0507(13)

O(7)-Co(1)#2	2.0330(13)	O(5)#1-Co(1)-O(7)#2	92.82(5)
O(5)#1-Co(1)-N(1)	105.52(6)	O(7)#2-Co(1)-O(6)#3	162.34(6)
O(7)#2-Co(1)-N(1)	102.77(6)	N(1)-Co(1)-O(6)#3	94.28(6)
O(5)#1-Co(1)-O(6)#3	86.91(5)	O(5)#1-Co(1)-O(4)	162.13(6)
O(7)#2-Co(1)-O(4)	86.65(5)	O(7)#2-Co(1)-Co(1)#1	81.31(4)
N(1)-Co(1)-O(4)	91.99(6)	N(1)-Co(1)-Co(1)#1	160.80(4)
O(6)#3-Co(1)-O(4)	88.25(6)	O(6)#3-Co(1)-Co(1)#1	81.07(4)
O(5)#1-Co(1)-Co(1)#1	92.88(4)	O(4)-Co(1)-Co(1)#1	69.36(4)

Symmetry codes: for **1**: #1 = -*x* + 1/2, *y* +,-*z* + 1/2; for **2**: #1 = -*x* + 1, -*y* + 1, -*z* + 1; #2 = -*x* + 1, -*y* + 1, -*z*; #3 = *x*, *y*, *z* + 1; #4 = *x*, *y*, *z* - 1; #5 = -*x* - 1,-*y*, -*z* + 1;

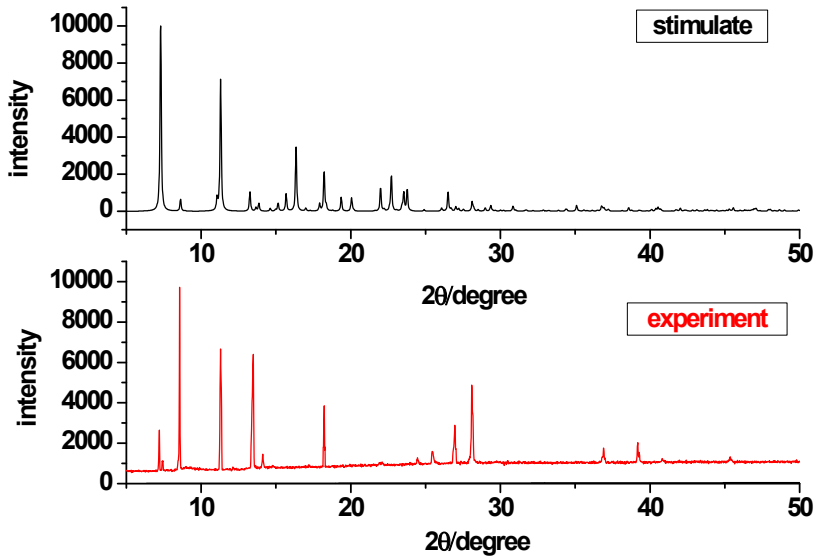

Fig. S1 Powder X-ray diffraction patterns of complex **1**

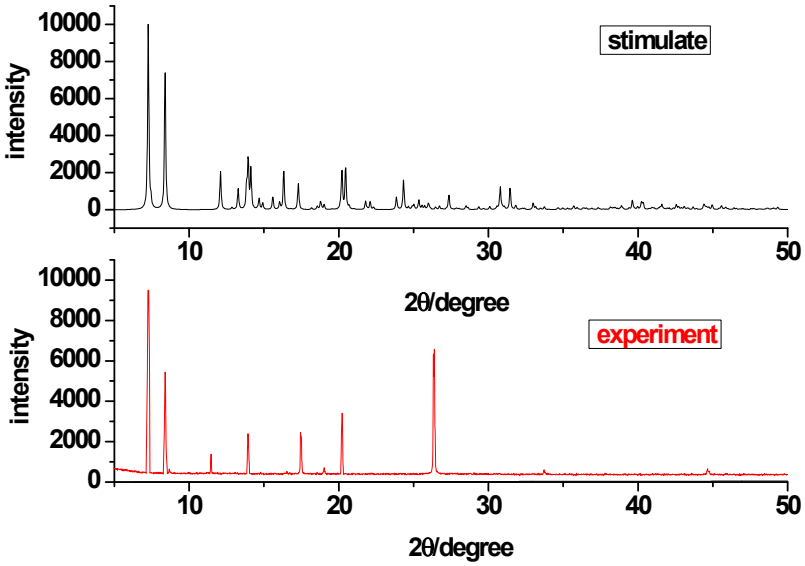

Fig. S2 Powder X-ray diffraction patterns of complex **2**

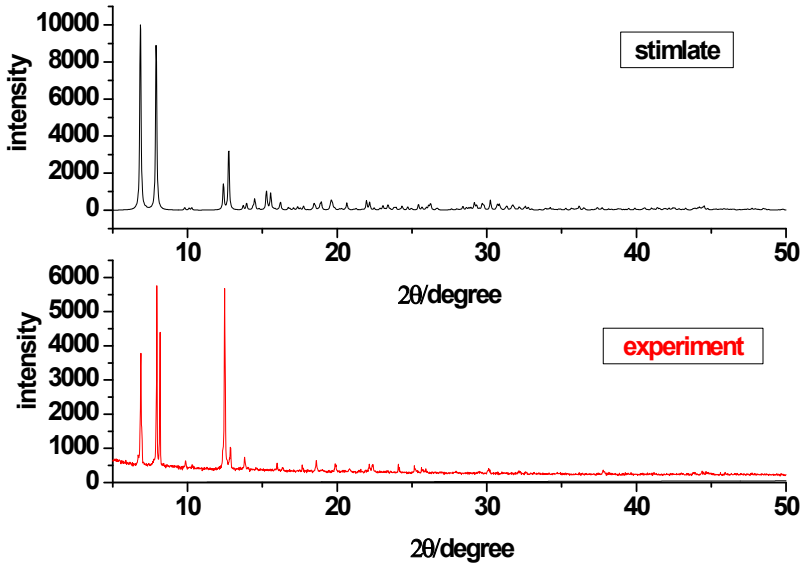

Fig. S3 Powder X-ray diffraction patterns of complex **3**

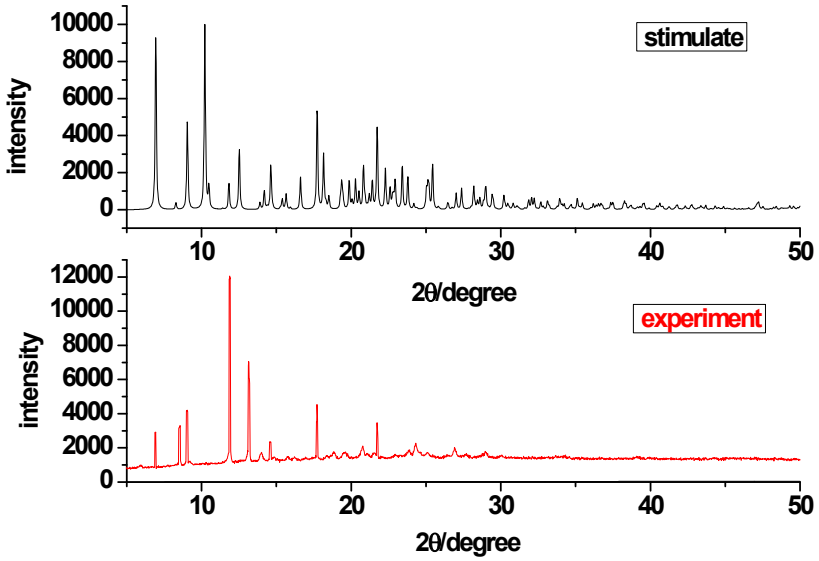

Fig. S4 Powder X-ray diffraction patterns of complex **4**

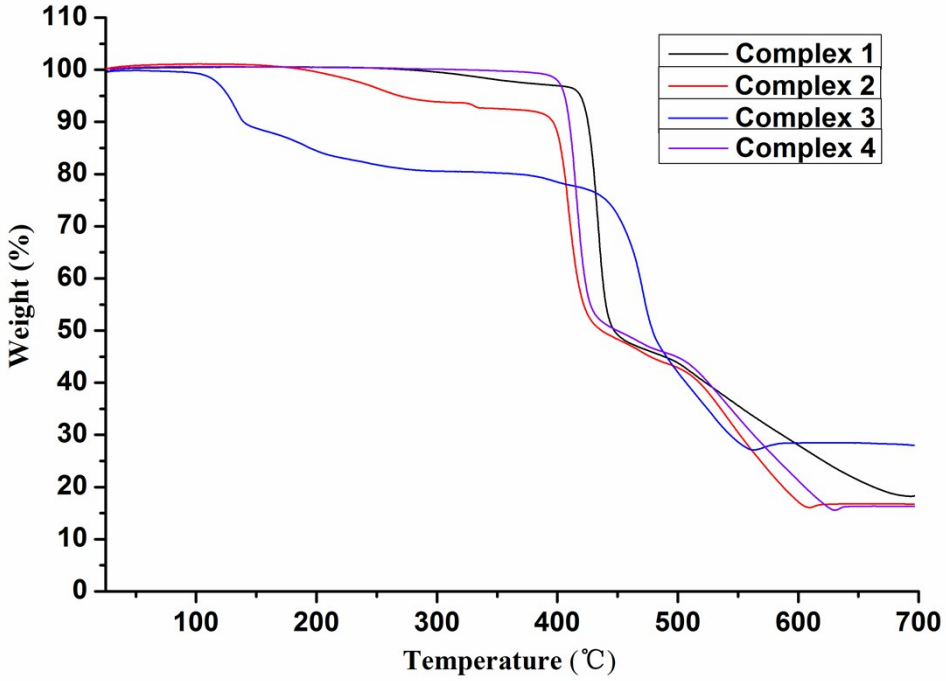

Fig. S5 The TGA diagrams of complexes **1-4.**

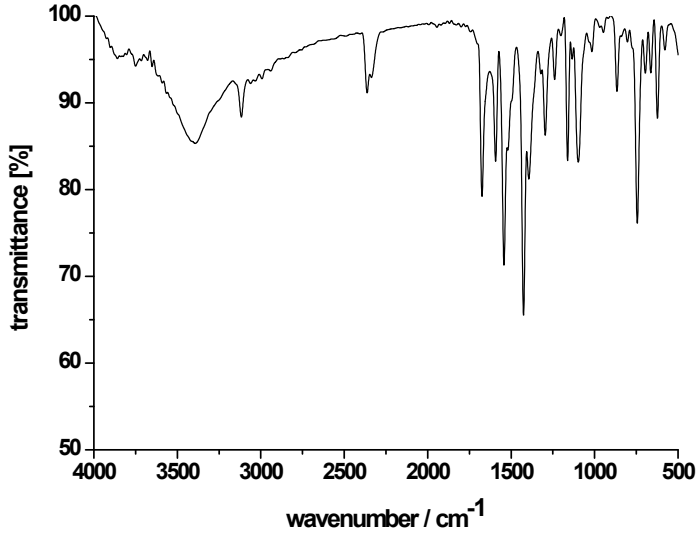

Fig. S6 IR spectra of complex **1**

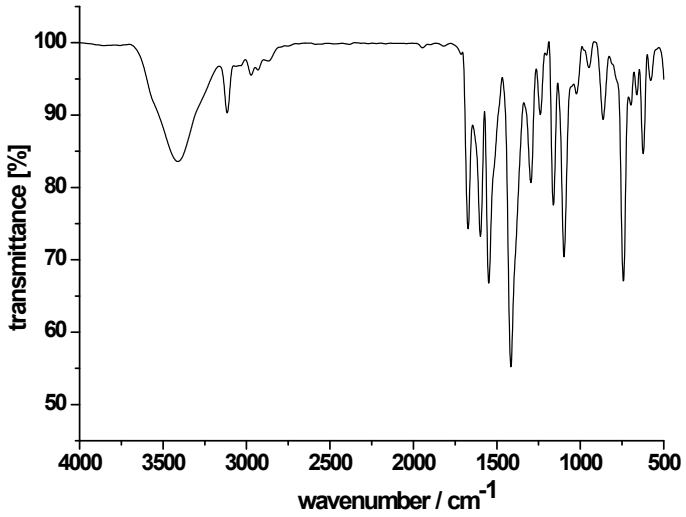

Fig. S7 IR spectra of complex **2**

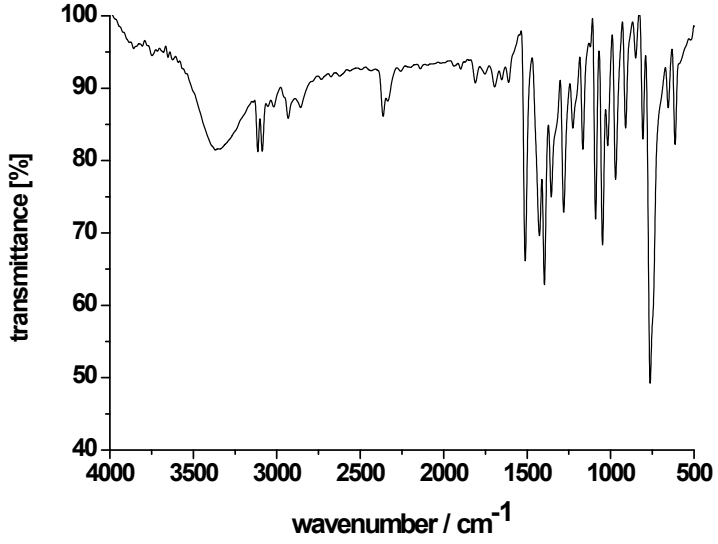

Fig. S8 IR spectra of complex **3**

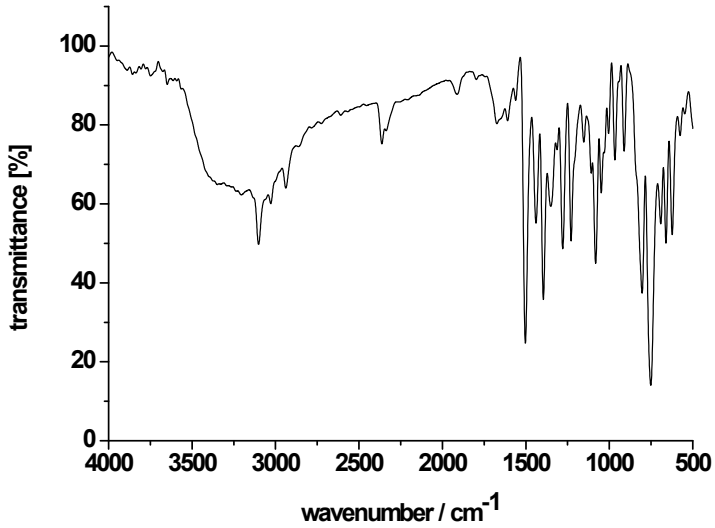

Fig. S9 IR spectra of complex **4**

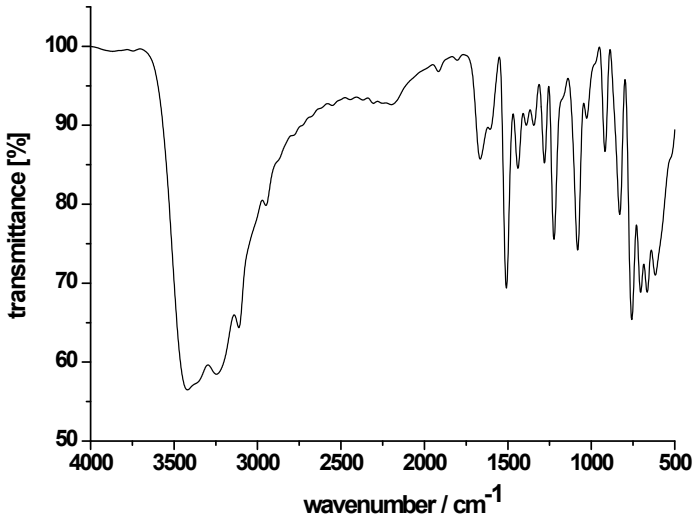

Fig. S10 IR spectra of BMB ligand

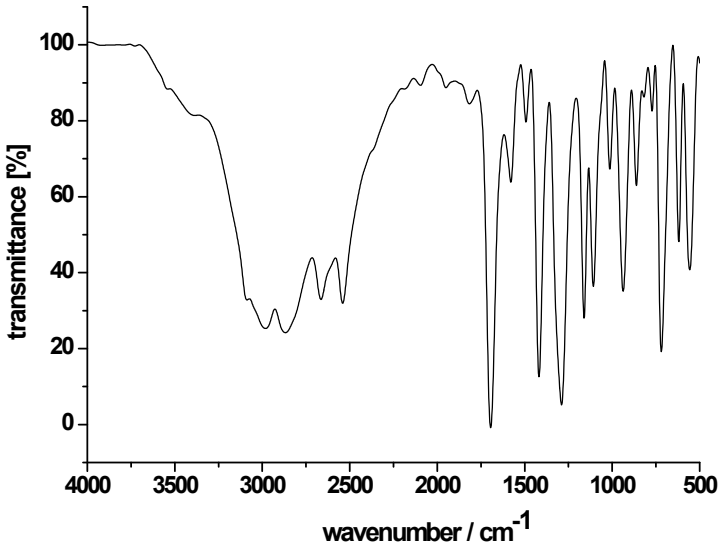

Fig. S11 IR spectra of 4,4'-sdb ligand

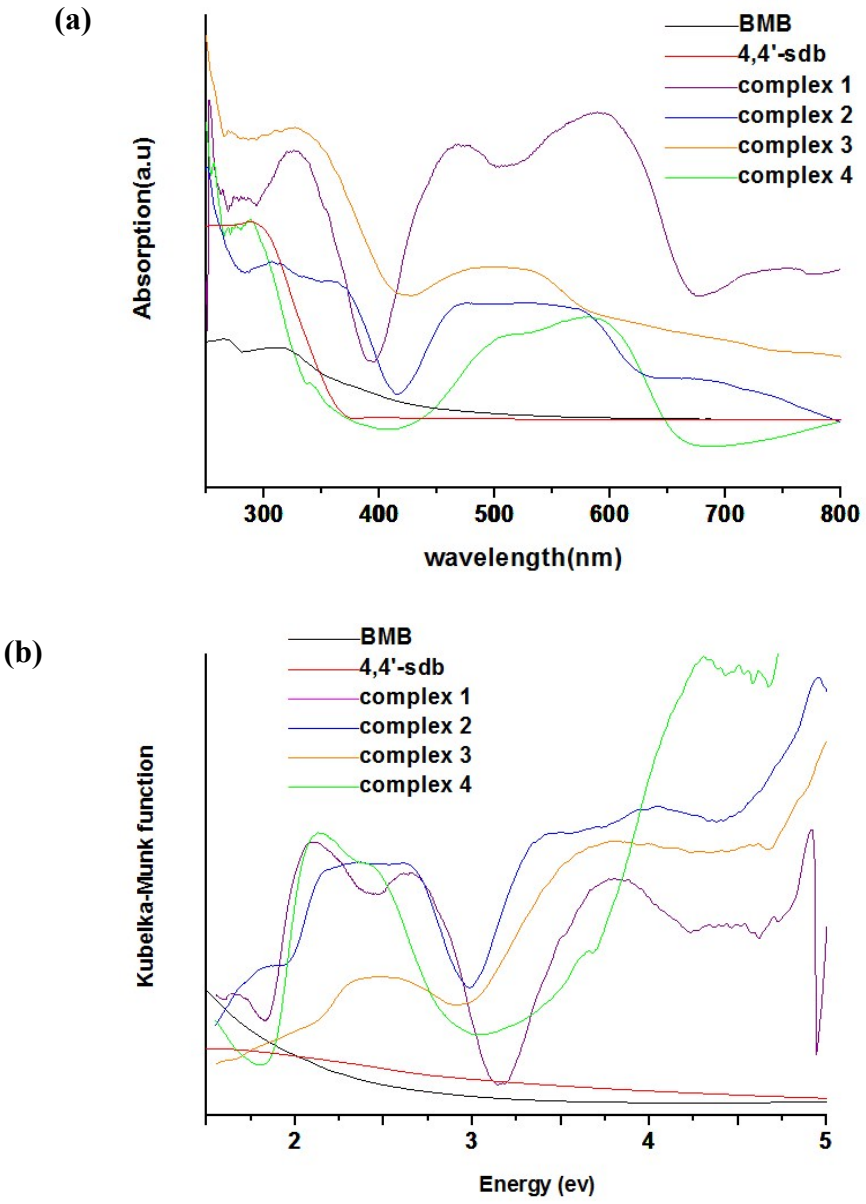

Fig. S12 (a) UV-vis absorbance spectra and (b) Plot of Kubelka-Munk as a function of energy of complexes **1-4** and corresponding ligands BMB, 4,4'-sdb at room temperature.

Table S2 Summary of the product isolated in different solvent systems at 95 °C.

Solvent / Ratio	DMF/H_2O	DMF/CH_3CN	Solvent / Ratio	DMF/ CH_3CN / H_2O
0/6	powder	powder	0/3/3	powder
1/5	[powder crystal] trace + impurities	powder	1/3/2	[1+2+3] many + impurities
2/4	[powder crystal] few + impurities	powder	1/2/3	[1+3] trace + [2] few
3/3	[powder crystal] many	powder	1/1/4	[2] trace+ [4] few
4/2	[powder crystal] many	powder	2/3/1	[1+3+4] few
5/1	[powder crystal] trace	powder	2/2/2	[1+3+4] many+ [2] few
6/0	clear solution	clear solution	2/1/3	[3] many + [1+2+4] trace
			3/2/1	[1+3] few
			3/1/2	[1] few + [3] trace
			4/1/1	[1] trace
			1/1.5/3.5	[2] few
			1/0.5/4.5	[4] few
			2/0.5/3.5	[3] few
			3/0.5/2.5	[1] few

References

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