Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting information

Magnetic Diversity in Three-dimensional 2-Fold Interpenetrated Structure: Story of Two Compounds

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[†] Both PCR and SPC made equal contribution to this work.

CONTENTS

1. Synthesis of 4, 4-oxybis (*N*-(pyridine-4-yl) benzamide (L2) :

To a 250 mL oven dried and nitrogen purged round bottom flask, 4, 4'-oxybisbezoyl chloride (1.77, 6 mmol) was added, and it was dissolved in 50 mL of dry DCM. In another oven dried flask, 4-aminopyridine (1.223 g, 13 mmol) was dissolved in 50 mL of dry THF. Then amino pyridyl solution was added slowly to the above reaction mixture with the syringe. Here, we have observed an immediate white colour precipitate. This reaction mixture was refluxed overnight at 60 ˚C. After that, it was cooled to room temperature and then filtered the precipitate. The resultant compound was washed with 1:1 THF/DCM (50 mL) solvent mixture and dried under the vacuum. To the suspension 40 mL of methanol and (excess) 2 mL of triethylamine was added dropwise. The resultant reaction mixture was stirred at room temperature overnight. After the reaction, the final compound was filtered and dried in the oven for 12h. The yield of the product (1.35 gm, 55%). The compound was analyzed by ^{1}HNMR (Fig: **S1**). The proton NMR data is consistent with the reported literature.

2. Single Crystal X-ray Diffraction. Suitable crystal for both the compounds were carefully selected under a polarizing microscope and glued to a thin glass fiber. The data were collected on a Bruker AXS Smart Apex CCD diffractometer at 298 K. The X-ray generator was operated at 50 kV and 35 mA using MoKα (λ = 0.71073 Å) radiation. Data were collected with ω scan width of 0.3 °.

The data were reduced using SAINTPLUS[1] and an empirical absorption correction was applied using the SADABS program.[2] The crystal structure was determined by direct methods using SHELXS2014 and refined using SHELXL2014 present in the SHELXTL V6.14[3] package. All hydrogen atoms were placed in calculated positions during the final step of the refinement process. For the final refinement, the hydrogen atoms were placed in geometrically ideal positions and refined using the riding mode. The last cycles of the refinement included atomic positions, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix-least-squares structure refinement against F^2 was carried out using the WINGX[4] package of programs. CCDC- 1548310 and 1548312 contain the crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif

References

1 SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc.: Madison, WI, 2004.

2 G. M. Sheldrick, Siemens Area Correction Absorption Correction Program; University of Göttingen: Göttingen, Germany, 1994.

3 G. M. Sheldrick, SHELXL-97 Program for Crystal Structure Solution and Refinement; University of Göttingen: Göttingen, Germany, 1997.

4 J. L. Farrugia, *J. App. Crystallography*. 1999, **32**, 837-838.

2. Crystallographic tables of compounds **1** and **2**, respectively.

Table S1. Crystallographic parameters of compound **1**.

Parameters	Compound 1
Empirical formula	$C_{76}H_{71}N_{12}Ni_2O_{18}$
Formula weight	1557.86
Wavelength	0.71073 Å
Crystal System	Triclinic
Space Group	*P(*-1) (No.2)
a(Å)	10.1996(3)
b(Å)	14.8778(5)
c(Å)	24.9089(7)
α(^{0})	90.7630(10)
β(^{0})	93.2890(10)
γ(^{0})	99.624(2)
Volume(Å3)	3719.52
Z	2
Calculated density (g/cm3)	1.391
θ range (^{0})	0.819 to 28.363
Absorption coefficient (mm-1)	0.585
Reflections collected	67242
Unique reflections	18191
Goodness-of-fit	0.799
Number of parameters	982
Final R indices [I>2sigma(I)]	R1 = 0.0554, wR2 = 0.1160
R indices (all data)	R1 = 0.1776, wR2 = 0.1613

[a]$R_1 = \Sigma||F_0| - |F_c||/ \Sigma|F_0|$; $wR_2 = \{[w(F_0^2 - F_c^2)^2]/ [w(F_0^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$; $P = [\max(F_0^2,0) + 2(F_c)^2]/3$, where a = 0.0686 and b = 0.0000 for compound **1**.

Table S2. Selected bond lengths for compound **1**.

Moiety	**Bond lengths (Å)**
Ni(1)-O(56)	2.013(3)
Ni(1)-O(70)	2.032(3)
Ni(1)-N(4)	2.076(3)
Ni(1)-N(3)	2.091(3)
Ni(1)-O(15)	2.146(3)
Ni(1)-O(16)	2.150(3)
Ni(2)-O	2.025(3)
Ni(2)-O(58)	2.002(3)
Ni(2)-N(6)	2.093(3)
Ni(2)-O(3)	2.136(3)
Ni(2)-O(4)	2.146(3)
Ni(2)-N(8)	2.079(3)

Table S3. Crystallographic parameters of compound **2**.

Parameters	Compound 3
Empirical formula	$C_{36}H_{34}CoN_6O_9S$
Formula weight	785.68
Wavelength	0.71073 Å
Crystal System	Orthorhombic
Space Group	*Pbca* (No.61)
a(Å)	15.4896(5)
b(Å)	18.1048(5)
c(Å)	24.9836(8)
α(^{0})	90
β(^{0})	90
γ(^{0})	90
Volume(Å3)	7006.3 (4)
Z	8
$_{Calculated}$ density (g/cm3)	1.490
θ range (^{0})	1.630 to 28.350
Absorption coefficient (mm-1)	0.615
Reflections collected	64745
Unique reflections	8730
Goodness-of-fit	0.915
Number of parameters	473
Final R indices [I>2sigma(I)]	R_1 = 0.0431, wR_2 = 0.0971
R indices (all data)	R_1 = 0.0858, wR_2 = 0.1201

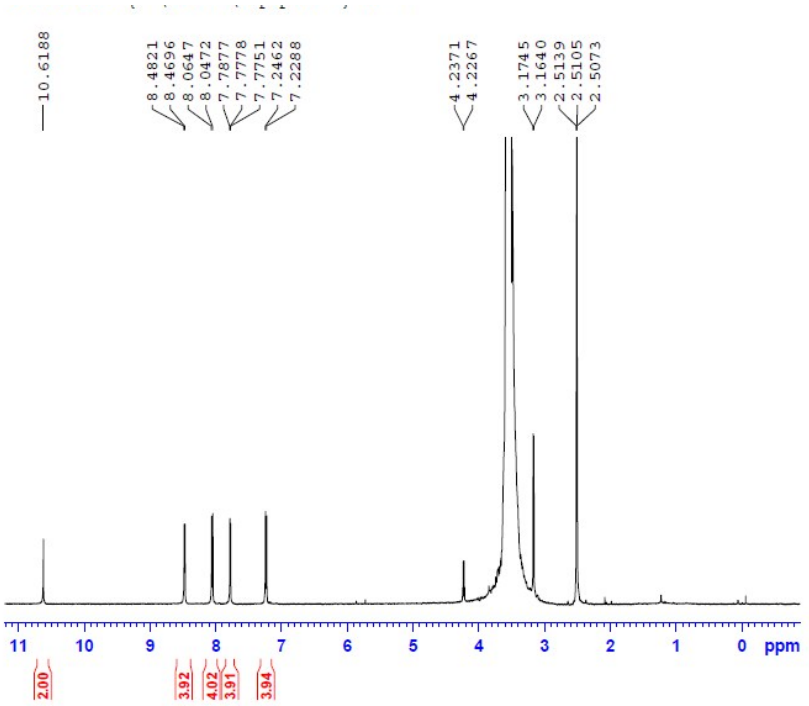
[a]$R_1 = \Sigma||F_0| - |F_c||/ \Sigma|F_0|$; $wR_2 = \{[w(F_0^2 - F_c^2)^2]/ [w(F_0^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_0)^2 + (aP)^2 + bP]$; $P = [\max(F_0^2,0) + 2(F_c)^2]/3$, where a = 0.0627and b = 0.0000 for compound **3**.

Table S4. Selected bond lengths for compound **2**.

Moiety	**Bond lengths (Å)**
Co(1)- O(2)	2.0280(15)
Co(1)-O(1)	2.0088(17)
Co(1)-N(1)	2.132(2)
Co(1)-N(4)	2.140(2)
Co(1)-O(4)	2.1835(17)
Co(1)-O(3)	2.2011(15)

(A) NMR spectra of the L2 ligand

(a)

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P1                    9.04 use
PLW1           27.16399956 W

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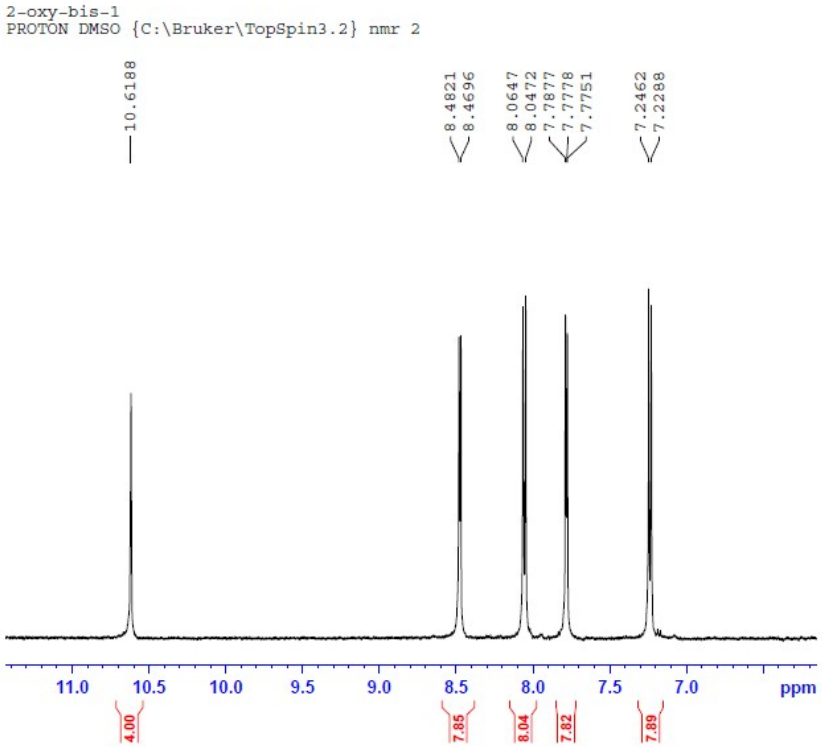


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Current Data Parameters
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EXPNO                    6
PROCNO                   1

F2 - Acquisition Parameters
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Time                 15.10
INSTRUM              spect
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PULPROG                zg30
TD                    65536
SOLVENT                DMSO
NS                       16
DS                        2
SWH              10000.000 Hz
FIDRES               0.152588 Hz
AQ                3.2767999 sec
RG                       32
DW                   50.000 use
DE                    6.50 use
TE                   296.0 K
D1              1.00000000 sec
TD0                      1

-------- CHANNEL f1 --------
SFO1           500.2330891 MHz
NUC1                   1H
P1                    9.04 use
PLW1           27.16399956 W

F2 - Processing parameters
SI                    65536
SF             500.2300000 MHz
WDW                    EM
SSB          0
LB                    0.30 Hz
GB           0
PC                    1.00
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(b)

Figure S1 (a) and (b) ^{1}H NMR spectra of ligand L2.

4. Characterization of compounds **1** and **2**, respectively.

(B) PXRD analysis

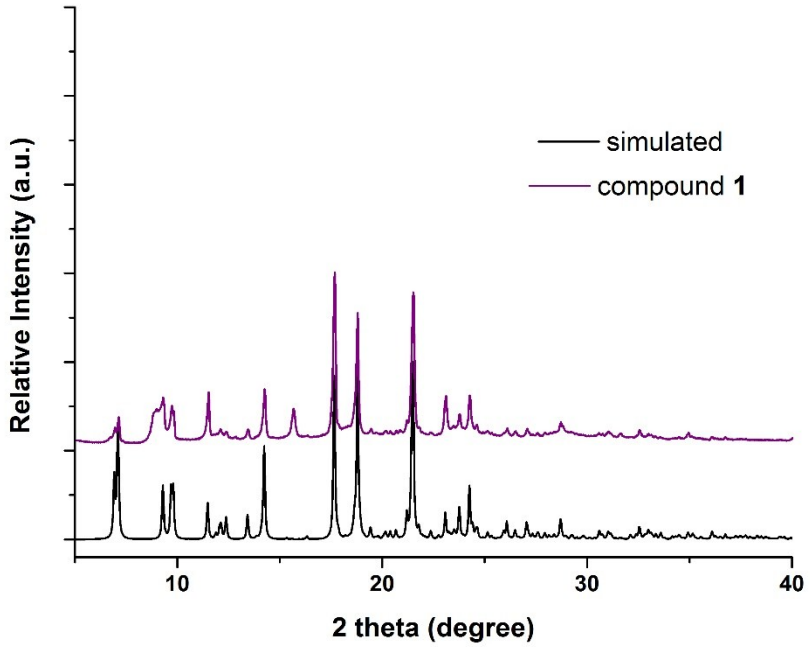


Figure S2. The powder XRD pattern of compound **1,** simulated (black in colour) and experimental (purple in colour).

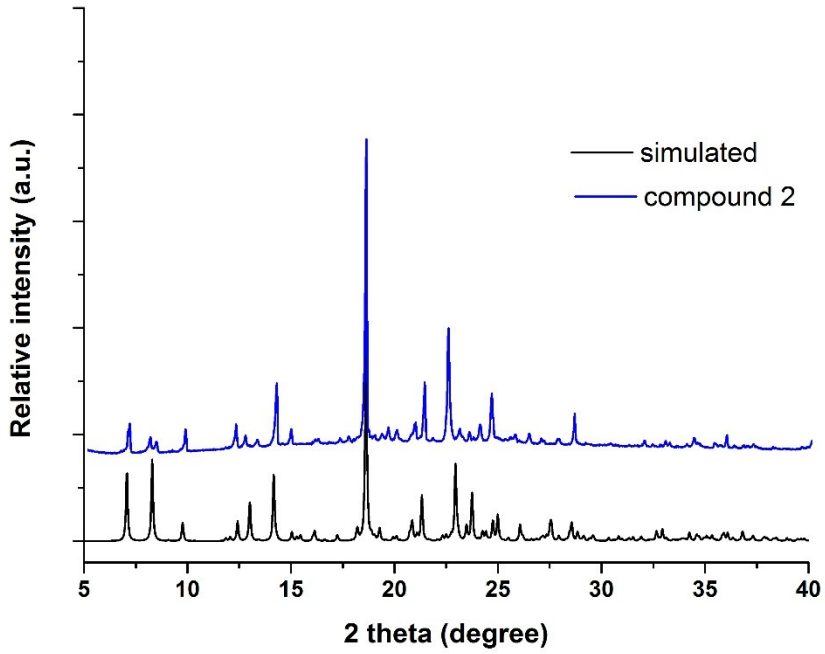


Figure S3. The powder XRD pattern of compound **2,** simulated (black in colour) and experimental (blue in colour).

(C) Thermogravimetric analysis (TGA)

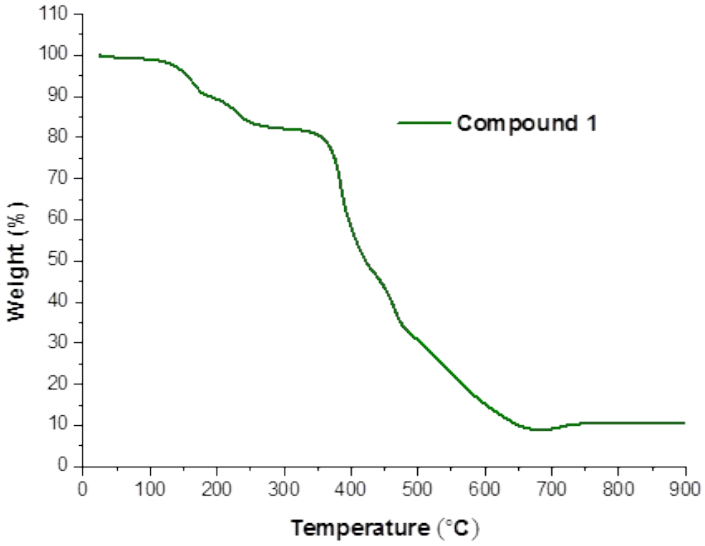


Figure S4. Thermogravimetric analysis plot of compound **1**.

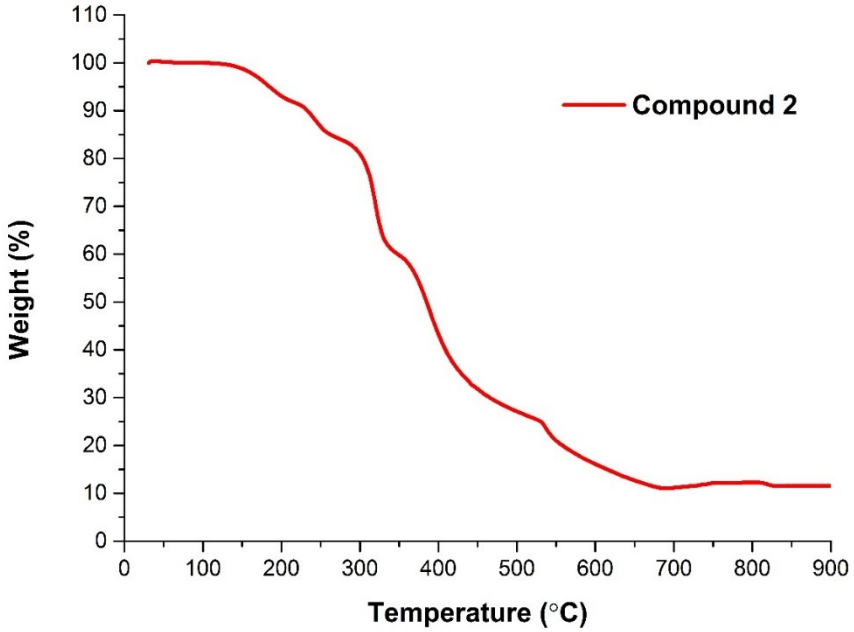


Figure S5. Thermogravimetric analysis plot of compound **2**.

(D) Infrared (IR) spectroscopy studies

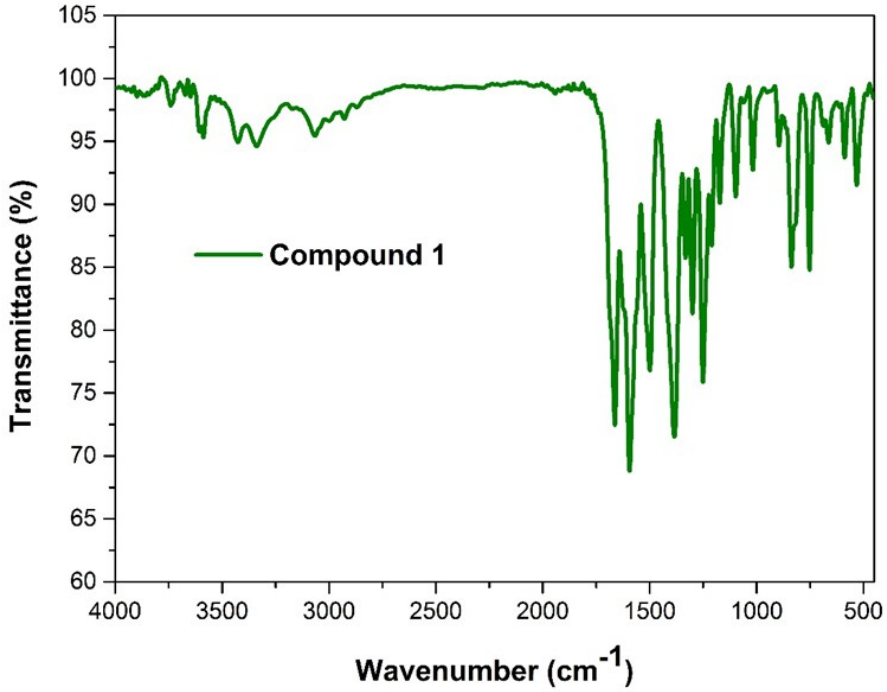


Figure S6. The IR spectrum of compound **1**.

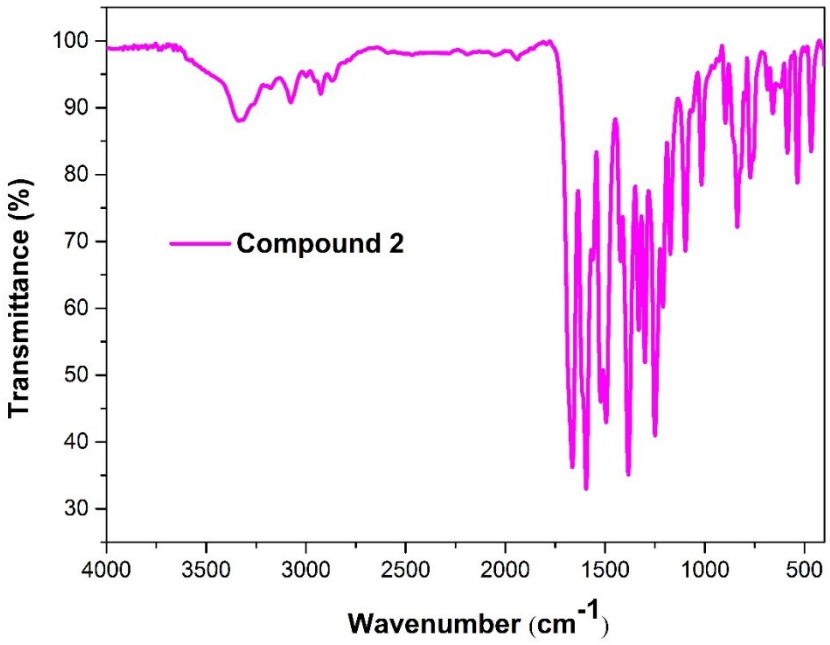
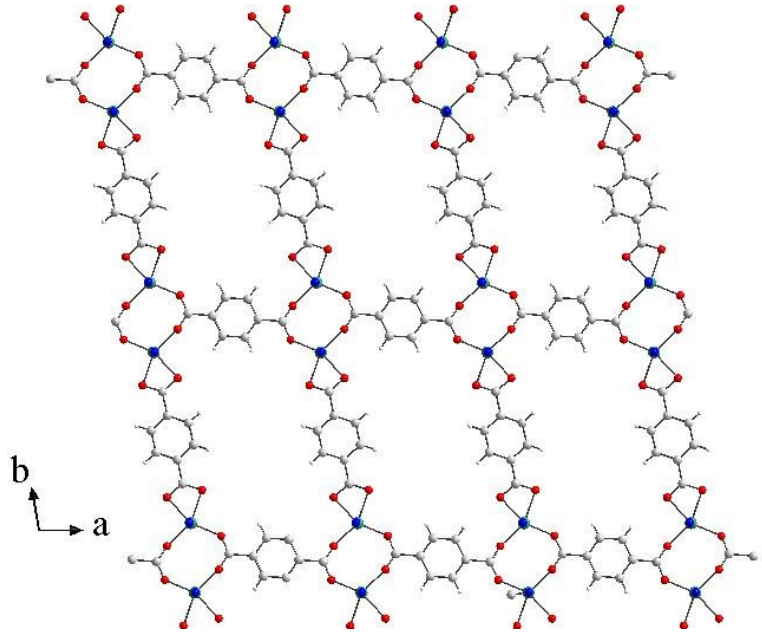
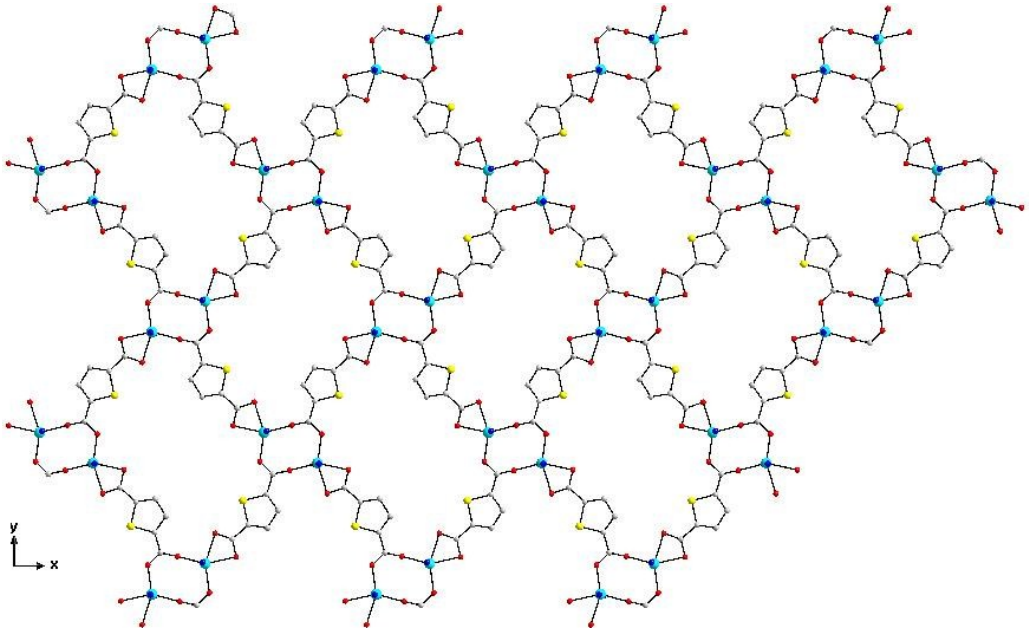


Figure S7. The IR spectrum of compound **2**.

(E) Additional structural figures

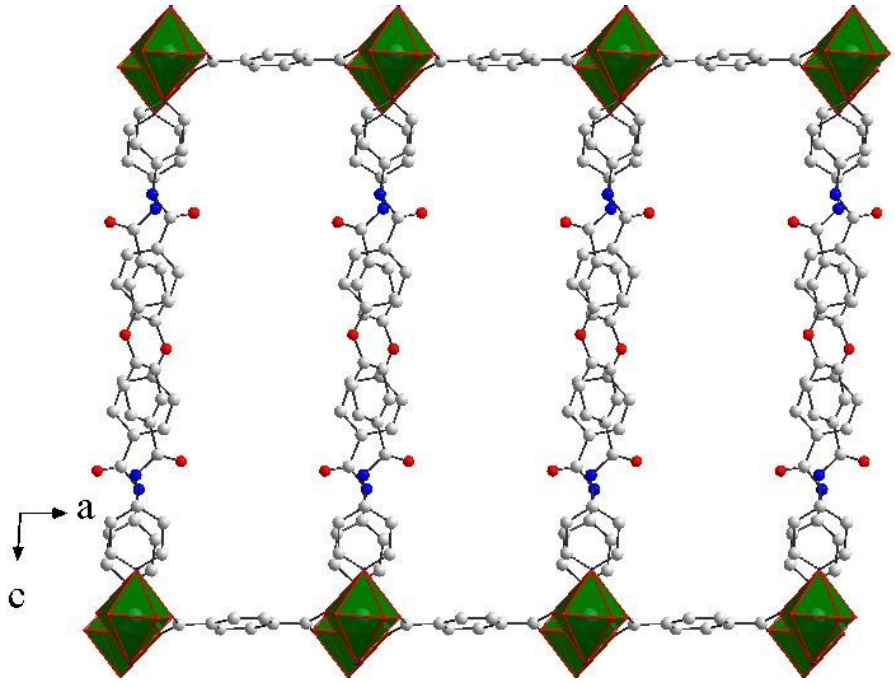


(a)

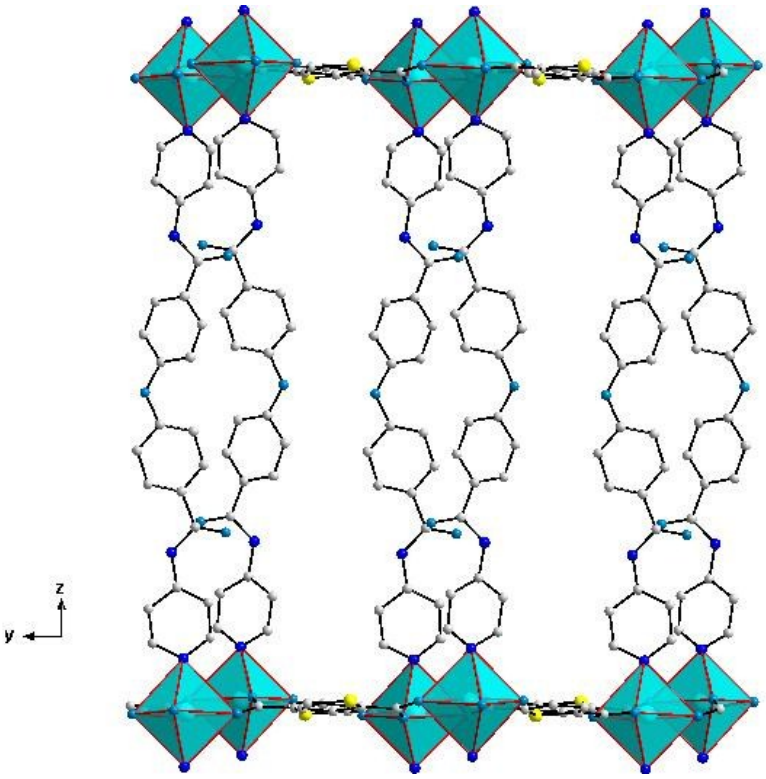


(b)

Figure S8. Two-dimensional architecture of (a) compound **1** and (b) compound **2**, respectively.



(a)



(b)

Figure S9. Pillared layered architectures of (a) compound **1** and (b) compound **2**, respectively.