A Structurally versatile coordination polymer: demonstrating spontaneous resolution, conformational polymorphism and gel formation

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SI 1

Experimental Section

Chemicals: All the chemicals were obtained from Aldrich and used as received. Solvents were used without purifications or drying. *O, O*-bis-cyanophenoxy benzonitrile (*O, O*-CPBN) was synthesized following the literature procedure.[1]

Synthesis of Ag(I)-O, O-CPBN coordination polymer (1-7): $Ag(I)CF_3SO_3$ (102 mg, 0.4 millimoles) and *O, O*-CPBN (88 mg. 0.4 millimoles) were dissolved separately in hot toluene (5 ml each) and brought to room temperature before the solutions mixed together. On standing needle-shaped single crystals of **1** were formed after 12 h (yield = 95%). Recrystallization of **1** (dissolving under hot conditions, but with crystal formation at room temperature) or repeating the procedure using ethyl acetate produced crystals of **2** (yield = 95%). The addition of toluene solutions of $Ag(I)CF_3SO_3$ (102 mg, 0.4 millimoles, 5 ml) and *O, O*-CPBN (176 mg, 0.8 millimoles, 5 ml) at room temperature produced coordination polymer gel (**3**) after standing for 20 h. **3** slowly transformed into single crystals of **4** on standing at room temperature for more than two weeks (yield = 50%).

SI 2

Characterization:

X-ray diffraction: PXRD measurements were recorded using a Siemens diffraktometer-D500 at room temperature. Single crystals were carefully chosen after they were viewed through a polarizing microscope. The crystals were glued to a thin glass fibre using an adhesive (cyano acrylate) and mounted on a diffractometer equipped with an Bruker SMART APEX CCD area detector (O, O-CPBN, 1, 2, 5, 6) and Rigaku Saturn-724 HG CCD detector (4 and 6. The data collections were carried out at 150K and no extraordinary methods were employed, except that the crystals were smeared in NIH immersion oil to protect them from ambient laboratory conditions. The intensity data were processed using Bruker's suite of data processing programs (SAINT), and absorption corrections were applied using SADABS.[2] The

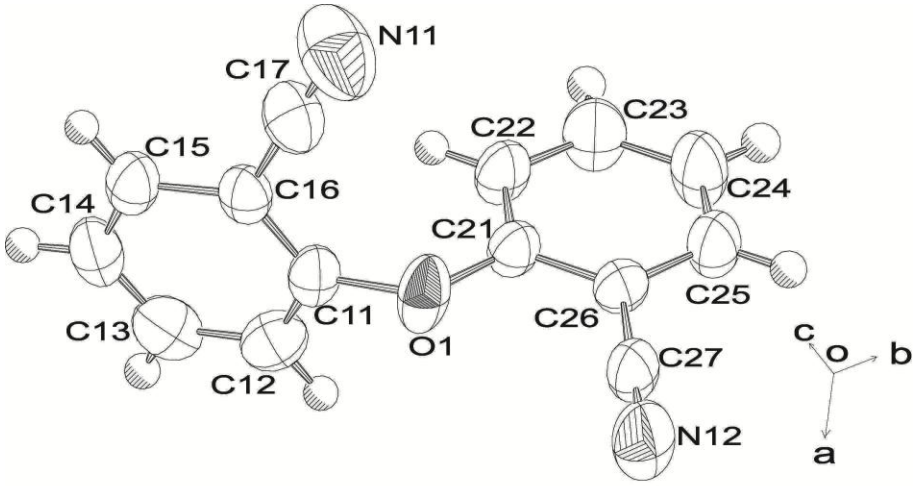
structure solution of all the complexes was carried out by direct methods, and refinements were performed by full-matrix least-squares on F^2 using the SHELXTL-PLUS[2] suite of programs. All the structures converged to good *R* factors. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were fixed on calculated positions using appropriate HFIX options in Shelxtl and were refined isotropically. Intermolecular interactions were computed using the PLATON program.[3]

TGA was carried out using Perkin-Elmer Pyris 1 TG analyzer and the experiments were carried out in an inert atmosphere with a heating rate of 10 ^{o}C/min. IR spectra were recorded on a Perkin-Elmer spectrometer with ATS Sampling Accessory. The morphology of coordination polymer gel was examined using field emission scanning electron microscopy (FE-SEM, Hitachi S-4300) at acceleration voltage at 5 kV. Prior to analysis, the samples were coated with a thin layer of gold. CD was carried out using Jasco-J815 CD spectrometer by spreading the crystalline sample on glass plate.

SI 3 Crystallographic table ***O, O*-CPBN**, **1**, **2** and **4**

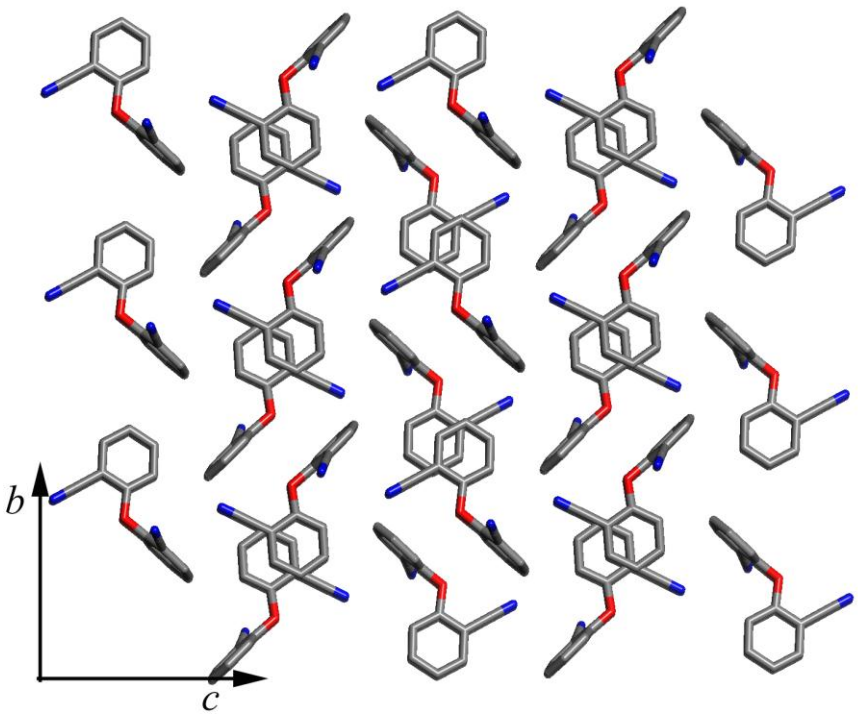
	***O, O*-CPBN**	**1**	**2**	**4**
CCDC No.	895074	895068	895069	895070
Formula	$C_{14}H_8N_2O$	$C_{15}H_8AgF_3N_2O_4S$	$C_{15}H_8AgF_3N_2O_4S$	$C_{59}H_{34}Ag_3F_9N_8O_{15}S_3$
Size (mm^3)	0.23 × 0.17 × 0.02	0.15 × 0.10 × 0.05	0.23 × 0.12 × 0.08	0.23 × 0.19 × 0.16
F. W.	220.22	477.16	477.16	1683.72
Crys. Sys.	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	P2(1)/c	C222(1)	P2(1)/n	P-1
a [Å]	7.9698(17)	5.1665(10)	11.093(4)	14.125(3)
b [Å]	9.389(2)	18.453(4)	12.530(4)	15.669(3)
c [Å]	15.464(3)	18.155(3)	12.330(4)	16.371(3)
α[°]	90	90	90	75.12(3)
β[°]	92.310(5)	90	91.45(3)	71.49(3)
γ[°]	90	90	90	81.75(3)
V [$Å^3$]	1156.3(4)	1730.8(6)	1710.5(9)	3313.0(11)
Z	4	4	4	2
$D_{calculd.}$[g/cm^3]	1.265	1.831	1.853	1.688
μ [mm^{-1}]	0.082	1.339	1.355	1.067
F(000)	456	936	936	1664
θ range [°.]	2.56 to 25.65	2.21 to 24.97°.	2.32 to 25.05	1.35 to 25.00
Refls. Colled.	12578	4900	17879	50889
R_{int}	0.0362	0.0241	0.0258	0.0603
Indept. Refls.	2181	1510	3023	11531
GOF on F^2	1.080	1.034	1.079	1.004
Final *R*	0.0548	0.0667	0.0272	0.0552
Final *R*w	0.1436	0.1935	0.0720	0.1622

(a)



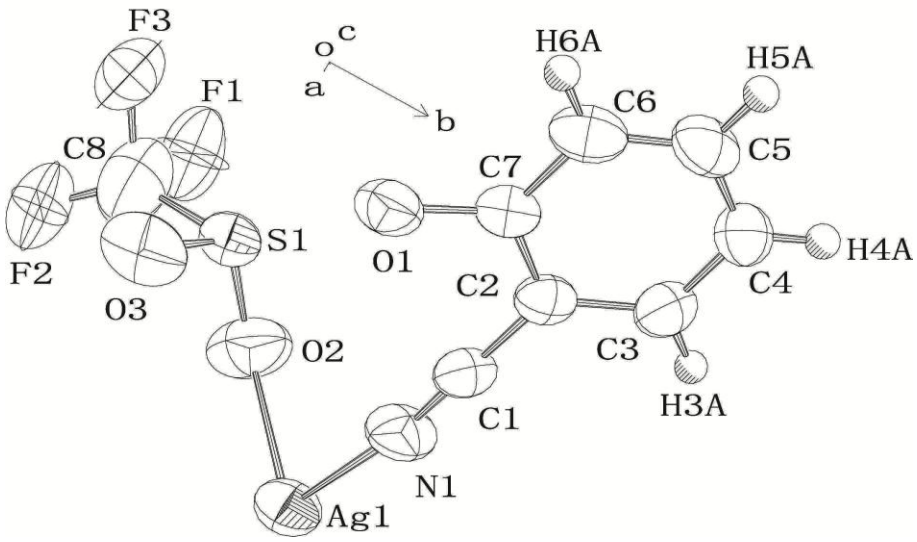
SI 4a. Ortep representation of asymmetric unit of ***O, O*-CPBN**

(b)



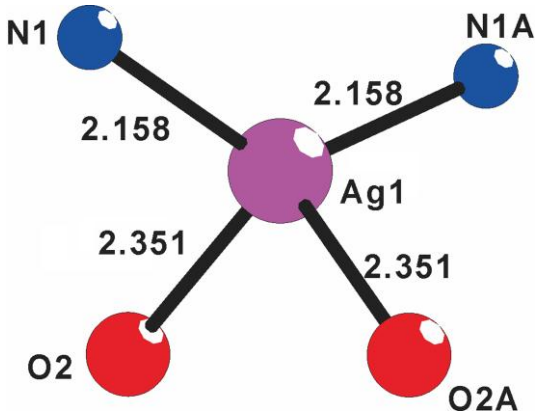
SI 4b. Crystal packing of ***O, O*-CPBN**

(a)



SI 5a. Ortep representation of asymmetric unit of **1**.

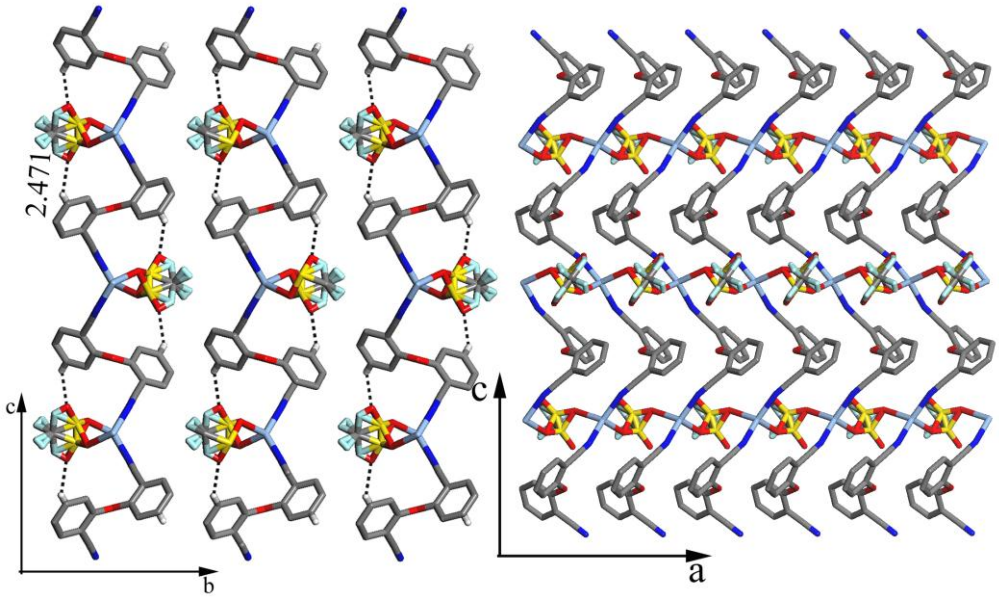
(b)



	N_1-Ag_1-O_2	O_2-Ag_1-O_2	N_1-Ag_1-N_1
Bond angles (°)	99.795	98.344	127.501

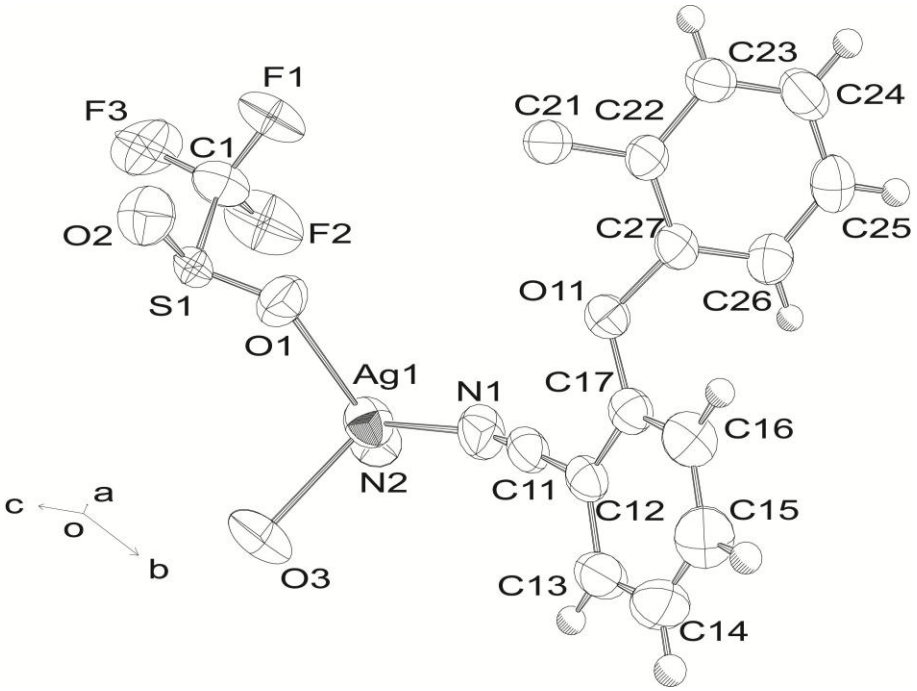
SI 5b. Ag(I) coordination bond lengths and bond angles of **1**.

(c)



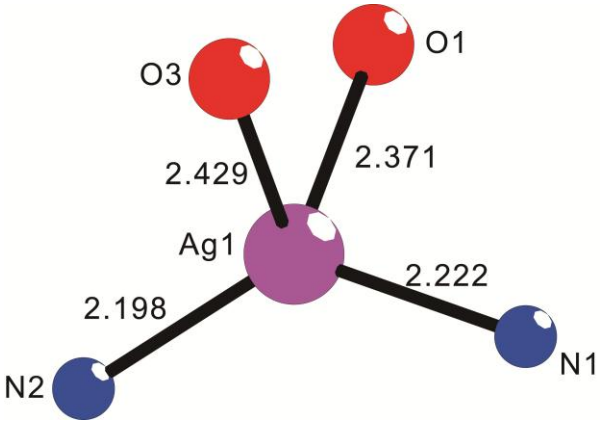
SI 5c. Crystal packing of **1.**

(a)



SI 6a. Ortep representation of asymmetric unit of **2**.

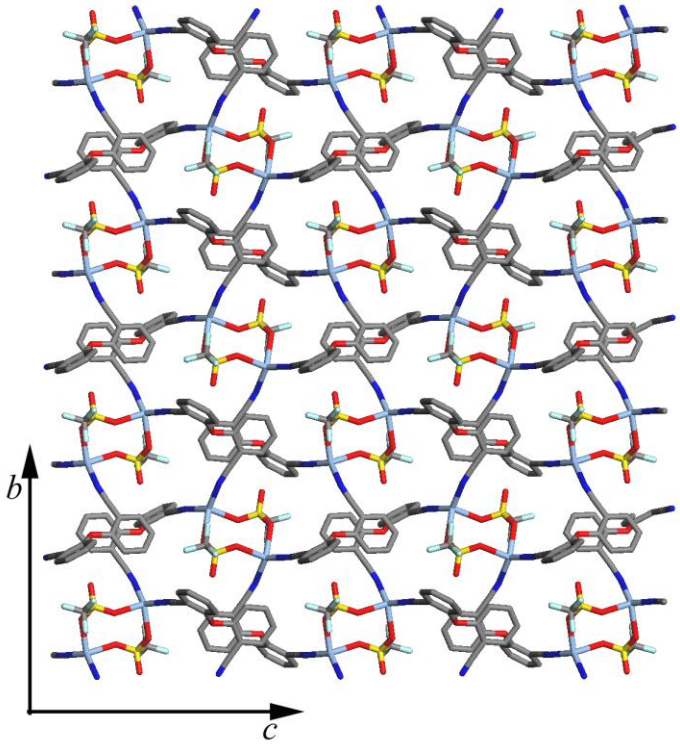
(b)



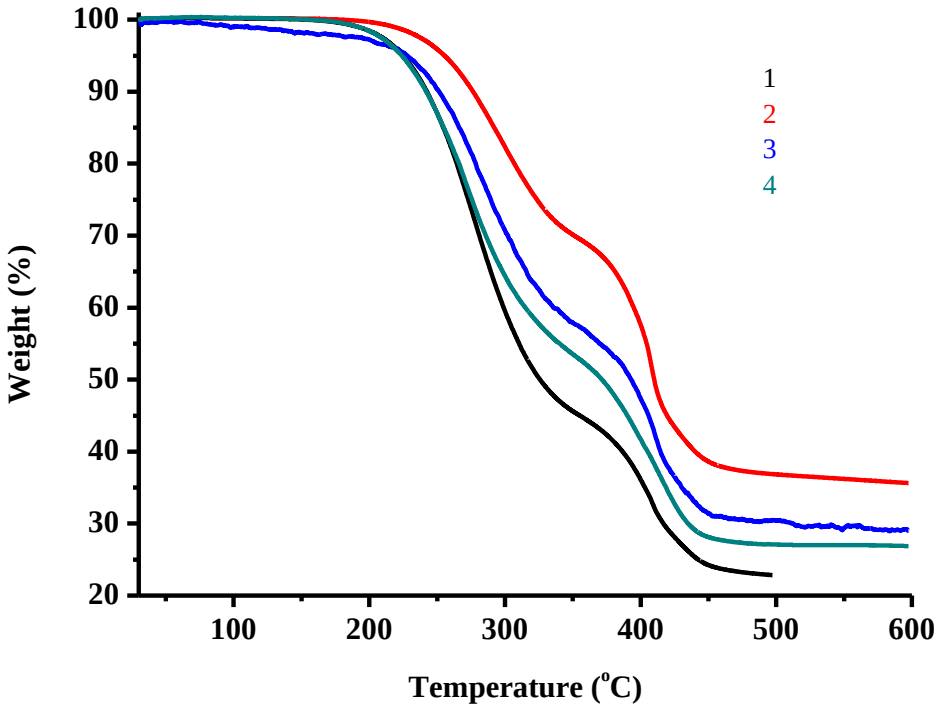
	N_1-Ag_1-O_1	O_1-Ag_1-N_2	N_1-Ag_1-N_2	O_1-Ag_1-O_3	N_1-Ag_1-O_3	N_2-Ag_1-O_3
Bond angles (°)	98.448	122.325	129.295	91.115	101.089	106.59

SI 6b. Ag(I) coordination bond length and bond angles of **2**.

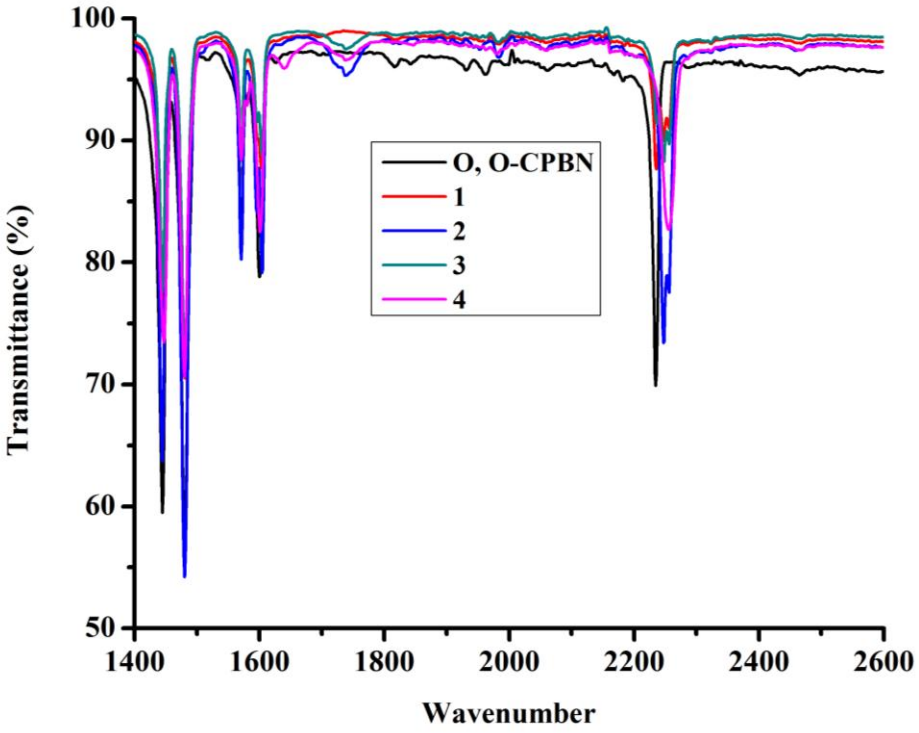
(c)



SI 6c. Crystal packing of **2.**

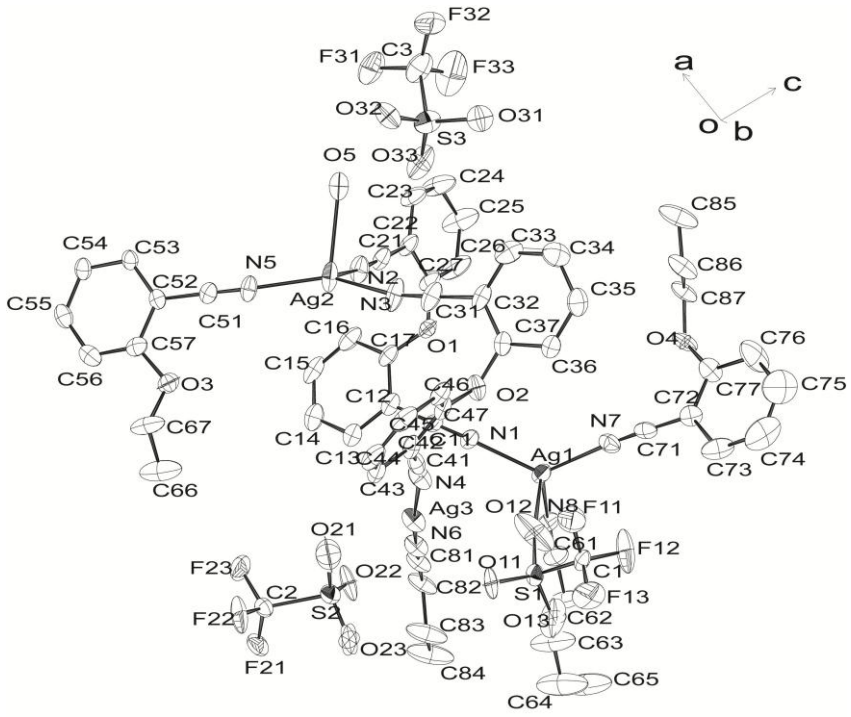


SI 7. Thermo-gravimetric analysis of **1-4**



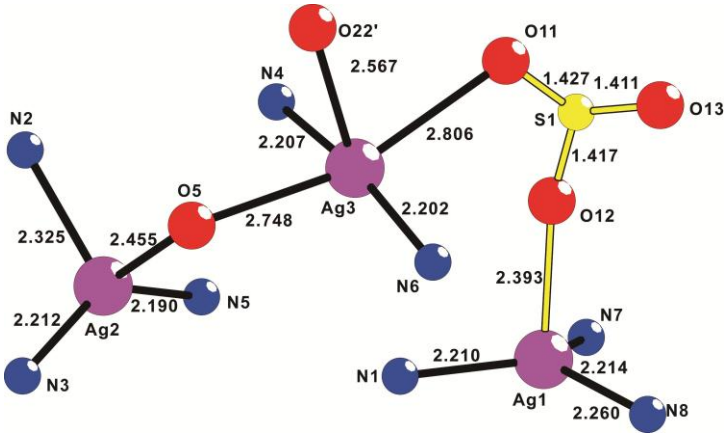
SI 8. IR spectra of **1-4**

(a)



SI 9a. Ortep representation of asymmetric unit of **4**.

(b)



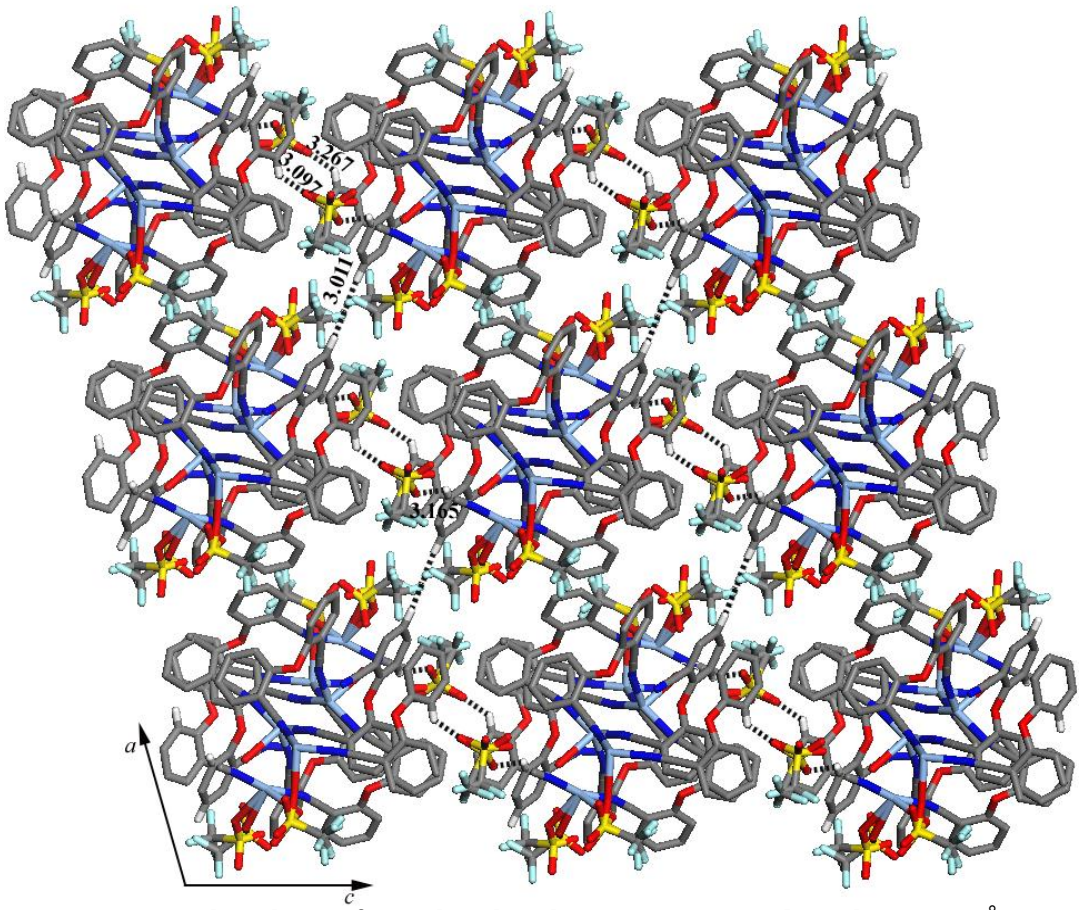
	N_1-Ag_1-N_7	N_1-Ag_1-N_8	N_8-Ag_1-N_7	N_1-Ag_1-O_{12}	N_7-Ag_1-O_{12}	N_8-Ag_1-O_{12}
Bond angles (°)	122.815	116.259	117.457	106.205	97.035	84.197

	N_2-Ag_2-N_3	N_3-Ag_2-N_5	N_5-Ag_2-N_2	N_2-Ag_2-O_5	N_3-Ag_2-O_5	N_5-Ag_2-O_5
Bond angles (°)	107.292	138.823	109.546	90.397	93.236	104.087

	O_5-Ag_3-N_6	N_6-Ag_3-O_{11}	O_{11}-Ag_3-N_4	N_4-Ag_3-O_5	O_{22}-Ag_3-N_4	O_{22}-Ag_3-O_5	O_{22}-Ag_3-N_6	O_{22}-Ag_3-O_{11}
Bond angles (°)	94.20	95.08	89.60	84.79	88.06	92.72	103.66	78.24

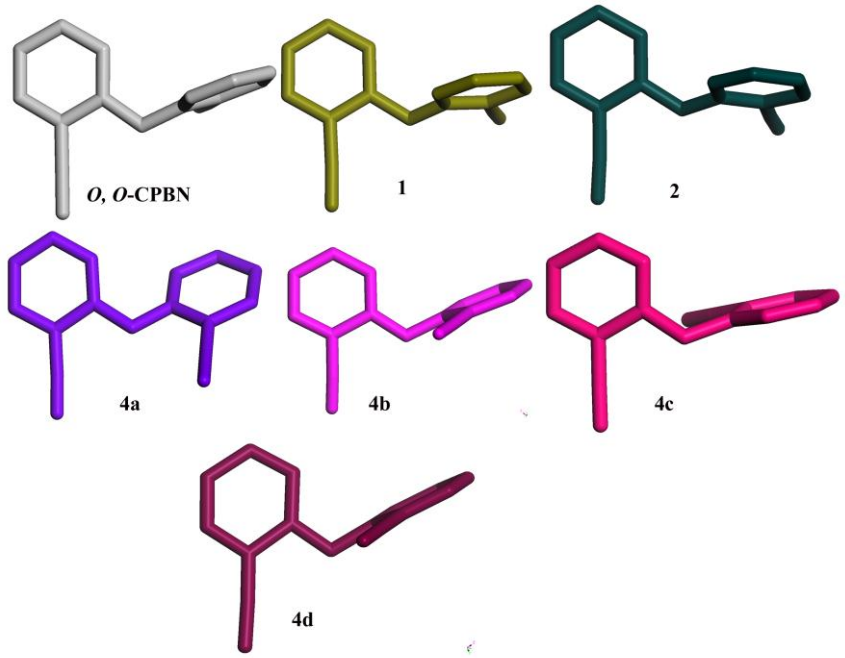
SI 9b. Ag1(I) coordination bond length and bond angles of **4**.

(c)



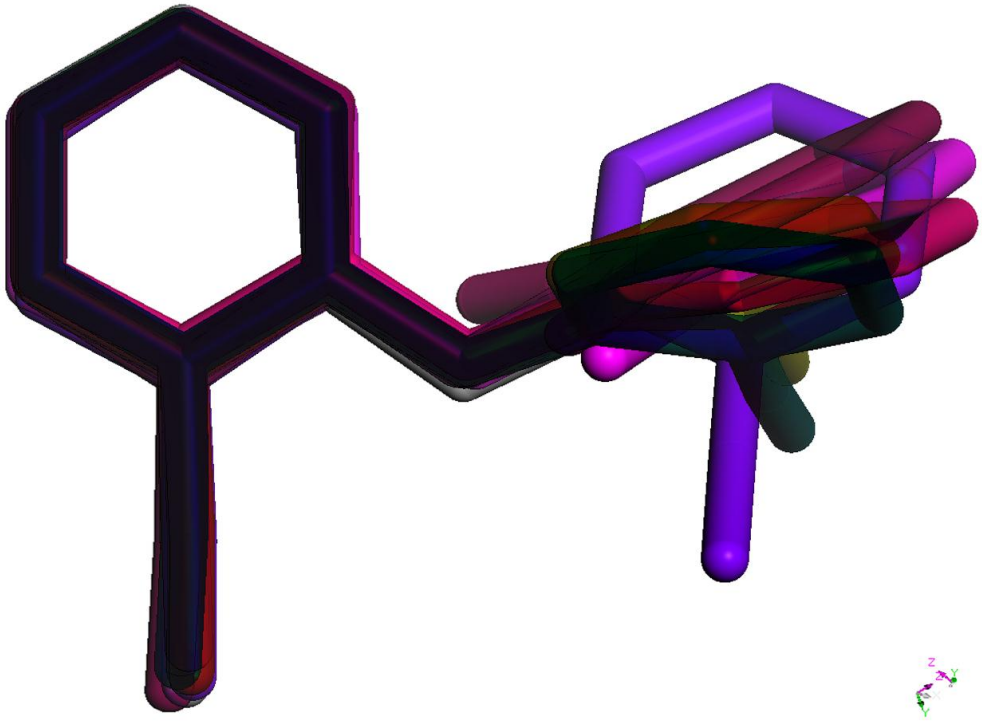
SI 9c. Crystal packing of **4** with H-bonding interactions; $d_{D\cdots A}$ distances (Å) are marked.

(a)



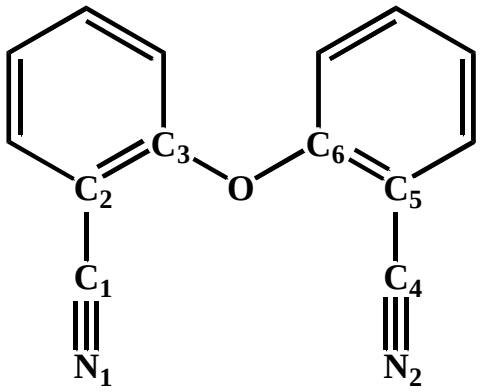
SI 10a. Different conformation displayed by *O, O*-CPBN in the crystal structure of *O, O*-CPBN and **1, 2, 4-7.** and **4-7**.

(b)



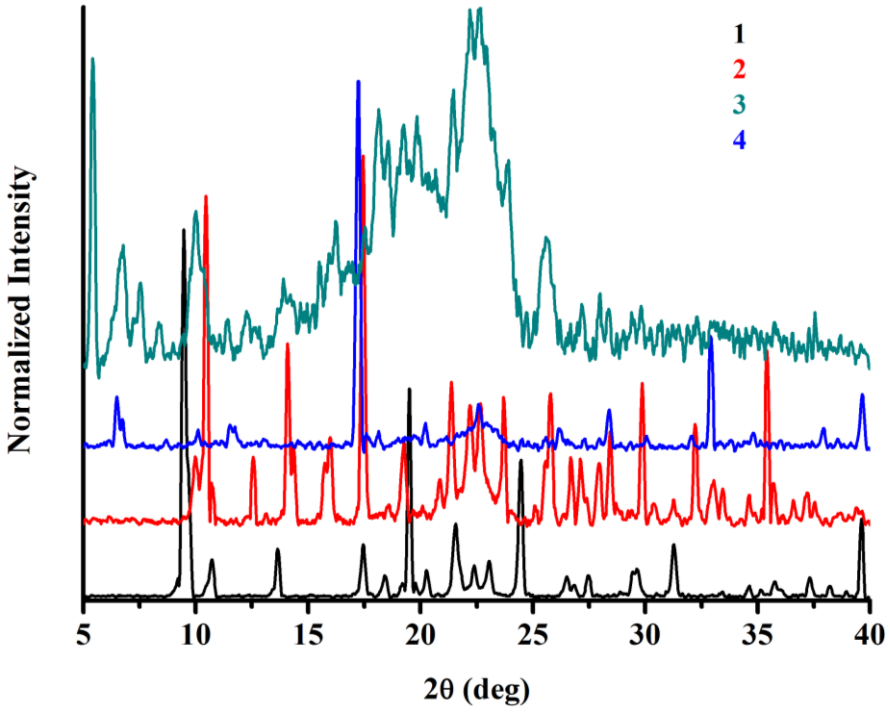
SI 10 b. Superimposing different conformation of *O, O*-CPBN in the crystal lattice of *O, O*-CPBN, 1, 2 and 4.

(c)

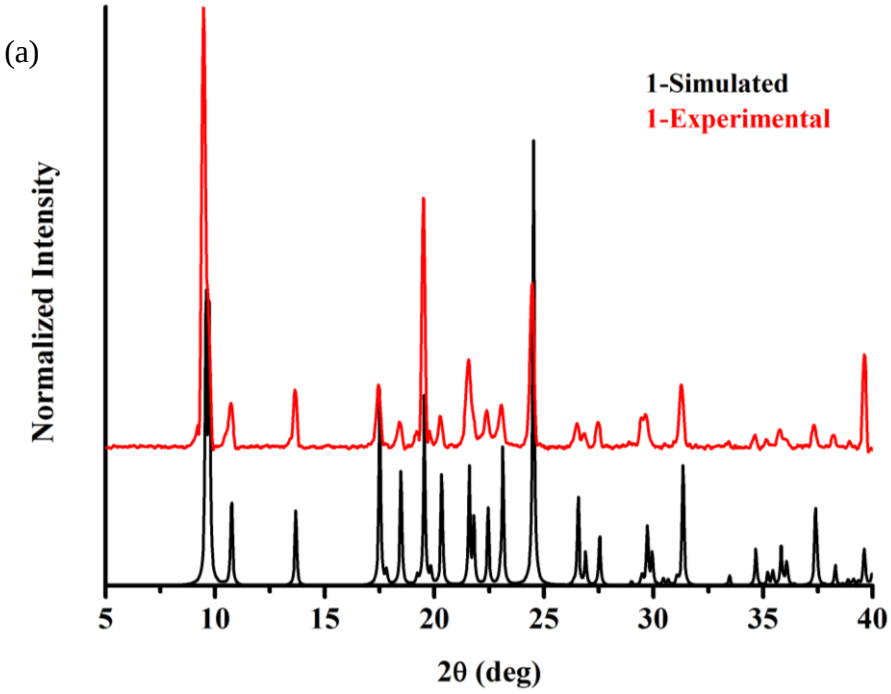


Compounds		τ_1 (°, C_1-C_2-C_3-O)	τ_1 (°, C_4-C_5-C_6-O)
***O, O*-CPBN**		8.7(2)	1.1(3)
1		8.3(11)	
2		4.8(3)	4.3(3)
4	**a**	-3.5(11)	-0.9(17)
	b	8.6(11)	2.8(13)
	c	4.8(12)	1.1(12)
	d	0.4(9)	4.7(10)

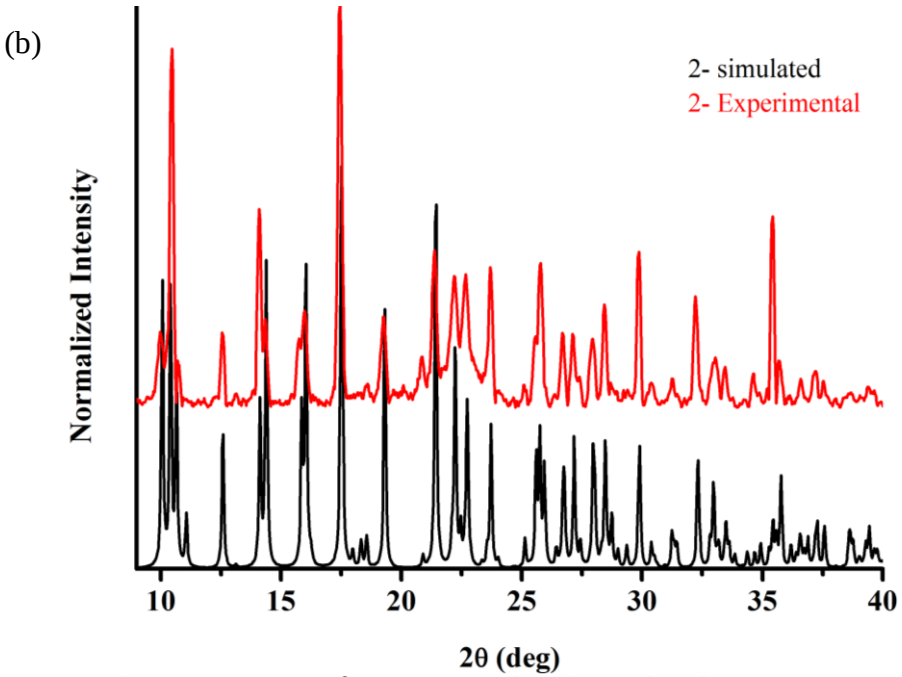
SI 10c. Molecular structure of ***O, O*-CPBN** with torsion angle numbering and torsion angle of ***O, O*-CPBN** in the different crystal lattices.



SI 11. PXRD patterns of **1-4**

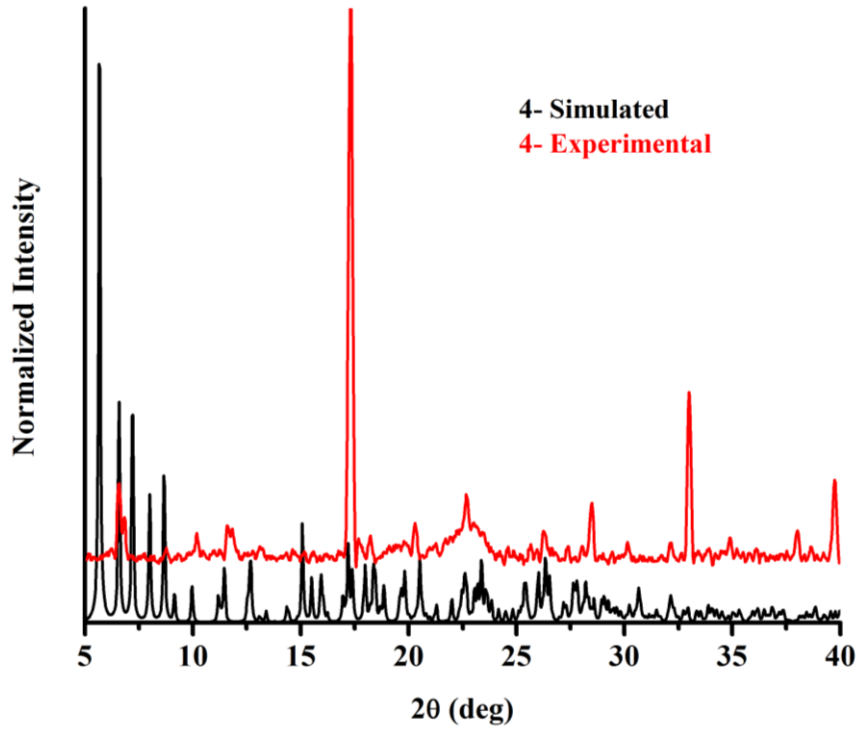


SI 12a. Comparison of experimental and simulated PXRD patterns of **1.**



SI 12b. Comparison of experimental and simulated PXRD patterns of **2.**

(c)



SI 12c. Comparison of experimental and simulated PXRD patterns of **4.**

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