Supporting Information

Remarkable solvent-size effects in constructing novel porous 1,3,5-benzenetricarboxylate metal-organic frameworks

Xiang-Rong Hao,[a,b] Xin-Long Wang,[a] Kui-Zhan Shao,[a] Guang-Sheng Yang,[a] Zhong-Min Su,[*a] Gang Yuan.[a]

Institute of Functional Materials, College of Chemistry, Northeast Normal University, Changchun 130024, China. Email: zmsu@nenu.edu.cn

Table S1 Crystallographic data of the compound **1**, **1′**, **1′′,** **2**, **2′** and **4**, **4′**

Compound	**1**	**1′***	**1′′***	**2**	**2′***	**4**	**4′***
Chemical formula	**$Zn_2(C_9H_3O_6)(NO_3)(C_4H_9NO)_3$**	**$Zn_2(C_9H_3O_6)(NO_3)$ •5(C_2H_5OH) •H_2O**	**$Mg_2(C_9H_3O_6)(CH_3COO)$ •3(C_4H_9NO)(H_2O)**	**$Zn_{11}(C_9H_3O_6)_6(NO_3)_4(C_6H_{13}NO)_9$**	**$C_{155}{\cdot}_{17}H_{36}N_8O_{98}Zn_{22}$**	**$ZnC_9H_3O_6$• C_4H_9NO •C_2H_8N**	**$ZnC_9H_3O_6$• C_3H_7NO •C_2H_8N**
Formula Mass	661.23	648.22	576.14	3246.36	5018.10	405.70	391.67
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Cubic	Cubic	Monoclinic	Monoclinic
a/Å	12.935(5)	14.728(4)	12.537(5)	20.573(5)	20.4582(13)	9.320(5)	9.4550(6)
b/Å	14.708(5)	14.728(4)	14.977(5)	20.573(5)	20.4582(13)	16.107(5)	16.0074(11)
c/Å	15.359(5)	14.728(4)	15.404(6)	20.573(5)	20.4582(13)	12.608(5)	11.0347(7)
α/°	90.000(5)	90.000(5)	90.00	90.000(5)	90.00	90.000(5)	90.000(5)
β/°	90.000(5)	90.000(5)	90.00	90.000(5)	90.00	100.942(5)	98.4660(10)
γ/°	90.000(5)	90.000(5)	90.00	90.000(5)	90.00	90.000(5)	90.000(5)
Unit cell volume/Å^3	2922.0(18)	3195(2)	2892.3(18)	8707(4)	8562.5(9)	1858.3(14)	1651.90(19)
Temperature/K	293(2)	293(2)	213(2)	293(2)	173(2)	293(2)	293(2)
Space group	*P*212121	*P*213	*P*212121	*Pm*$\bar{3}$ *m*	*Pm*$\bar{3}$ *m*	*P*21/*n*	*P*21/*n*
Z	4	4	4	1	1	4	4
No. of reflections measured	14745		9123	44723	14454	9299	
No. of independent reflections	5143		3725	1582	740	3281	
R_{int}	0.0360		0.0224	0.1422	0.0359	0.0630	
Final R_1 values ($I > 2\sigma(I)$) [a]	0.0383		0.0599	0.1016	0.1278	0.0486	
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.0995		0.1517	0.2972	0.3523	0.1101	
Final R_1 values (all data)	0.0468		0.0704	0.1762	0.1423	0.0874	
Final $wR(F^2)$ values (all data)	0.1063		0.1628		0.3648	0.1269	

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. * compound 1′**,** 1′′**,** 2′ and 4′ have been reported previously.

Table S2. The relationship between the and different size of solvents.

	DMF	DMA	DEE	DEP	DPE	DPP
btc-Zn / Method **I**	**1′***	**1**	**2**	**3**	X	X
btc-Zn / Method **II**	**4′***	**4**, **5** **6**$^{\#}$,	**6**$^{\#}$, **7**	X	X	X

* **1′** and **4′** have been reported previously. **1′** is prepared in alcohol. $^{\#}$**6** was first obtained in a mixture of DMA and DEE (3:1 v/v) solvent, it also can obtained DMA solvent occasionally. Symbol "X" indicates no single crystal samples suitable for measuring can be obtained.

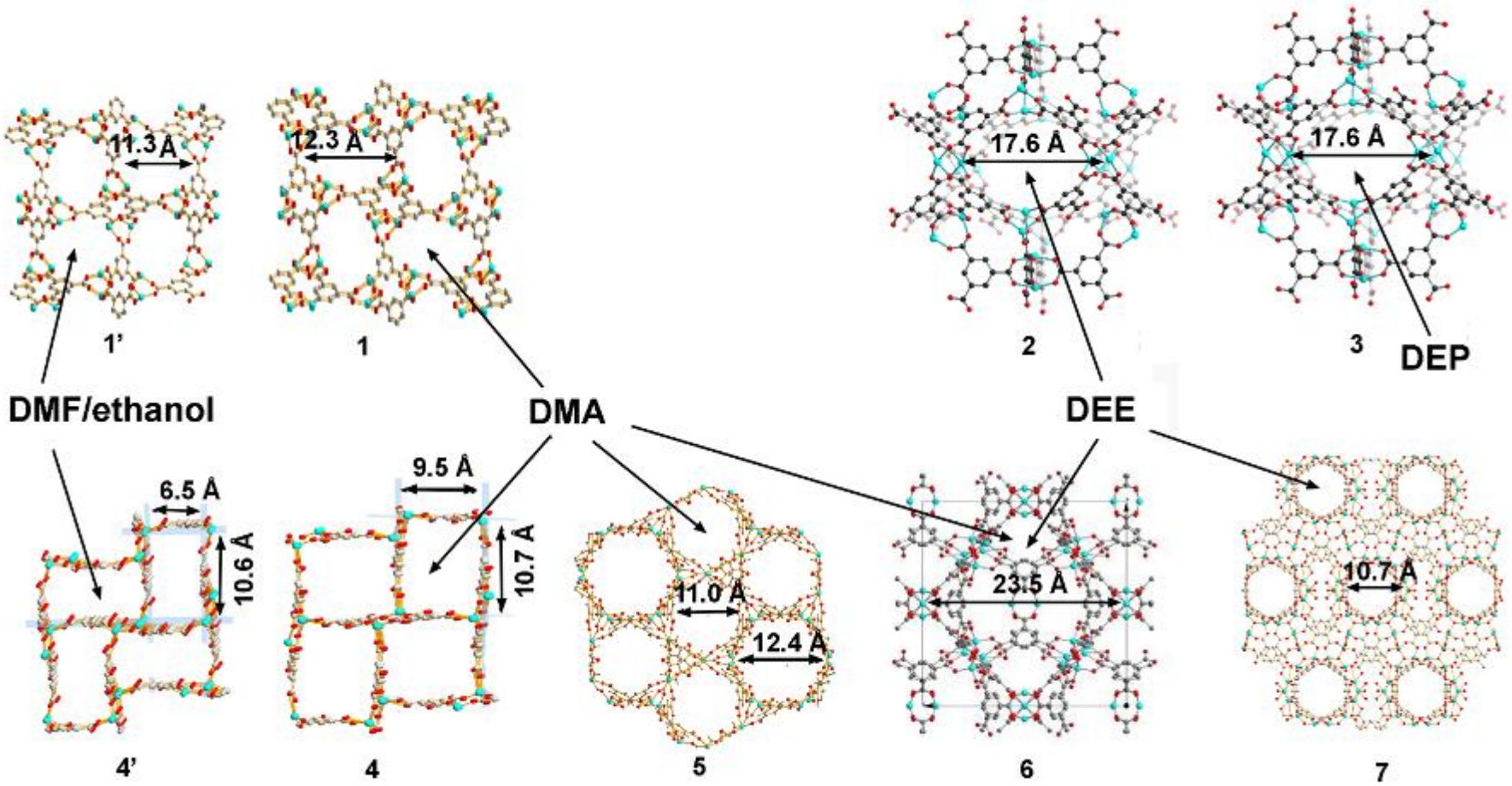


Fig. S1 A view of frameworks **1-7** showing the different pore size introduced by solvents and breathing phenomenon.

PXRD analysis:

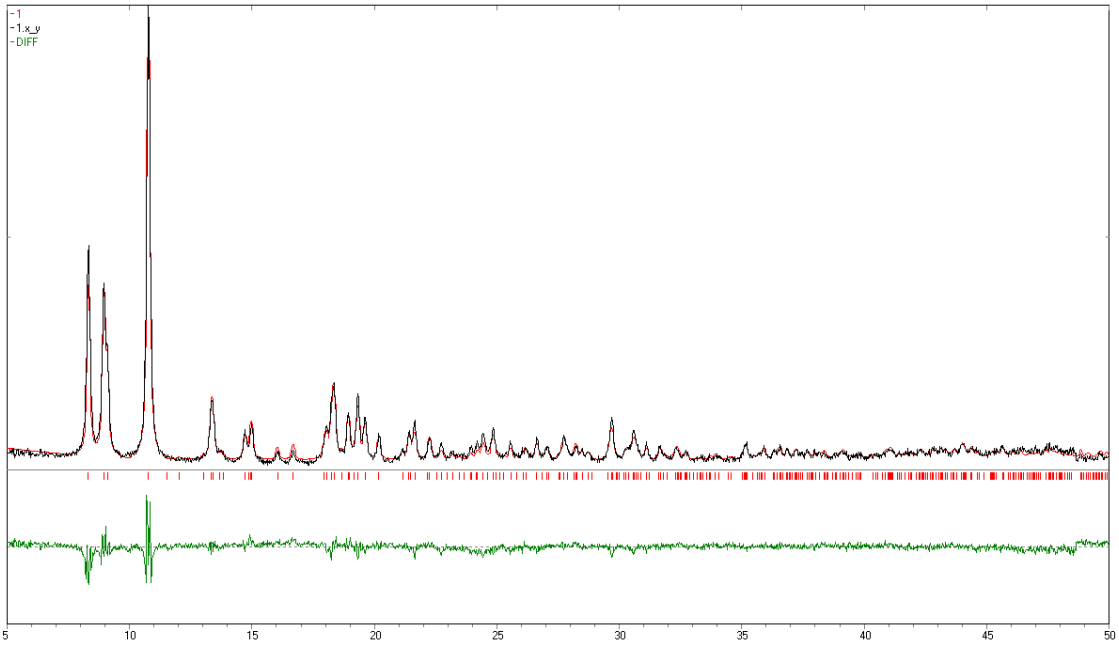


Fig. S2. PXRD patterns for **1**: the calculated X-ray crystal structure (red), experimental XRPD pattern (black) and difference (green) of the bulk material.

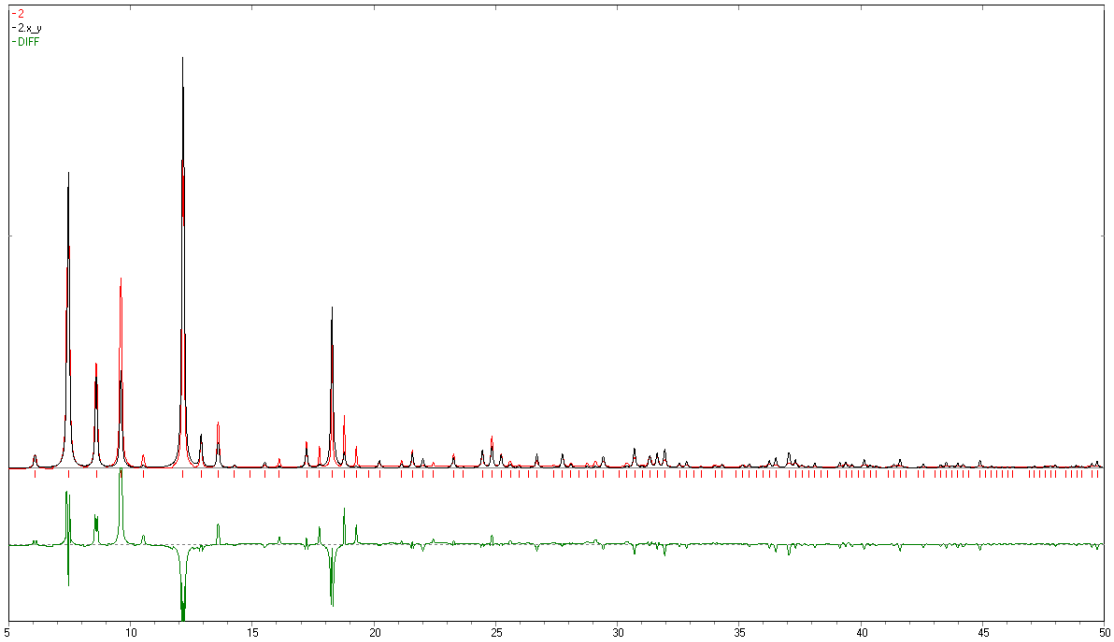


Fig. S3. PXRD patterns for **2**: the calculated X-ray crystal structure (red), experimental XRPD pattern (black) and difference (green) of the bulk material.

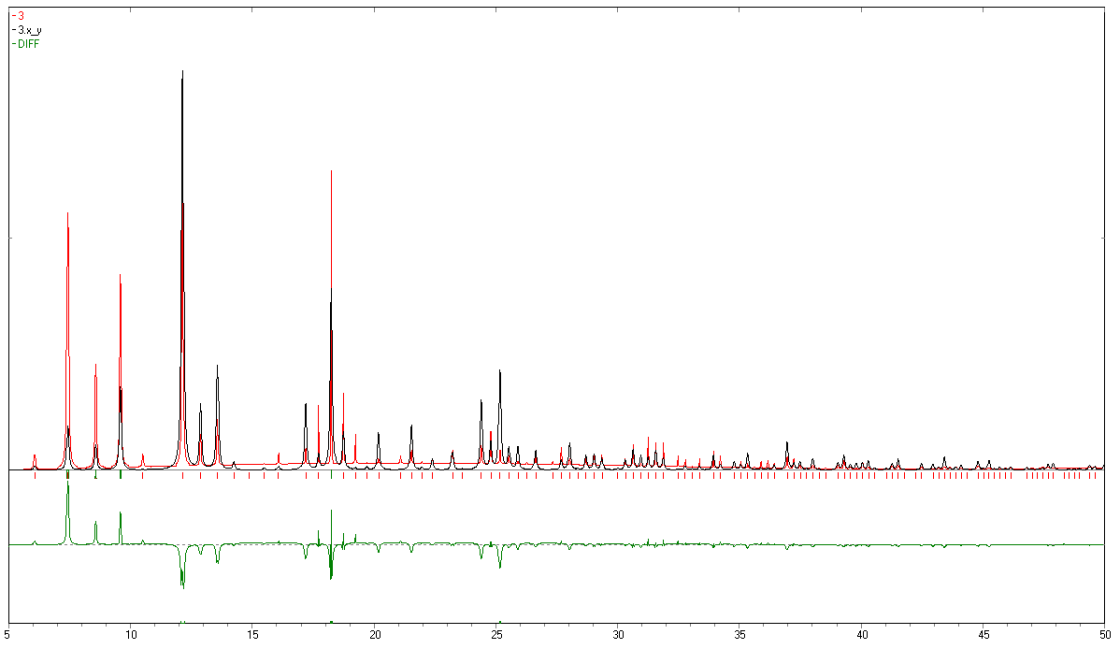


Fig. S4. PXRD patterns for **3**: the calculated X-ray crystal structure (red), experimental XRPD pattern (black) and difference (green) of the bulk material.

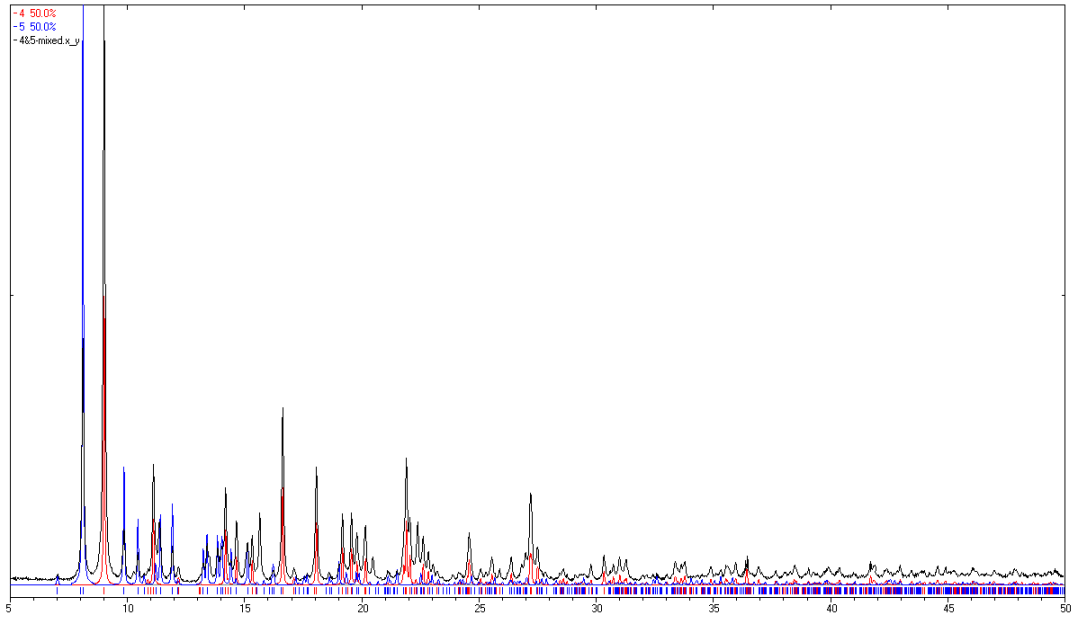


Fig. S5. PXRD patterns for the bulk of **4** (or **5**) present a mixed-phase characterization: the calculated X-ray crystal structure of **4** (red), the calculated X-ray crystal structure of **5** (blue), the experimental XRPD pattern (black) showing that the bulk probably is a mixture of **4** and **5**.

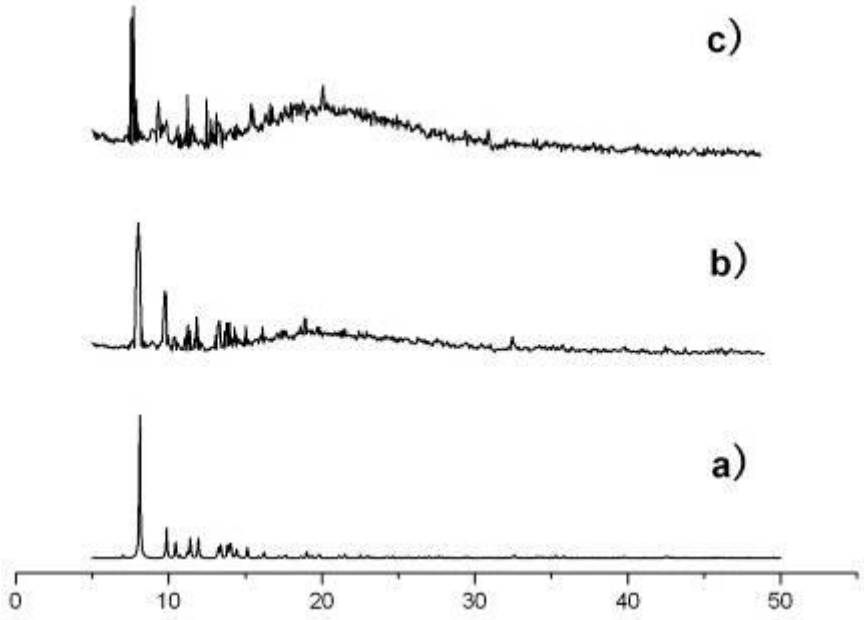


Fig. S6. PXRD patterns for **5**: (a) simulated from single-crystal X-ray diffraction data, (b) as-synthesized solids, (c) after the ammonium acetate added in dmso-D6.

IR analysis:

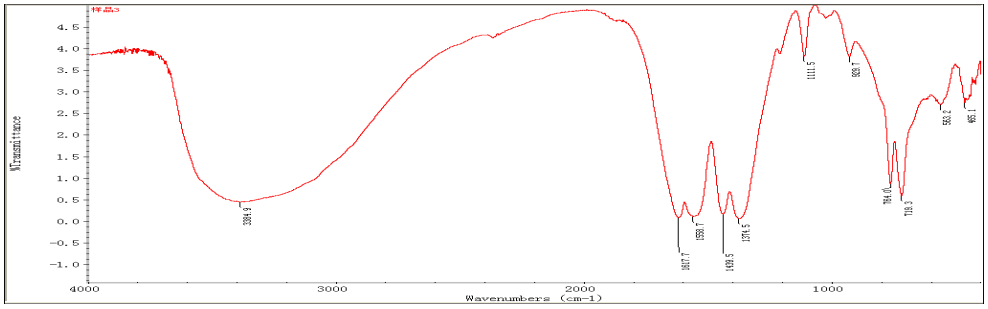


Fig. S16. FT-IR spectrum of as-synthesized **-1**.

Fig. S17. FT-IR spectrum of as-synthesized **-2**.

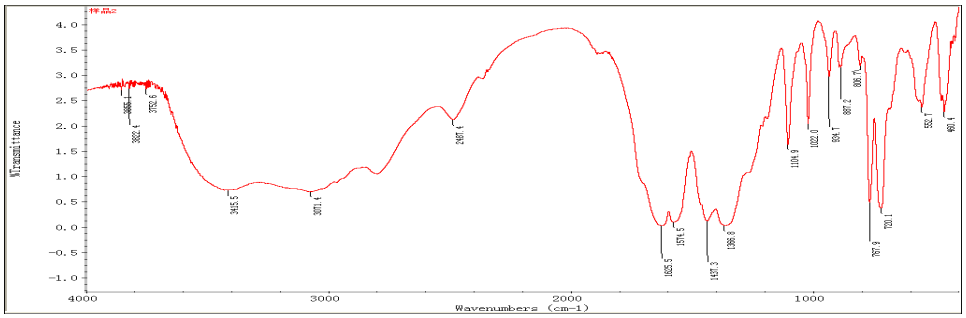


Fig. S18. FT-IR spectrum of as-synthesized **-3**.

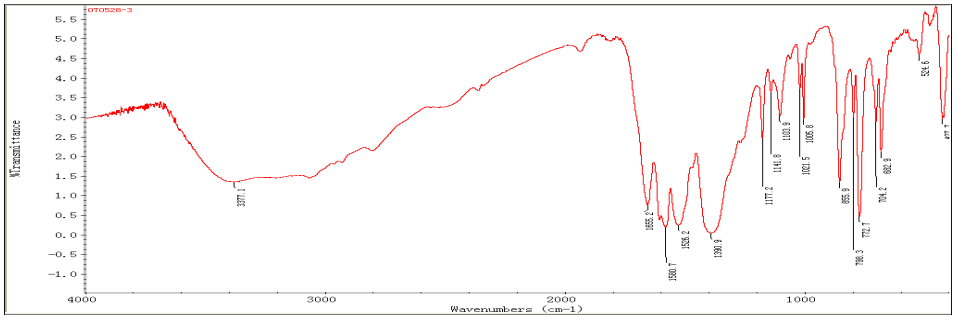


Fig. S19. FT-IR spectrum of as-synthesized **-4**.

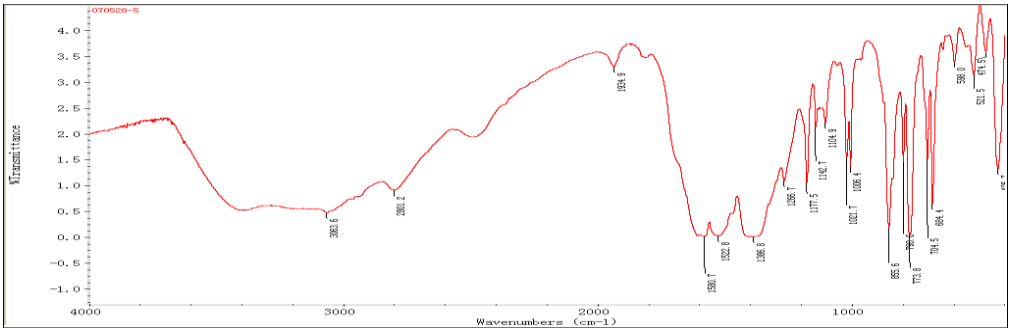
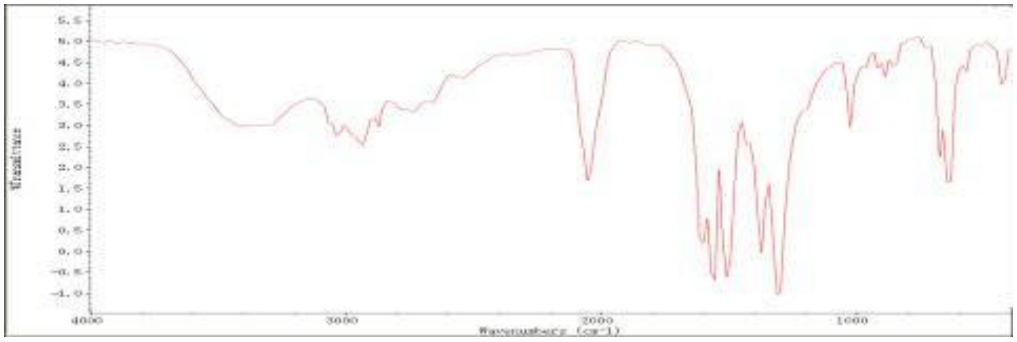


Fig. S20. FT-IR spectrum of as-synthesized **-5**.



.**Fig. S21.** FT-IR spectrum of as-synthesized **-6**

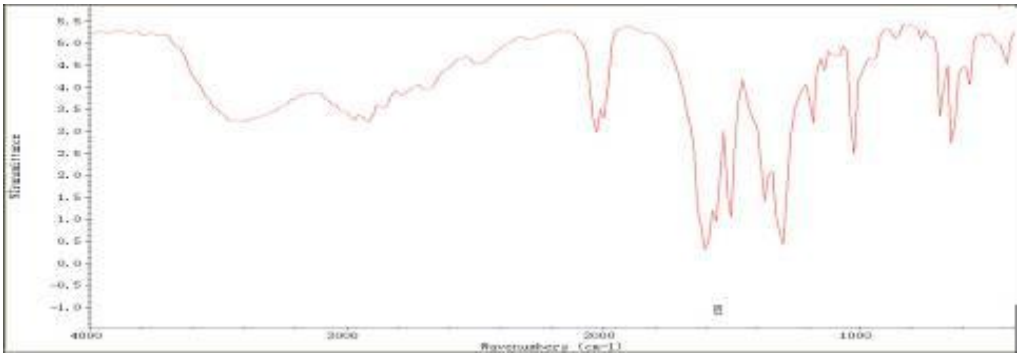


Fig. S22. FT-IR spectrum of as-synthesized **-7**

TGA analysis:

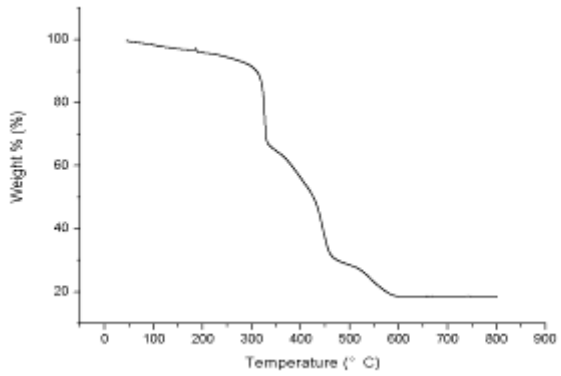


Fig. S23. TG curve of **2**.

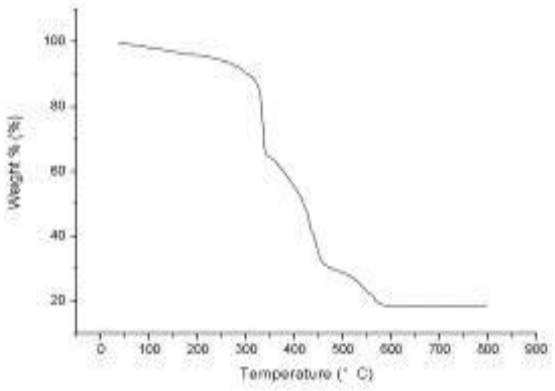


Fig. S24. TG curve of **3**

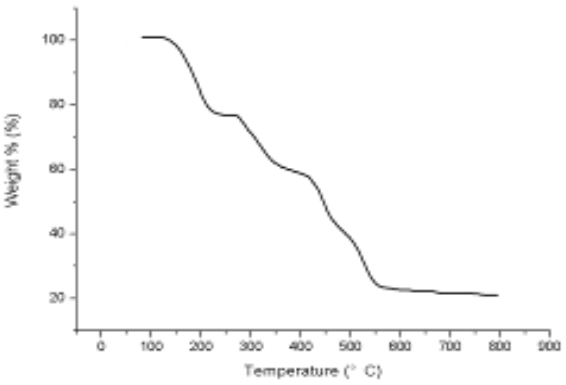


Fig. S25. TG curve of **4**

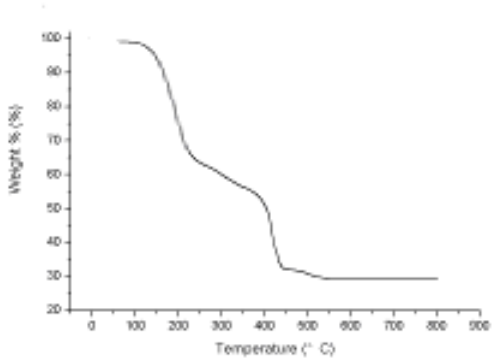


Fig. S26. TG curve of **5**

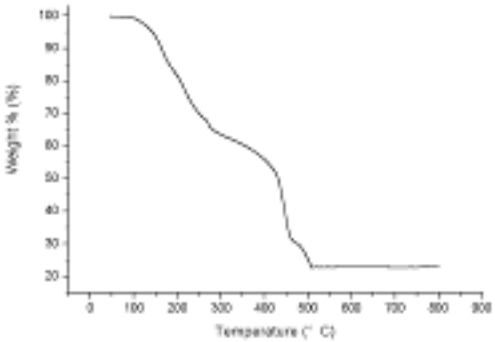


Fig. S27. TG curve of **6**

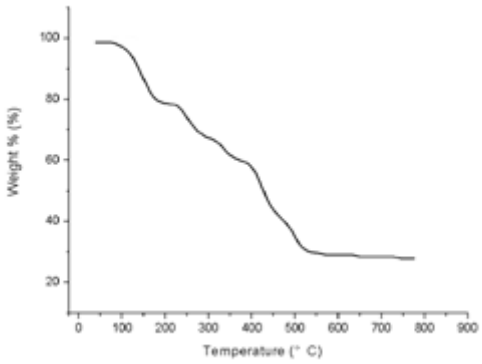


Fig. S28. TG curve of **7**

The coordinates for idealized net computed with Systre (Compounds 5, 6 and 7)

```
CRYSTAL
NAME "Compound 5 (3,3,4,5)-c trans [45]"
GROUP R-3c:H
CELL 7.91537 7.91537 2.73089 90.0000 90.0000 120.0000
NODE 1 3 0.12080 0.18671 0.07543
NODE 3 5 0.00000 0.16359 0.25000
NODE 2 3 0.28992 0.00000 0.25000
NODE 4 4 0.00000 0.24902 0.75000
EDGE 0.00000 0.16359 0.25000 -0.00000 0.28992 0.25000
EDGE 0.00000 0.24902 0.75000 0.06591 0.18671 0.57543
EDGE 0.28992 0.00000 0.25000 0.41765 0.08432 0.08333
EDGE 0.00000 0.16359 0.25000 0.12080 0.18671 0.07543
EDGE 0.00000 0.16359 0.25000 0.06591 0.18671 0.57543
# EDGE_CENTER 0.00000 0.22675 0.25000
# EDGE_CENTER 0.03296 0.21786 0.66271
# EDGE_CENTER 0.35379 0.04216 0.16667
# EDGE_CENTER 0.06040 0.17515 0.16271
# EDGE_CENTER 0.03296 0.17515 0.41271
END

CRYSTAL
NAME "Compound 6 (3,4,6)-c trans [3222]; 6[6^6]+[6^12]"
GROUP Im-3
CELL 3.77123 3.77123 3.77123 90.0000 90.0000 90.0000
NODE 2 6 0.25000 0.25000 0.25000
NODE 1 3 0.00000 0.18764 0.31263
NODE 3 4 0.00000 0.00000 0.50000
EDGE 0.00000 0.00000 0.50000 0.00000 0.18764 0.31263
EDGE 0.00000 0.18764 0.31263 0.25000 0.25000 0.25000
# EDGE_CENTER 0.00000 0.09382 0.40632
# EDGE_CENTER 0.12500 0.21882 0.28132
END

CRYSTAL
NAME "Compound 7 (3,3,3,5,6)-c trans [59]"
GROUP Pnma
CELL 2.86160 4.87780 2.88729 90.0000 90.0000 90.0000
NODE 5 3 0.29588 0.08602 0.27164
NODE 2 6 0.12278 0.56272 0.43712
NODE 4 3 0.01637 0.25000 0.53407
NODE 1 5 0.35973 0.25000 0.46964
```

NODE 3 3 0.44449 0.62084 0.34412
EDGE 0.29588 0.08602 0.27164 0.37722 0.06272 -0.06288
EDGE 0.01637 0.25000 0.53407 -0.12278 0.06272 0.56288
EDGE 0.01637 0.25000 0.53407 0.35973 0.25000 0.46964
EDGE 0.12278 0.56272 0.43712 0.44449 0.62084 0.34412
EDGE 0.12278 0.56272 0.43712 -0.12278 0.43728 0.56288
EDGE 0.29588 0.08602 0.27164 0.12278 -0.06272 0.43712
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EDGE 0.35973 0.25000 0.46964 0.55551 0.12084 0.65588
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EDGE_CENTER 0.28363 0.59178 0.39062
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EDGE_CENTER 0.03363 0.59178 0.29650
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END