Supplementary Material for CrystEngComm

Electronic Supplementary Information for:

Design and constructions of three novel metal–organic frameworks based on the pillared-layer motifs†

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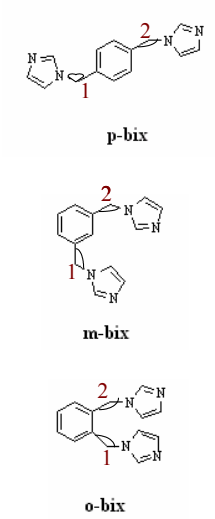
Table S1. Selected Distances (Å) and Angles (deg) of Hydrogen Bonding for Compound **1-3**[c]

D – H	*d*(D – H)	*d*(H … A)	∠DHA	*d*(D … A)	A
		Complex **1**			
O(5)－H(5D)	0.85	2.23	123	2.780(3)	O(2)#1
O(7)－H(7D)	0.85	2.18	115	2.649(5)	O(5)#2
O(6)－H(6A)	0.85	2.17	149	2.933(5)	O(7)#3
O(6)－H(6C)	0.85	2.06	149	2.820(3)	O(3)#4
O(8)－H(8F)	0.85	2.18	138	2.865(4)	O(1)#5
O(8)－H(8C)	0.85	2.12	123	2.689(5)	O(5)#6
		Complex **2**			
O(1W)－H(1WB)	0.85	2.09	133	2.739(6)	O(2W)#1
O(2W)－H(2WD)	0.85	2.00	145	2.739(6)	O(1W)#2
		Complex **3**			
O(9)－H(9A)	0.85	1.92	175	2.762(7)	O(14)#1
O(9)－H(9B)	0.85	2.13	162	2.949(2)	O(16)#2
O(10)－H(10D)	0.85	2.12	133	2.766(8)	O(15)#3
O(11)－H(11D)	0.85	2.49	126	3.071(4)	O(15)#3
O(11)－H(11B)	0.85	1.81	152	2.588(0)	O(3)#2
O(12)－H(12C)	0.85	2.28	149	3.046(5)	O(13)#3
O(13)－H(13D)	0.85	2.47	125	3.046(5)	O(12)#3
O(14)－H(14A)	0.85	2.36	112	2.762(7)	O(9)#4
O(14)－H(14C)	0.85	2.44	119	2.944(9)	O(10)#3
O(15)－H(15A)	0.85	2.33	115	2.802(9)	O(5)#5
O(15)－H(15A)	0.85	2.36	161	3.178(5)	O(4)#3
O(16)－H(16B)	0.85	2.42	121	2.949(2)	O(9)#6

[c] Symmetry codes: (1) #1 x, -y + 1/2, z - 1/2; #2 –x + 1, y + 1/2, -z + 1/2; #3 x, y + 3/2, z + 1/2; #4 x, y + 1, z; #5 –x + 1, -y + 1, -z + 1; #6 x, -y + 3/2, z + 1/2; (2) #1 –x + 1, -y + 1, -z + 1; #2 –x + 1, -y + 1, -z + 1; (3) #1 –x + 1/2, y - 1/2, -z + 1/2; #2 x - 1/2, -y + 1/2, z - 1/2; #3 –x + 1, -y + 1, -z + 1; #4 –x + 1/2, y + 1/2, -z + 1/2; #5 –x + 3/2, y + 1/2, -z + 3/2; #6 x + 1/2, -y + 1/2, z + 1/2.

Table S2. Selected Bond angles (°) and Dihedral angles (°) of the bix ligands and their tendences in Complexes **1-3**.

Complexes		**3**	**1**	**2**
Dihedral angles (°)	phenyl ring and imidazole ring	65.1(6)	75.3(2)	80.6(4)
		64.7(4)	67.8(9)	79.0(1)
	imidazole ring and imidazole ring	53.4(3)	56.7(5)	60.0(4)
Bond angles (°)	<1	114.6(4)	112.3(2)	111.5(3)
	<2	114.0(4)	112.22(18)	115.5(3)



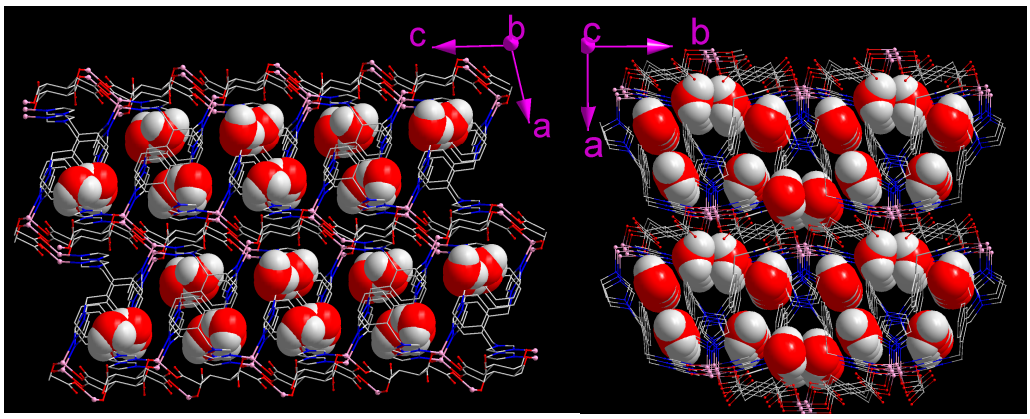


Fig. S1. Perspective view of **1** along different directions showing the cavities encapsulating free water molecules. Interestingly, three kinds of rectangle cavities have been found and their dimensions looking down the *c*- and *b*-axis are approximately 6.26 × 8.64 Å, 7.47 × 6.76 Å and 7.20 × 11.35 Å, respectively.

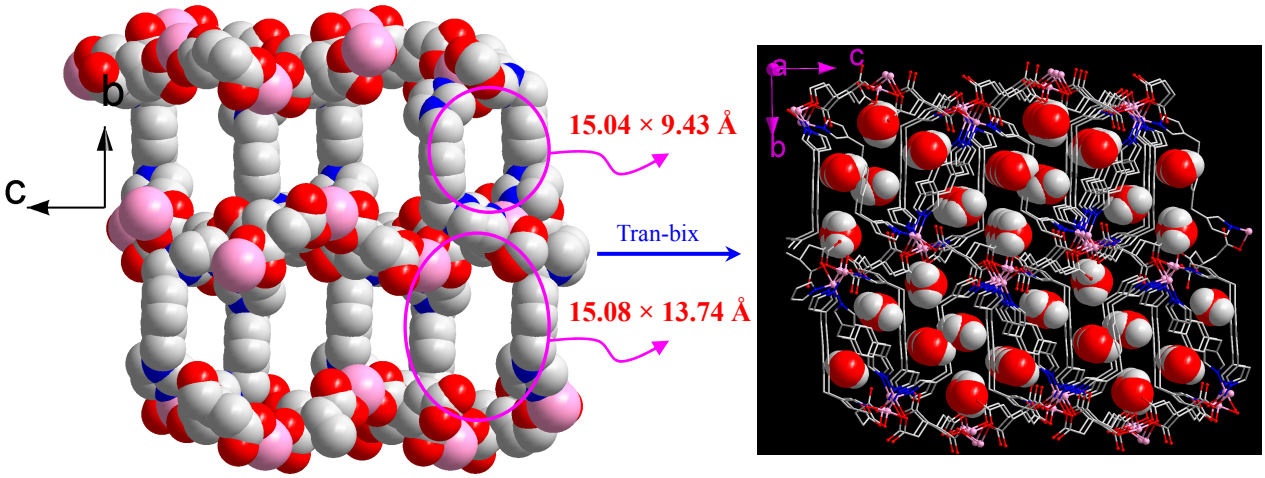


Fig. S2. The space-filling model of **3** with tran-bix omited along the [100] direction (two kinds of channels being about 15.08 × 13.74 Å and 15.04 × 9.43 Å were found if the *trans*-bix pillars were

omited. In fact, it is *tran*-bix that make the cavities of framework **3** smaller and complicated).

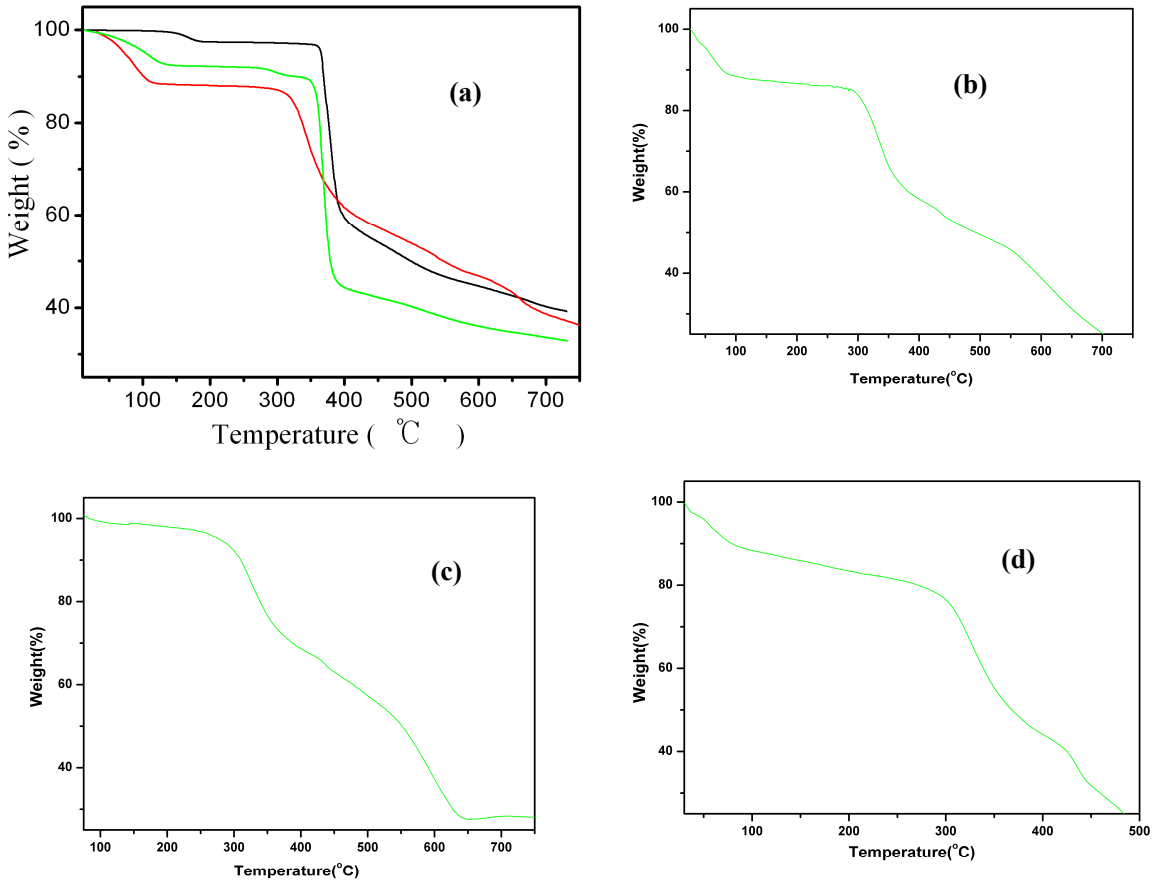
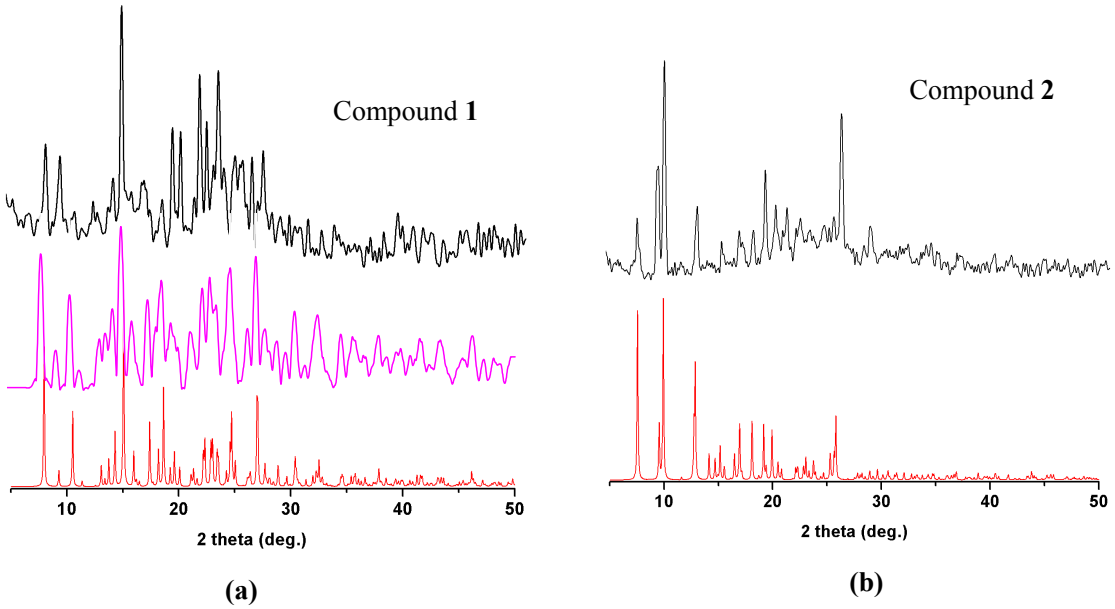
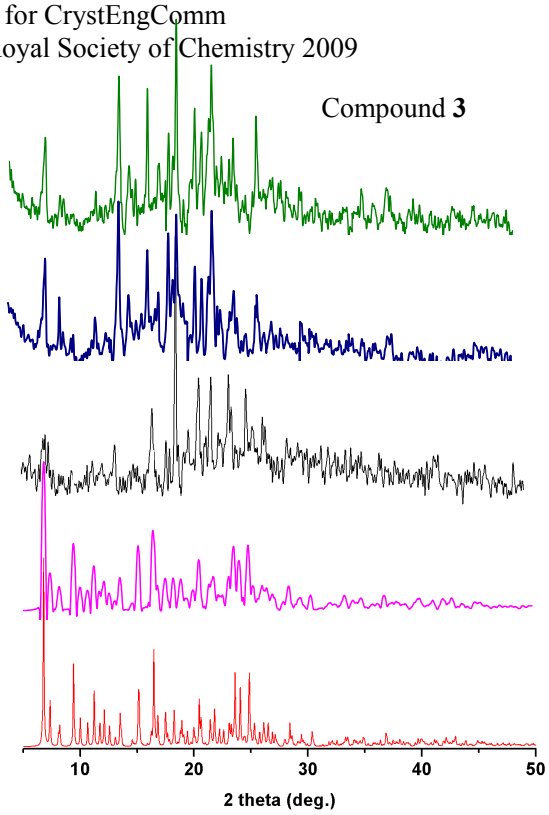


Fig. S3. (a) TG curves of compounds **1** (red), **2** (black) and **3** (green); TG curves of dehydrated compounds **3** with other solvent molecules: (b) methanol; (c) acetonitrile; (d) chloroform.

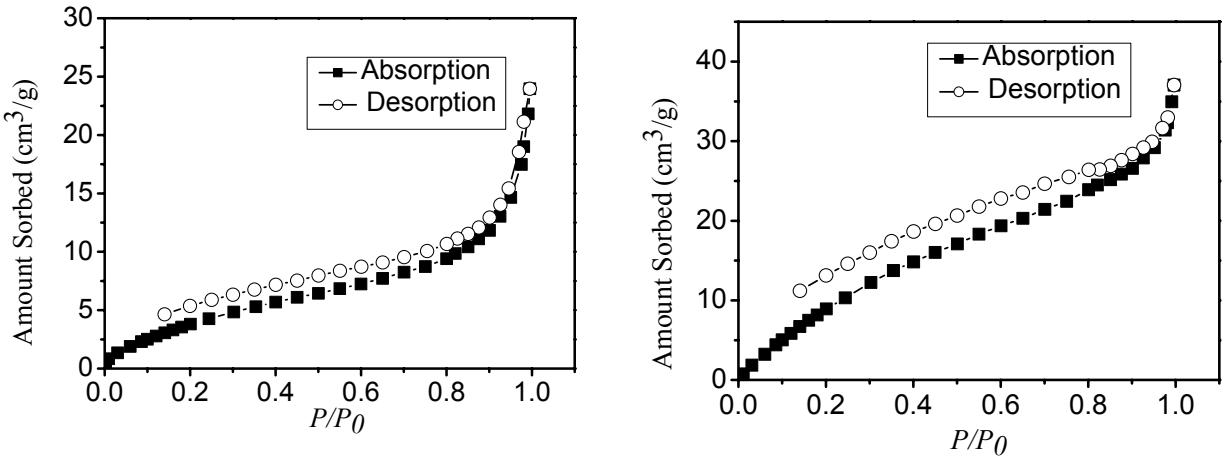




(c)

Fig. S4 The PXRD for **1** (a), **2** (b) and **3** (c). red: simulated; magenta: taken at room temperature; black: after heating to 150℃ under vacuum for 5h.; royal: adsorbed methanol; olive: adsorbed chloroform.

* For 3 with adsorpted methanol and chloroform, the powder XRD patterns show some differences from structures of 3 without adsorpted methanol and chloroform (S4c).That, probably, comes from the flexible ligands.



(a) **(b)**

Fig. **S5**. Adsorption/desorption isotherm of nitrogen gas (77 K) for **1** (a) and **3** (b).

* Compouds 1 and 2 both show type II physisorption isotherms