Electronic supplementary information (ESI)

Synthesis, structure, magnetic and catalytic properties of metal frameworks with 2,2'-dinitro-4,4'-biphenyldicarboxylate and imidazole-containing tripodal ligands

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Table S1 Selected bond lengths (Å) and angles (°) for **1-4.**[a]

Complex **1**			
Mn(1)-O(10)	2.081(3)	Mn(1)-O(19)#1	2.085(3)
Mn(1)-O(1)	2.209(3)	Mn(1)-O(11)#2	2.223(2)
Mn(1)-O(2)	2.267(2)	Mn(1)-O(12)#2	2.342(2)
Mn(2)-O(4)#3	2.139(3)	Mn(2)-O(1W)	2.205(3)
Mn(2)-O(18)	2.208(2)	Mn(2)-O(9)	2.213(3)
Mn(2)-N(7)	2.240(3)	Mn(2)-O(20)#4	2.249(2)
Mn(3)-O(3)#3	2.075(3)	Mn(3)-O(17)	2.131(2)
Mn(3)-N(9)#5	2.207(3)	Mn(3)-O(2W)	2.279(3)
Mn(3)-O(12)#2	2.292(3)	Mn(3)-O(10)	2.477(3)
O(10)-Mn(1)-O(19)#1	99.75(10)	O(10)-Mn(1)-O(1)	124.57(11)
O(19)#1-Mn(1)-O(1)	127.48(10)	O(10)-Mn(1)-O(11)#2	129.97(9)
O(19)#1-Mn(1)-O(11)#2	85.78(10)	O(1)-Mn(1)-O(11)#2	85.57(10)
O(10)-Mn(1)-O(2)	103.45(10)	O(19)#1-Mn(1)-O(2)	87.49(10)

O(1)-Mn(1)-O(2)	58.26(9)	O(11)#2-Mn(1)-O(2)	126.54(10)
O(10)-Mn(1)-O(12)#2	78.04(9)	O(19)#1-Mn(1)-O(12)#2	119.89(9)
O(1)-Mn(1)-O(12)#2	78.04(9)	O(11)#2-Mn(1)-O(12)#2	57.28(9)
O(2)-Mn(1)-O(12)#2	152.22(10)	O(4)#3-Mn(2)-O(1W)	81.30(11)
O(4)#3-Mn(2)-O(18)	107.85(10)	O(1W)-Mn(2)-O(18)	79.57(11)
O(4)#3-Mn(2)-O(9)	94.09(10)	O(1W)-Mn(2)-O(9)	155.75(10)
O(18)-Mn(2)-O(9)	79.26(10)	O(4)#3-Mn(2)-N(7)	163.60(11)
O(1W)-Mn(2)-N(7)	92.31(11)	O(18)-Mn(2)-N(7)	85.60(10)
O(9)-Mn(2)-N(7)	97.72(10)	O(4)#3-Mn(2)-O(20)#4	81.03(10)
O(1W)-Mn(2)-O(20)#4	115.99(10)	O(18)-Mn(2)-O(20)#4	163.57(10)
O(9)-Mn(2)-O(20)#4	86.44(9)	N(7)-Mn(2)-O(20)#4	88.37(10)
O(3)#3-Mn(3)-O(17)	99.08(11)	O(3)#3-Mn(3)-N(9)#5	170.97(11)
O(17)-Mn(3)-N(9)#5	84.30(10)	O(3)#3-Mn(3)-O(2W)	86.34(11)
O(17)-Mn(3)-O(2W)	81.81(10)	N(9)#5-Mn(3)-O(2W)	102.47(10)
O(3)#3-Mn(3)-O(12)#2	90.66(10)	O(17)-Mn(3)-O(12)#2	156.96(9)
N(9)#5-Mn(3)-O(12)#2	89.28(10)	O(2W)-Mn(3)-O(12)#2	78.00(9)
O(3)#3-Mn(3)-O(10)	80.50(10)	O(17)-Mn(3)-O(10)	130.51(9)
N(9)#5-Mn(3)-O(10)	90.92(9)	O(2W)-Mn(3)-O(10)	146.51(9)
O(12)#2-Mn(3)-O(10)	71.54(9)		

Symmetry codes: #1 3/2-x,-1/2+y,1/2-z; #2 1/2+x,1/2-y,1/2+z; #3 -x,1-y,1-z; #4 -1+x,y,z; #5 1-x,1-y,-z.

Complex **2**

Cd(1)-O(1)	2.173(2)	Cd(1)-O(18)	2.269(2)
Cd(1)-N(5)#1	2.242(2)	Cd(1)-O(1W)	2.386(2)
Cd(1)-O(12)#2	2.496(2)	Cd(1)-O(9)	2.531(2)
Cd(1)-O(10)	2.362(2)	Cd(2)-O(2)	2.271(2)
Cd(2)-N(1)	2.296(2)	Cd(2)-O(2W)	2.303(3)
Cd(2)-O(17)	2.330(2)	Cd(2)-O(20)#3	2.333(2)
Cd(2)-O(10)	2.362(2)	Cd(3)-O(9)#4	2.201(2)
Cd(3)-O(19)	2.243(2)	Cd(3)-O(3)#5	2.294(2)
Cd(3)-O(11)#1	2.335(2)	Cd(3)-O(11)#1	2.335(2)
Cd(3)-O(4)#5	2.358(2)	Cd(3)-O(12)#1	2.387(2)
O(1)-Cd(1)-N(5)#1	170.00(10)	O(1)-Cd(1)-O(18)	103.47(9)

N(5)#1-Cd(1)-O(18)	85.84(8)	O(1)-Cd(1)-O(1W)	85.45(9)
N(5)#1-Cd(1)-O(1W)	99.50(8)	O(18)-Cd(1)-O(1W)	82.96(8)
O(1)-Cd(1)-O(12)#2	83.72(9)	N(5)#1-Cd(1)-O(12)#2	89.20(9)
O(18)-Cd(1)-O(12)#2	155.89(8)	O(1W)-Cd(1)-O(12)#2	74.61(7)
O(1)-Cd(1)-O(9)	78.45(9)	N(5)#1-Cd(1)-O(9)	92.57(8)
O(18)-Cd(1)-O(9)	133.01(7)	O(1W)-Cd(1)-O(9)	143.02(8)
O(12)#2-Cd(1)-O(9)	70.72(7)	O(1)-Cd(1)-O(10)	93.31(8)
N(5)#1-Cd(1)-O(10)	84.07(8)	O(18)-Cd(1)-O(10)	83.20(7)
O(1W)-Cd(1)-O(10)	165.40(7)	O(12)#2-Cd(1)-O(10)	119.76(6)
O(9)-Cd(1)-O(10)	50.03(6)	O(2)-Cd(2)-N(1)	165.39(8)
O(2)-Cd(2)-O(2W)	80.52(10)	N(1)-Cd(2)-O(2W)	95.99(10)
O(2)-Cd(2)-O(17)	109.61(8)	N(1)-Cd(2)-O(17)	83.54(8)
O(2W)-Cd(2)-O(17)	80.36(9)	O(2)-Cd(2)-O(20)#3	78.81(8)
N(1)-Cd(2)-O(20)#3	90.98(8)	O(2W)-Cd(2)-O(20)#3	120.25(9)
O(17)-Cd(2)-O(20)#3	159.21(9)	O(2)-Cd(2)-O(10)	93.11(8)
N(1)-Cd(2)-O(10)	96.13(8)	O(2W)-Cd(2)-O(10)	152.97(8)
O(17)-Cd(2)-O(10)	77.12(8)	O(20)#3-Cd(2)-O(10)	83.57(7)
O(9)#4-Cd(3)-O(19)	96.38(8)	O(9)#4-Cd(3)-O(3)#5	132.90(9)
O(19)-Cd(3)-O(3)#5	122.21(8)	O(9)#4-Cd(3)-O(11)#1	127.15(8)
O(19)-Cd(3)-O(11)#1	85.06(8)	O(3)#5-Cd(3)-O(11)#1	85.47(8)
O(9)#4-Cd(3)-O(4)#5	107.05(8)	O(19)-Cd(3)-O(4)#5	85.81(8)
O(3)#5-Cd(3)-O(4)#5	56.04(7)	O(11)#1-Cd(3)-O(4)#5	125.69(7)
O(9)#4-Cd(3)-O(12)#1	78.60(7)	O(19)-Cd(3)-O(12)#1	117.82(7)
O(3)#5-Cd(3)-O(12)#1	102.19(7)	O(11)#1-Cd(3)-O(12)#1	55.46(7)
O(4)#5-Cd(3)-O(12)#1	155.41(8)		

Symmetry codes: #1 -x,-y,2-z; #2 -1/2+x,-1/2-y,-1/2+z; #3 1+x,y,z; #4 -1/2-x,1/2+y,3/2-z; #5 -3/2+x,1/2-y,1/2+z.

Complex **3**

Zn(1)-O(24)#1	1.948(3)	Zn(1)-N(1)	1.991(3)
Zn(1)-O(22)	2.002(3)	Zn(1)-N(7)	2.014(4)
Zn(2)-O(7)#2	1.936(3)	Zn(2)-O(5)	1.958(3)
Zn(2)-N(3)#3	2.010(3)	Zn(2)-N(11)	2.050(4)
Zn(3)-O(21)	1.981(4)	Zn(3)-N(5)	2.010(4)

Zn(3)-O(13)	2.002(5)	Zn(3)-N(9)	2.024(4)
Zn(3)-O(14)	2.469(6)	O(24)#1-Zn(1)-N(1)	116.38(13)
O(24)#1-Zn(1)-O(22)	102.77(12)	N(1)-Zn(1)-O(22)	115.62(12)
O(24)#1-Zn(1)-N(7)	97.36(14)	N(1)-Zn(1)-N(7)	112.46(14)
O(22)-Zn(1)-N(7)	110.46(12)	O(7)#2-Zn(2)-O(5)	110.47(13)
O(7)#2-Zn(2)-N(3)#3	125.78(14)	O(5)-Zn(2)-N(3)#3	105.38(14)
O(7)#2-Zn(2)-N(11)	107.35(14)	O(5)-Zn(2)-N(11)	105.03(12)
N(3)#3-Zn(2)-N(11)	100.80(13)	O(21)-Zn(3)-N(5)	119.87(17)
O(21)-Zn(3)-O(13)	106.9(2)	N(5)-Zn(3)-O(13)	116.76(19)
O(21)-Zn(3)-N(9)	109.06(17)	N(5)-Zn(3)-N(9)	104.43(14)
O(13)-Zn(3)-N(9)	97.2(2)	O(21)-Zn(3)-O(14)	89.73(18)
N(5)-Zn(3)-O(14)	86.00(17)	O(13)-Zn(3)-O(14)	51.6(2)
N(9)-Zn(3)-O(14)	148.81(18)		

Symmetry codes: #1 2-x,1/2+y,1/2-z; #2 -1-x,1/2+y,1/2-z; #3 -1+x,3/2-y,-1/2+z.

Complex **4**

Cd(1)-O(1W)	2.277(2)	Cd(1)-N(3)	2.298(2)
Cd(1)-N(5)	2.305(2)	Cd(1)-N(1)	2.312(2)
Cd(1)-O(1)	2.348(2)	Cd(1)-O(2)	2.434(2)
O(1W)-Cd(1)-N(3)	87.84(6)	O(1W)-Cd(1)-N(5)	104.49(6)
N(3)-Cd(1)-N(5)	97.11(6)	O(1W)-Cd(1)-N(1)	86.61(6)
N(3)-Cd(1)-N(1)	174.30(6)	N(5)-Cd(1)-N(1)	85.57(6)
O(1W)-Cd(1)-O(1)	147.58(6)	N(3)-Cd(1)-O(1)	93.57(7)
N(5)-Cd(1)-O(1)	107.45(6)	N(1)-Cd(1)-O(1)	90.41(6)
O(1W)-Cd(1)-O(2)	92.79(5)	N(3)-Cd(1)-O(2)	88.76(6)
N(5)-Cd(1)-O(2)	161.91(6)	N(1)-Cd(1)-O(2)	90.19(6)
O(1)-Cd(1)-O(2)	54.92(6)		

Table S2 Hydrogen bonding data of **4**.

Complex **4**				
D–H ··A	d(*D*–H) (Å)	d(H ··A) (Å)	d(*D* ··A)(Å)	*D*–H ··A (°)
O(1W)-H(1A) ··O(4)	0.81	1.84	2.644(3)	171
O(1W)-H(1B) ··O(3)	0.91	1.85	2.744(3)	167
C(7)-H(7) ··O(3)	0.93	2.45	3.378(3)	175
C(15)-H(15) ··O(1W)	0.93	2.51	3.324(4)	146
O(2W)-H(2WB) ··O(9)	0.90	1.95	2.843(5)	175
O(2W)-H(2WA) ··O(4)	0.94	1.91	2.835(3)	166
C(5)-H(5) ··O(2W)	0.93	2.53	3.455(4)	172
C(13)-H(13) ··O(2W)	0.93	2.56	3.484(4)	172

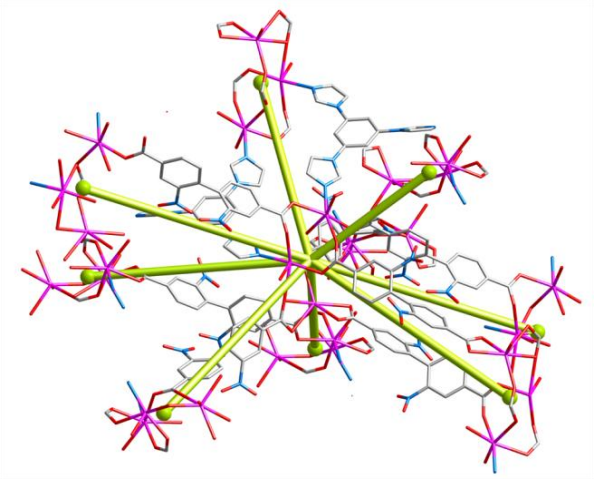


Fig. S1 The 8-node of SBU in **1**.

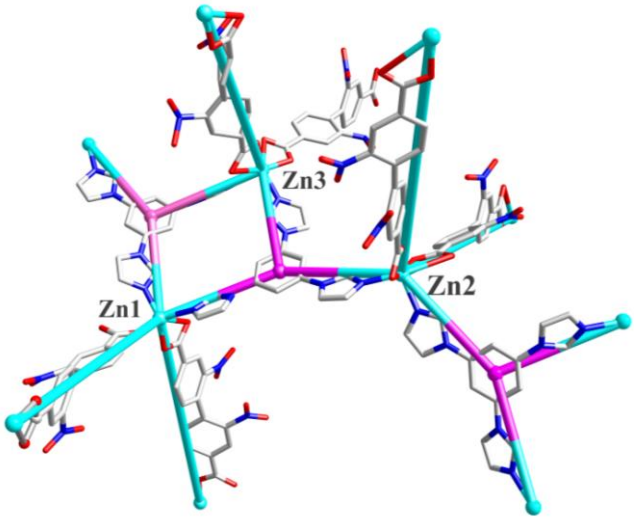


Fig. S2 Four-, four-, three-, three- and two-connectors in **3**.

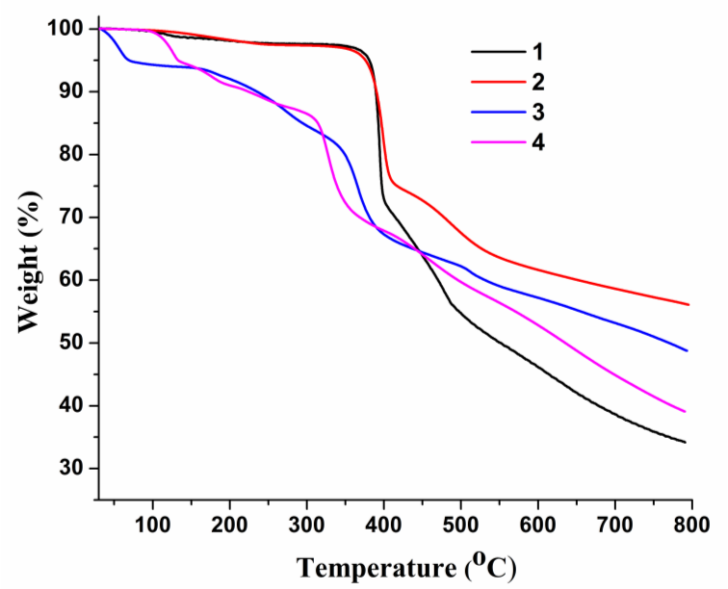


Fig. S3 TG curves of **1**, **2**, **3** and **4**.

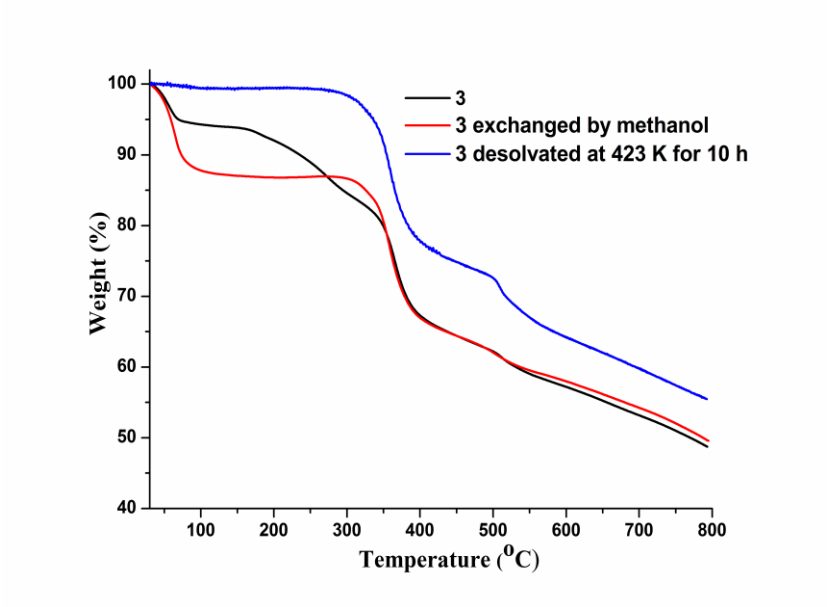
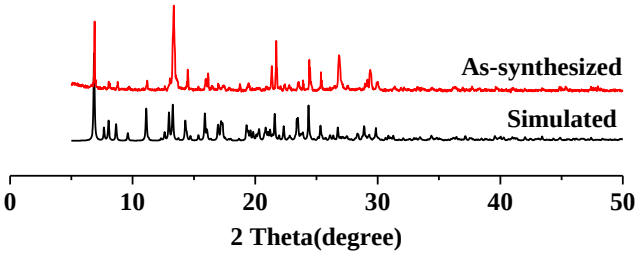
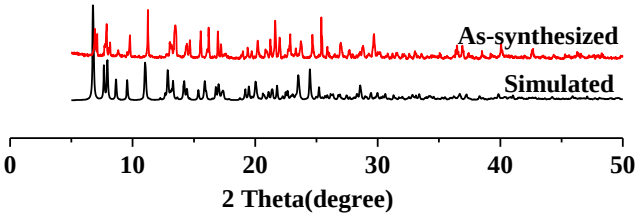


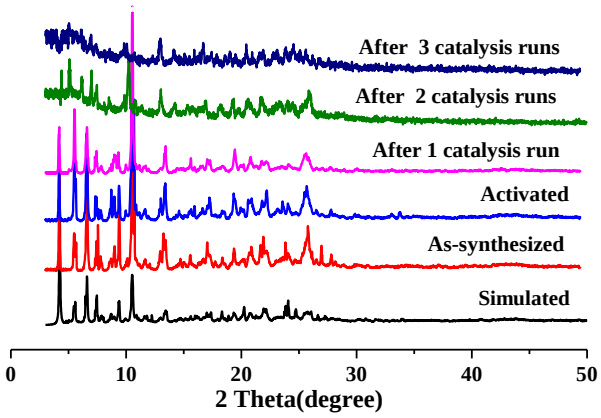
Fig. S4 TG curves of **3** (black: as-synthesized, red: exchanged by methanol, blue: desolvated at 423 K for 10 h).



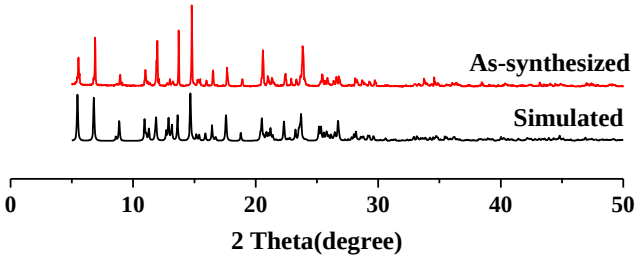
(a)



(b)



(c)



(d)

Fig. S5 PXRD patterns of **1** (a), **2** (b), **3** (c) and **4** (d).

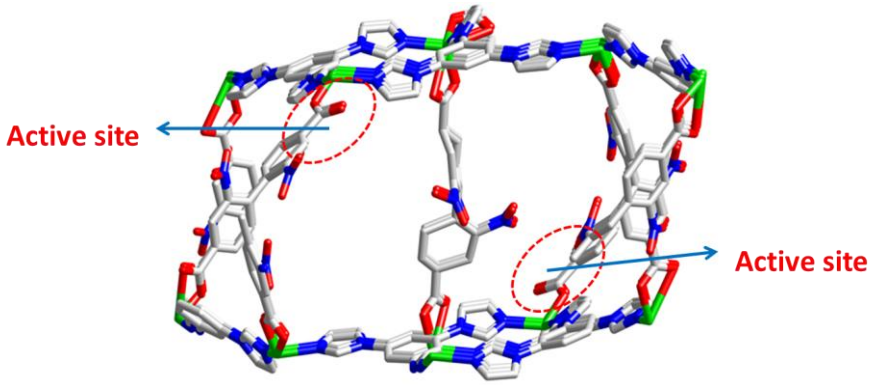


Fig. S6 The C=O group in the 1D channel of **3**.

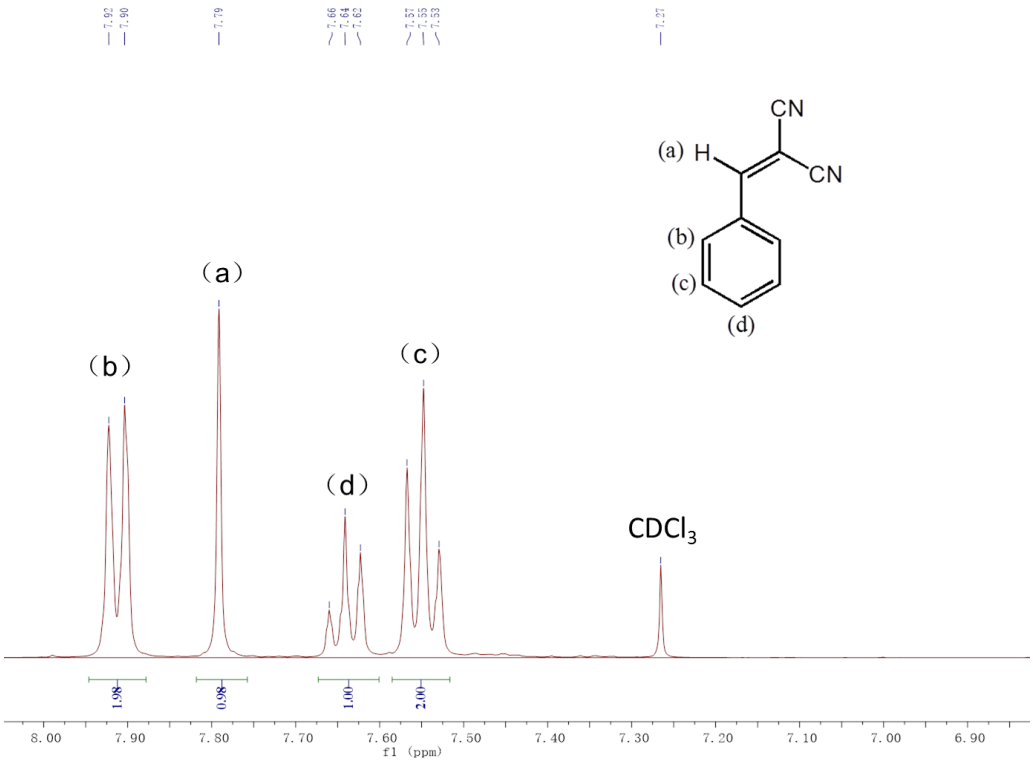


Fig. S7 ^{1}H NMR characterization of Knoevenagel condensation reaction of benzlaldehyde with malononitrile, catalyzed by **3'**.

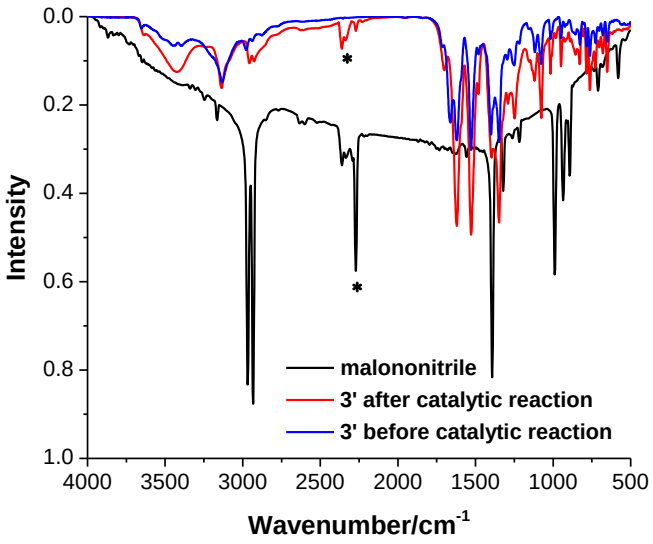
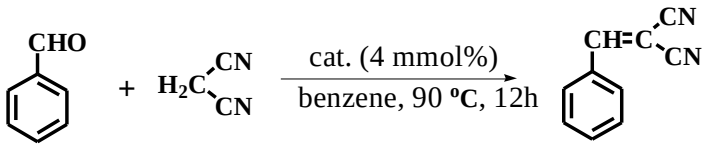


Fig. S8 IR spectra at room temperature of malononitrile (black), **3'** after catalytic reaction (red) and **3'** before catalytic reaction (blue). The bands marked with an asterisk indicate the -CN stretching vibration bands.



entry	cat.	yield
1		NR
2	$Zn(NO_3)_2$	Trace
3	H_2dnbpdc	Trace
4	tib	7.2%
5	**3'**	84.5%

Fig. S9 Knoevenagel condensation reaction of benzlaldehyde with malononitrile, catalyzed by various compounds.

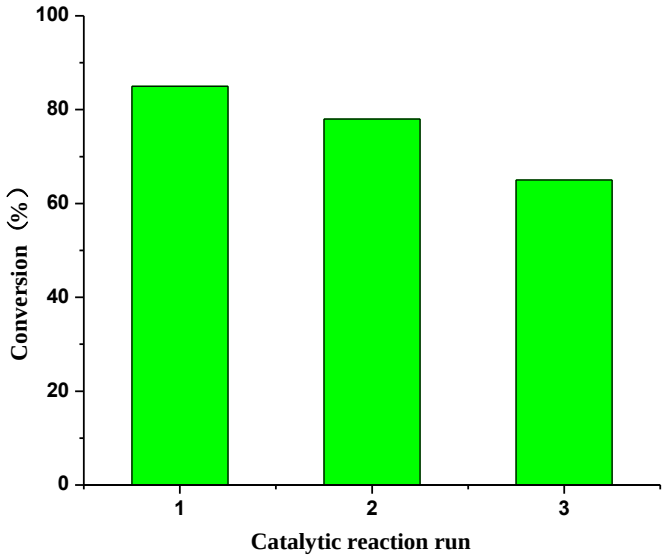
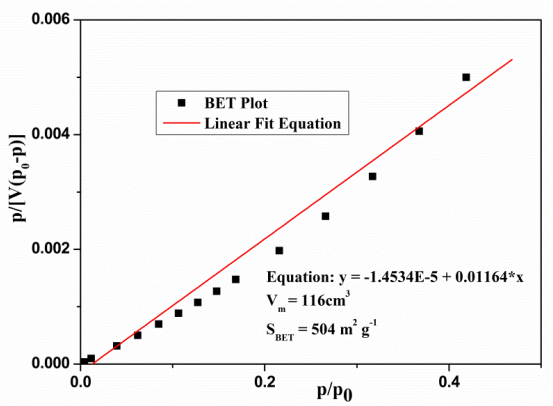
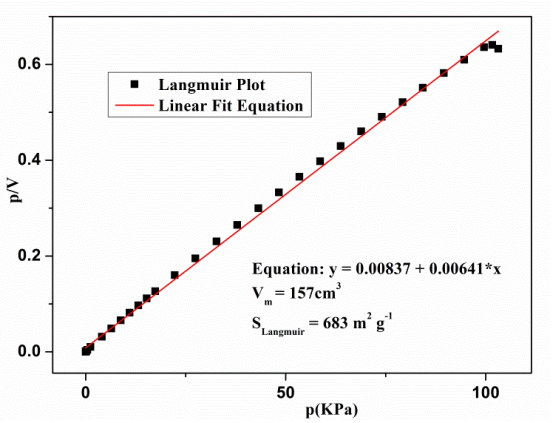


Fig. S10 The recycled catalysis experiments of **3'**.



(a)



(b)

Fig. S11 (a) The BET plot calculated from N_2 isotherm of **3'**. (b) The Langmuir plot calculated from N_2 isotherm of **3'**.

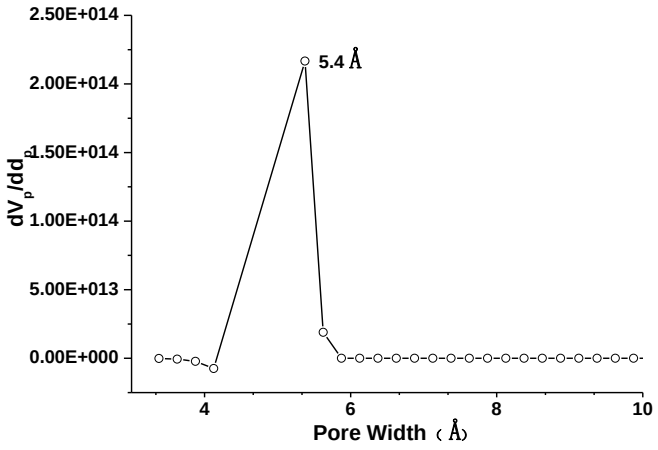


Fig. S12 Calculated pore size distributions of **3'** according to N_2 isotherm.