Supplementary Information

Three-dimensional Pillared-layer Supramolecular Network Comprising Polymeric Layers and $\{H_2O\}_4$ Tetramer Pillars

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Table S1 Crystal data and structure refinements for **1–3**

Compound	**1**	**2**	**3**
Formula	$C_{18}H_{12}La_2O_{15}S_3$	$C_{18}H_{12}Ce_2O_{15}S_3$	$C_{18}H_{12}Pr_2O_{15}S_3$
M_r	842.28	844.70	846.28
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a (Å)	9.1069(12)	9.0536(11)	9.0148(15)
b (Å)	10.5452(13)	10.4806(12)	10.4259(18)
c (Å)	13.5137(17)	13.4765(16)	13.458(2)
	100.4410(10)	100.3860(10)	100.259(2)
B (°)	102.8500(10)	102.3950(10)	102.113(2)
	102.9220(10)	103.0420(10)	103.114(2)
V (Å^3)	1196.3(3)	1181.0(2)	1170.1(3)
Z	2	2	2
ρ(g cm^{-3})	2.338	2.375	2.402
μ (mm^{-1})	3.862	4.149	4.461
F(000)	804	808	812
GOF(F^2)	1.001	1.052	1.059
R_1[a] [$I>2\sigma(I)$]	0.0179	0.0210	0.0216
wR_2[b][$I>2\sigma(I)$]	0.0446	0.0514	0.0554

[a] $R_1 = \sum \left| |F_o| - |F_c| \right| / \sum |F_o|$. [b] $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$

Table S2 Selected bond lengths (Å) for **1–3**[a]

Compound	**1**	**2**	**3**
Ln(1)- O(9)	2.4570(19)	2.435(2)	2.418(3)
Ln(1)- O(6)	2.4635(19)	2.440(2)	2.423(3)
Ln(1)- O(7)	2.4885(18)	2.454(2)	2.442(3)
Ln(1)-O(13)	2.4943(19)	2.473(2)	2.451(3)
Ln(1)-O(3) #1	2.5095(18)	2.491(2)	2.466(3)
Ln(1)-O(5)#2	2.578(2)	2.551(3)	2.532(3)
Ln(1)-O(2)	2.6502(18)	2.629(2)	2.613(2)
Ln(1)-O(6)#2	2.7233(19)	2.709(2)	2.690(3)
Ln(1)-O(1)	2.7324(19)	2.719(2)	2.701(3)
Ln(1)-O(11)	2.4985(18)	2.479(2)	2.462(2)
Ln(2)-O(10)	2.5082(19)	2.486(2)	2.464(3)
Ln(2)-O(8)	2.554(2)	2.523(2)	2.505(3)
Ln(2)-O(4)#3	2.5381(19)	2.521(2)	2.508(3)
Ln (2)-O(12)#3	2.568(2)	2.545(3)	2.530(3)
Ln (2)-O(1)#1	2.6154(19)	2.588(2)	2.570(3)
Ln (2)-O(2)	2.5920(18)	2.583(2)	2.577(2)
Ln (2)-O(3)	2.6966(18)	2.681(2)	2.671(3)
Ln (2)-O(11)#3	2.7520(18)	2.729(2)	2.706(2)
Ln (2)-O(7)	2.8093(19)	2.806(2)	2.795(3)

[a] Symmetry codes: #1 -x+2,-y+1,-z #2 -x+2,-y,-z #3 -x+1,-y+1,-z

Table S3 Hydrogen bonds for **1-3**[a]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Compound **1**				
O(13)-H(1W)...O(10)#4	0.85	2.10	2.853(3)	146.8
O(13)-H(1W)...O(4)#1	0.85	2.42	3.016(3)	127.4
O(13)-H(1W)...O(11)#4	0.85	2.57	3.170(3)	128.2
O(13)-H(2W)...O(9)#2	0.85	1.94	2.693(3)	147.8
O(14)-H(3W)...O(8)#5	0.85	2.25	3.037(4)	154.4
O(14)-H(4W)...O(15)	0.85	1.94	2.786(5)	174.2
O(15)-H(5W)...O(5)#6	0.85	2.13	2.964(4)	168.3
O(15)-H(6W)...O(14)#7	0.85	1.99	2.825(4)	167.0
Compound **2**				
O(13)-H(1W)...O(10)#4	0.85	2.11	2.850(3)	146.8
O(13)-H(1W)...O(4)#1	0.84	2.42	3.010(4)	127.5
O(13)-H(1W)...O(11)#4	0.84	2.54	3.138(3)	128.7
O(13)-H(2W)...O(9)#2	0.84	1.93	2.682(3)	147.7
O(14)-H(3W)...O(8)#5	0.85	2.30	3.083(6)	154.5
O(14)-H(4W)...O(15)	0.84	1.82	2.659(10)	172.6
O(15)-H(5W)...O(5)#6	0.85	2.15	2.982(7)	167.5
O(15)-H(6W)...O(14)#7	0.85	1.99	2.820(8)	166.5
Compound **3**				
O(13)-H(1W)...O(10)#4	0.84	2.12	2.854(4)	146.9
O(13)-H(1W)...O(4)#1	0.84	2.42	3.005(4)	127.7
O(13)-H(1W)...O(11)#4	0.84	2.52	3.115(4)	129.1
O(13)-H(2W)...O(9)#2	0.84	1.93	2.677(4)	147.3
O(14)-H(3W)...O(8)#5	0.84	2.30	3.086(6)	154.9
O(14)-H(4W)...O(15)	0.84	1.81	2.646(12)	172.6
O(15)-H(5W)...O(5)#6	0.85	2.16	2.993(8)	167.1
O(15)-H(6W)...O(14)#7	0.85	2.00	2.830(9)	166.2

[a] Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z #2 -x+2,-y,-z #3 -x+1,-y+1,-z #4 x+1,y,z #5 x,y,z+1 #6 x,y+1,z+1 #7 -x+1,-y+1,-z+1

Fig.S1 1D polymeric chain built by tdc-1 (All H atoms are omitted for clarity).

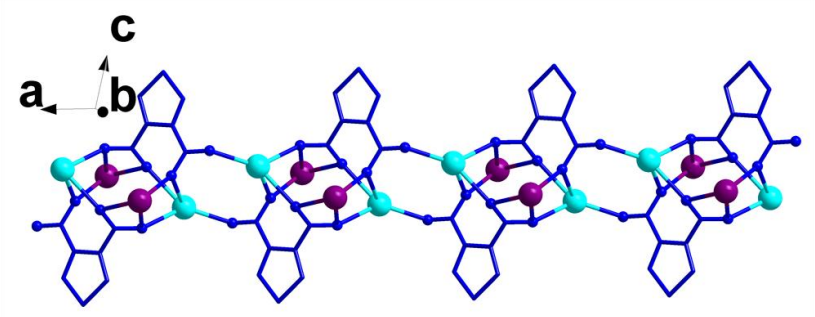

Fig.S2 2D polymeric layer structure constructed from tdc-1and tdc-2 (All H atoms are omitted for clarity).

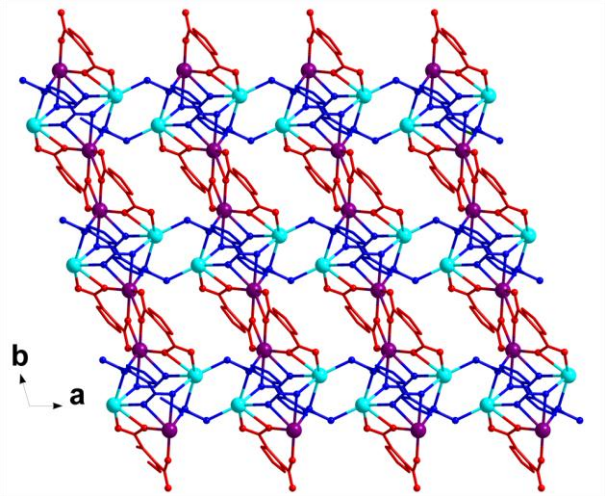

Fig.S3 2D polymeric layer where tdc-3 acting as μ_3-auxiliary supporting bridges (All H atoms are omitted for clarity).

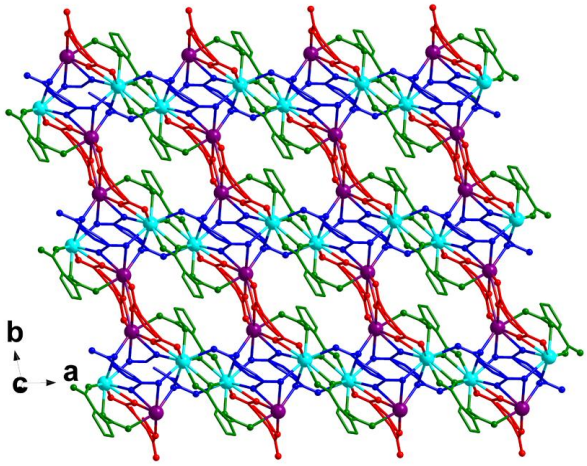

Fig. S4 O–H···O hydrogen bonding between coordinated water and carboxyl oxygen atoms (All thiophene rings and C atoms are omitted for clarity).

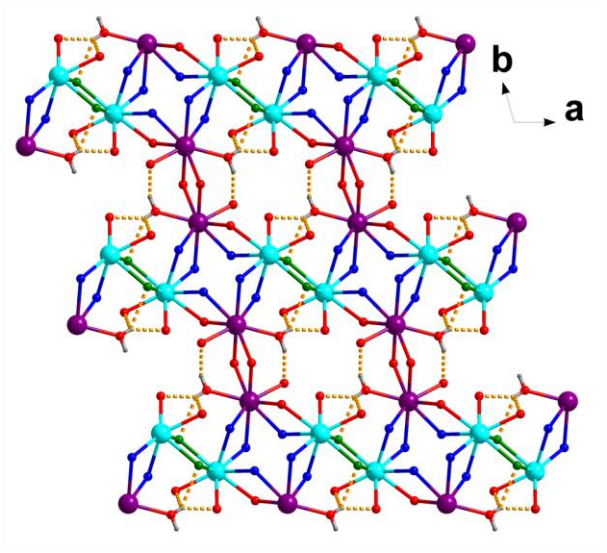

Fig. S5 TGA curves of **1**.

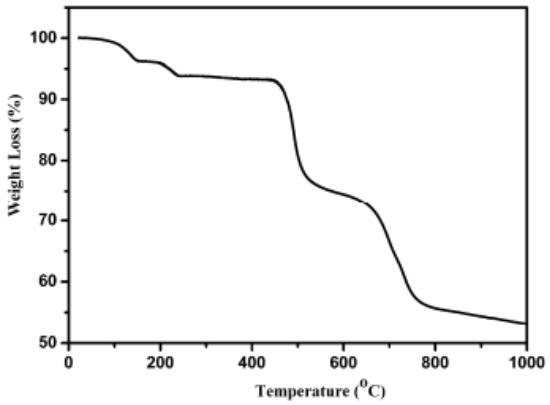

Fig. 6 Simulated, experimental, dehydrated and recovered PXRD patterns of **1**.

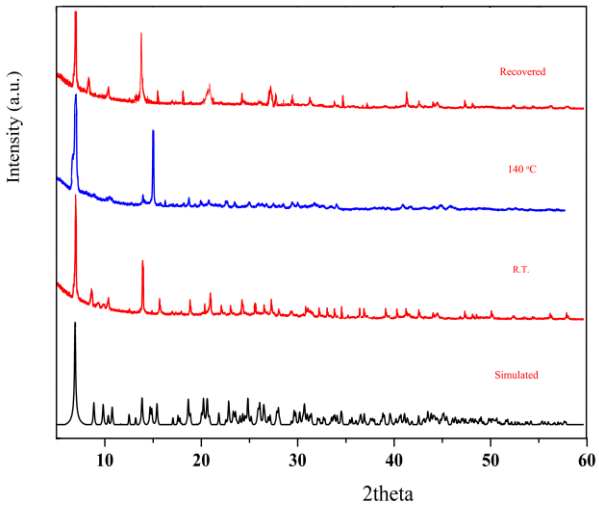

Fig. S7 Initial, dehydrated, and recovered IR spectra of **1**.