Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information

Formation of 1D-polymeric chain of Hg building blocks through C-C coupling under ambient condition

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Experimental Section:

Materials and Physical Measurements. The commercially available starting materials, $HgCl_2$, 2-methylhydroxy pyridine (hmp-H) methanol were used. Elemental analyses were carried out with a Thermoscientific elemental analyzer. X-ray (powder) diffraction data were collected on a Philips X'Pert Pro X-ray diffraction system using monochromated Cu-Kα radiation (λ = 1.5406 Å). Inductively Coupled Plasma: Atomic Emission Spectrometer (ICP-AES) were recorded on CCD equipped ARCOS System.

Synthesis of 1. A solution of hmp-H (109 mg, 1 mmol) in MeOH (4 ml) was added to a solution of $HgCl_2$ (271 mg, 1 mmol) in MeOH (40 ml). and the resultant solution was stirred for overnight at room temperature. The solution was then passed through the filter paper in order to remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallization. Transparent colourless crystals of insoluble **1** were obtained within 15 days by slow evaporation of the solvent.Yield 59%, M.P.: >300-302 ^{o}C. Anal. Calcd for C_{12} H_{10} Cl_4 Hg_2 N_2 $O_2 \cdot 2H_2O$, (Mw =793.23): C, 18.17; H, 1.78; N, 3.53. Found: C, 18.31; H, 1.75; N, 3.32. ICP-AES: Hg, 50.63% (Calcd: Hg, 50.57).

Synthesis of 2. A solution of hmp-H (218 mg, 2 mmol) in MeOH (4 ml) was added to a solution of $HgCl_2$ (271 mg, 1 mmol) in MeOH (40 ml) and the resultant solution was stirred for overnight at room temperature. The solution was then passed through the filter paper in order to remove any unreacted materials. The filtrate was allowed to stand at room temperature for crystallization. Transparent colourless crystals of insoluble **2** were obtained within 7 days by slow evaporation of the solvent. Yield 63%, M.P.: >190-192 ^{o}C. Anal. Calcd for C_{12} H_{12} Cl_{l4} Hg_2 N_2 O_2, (Mw =759.22): C, 18.98; H, 1.59; N, 3.69. Found: C, 18.87; H, 1.47; N, 3.58. ICP-AES: Hg, 52.43% (Calcd: Hg, 52.84%).

X-ray Crystallography: Single crystal X-ray structural studies of **1** and **2** were performed on a CCD Agilent technology supernova diffractometer equipped with a low-temprature attachment. Data were collected at 150(2) K using graphite-monochromoated Mo Kα

radiation (λ_{α} = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least squares with SHELXL-97, refining on F^{2}[1].

The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2 x U_{eq} of their parent atoms. All the H-bonding interactions, mean plane analyses, and molecular drawings were obtained using the program Diamond (ver 3.1d). The crystal and refinement data are summarized in **Table S1**, and selected bond distances and bond angles are shown in **Table S2.** Intermolecular and Intramolecular Hydrogen bond distances and bond angles are shown in **Table S3.**

Reference

1 Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *A64*, 112-122. *Program for Crystal Structure Solution and Refinement;* University of Goettingen: Goettingen, Germany, 1997.

Table S1. Crystallographic Parameters for 1 and 2

Identification code	**1 (150 K)**	**2 (150 K)**
Empirical formula	C_{12} H_{14} C_{l4} Hg_2 N_2 O_4	C_{12} H_{12} C_{l4} Hg_2 N_2 O_2
Formula weight	793.23	759.22
Wavelength	0.71073 A	0.71073 A
Crystal system, space group	Monoclinic, C 2/c	Triclinic, P -1
Unit Cell Parameter		
a/Å	11.6344(5)	7.2128(4)
b/Å	11.0503(5)	7.3831(4)
c/Å	15.0011(14)	9.4701(4)
$\alpha/^{o}$	90	107.164(4)
$\beta/^{o}$	96.075(6)	92.654(4)
$\gamma/^{o}$	90	112.675(5)
$V/Å^3$	1917.8(2)	437.07(4)
Z, d_{calcd} (mg/m^3)	4, 2.747	1, 2.884
μ/ mm^{-1}	16.567	18.158
F(000)	1440	342
Crystal size (mm^3)	0.23 x 0.18 x 0.13	0.12 x 0.08 x 0.07
θ range	2.98 to 24.98 deg.	3.11 to 25.00 deg.
Index ranges	-13<=h<=13, -12<=k<=13, -17<=l<=17	-7<=h<=8, -8<=k<=8, -11<=l<=10
Reflections collected / unique	5737 / 1687 [R(int) = 0.0262]	2875 / 1538 [R(int) = 0.0560]
Data collection Instrument	Oxford XCalibur-S	Oxford XCalibur-S
Absorption correction	Semi-empirical from equivalents	Semi-empiricalfrom

		equivalents
Max. and min. transmission	0.2220 and 0.1150	0.3630 and 0.2192
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	1687 / 2 / 117	1538 / 0 / 100
GOF, F^2	1.046	1.091
R1, wR2 [I>2σ(I)]	0.0452, 0.0989	0.0210, 0.0545
R1, wR2 (all data)	R1 = 0.0527, wR2 = 0.1039	R1 = 0.0213, wR2 = 0.0546
Largest diff. peak and hole	2.044 and -1.526 e.A^-3	1.514 and -2.270 e.A^-3

Table S2. Selected bond distances and angles for 1 and 2

Bond distance	**1**	**2**
Hg(1)-N(1)	2.206(8)	2.180(4)
Hg(1)-Cl(1)	2.351(3)	2.350(12)
Hg(1)-Cl(2)	2.682(3)	2.760(12)
Hg(1)-Cl(2)#1	2.764(3)	2.801(13)
Hg(1)-O(1)	2.740 (2)	2.618(4)
Selected bond angles (°) for 1 and 2		
N(1)-Hg(1)-Cl(1)	149.7(2)	163.2(12)
N(1)-Hg(1)-Cl(2)	96.5(2)	96.26(11)
Cl(1)-Hg(1)-Cl(2)	105.94(11)	98.19(4)
N(1)-Hg(1)-Cl(2)#1	101.5(2)	91.08(11)
Cl(1)-Hg(1)-Cl(2)#1	100.81(10)	97.60(4)
Cl(2)-Hg(1)-Cl(2)#1	84.10(9)	89.28(4)
Hg(1)-Cl(2)-Hg(1)#1	93.57(9)	90.72(4)
C(1)-N(1)-Hg(1)	118.0(7)	118.0(3)
C(5)-N(1)-Hg(1)	122.2(6)	123.2(3)
N(1)-Hg(1)-O(1)	-	68.88(13)
Cl(1)-Hg(1)-O(1)	-	94.36(9)
O(1)-Hg(1)-Cl(2)	-	150.13(2)
O(1)-Hg(1)-Cl(2)#1	-	115.83(9)
C(6)-O(1)-Hg(1)	-	106.5(3)

Table S3. Hydrogen bonding parameters for 1 and 2 [Å and (°)]-

	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
			1		
1	C(1)-H(1)…Cl(2) #(1)	0.95(10)	2.758(3)	3.495(12)	134.98(67)
2	O(101)-H(111)…O(1) # (1)	0.880(45)	1.887(49)	2.669(17)	147.09(40)
3	C(2)-H(2)…O(1) #(2)	…0.950(11)	2.951(13)	…..3.583(18)	127.77(73)
	C(3)-H(3)…O(1) #(2)	…0.950(12)	2.996(8)	…..3.458(14)	111.43(71)
	C(3)-H(3)…O(101) #(2)	…0.950(12)	2.951(13)	….3.583(18)	125.09(71)
3	O(101)-H(222)…Cl(1) #(3)	0.820(117)	2.834(30)	3.517(14)	142.03(7.63)
4	O(101)-(H222)…Cl(2) #(4)	0.820(117)	2.827(.251)	3.255(.014)	102.88(15.10)
Equivalent positions: (1) x,y,z (2) x+1/2, +y+1/2,+z (3) -x+1/2+1,+y+1/2,-z+1/2 (4) x-1/2,+y+1/2,+z					
			2		
1	C(1)-H(1)...Cl(2) #(0)	0.95(6)	2.747(1)	3.506(2)	137.64(3)
2	C(2)-H(2)…Cl(1) # (1)	0.95(6)	2.742(1)	3.515(6)	139.05(4)
3	C(3)-H(3)…Cl(2) # (2)	0.95(5)	2.782(1)	3.665(6)	154.97(3)
4	C(6)-H(6A)---Cl(1)#(3)	0.990(7)	2.706(2)	3.671(7)	165.08(4)
Equivalent Position (0) x,y,z (1) x,+y+1, +z+1 (2) x,+y,+z+1 (3) -x+2, -y, -z+1					

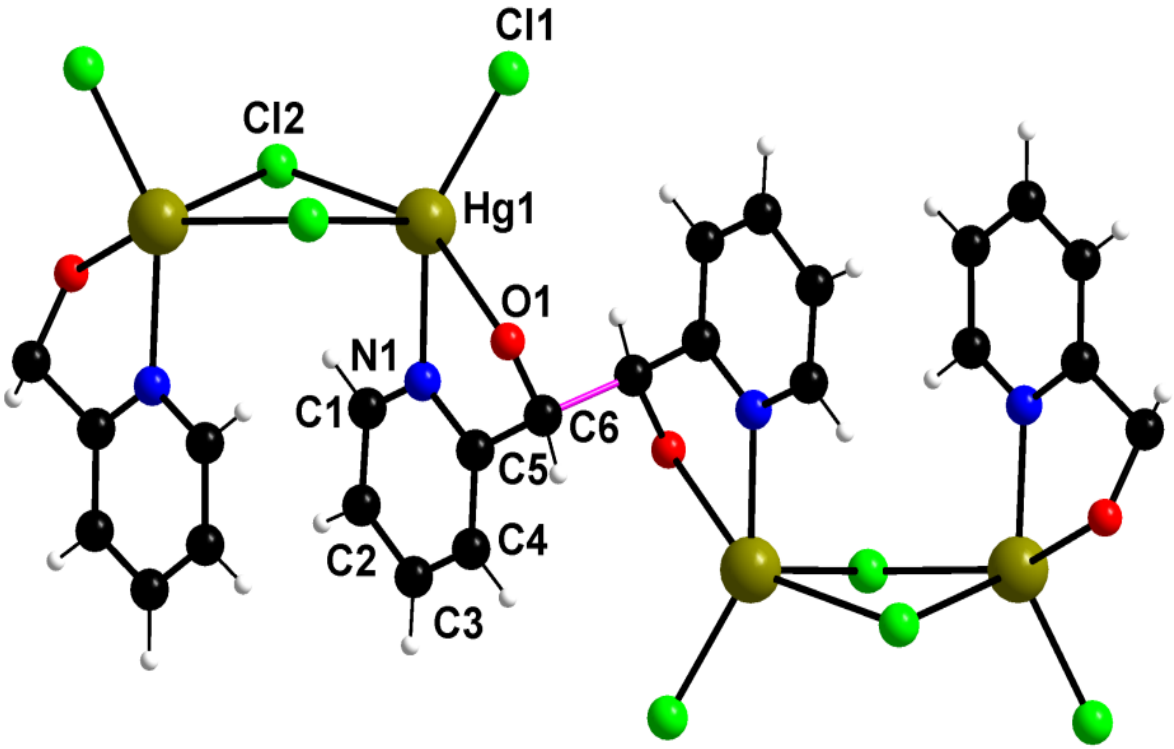

Fig.S1 Showing C-C coupling in **1**

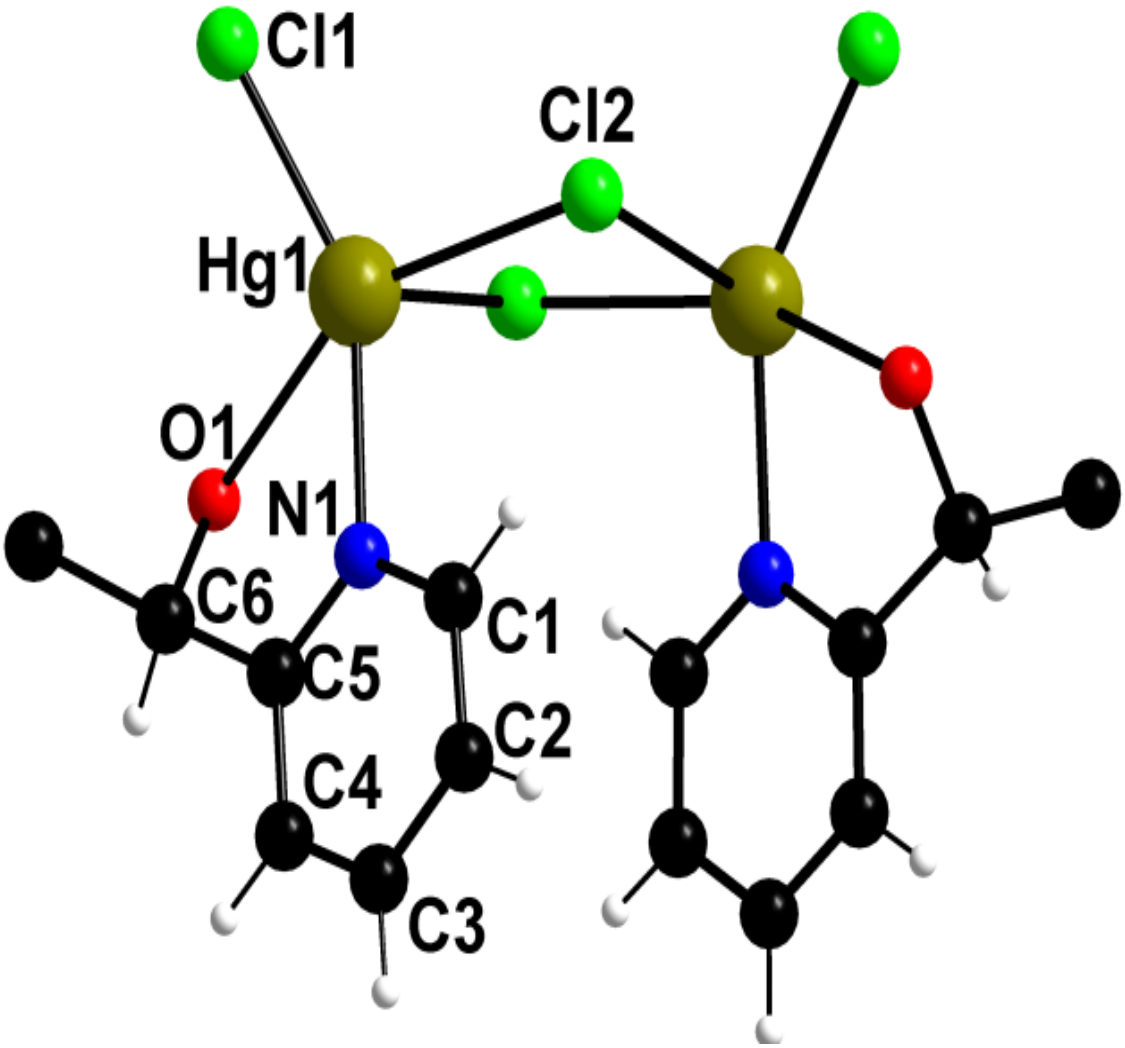

Fig. S2 Formation of intermediate dimer in **1**

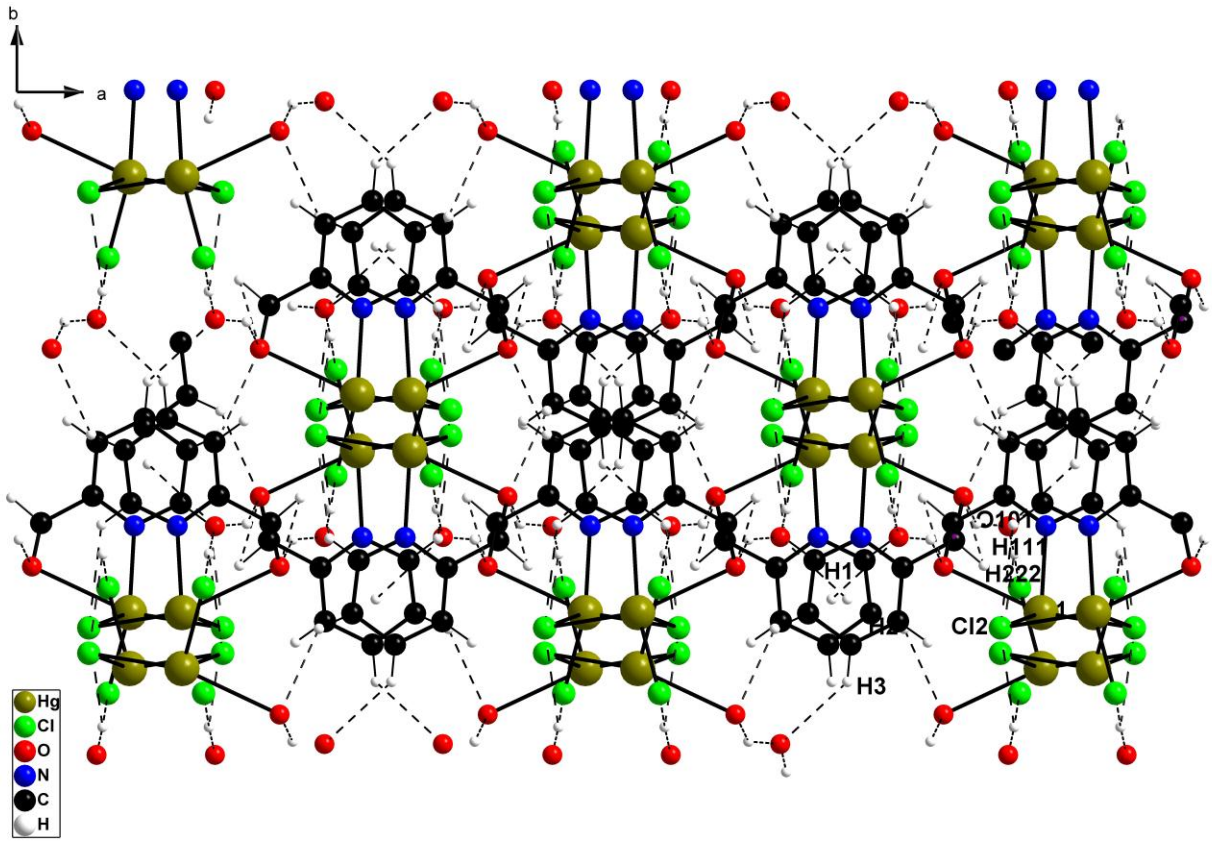

Fig. S3 The perspective view of hydrogen bonded 2D-network in **1**.

The pyridine H atoms (H(2) and H(3)) of hmp^- involve in C-H---O interactions with the coordinated O(1) atom of hmp^- and the oxygen atom (O(101)) of the lattice water molecule. The hydrogen atom H(222) of the lattice water molecule involves in intermolecular interactions with both the terminal Cl(1) and bridging Cl(2) of one layer and the other hydrogen atom H(111) of the lattice water molecule is hydrogen bonded to the coordinated oxygen atom O(1) of hmp^- in the adjacent layer.

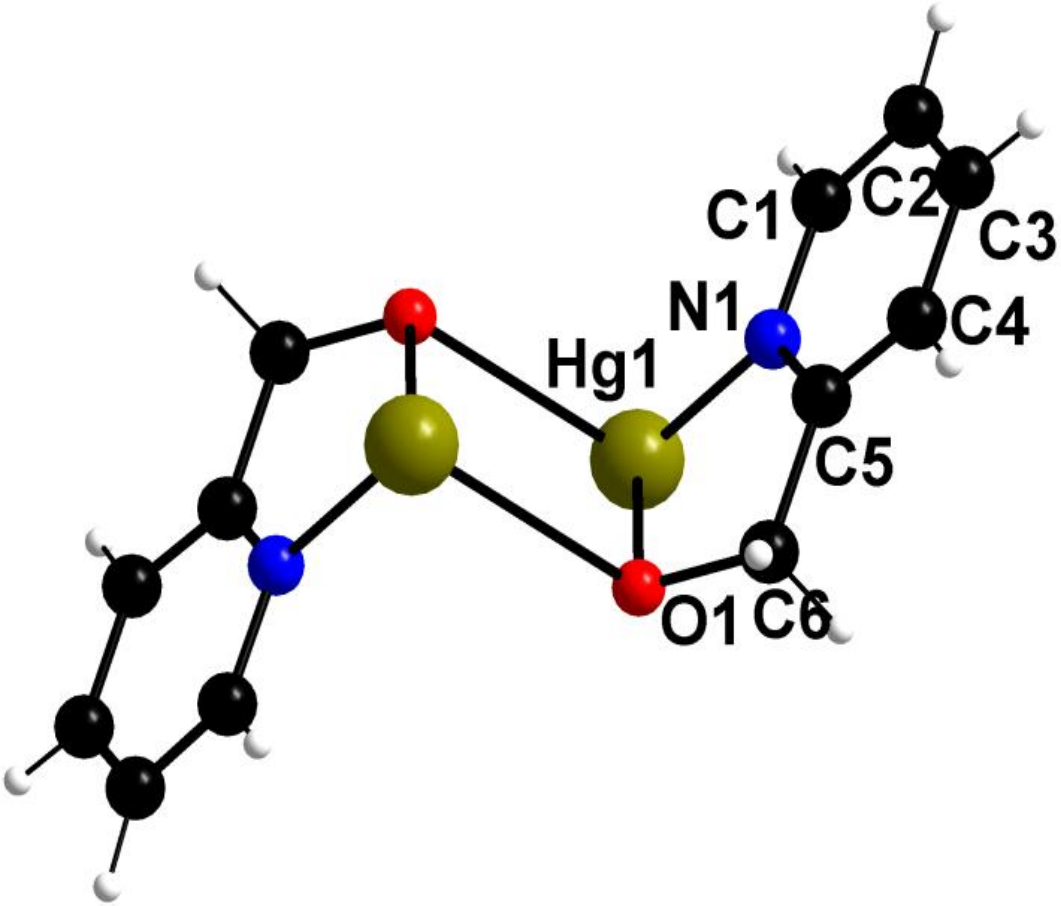

Fig. S4 The chair-like conformation of the Hg_2O_2coreand hmp^- in **2**

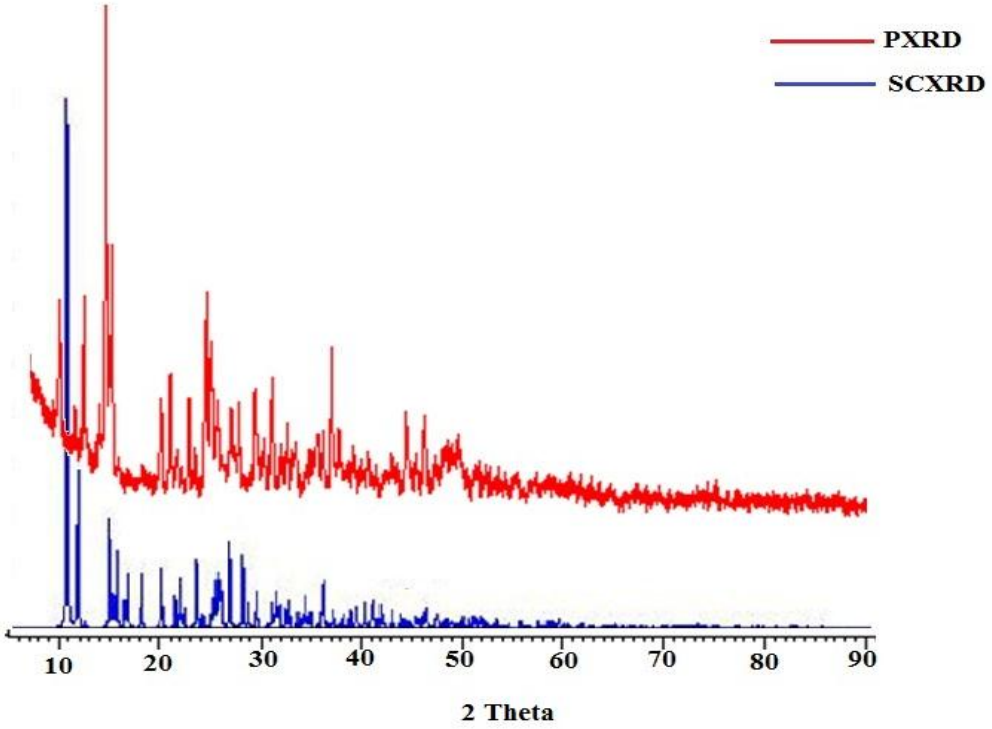

Fig. S5 The PXRD (red) patterns and simulated SCXRD (blue) patterns