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1D, 2D and 3D coordination polymers of 1,3-phenylene diisonicotinate with Cu(I)/Cu(II): Cu_2I_2 building block, anion influence and guest inclusions

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Supporting Information

Experimental details, IR Spectra. TGA, and XRPD patterns of the complexes.

General.

Fourier transform IR (FTIR) spectra was recorded with an Perkin-Elmer instrument. Elemental analyses were obtained with a Perkin-Elmer instrument, series II, CHNS/O analyzer 2400. Thermogravimetric analysis (TGA) data were recorded under an Ar atmosphere at a heating rate of 5ºCmin^{-1} with a Perkin-Elmer instrument, Pyris Diamond TG/DTA. X-ray Powder diffraction (XRPD) data were recorded with a Bruker APEX-2 diffractometer.

The single crystal data was collected on Bruker APEX-2 CCD X-ray diffractometer that uses graphite monochromated MoKα radiation (λ =0.71073 Å) by hemisphere method. The structures are solved by direct methods and refined by least square methods on F^2 using SHELX-97.[1] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. PLATON was used for the calculation of guest available volumes. The platon squeeze option was used in final refinement by removing $CHCl_3$ (could not be located) in **1**, and anions (distorted with high thermal motions) and free water molecules (high thermal motions) in **6**.[2]

Synthetic Procedures.

1,3-phenylene diisonicotinate (L): The molecule **L** was prepared according to the previously reported method.[3]

Syntheses of Complexes 1-4 by Layering. 1.0 mL of acetonitrile was layered on to methanol (3.0 mL)/chloroform (2 mL) solution (5 mL) of **L** (0.009 g, 0.028 mmol). Over this solution an acetonitrile solution (1.0 mL) of CuI (0.005 g, 0.028 mmol) was carefully layered. Bright orange colored platy crystals of **1** were formed after 3-4 days.

Complex **2-4** were prepared in similar way taking nitrobenzene, cyanobenzene and bromobenzene, respectively in place of chloroform.

Complex **1**: Yield: 40%. Elemental analysis for $C_{38}H_{26}Cl_6Cu_2I_2N_4O_8$; calc (%) C 36.22, H 2.08, N 4.45; obs (%) C 36.27, H 2.19, N 5.03.

Complex **2**: Yield: 44%. Elemental analysis for $C_{48}H_{34}Cu_2I_2N_6O_{12}$; calc (%) C 45.48, H 2.70, N 6.63; obs (%)C 45.45, H 2.55, N 6.68.

Complex **3**: Yield: 44%. Elemental analysis for $C_{50}H_{34}Cu_2I_2N_6O_8$; calc (%) C 48.91, H 2.79, N 6.85; obs (%)C 48.94, H 2.73, N 6.81.

Complex **4**: Yield: 35%. Elemental analysis for $C_{48}H_{34}Br_2Cu_2I_2N_4O_8$; calc (%) C 43.17, H 2.57, N 4.20; obs (%)C 43.66, H 2.50, N 4.44.

Complex **5**: Yield: 56%. Elemental analysis for $C_{37}H_{29}Cl_3CuF_{12}N_4O_{10}P_2$; calc (%) C 38.66, H 2.54, N 4.87; obs (%)C 38.56, H 2.09, N 5.12.

Complex **6**: Yield: 52%. Elemental analysis for $C_{108}H_{106}Cl_6Cu_3N_{12}O_{65}$; calc (%) C 43.02, H 3.54, N 5.57; obs (%)C 43.16, H 3.78, N 5.07.

Syntheses of Complexes 5-6 by Direct Mixing.

Methanolic solution (1 mL) of $Cu(PF_6)_2$ (0.028 mmol) was added to a stirred solution of ligand **L** (0.009 g, 0.028mmol) in $CHCl_3$. This resulted in the formation of a blue precipitate. After 5-10 min of stirring, water was added drop wise to obtain a clear solution. This solution was filtered and kept for slow evaporation. $Cu(PF_6)_2$ solution was prepared by taking nitrate salts of Cu(II) and $NaPF_6$ in a 1:2 ratio. Blue needle shaped crystals were afforded in 2 days.

Methanolic solution (1 mL) of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.008 g, 0.028 mmol) was added to a stirred solution of ligand **L** (0.009 g, 0.028mmol) in $CHCl_3$. This resulted in the formation of a blue precipitate. After 5-10 min of stirring, water was added drop wise to obtain a clear solution. This solution was filtered and kept for slow evaporation. Blue block shaped crystals of **6** were afforded in 2 days.

Table S1: Crystallographic parameters for 1-6.

Compounds	**1**	**2**	**3**
Formula	$C_{38}H_{26}Cl_6Cu_2I_2N_4O_8$	$C_{48}H_{34}Cu_2I_2N_6O_{12}$	$C_{50}H_{34}Cu_2I_2N_6O_8$
Mol.Wt.	1260.21	1267.69	1227.71
T (K)	293(2)	293(2)	293(2)
System	Monoclinic	Monoclinic	Monoclinic

Space Group	*P*2(1)/*c*	*P*2(1)/*n*	*P*2(1)/*n*
a(Å)	9.236(2)	9.608(2)	9.470(3)
b(Å)	8.784(2)	8.3895(18)	8.587(3)
c(Å)	29.629(7)	30.122(6)	30.417(9)
α(°)	90	90	90
β(°)	96.361(8)	97.841(6)	100.186(12)
γ(°)	90	90	90
V (Å^3)	2389.12	2405.32	2434.49
Z	2	2	4
D (g/cc)	1.752	1.750	1.675
R_1 (I>2σ(I))	0.1241	0.0985	0.1335
wR_2 (on F^2, all data)	0.2529	0.2384	0.3166
independent reflns	2279	3761	2965
reflns used[I>2σ(I)]	4340	4049	4422
R_{int}	0.1125	0.0541	0.1456

Compounds	**4**	**5**	**6**
Formula	$C_{48}H_{34}Br_2Cu_2I_2N_4O_8$	$C_{37}H_{29}Cl_3CuF_{12}N_4O_{10}P_2$	$C_{108}H_{106}Cl_6Cu_3N_{12}O_{65}$
Mol.Wt.	1335.49	1149.47	3015.37
T (K)	293(2)	293(2)	293(2)
System	Monoclinic	Monoclinic	Monoclinic
Space Group	*P*2(1)/*n*	*C*2/*c*	*C*2
a(Å)	9.6255(19)	17.615(3)	16.835(8)
b(Å)	8.4480(17)	15.560(2)	9.707(5)
c(Å)	29.784(6)	19.211(3)	39.767(19)
α(°)	90	90	90

β(°)	94.921(7)	115.087(4)	90.522(10)
γ(°)	90	90	90
V (Å^3)	2413	4768.81	6498.35
Z	2	4	12
D (g/cc)	1.838	1.601	1.541
R_1 (I>2σ(I))	0.0672	0.0806	0.0956
wR_2 (on F^2, all data)	0.2177	0.2448	0.2340
independent reflns	3353	3141	7241
reflns used[I>2σ(I)]	4859	4523	11120
R_{int}	0.0609	0.0365	0.1303

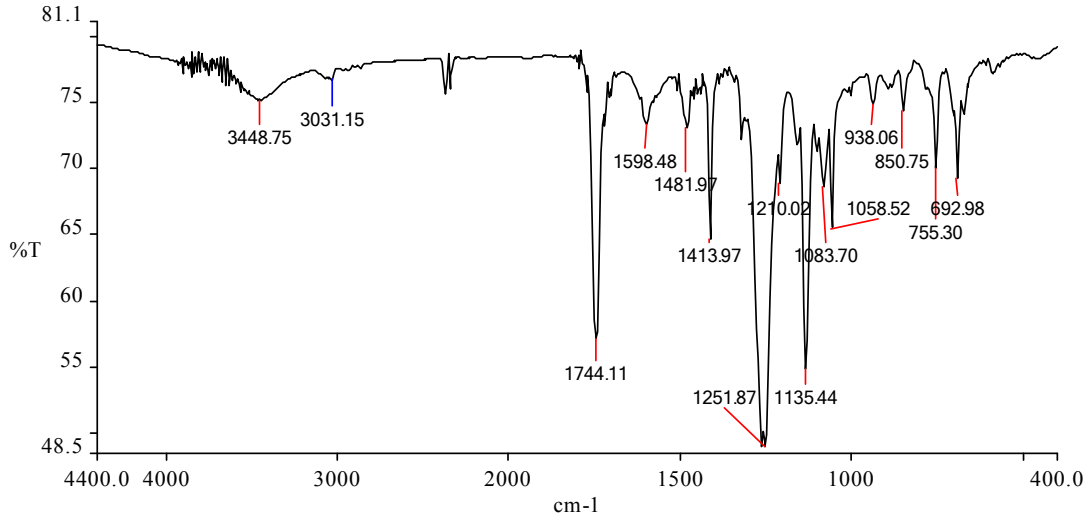

Figure S1. FT-IR spectra for **1**: 3031 cm^{-1} (aromatic C-H str); 1744 cm^{-1} (ester C=O); 1598- 1413 cm^{-1}(C=C, C=N pyridine ring str).

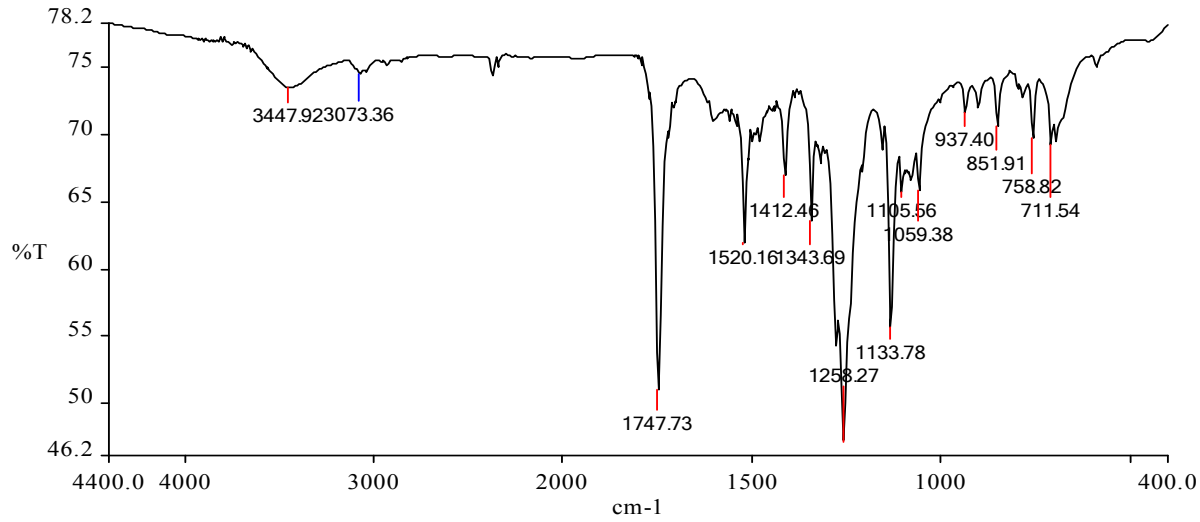

Figure S2. FT-IR spectra for **2**: 3073 cm^{-1} (aromatic C-H str); 1747 cm^{-1} (ester C=O); 1596- 1414 cm^{-1}(C=C, C=N pyridine ring str); 1520 cm^{-1} (asym $(N\text{-}O)_2$ str); 1343 cm^{-1} (sym $(N\text{-}O)_2$ str).

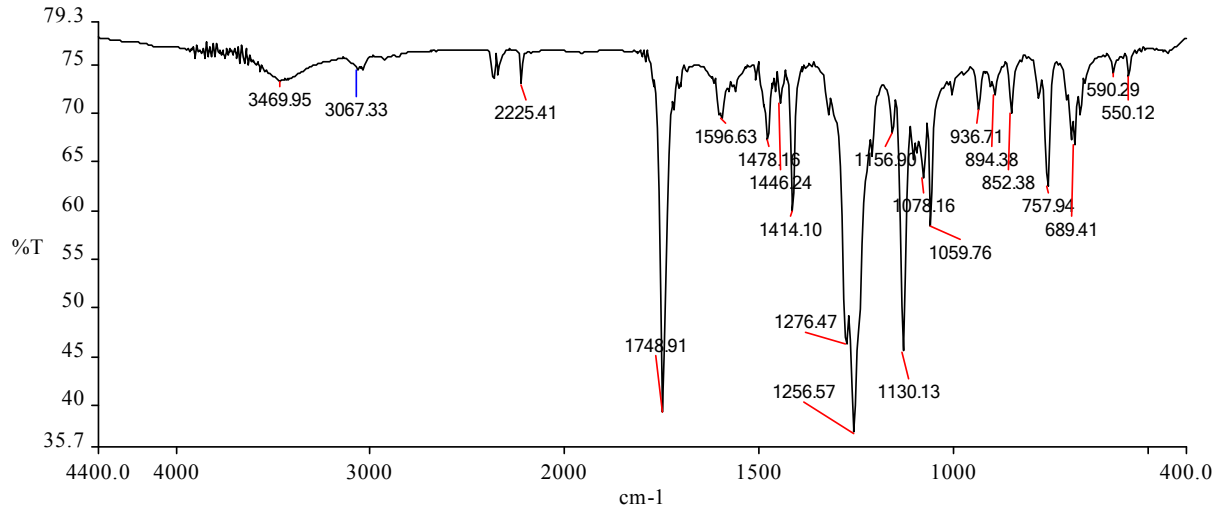

Figure S3. FT-IR spectra for **3**: 3067 cm^{-1} (aromatic C-H str); 2225 cm^{-1} (CN stretch); 1748 cm^{-1} (ester C=O); 1596-1414 cm^{-1}(C=C, C=N pyridine ring str).

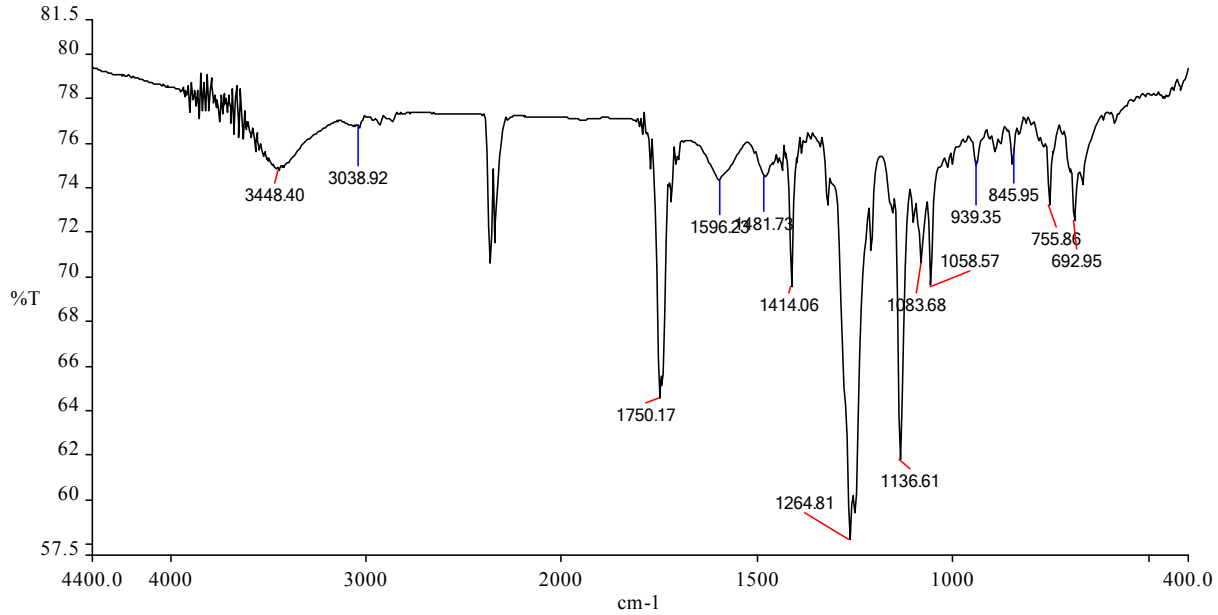

Figure S4. FT-IR spectra for **4**: 3038 cm^{-1} (aromatic C-H str); 1750 cm^{-1} (ester C=O); 1596- 1414 cm^{-1}(C=C, C=N pyridine ring str).

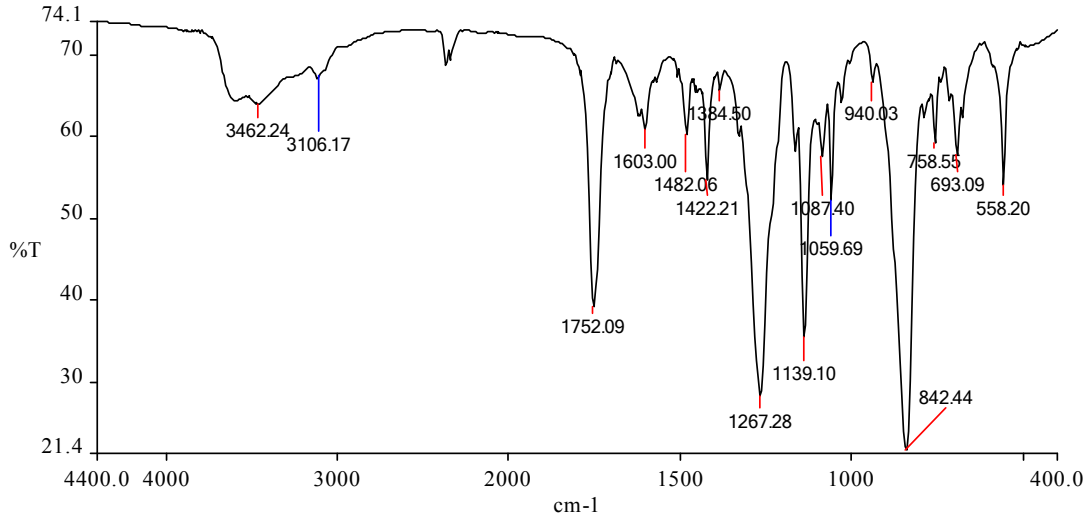

Figure S5. FT-IR spectra for **5**: 3106 cm^{-1} (aromatic C-H str); 1752 cm^{-1} (ester C=O); 1603- 1422 cm^{-1}(C=C, C=N pyridine ring str); 842, 558 (PF_6).

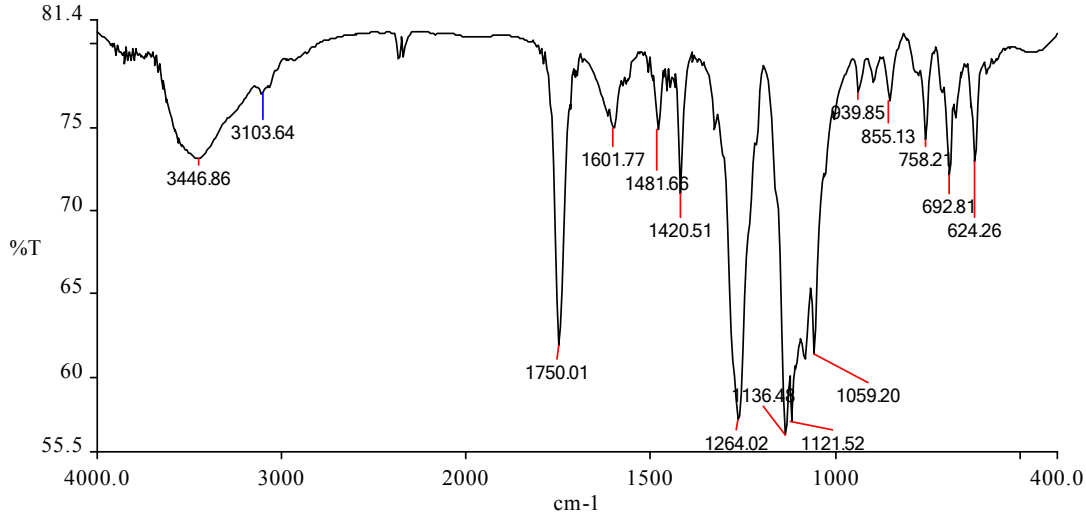

Figure S6. FT-IR spectra for **6**: 3103 cm^{-1} (aromatic C-H str); 1750 cm^{-1} (ester C=O); 1601- 1420 cm^{-1}(C=C, C=N pyridine ring str); 1121-1059 cm^{-1} (ClO_4).

TGA curve.

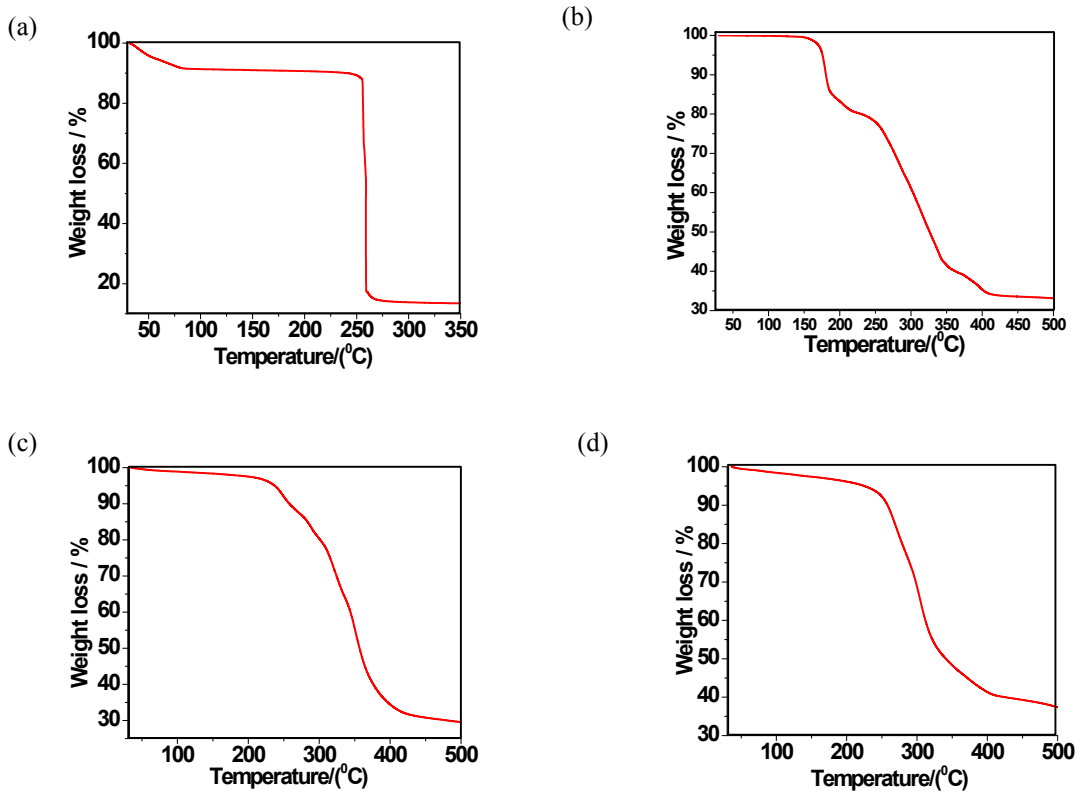

Figure S7. TGA curves of (a) **1**, (b) **2**, (c) **3**, (d) **4**.

XRPD patterns.

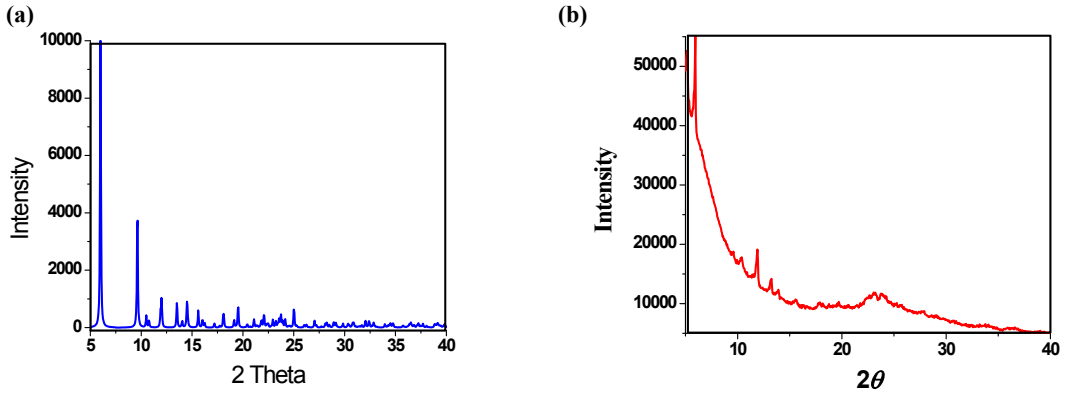

Figure S8. (a) Simulated and (b) experimental XRPD patterns of **1**.

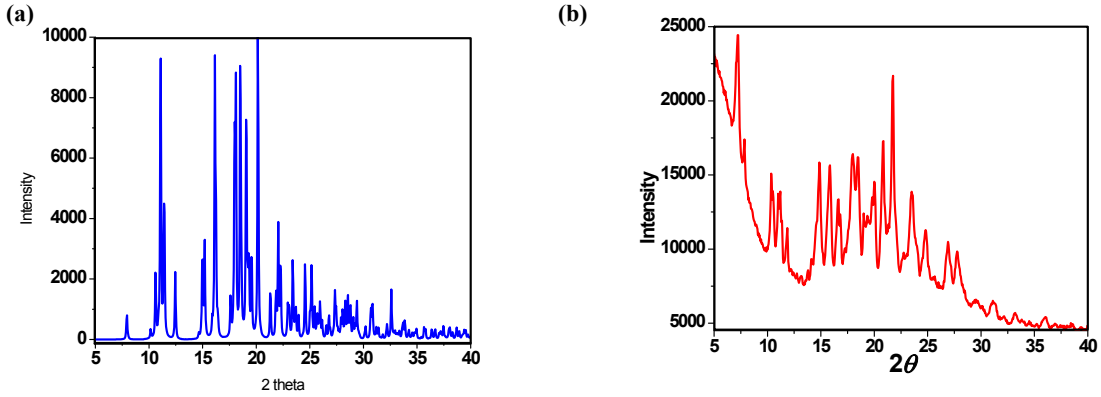

Figure S9. (a) Simulated and (b) experimental XRPD patterns of **5**.

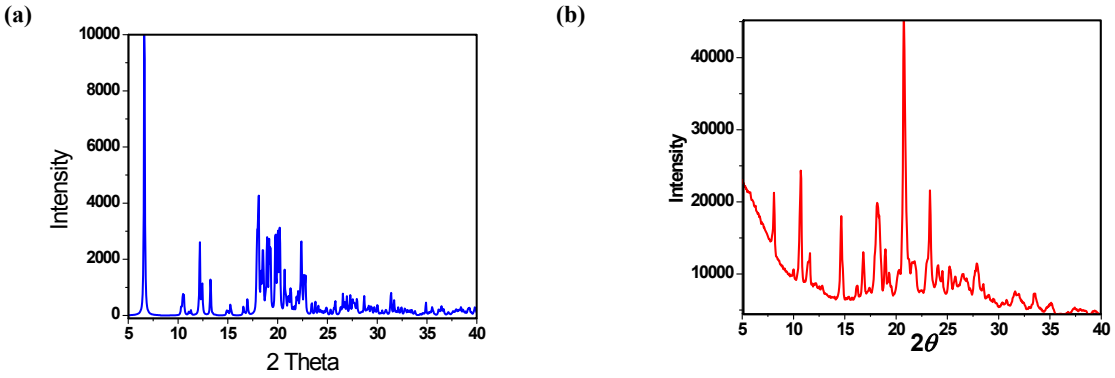

Figure S10. (a) Simulated and (b) experimental XRPD patterns of **6**.

References:

(1) G. M. Sheldrick, SHELX-97, *Program for the Solution and Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, **1997**.

(2) A. L. Spek, *PLATON-A Multi Purpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, **2002**.

(3) D. Sui, Q. Hou, J. Chai, L. Ye, L. Zhao, M. Li, S. Jiang, *Journal of Molecular Structure*, **2008**, *891*, 312–316.