Electronic Supplementary Information for MS:

Guest-induced expanding and shrinking porous modulation based on interdigitated metal-organic frameworks constructed by 4,4'-sulfonyldibenzoate and barium ions

Dongrong Xiao,*[a] Haiyan Chen,[a] Dianzhen Sun,[a] Jianghong He,[a] Shiwei Yan,[a] Juan Yang,[a] Xin Wang,[a] Ruo Yuan[a] and Enbo Wang*[b]

[a] *College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, P. R. China. E-mail: xiaodr98@yahoo.com.cn*

[b] *Key Laboratory of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun, 130024, P. R. China. E-mail: wangeb889@nenu.edu.cn*

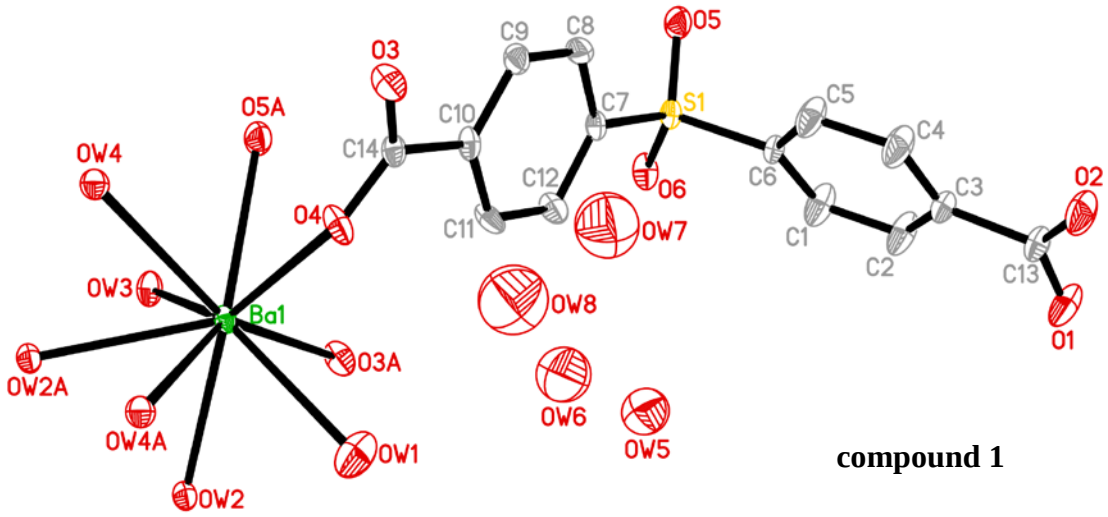
Table S1 Selected bond lengths [Å] for compounds **1–7**.[a]

compound **1**			
Ba(1)-O(4)	2.704(4)	Ba(1)-OW1	2.877(5)
Ba(1)-O(3)#1	2.737(4)	Ba(1)-OW4	2.891(4)
Ba(1)-OW2	2.837(4)	Ba(1)-O(5)#3	2.901(4)
Ba(1)-OW3	2.846(4)	Ba(1)-OW4#4	2.917(4)
Ba(1)-OW2#2	2.870(4)		
compound **2**			
Ba(1)-O(4)#1	2.717(2)	Ba(1)-OW2	2.843(2)
Ba(1)-O(3)#2	2.736(2)	Ba(1)-OW3	2.878(3)
Ba(1)-OW2#3	2.777(2)	Ba(1)-OW4	2.900(2)
Ba(1)-O(5)	2.810(2)	Ba(1)-OW4#4	2.906(2)
Ba(1)-OW1	2.834(3)		
compound **3**			
Ba(1)-O(3)#1	2.7140(17)	Ba(1)-OW2#3	2.8470(16)
Ba(1)-O(4)#2	2.7312(17)	Ba(1)-OW3	2.895(2)
Ba(1)-OW2	2.7838(16)	Ba(1)-OW4#4	2.9024(17)
Ba(1)-O(5)	2.8231(17)	Ba(1)-OW4	2.9112(18)
Ba(1)-OW1	2.833(2)		
compound **4**			

Ba(1)-O(3)#1	2.7241(18)	Ba(1)-OW1	2.8706(18)
Ba(1)-O(4)#2	2.7555(19)	Ba(1)-OW2	2.8756(18)
Ba(1)-OW3	2.822(2)	Ba(1)-OW2#4	2.8869(19)
Ba(1)-OW4	2.8215(18)	Ba(1)-O(5)	2.8943(18)
Ba(1)-OW1#3	2.8705(19)		
compound **5**			
Ba(1)-O(3)	2.7136(15)	Ba(1)-OW2	2.8666(16)
Ba(1)-O(4)#1	2.7502(16)	Ba(1)-O(5)#3	2.8666(16)
Ba(1)-OW4	2.789(3)	Ba(1)-OW2#4	2.8740(16)
Ba(1)-OW1#2	2.8352(17)	Ba(1)-OW1	2.8873(16)
Ba(1)-OW3	2.8385(17)		
compound **6**			
Ba(1)-O(4)	2.713(6)	Ba(1)-OW1#2	2.862(5)
Ba(1)-O(3)#1	2.738(6)	Ba(1)-OW2	2.872(6)
Ba(1)-OW4	2.816(7)	Ba(1)-OW2#3	2.898(6)
Ba(1)-OW1	2.841(5)	Ba(1)-O(5)#4	2.899(6)
Ba(1)-OW3	2.856(6)		
compound **7**			
Ba(1)-O(4)	2.724(4)	Ba(1)-O(5)#3	2.855(4)
Ba(1)-O(3)#1	2.756(4)	Ba(1)-OW1	2.868(4)
Ba(1)-OW4	2.789(6)	Ba(1)-OW2	2.880(4)
Ba(1)-OW3	2.845(4)	Ba(1)-OW1#4	2.894(4)
Ba(1)-OW2#2	2.850(4)		

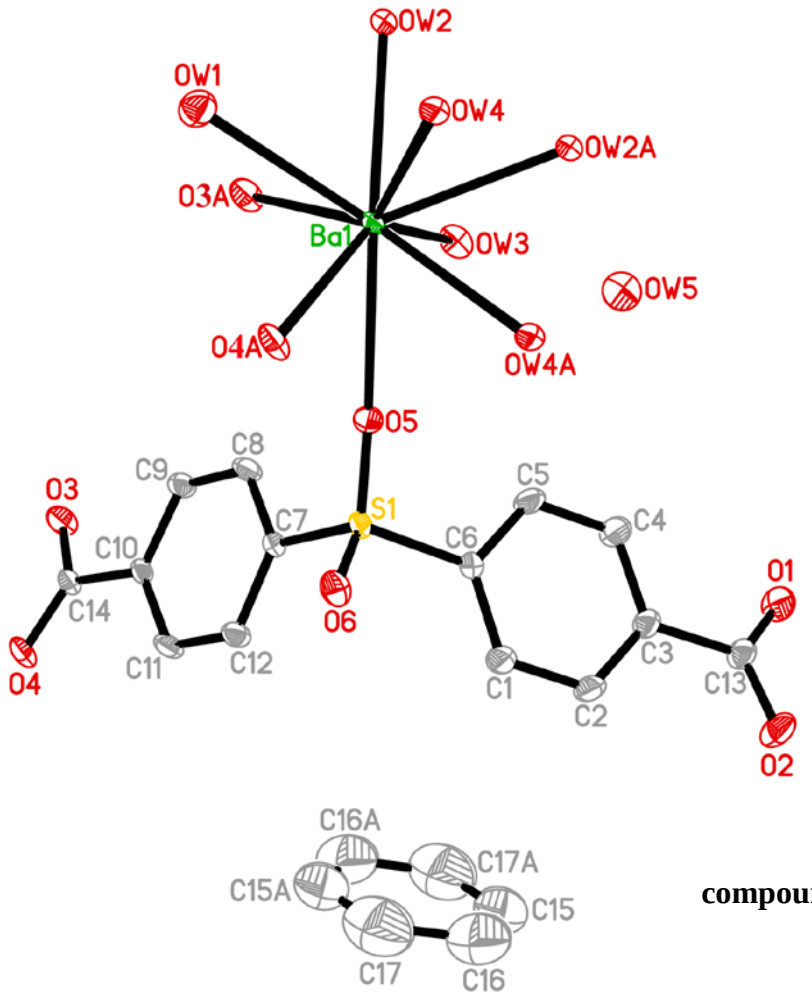
[a] Symmetry transformations used to generate equivalent atoms: for **1**: #1 x+1, y, z; #2 -x+1, -y+1, -z+1; #3 -x, -y+1, -z+2; #4 -x, -y+1, -z+1; #5 x-1, y, z; for **2**: #1 -x-1, -y-1, -z; #2 -x, -y-1, -z; #3 -x, -y-1, -z-1; #4 -x-1, -y-1, -z-1; for **3**: #1 -x, -y+2, -z+2; #2 -x+1, -y+2, -z+2; #3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

Supporting Figures



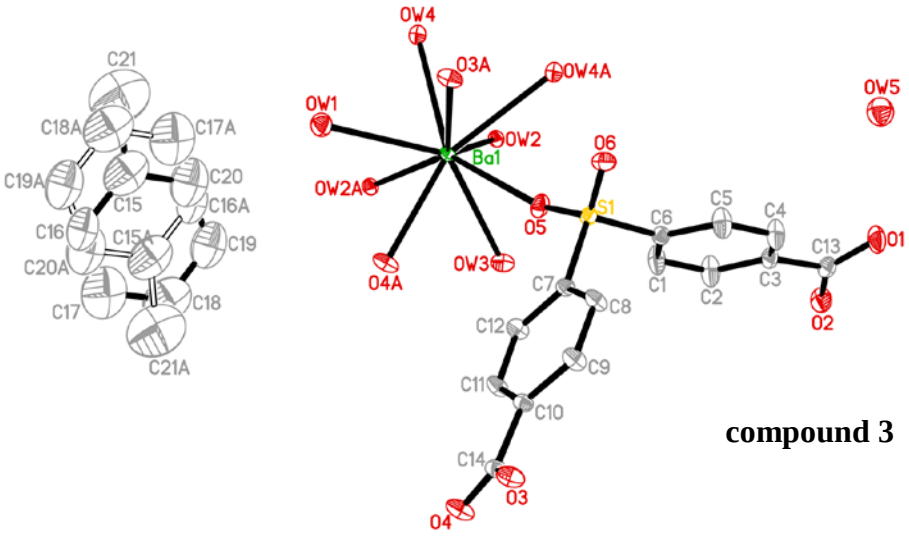
compound 1

(a)



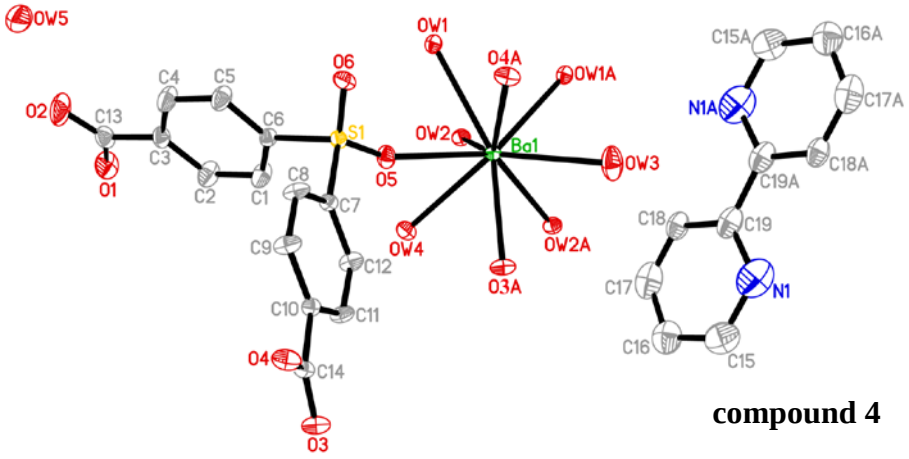
compound 2

(b)



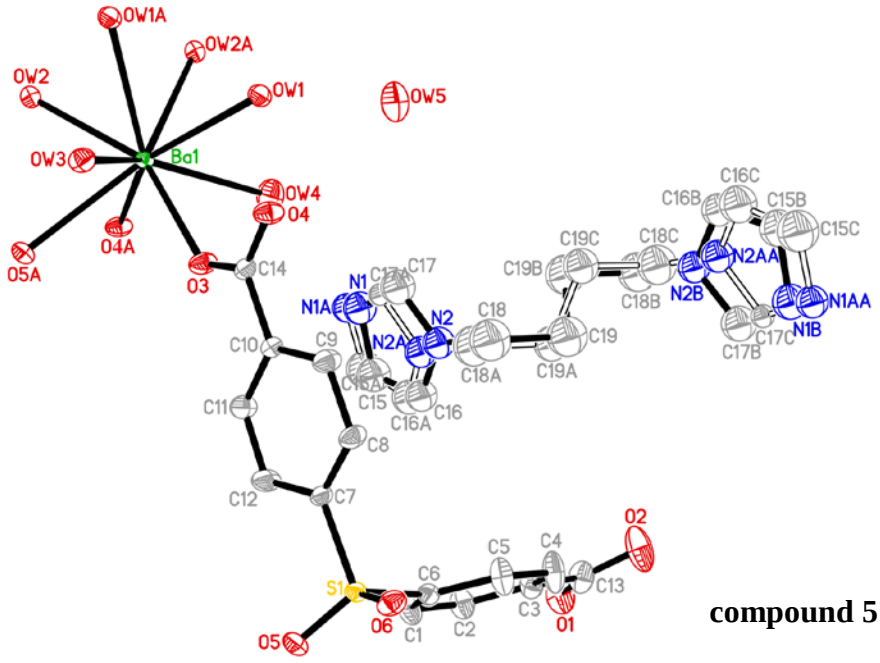
compound 3

(c)



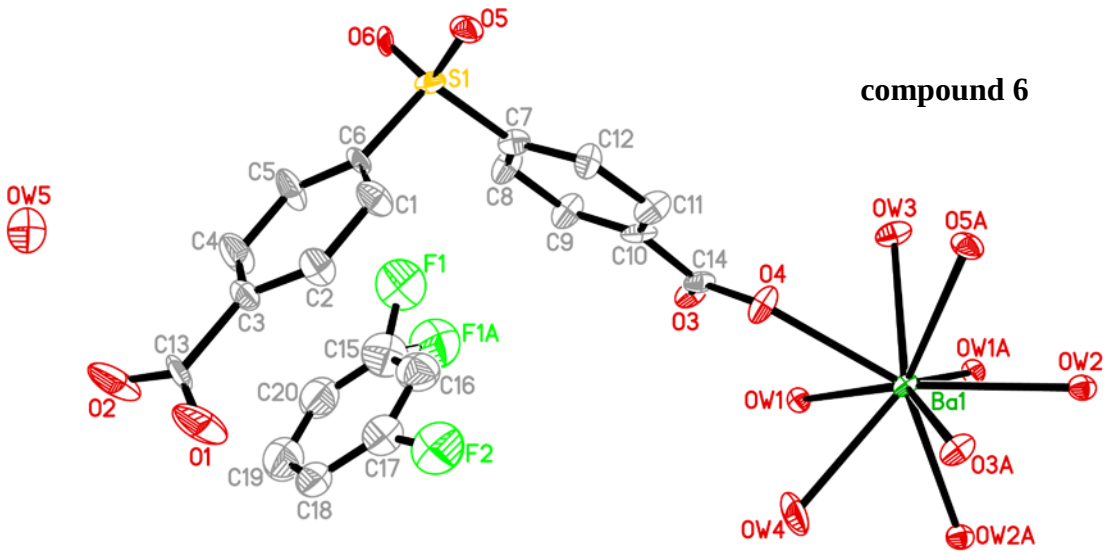
compound 4

(d)

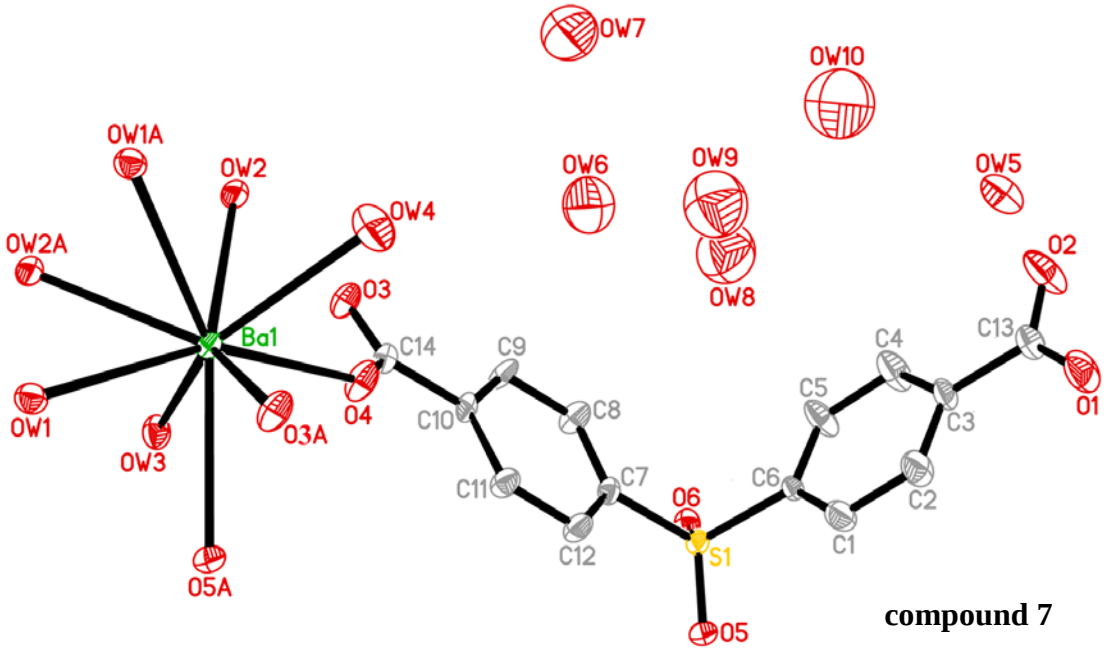


compound 5

(e)



(f)



(g)

Fig. S1 ORTEP drawing of the coordination environment for the Ba atom in **1**(a), **2**(b), **3**(c), **4**(d), **5**(e), **6**(f) and **7**(g) with thermal ellipsoids at the 30% probability level. The hydrogen atoms are omitted for clarity.

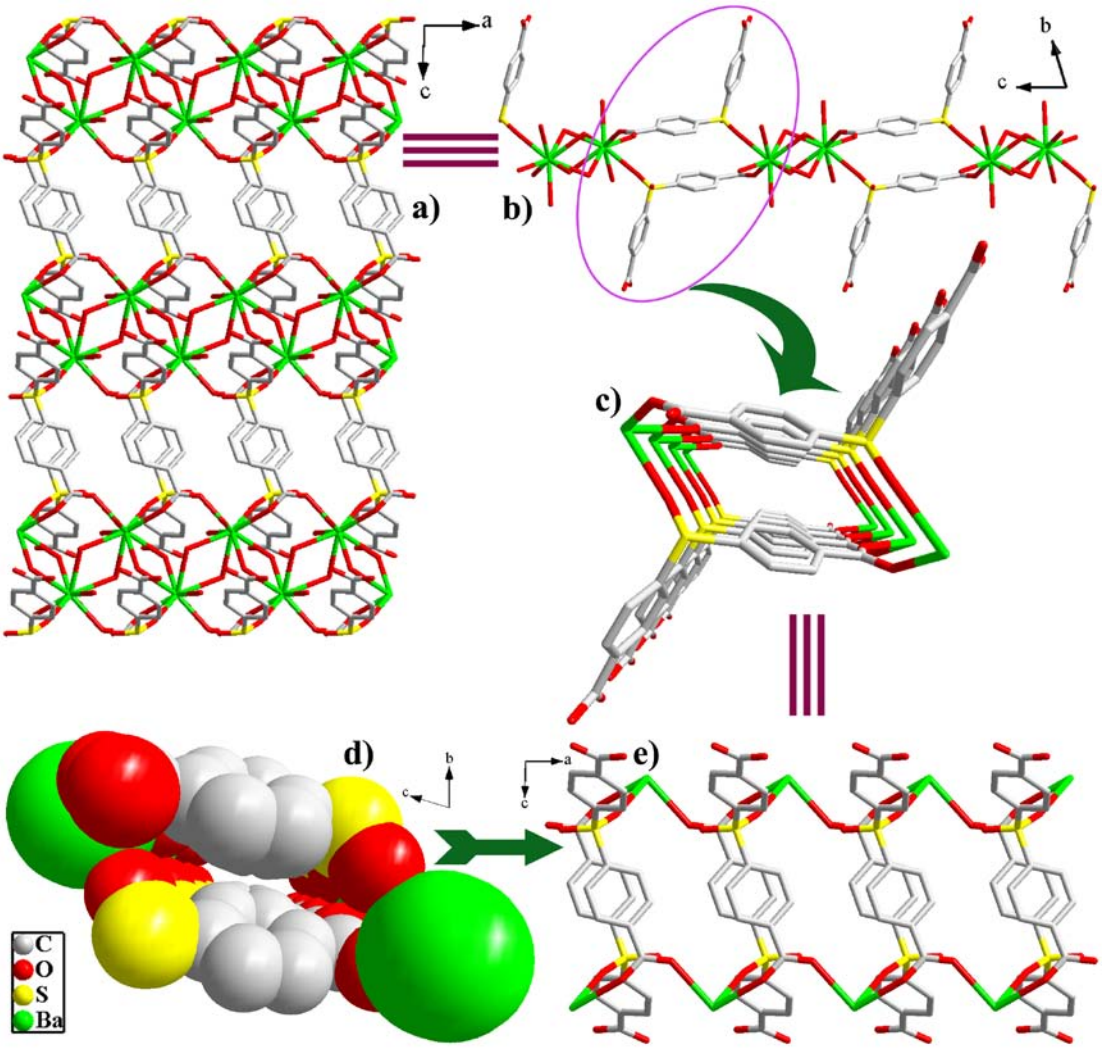


Fig. S2 Perspective views of (a, b) the single sidearm-containing 2D bilayer framework, and (c, d, e) the sidearm-containing 1D tubelike components.

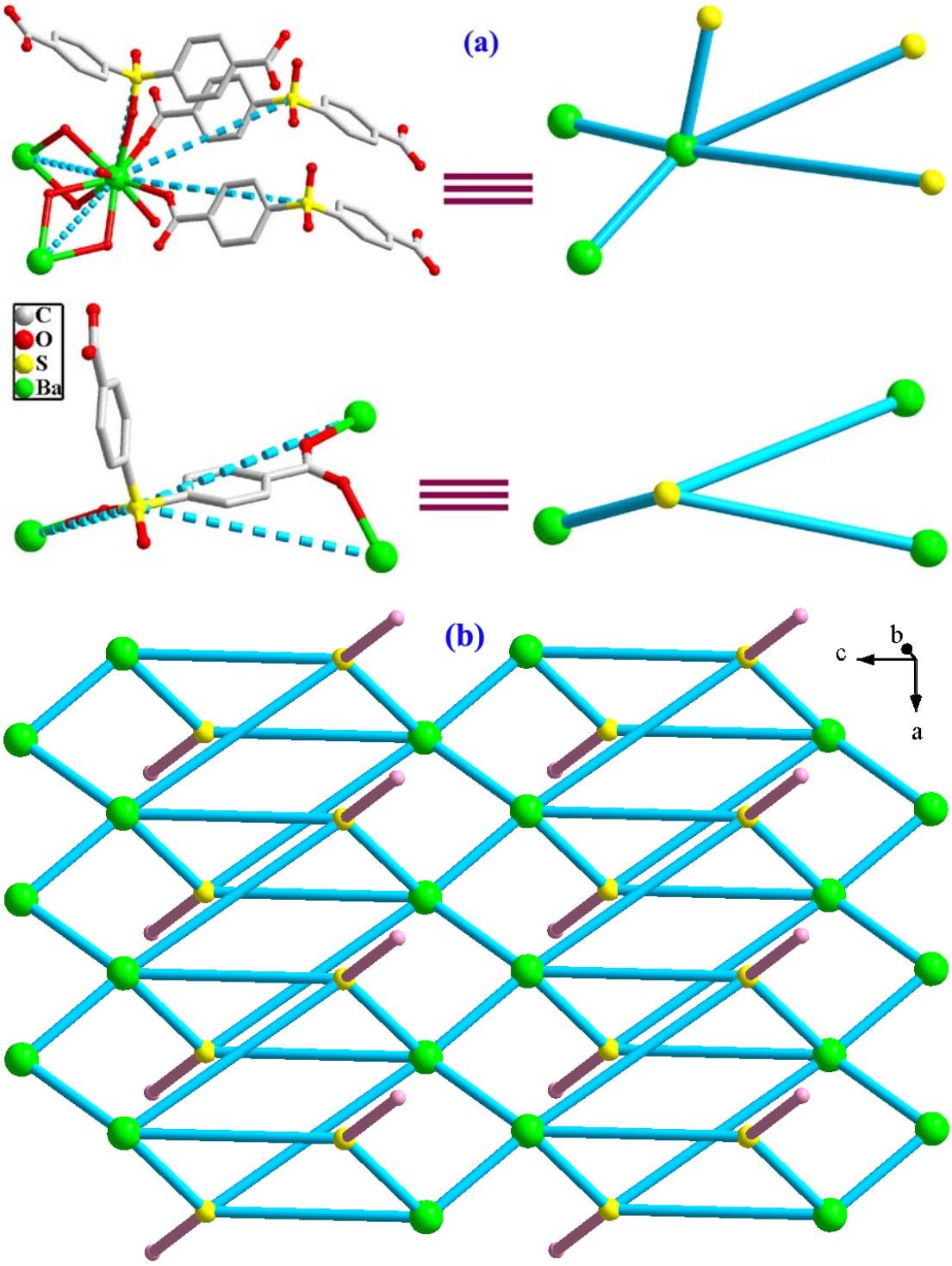
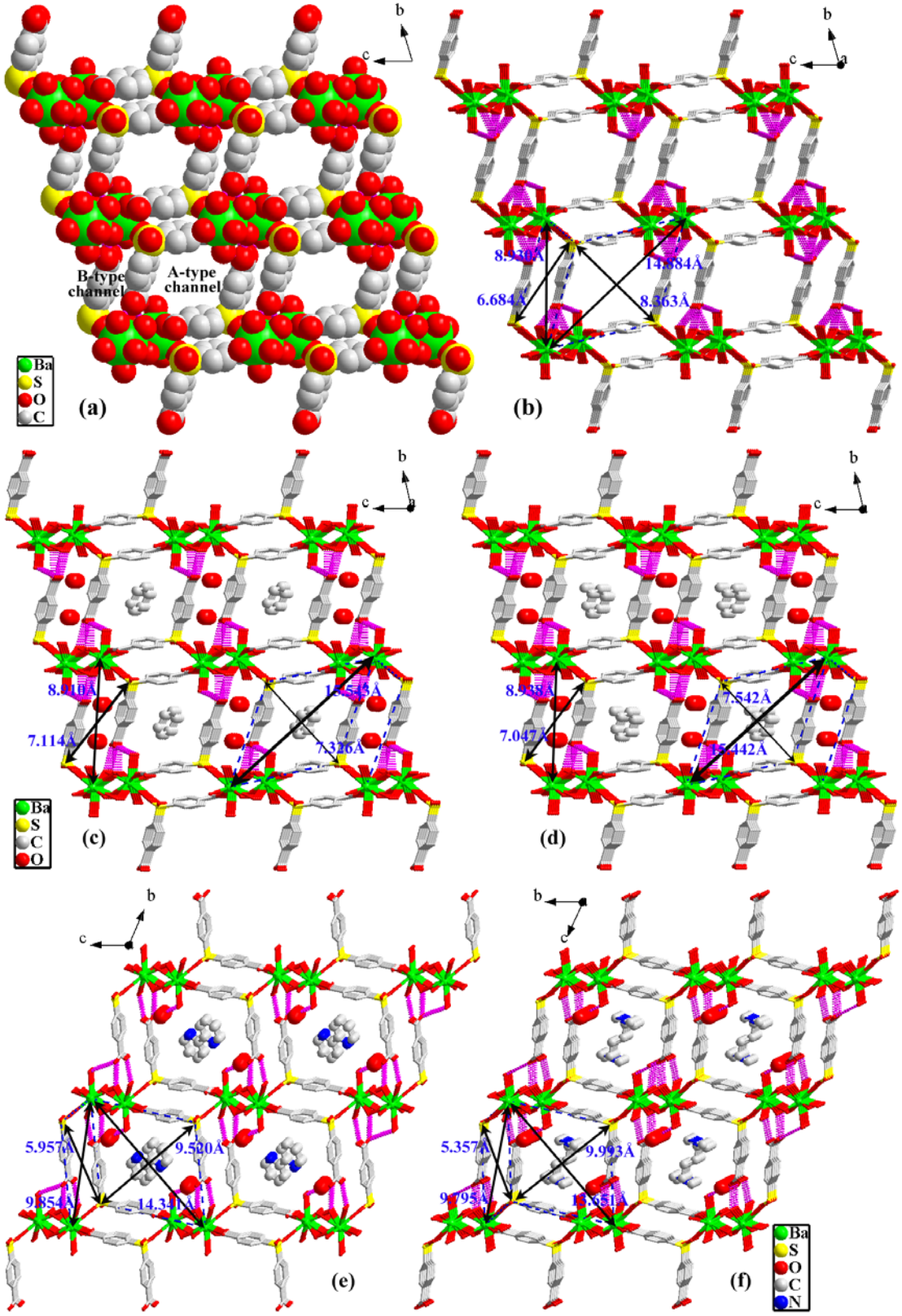


Fig. S3 (a) Perspective and simplified views of the five-connected Ba atom and three-connected sdba ligand. (b) Schematic representation of the single sidearm-containing 2D bilayer framework with (3,5)-connected $(4^3)(4^5.6^5)$ topology.



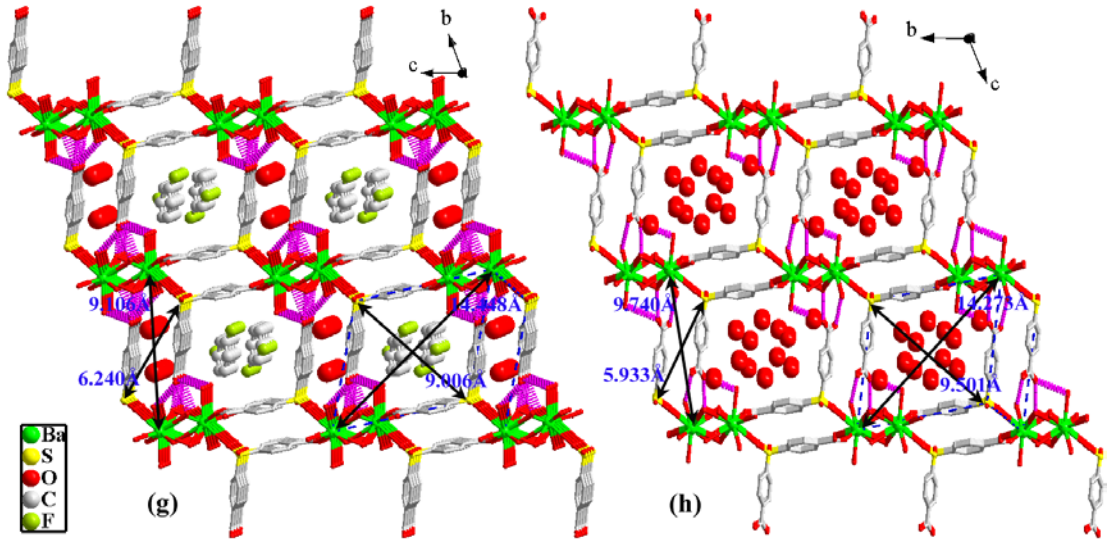


Fig. S4 Perspective views of the (2D→ 3D) interdigitated arrays with different dimensions of similar channels (A-type channel, B-type channel) in **1**(a, b), **2**(c), **3**(d), **4**(e), **5**(f), **6**(g) and **7**(h).

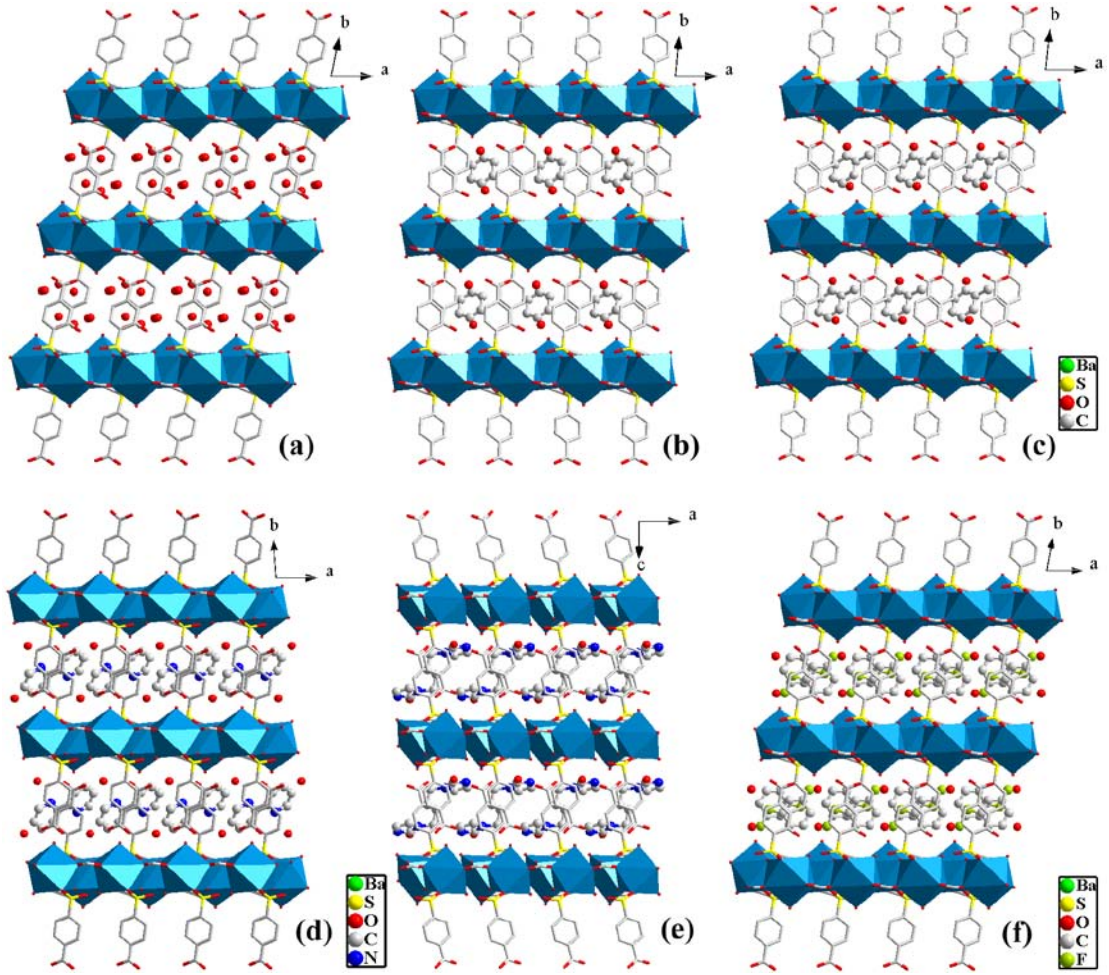


Fig. S5 Perspective views of the (2D→ 3D) interdigitated arrays with various guest molecules enwrapped in their interlayer channel space of **1**(a), **2**(b), **3**(c), **4**(d), **5**(e)

and **6**(f).

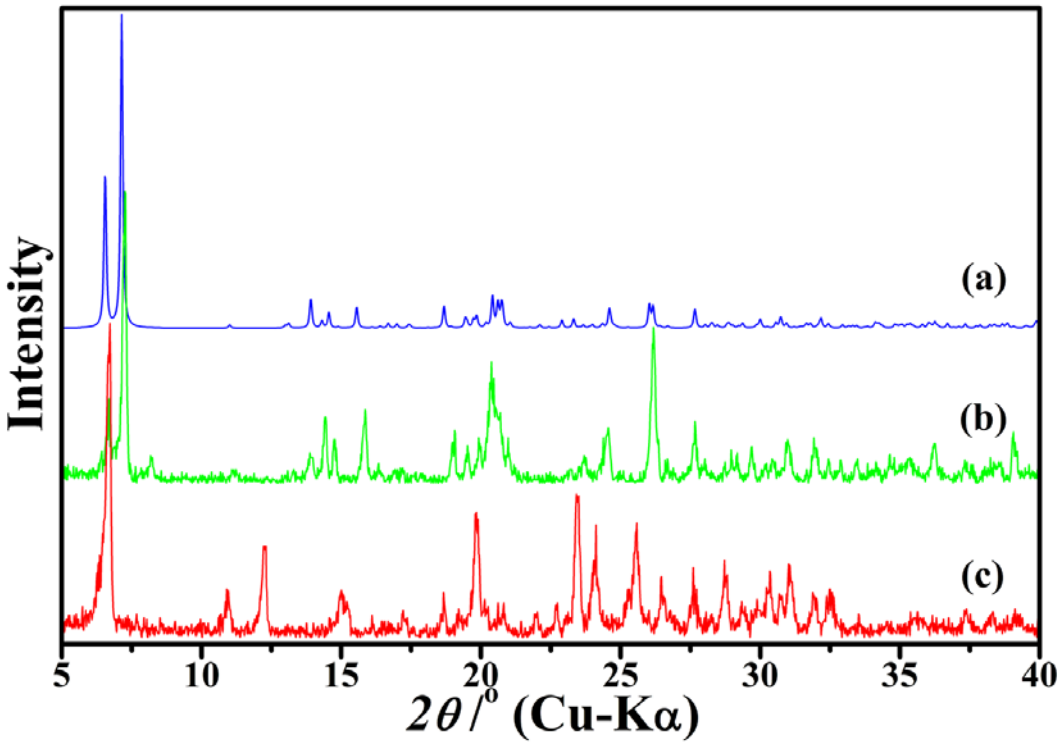


Fig. S6 The XRPD patterns for: (a) simulated one based on the single-crystal structure of **1**, (b) as-synthesized samples of **1**, and (c) dehydrated **1** at 100 ^{o}C for 12 hours.

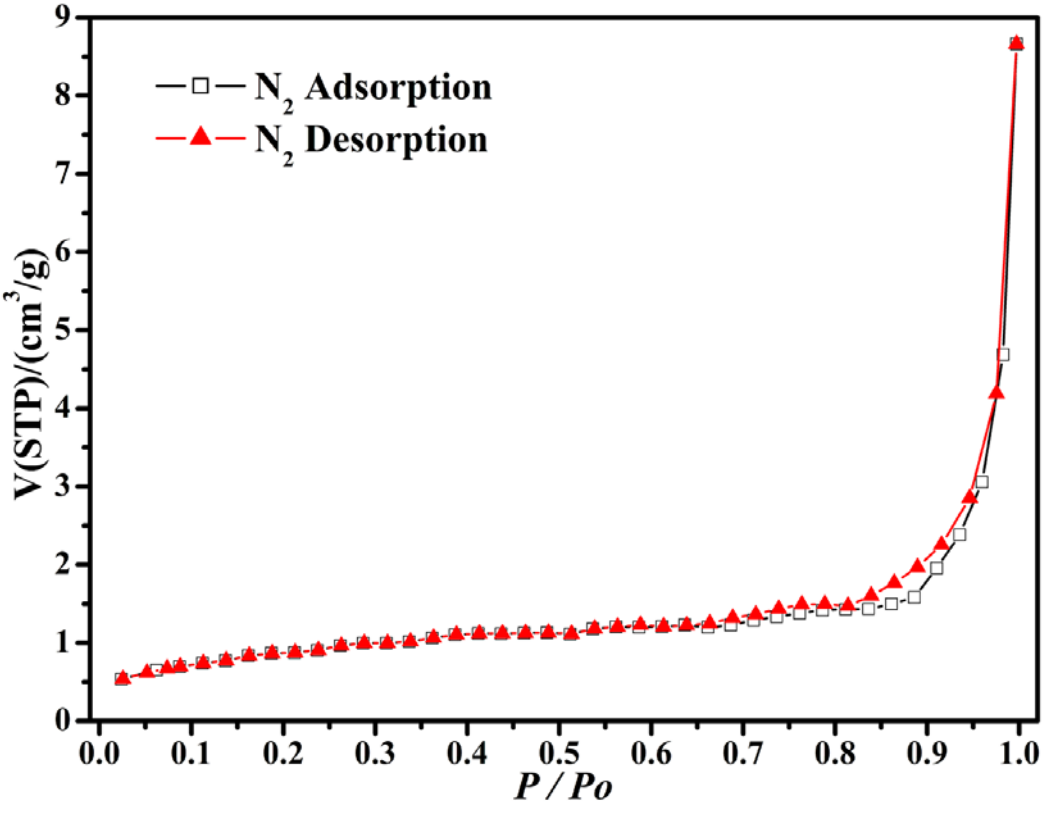


Fig. S7 The N_2 gas adsorption isotherms of dehydrated compound **1** at 77 K.

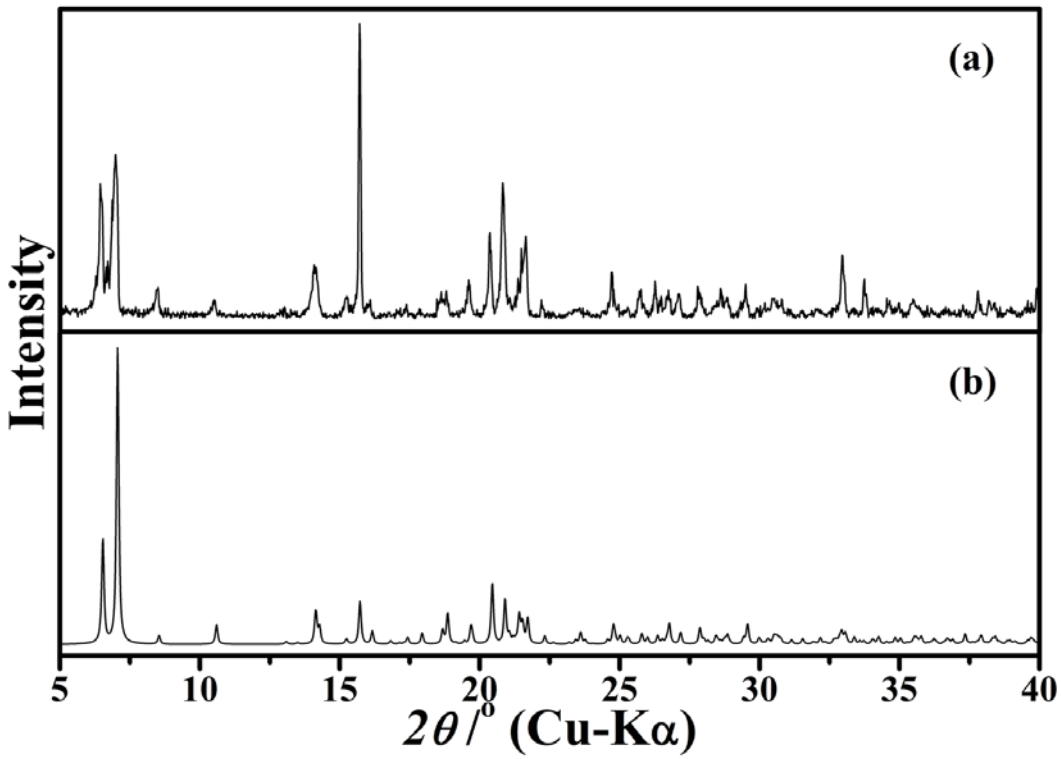


Fig. S8 The XRPD patterns for: (a) as-synthesized samples of **2**, and (b) simulated one based on the single-crystal structure of **2**.

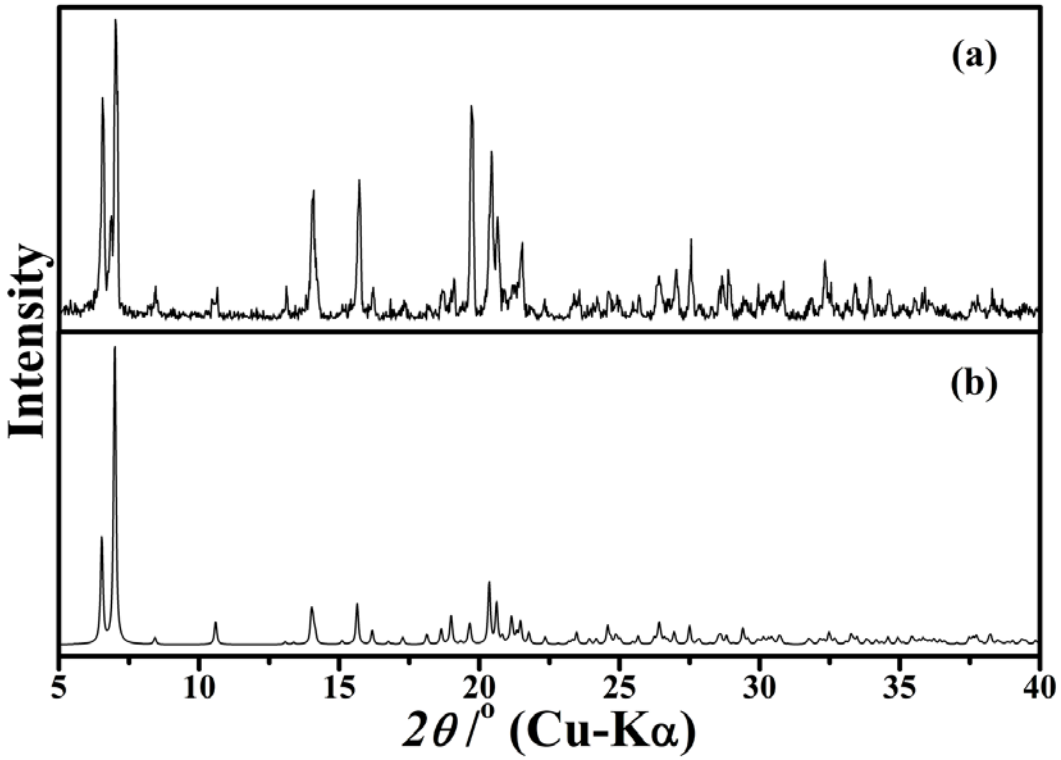


Fig. S9 The XRPD patterns for: (a) as-synthesized samples of **3**, and (b) simulated one based on the single-crystal structure of **3**.

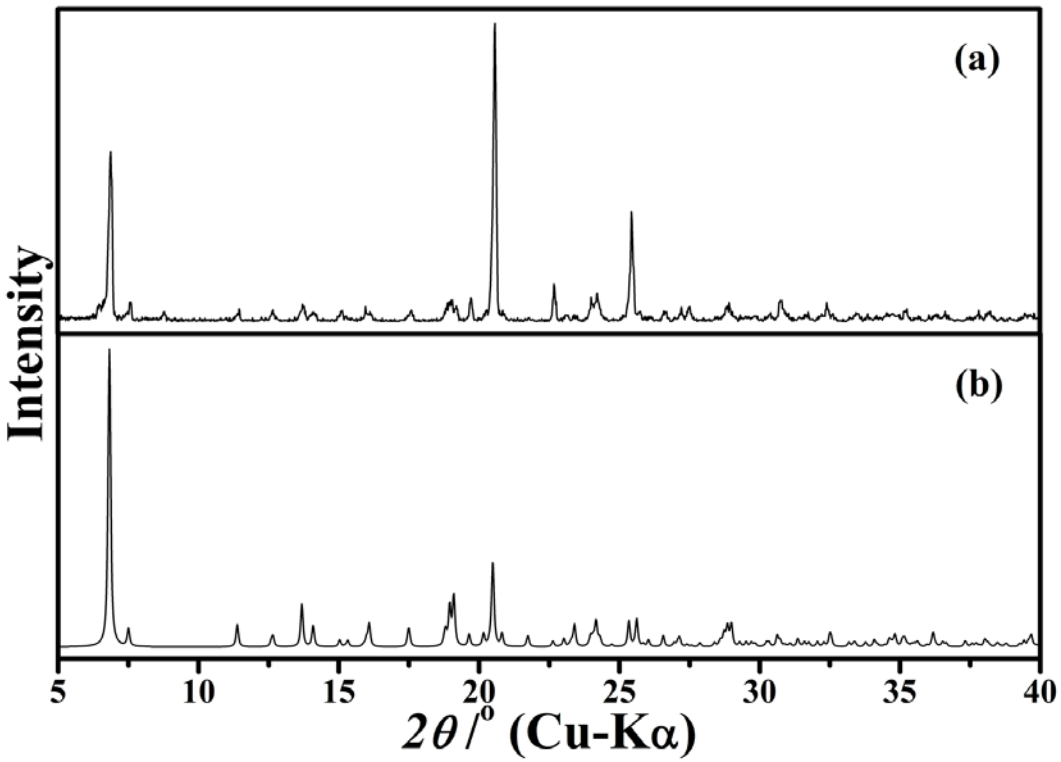


Fig. S10 The XRPD patterns for: (a) as-synthesized samples of **4**, and (b) simulated one based on the single-crystal structure of **4**.

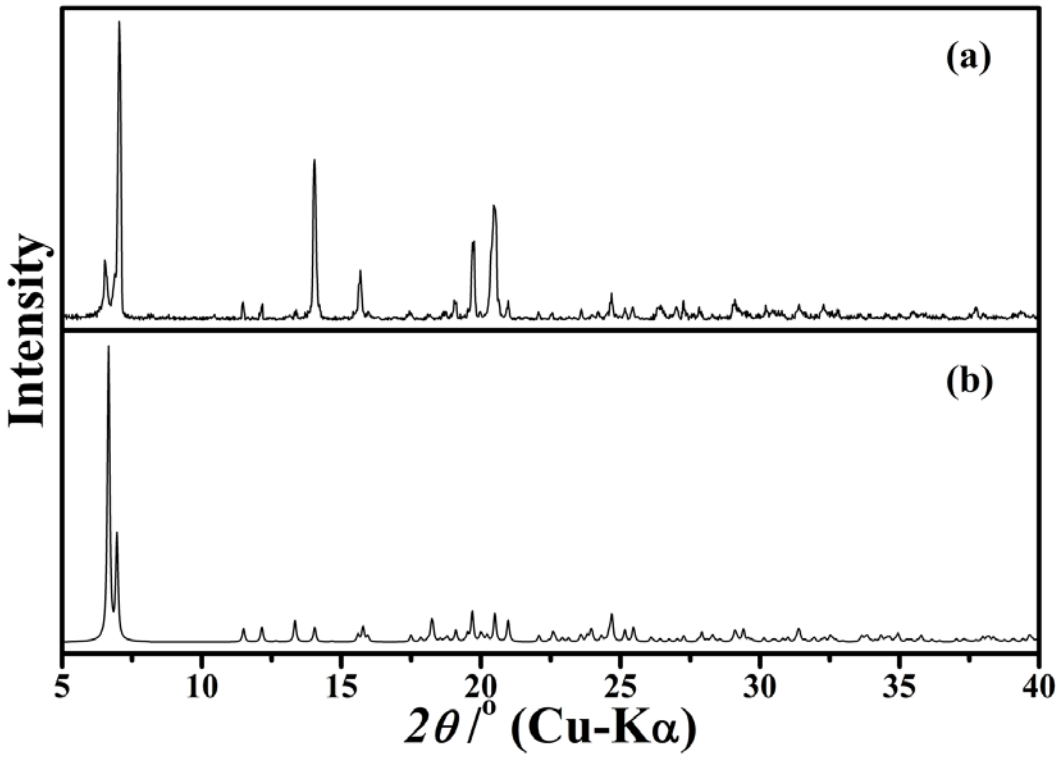


Fig. S11 The XRPD patterns for: (a) as-synthesized samples of **5**, and (b) simulated one based on the single-crystal structure of **5**.

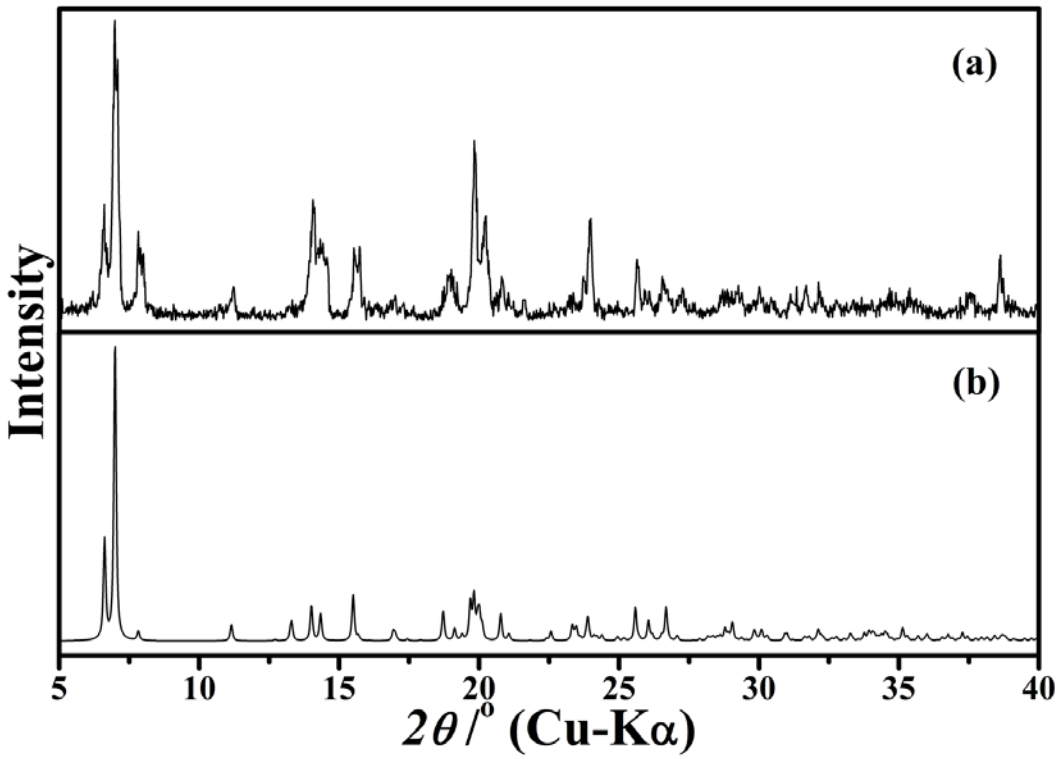


Fig. S12 The XRPD patterns for: (a) as-synthesized samples of **6**, and (b) simulated one based on the single-crystal structure of **6**.

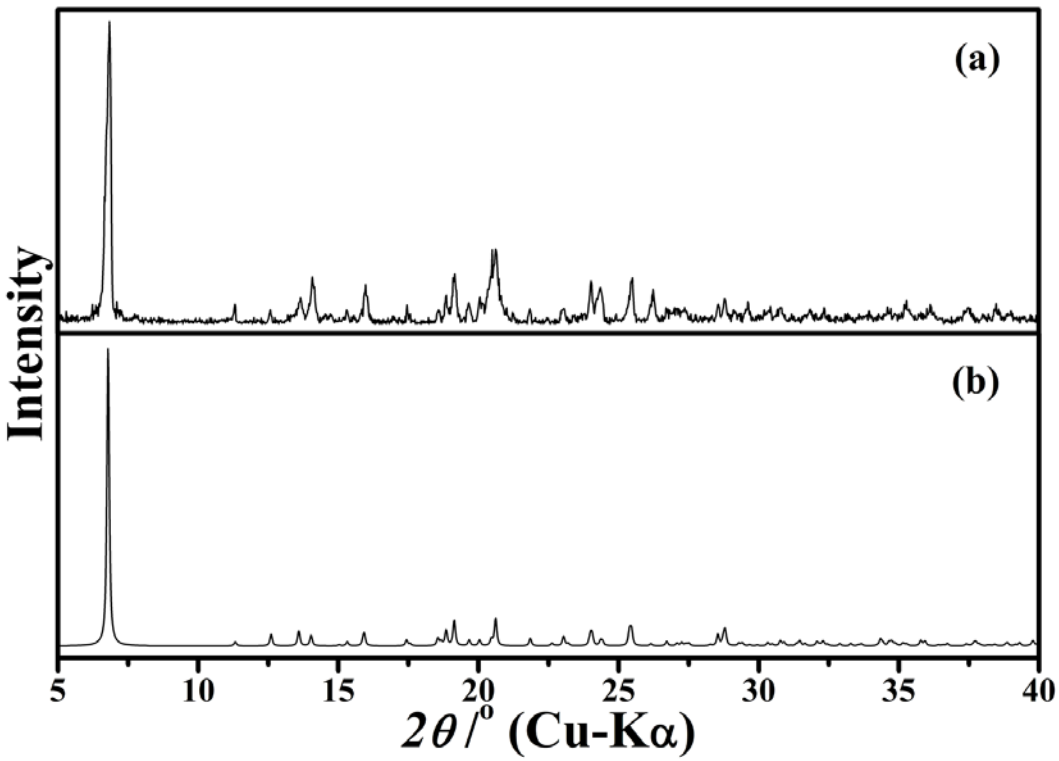
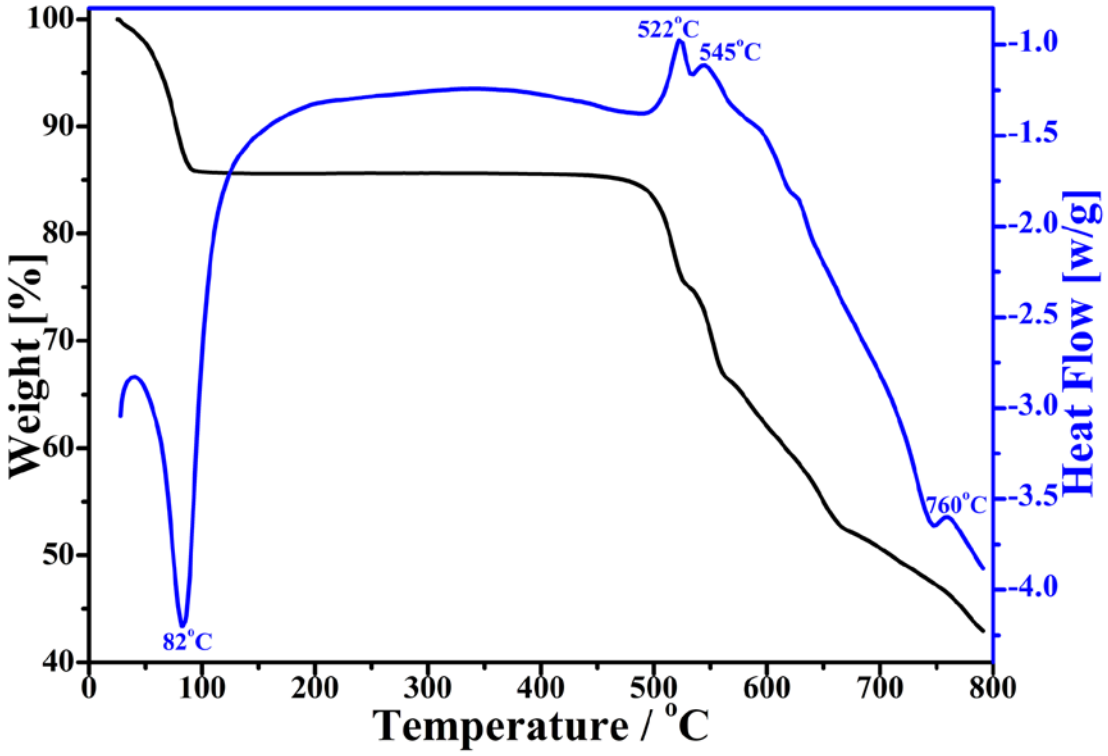
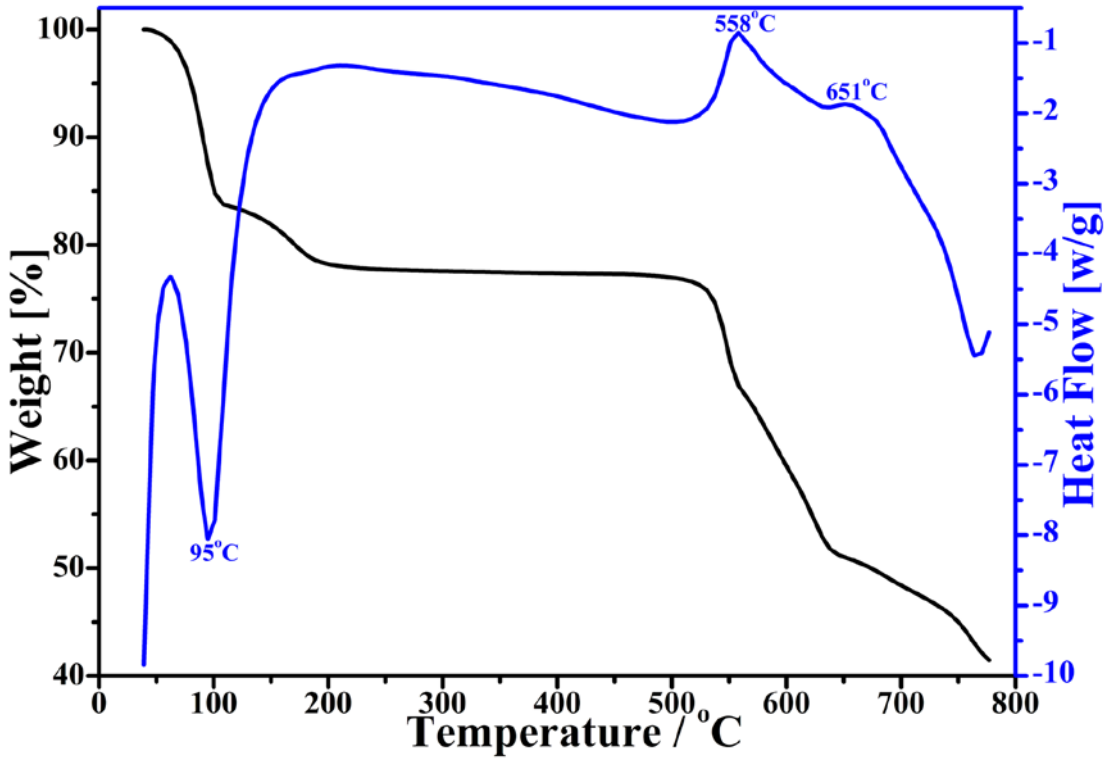


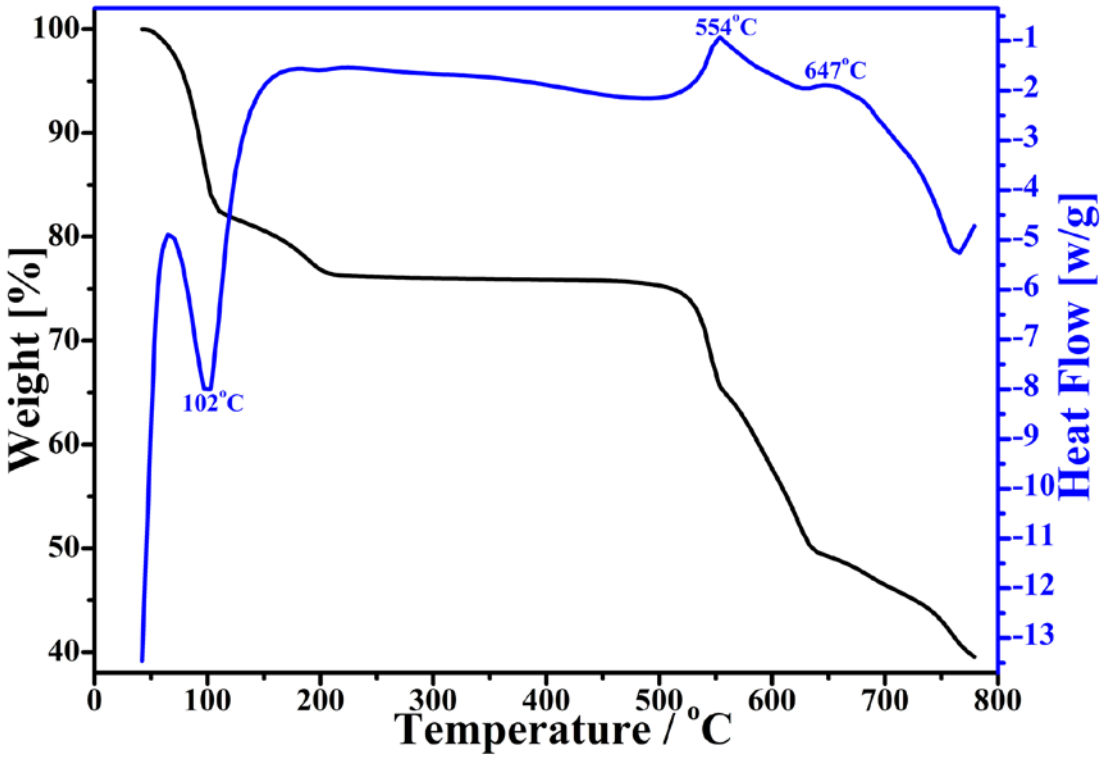
Fig. S13 The XRPD patterns for: (a) as-synthesized samples of **7**, and (b) simulated one based on the single-crystal structure of **7**.



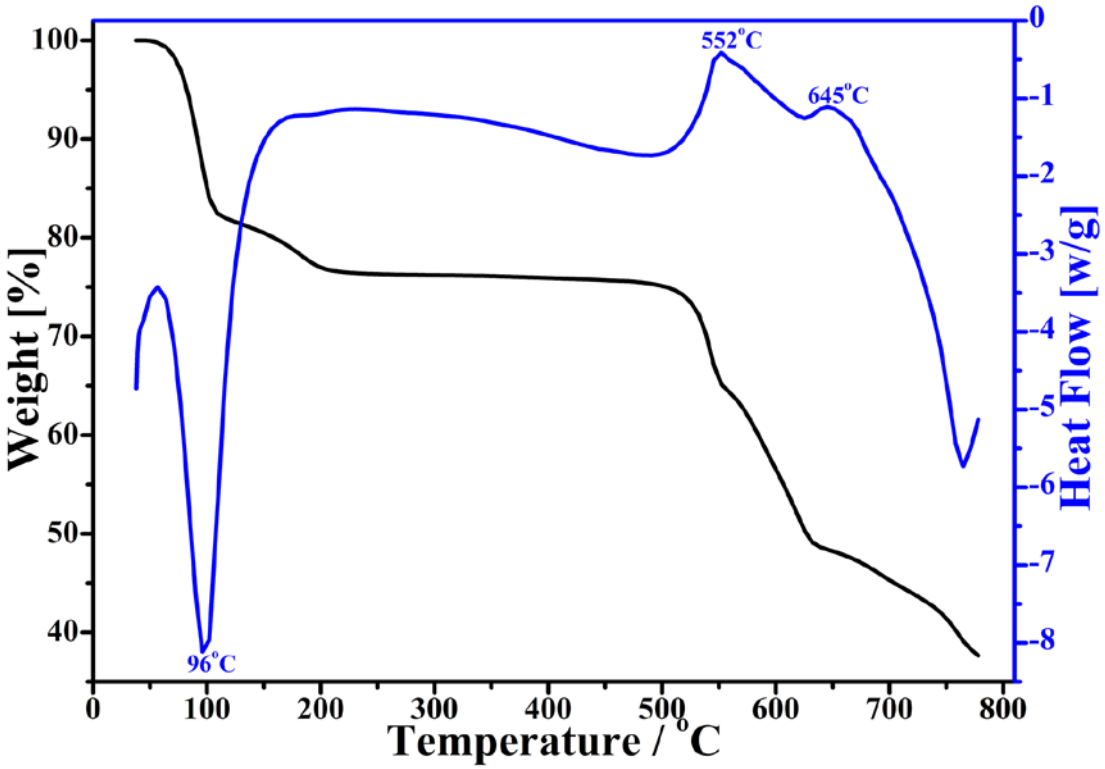
(a)



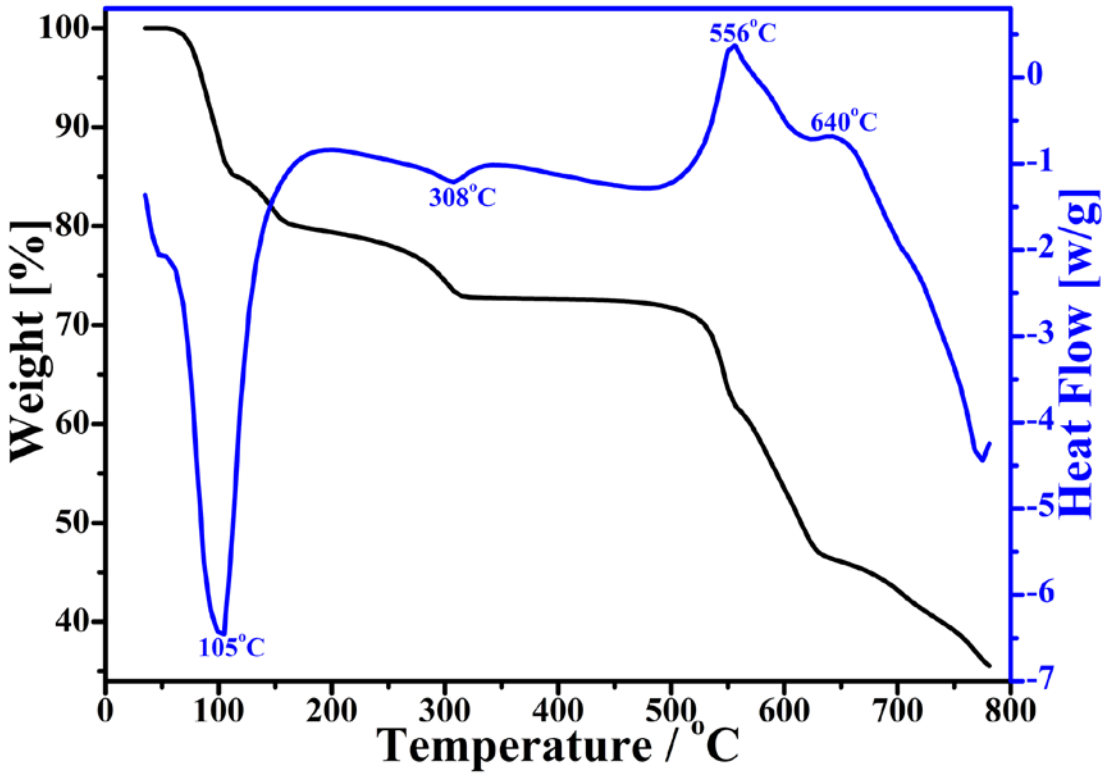
(b)



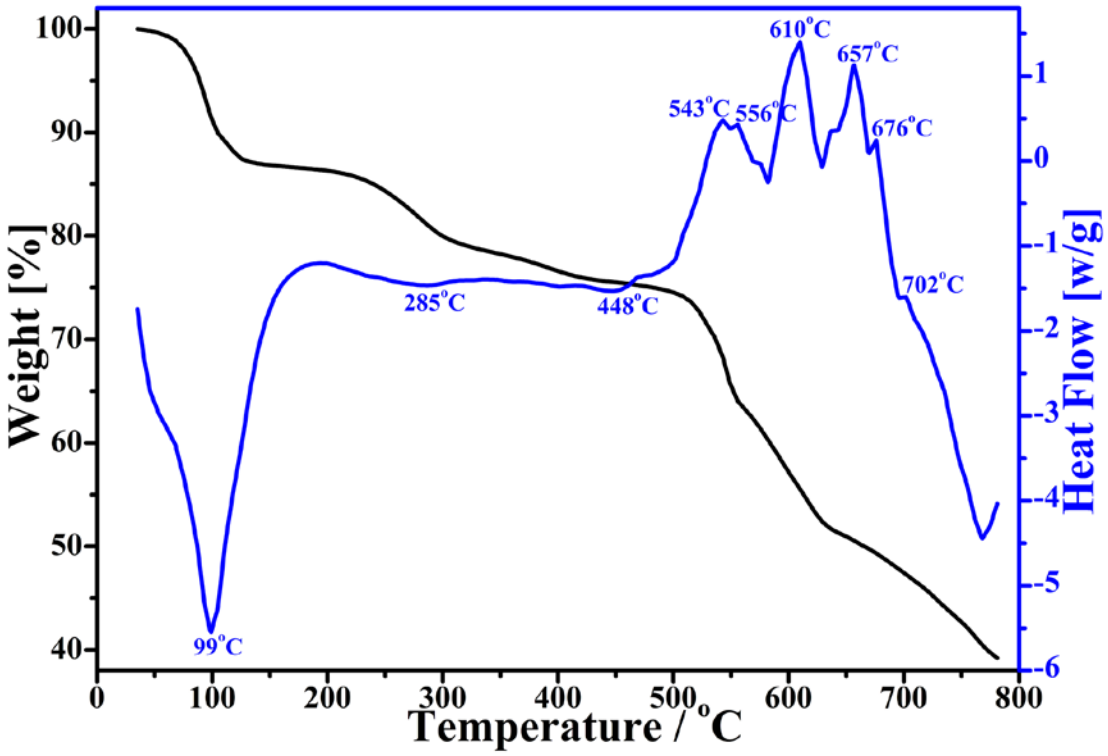
(c)



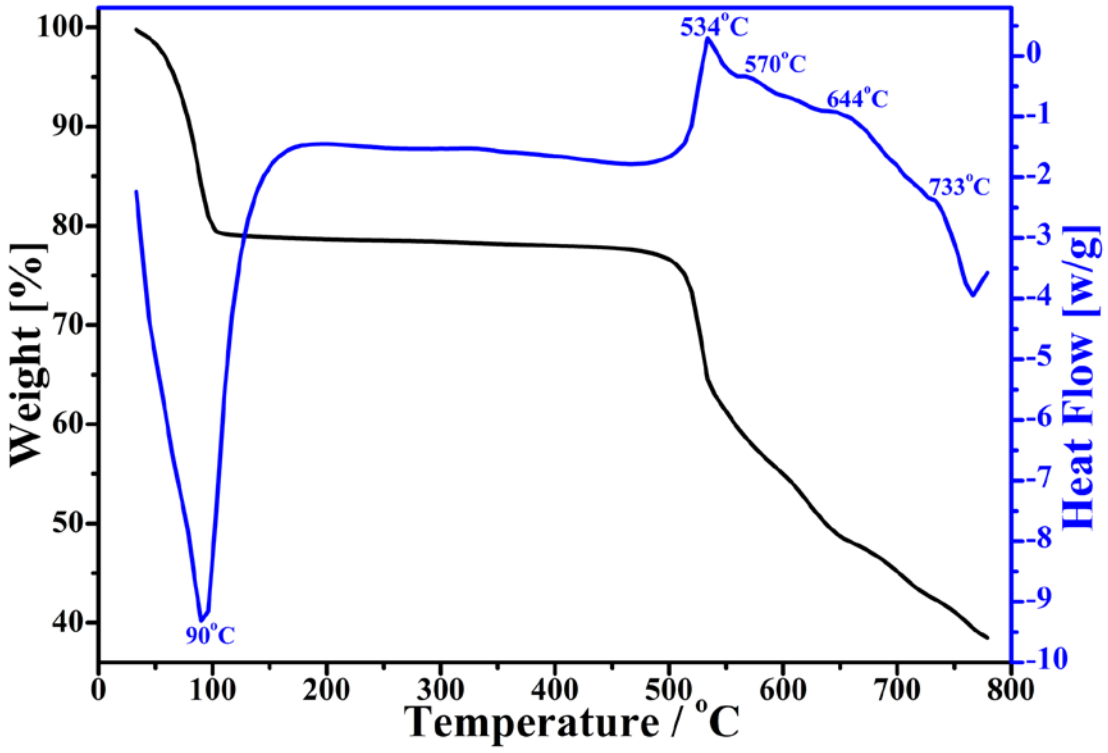
(d)



(e)

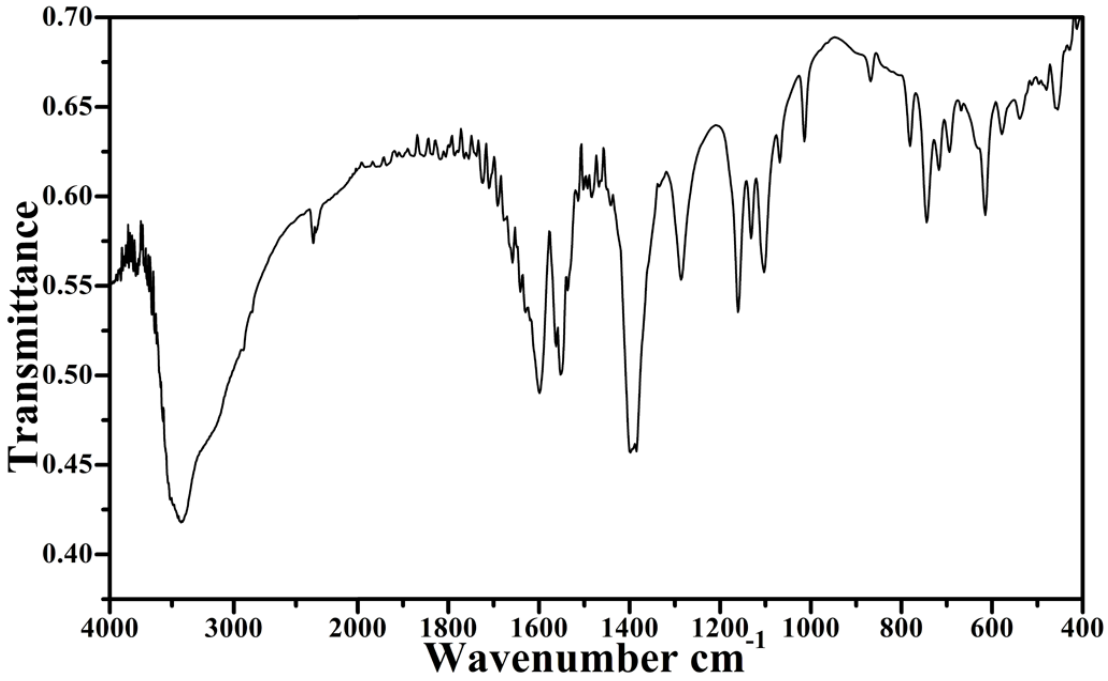


(f)

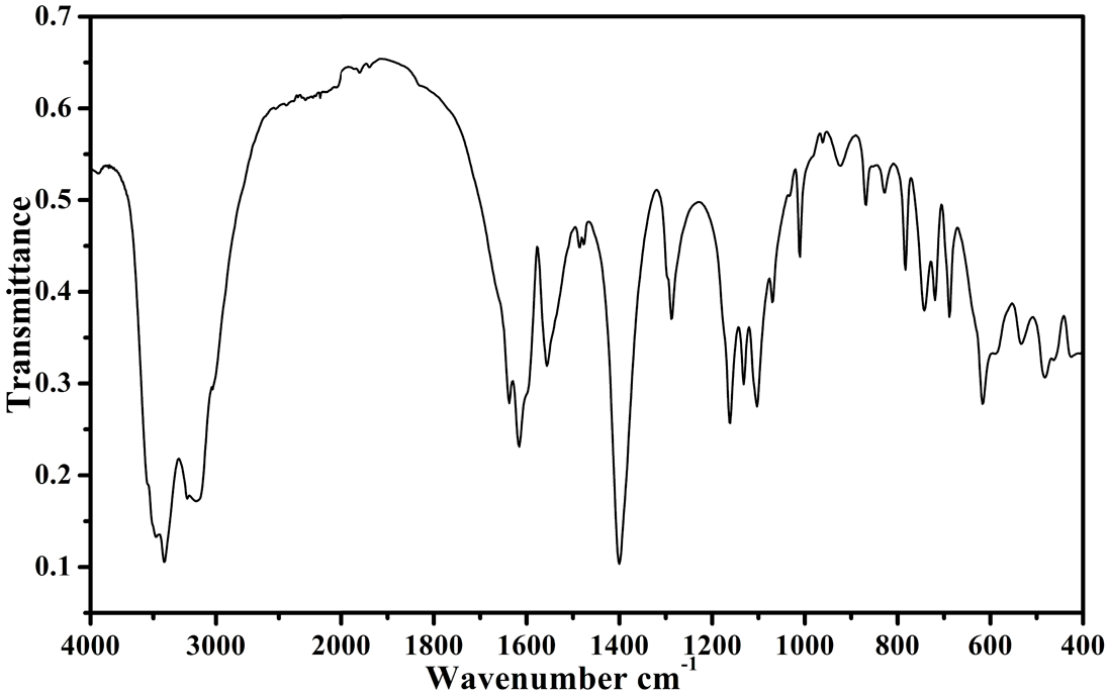


(g)

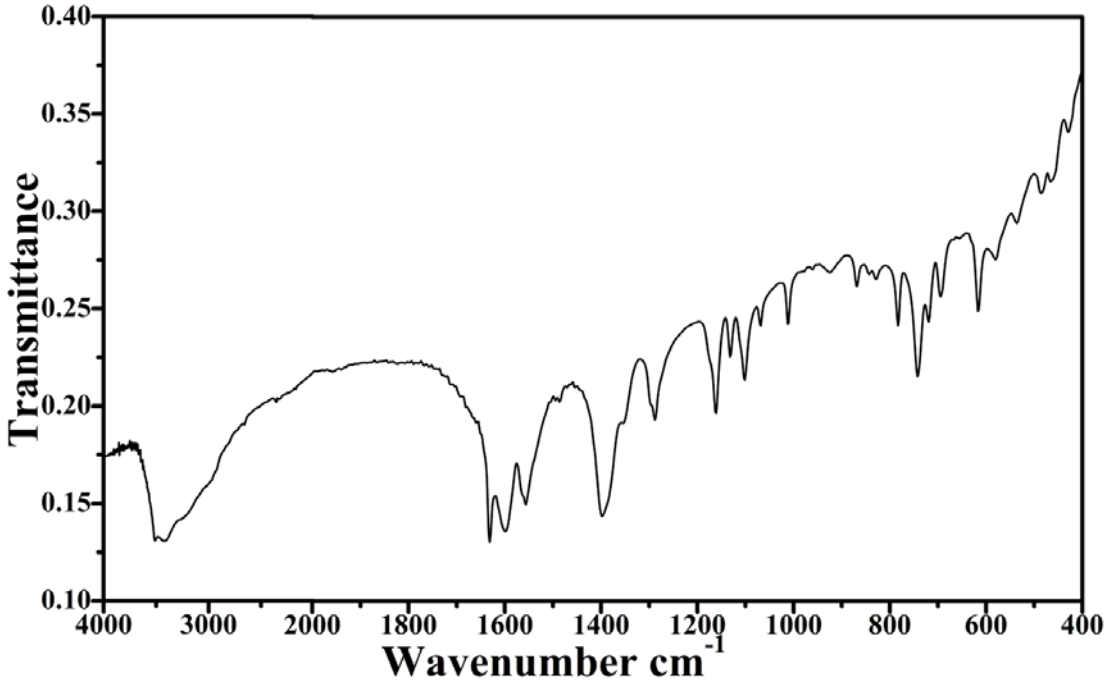
Fig. S14 The TG-DSC curves of compounds **1**(a), **2**(b), **3**(c), **5**(d), **4**(e), **6**(f) and **7**(g).



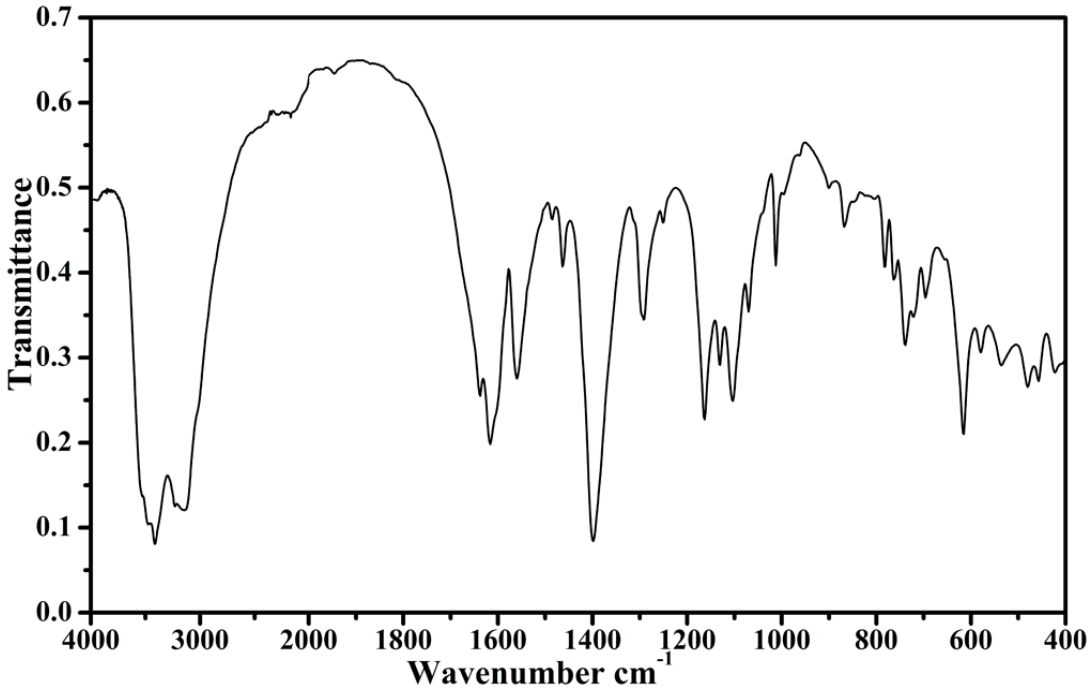
(a)



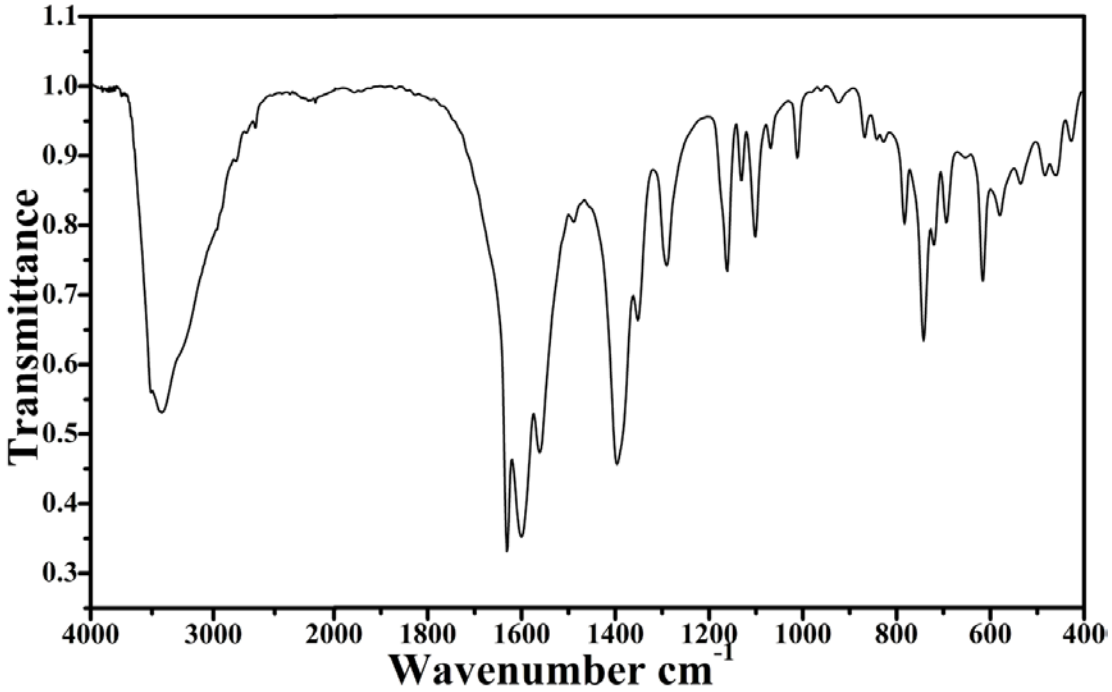
(b)



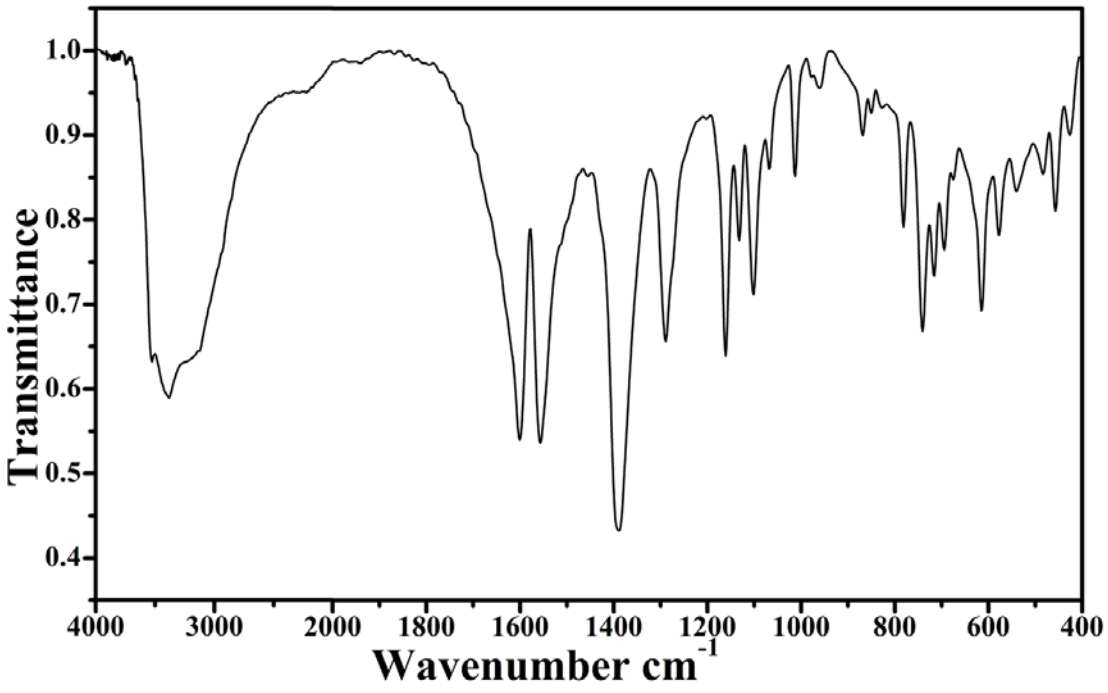
(c)



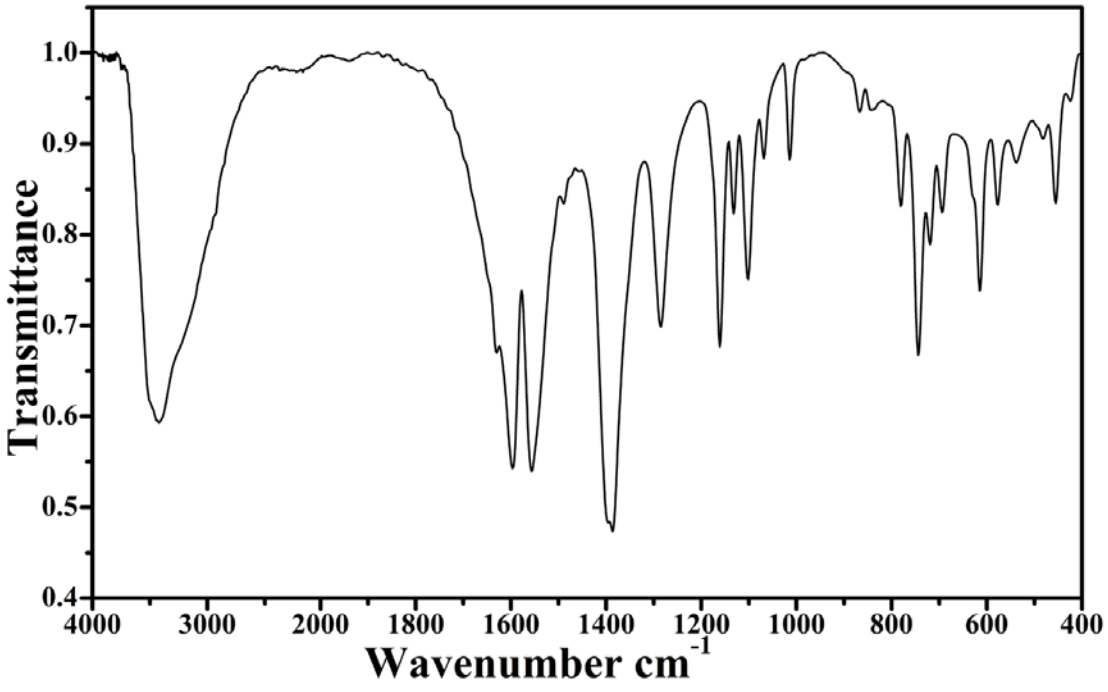
(d)



(e)



(f)



(g)

Fig. S15 The IR spectra of compounds **1**(a), **2**(b), **3**(c), **4**(d), **5**(e), **6**(f) and **7**(g).

Additional details for single-crystal structural refinements

During the process of structure refinement for all the compounds (**1**-**7**), the chemically equivalent O-H and non-bonding H···H distances within the H_2O molecules were refined with the restrained comment "DFIX" for giving a more reasonable chemically equivalent bond distance. The U_{iso}/U_{ij} restraints are used to give a more reasonable model of the aqua hydrogen atoms—that is, the aqua hydrogen atoms located from difference Fourier maps were refined with isotropic thermal parameters, 1.2 times those of their carrier atoms [i.e. $U_{iso}(H) = 1.2U_{eq}(OW)$].

The guest tolu molecule in **3** and bim molecule in **5**, are both disordered over two positions but lie disordered about an inversion centre, respectively. During the process of structure refinement, all the carbon atoms (C15, C16, C17, C18, C19, C20 and C21) of tolu molecule in **3** were treated by disorder with the occupancy factors of 0.5; while the carbon (C15, C16, C17, C18 and C19) and nitrogen atoms (N1 and N2) of bim molecule in **5** were all dealt with disorder with the occupancy factors of 0.3 and 0.2, respectively. And, the disordered one fluorin atom of the dfb molecule in **6** was dealt with disorder with the occupancy factors of 0.3 and 0.2, respectively. These disordered atoms were modeled by application of distance restraints for chemically equivalent bonding and non-bonding interactions (C-C, C-N, C-F and C···C); and many of them, including some non-disordered C and N atoms in **4**, **6** and **7**, were refined with restrained comments "DELU" to be sure that all the atoms have the similar environment. The restrained comments "FLAT" for the disorder imidazole rings (N1, N2, C15, C16 and C17; N1A, N2A, C15A, C16A and C17A) of bim molecules in **6** are used to make the geometry of the bim molecule close to ideal.

Moreover, the restrained refinement comment "ISOR" is common used during the refinement to restraint the Non-H atoms with the ADP problems, these atoms are as follows: OW5, OW6, OW7 and OW8 in **1**; C15, C16 and C17 in **2**; C15, C16, C17, C18, C19, C20 and C21 in **3**; C15, C15A, C16, C16A, C17, C17A, C18, C18A, C19, C19A, N1, N1A, N2 and N2A in **5**; C4, C13, C15, C16, C17, C18, C19, C20, F1, F1A, F2, O6 and OW5 in **6**; OW6, OW7, OW8, OW9 and OW10 in **7**.