Supporting Information

Series of Crystalline Beryllium Phosphates Including New Templates Generated by In Situ *N*-methylation Transformation

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Experimental Section

Synthesis of $[tmpip][Be_2(HPO_4)_2(H_2PO_4)]_2$ (4)

Compound **4** can also be obtained when the stating piperazine (*pip*) was replaced by 1,4-dimethyl-piperazine (*dmpip*) or 3-aminopyridine (*apy*) under similar conditions. The synthetic conditions are presented in Table S1.

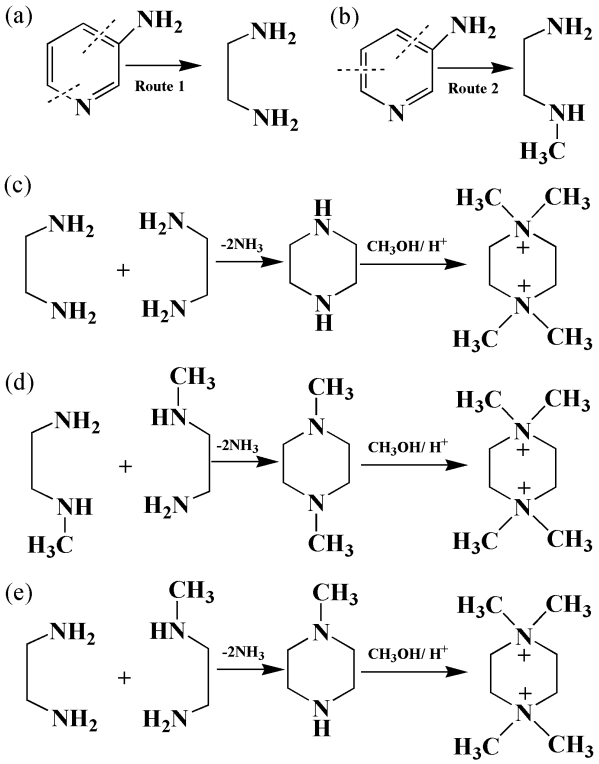
Table S1 Synthetic conditions of **4** synthesized from *dmpip* and *apy* amines

$BeSO_4·4H_2O$ [g]	H_3PO_4 [mL]	Methanol [mL]	H_2O [mL]	Amine	Temp [°C]	Time [days]	Yield (%based on Be)
0.178	0.26	1.80	2.20	*dmpip*, 0.38 mL	160	6	57.6
0.175	0.26	5.00	1.00	*apy*, 0.18 g	160	7	36.2

The formation of $tmpip^{2+}$ template from the starting *apy* amine in compound **4** is unexpected and interesting. However, the "black-box" nature of the sealed hydrothermal reactor makes it very difficult to truly master the reaction mechanisms or even isolate intermediate phases that appear prior to the onset of the product in most hydrothermal reactions. Based on the facts that **4** can be synthesized in the presence of *pip* or *dmpip* amine, the $tmpip^{2+}$ may presumably be generated *in situ* from unprecedented transformations (Scheme S1). Compared with routine synthetic methods, hydrothermal reactions create more chance for the cleavage of carbon-carbon bonds due to the relatively critical reaction conditions. In the present case, the *apy* starting amine may be decomposed to form ethylenediamine or 1-methylethylenediamine, which simultaneously undergoes *in situ* intramolecular deamination coupling reaction (DCR) to yield *pip*, 1-methyl-piperazine (*mpip*) and *dmpip*. Similar example including *in situ* DCR of organic amine to form *pip* has been observed under hydrothermal conditions.[1] The presences of *pip*, *mpip* and *dmpip* were also confirmed by the Mass spectrometry of the mother liquors of **4** from *apy* amine with or without $BeSO_4·4H_2O$ (Figure S1, 2). MS *m*/*z*: *pip*, 109.1 $(M + Na)^+$; *mpip*, 123.1 $(M + Na)^+$; *dmpip*, 137.1 $(M + Na)^+$. Thus, the *pip*, *mpip* and/or *dmpip* "intermediate" acting as the organic amine precursor participate in the subsequent methylation reactions under methanol-aqueous media. Similar *in situ* methylation reactions have also been observed in one zinc coordination polymer, several halometallates and zinc phosphates/phosphites under hydrothermal conditions.[2]

References:

1. S.T. Zheng, M.H. Wang, G.Y. Yang, *Inorg. Chem.*, 2007, **46**, 9503.
2. (a) O.R. Evans, W.B. Lin, *Cryst. Growth Des.*, 2001, **1**, 9; (b) Q. Hou, F.Q. Bai, M. J. Jia, J. Jin, J.H. Yu, J. Q. Xu, *CrystEngComm*, 2012, **14**, 4000; (c) G.M. Wang, J.H. Li, X. Zhang, P. Wang, B.B. Pang, Z.H. Wang, Y.X. Wang, J.H. Lin, C.Y. Pan, *Dalton Trans.*, 2013, **42**, 13084; (d) L.M. Li, K. Cheng, F. Wang, J. Zhang, *Inorg. Chem.*, 2013, **52**, 5654; (e) J.B. Wu, Y. Yan, B.K. Liu, X.L. Wang, J.Y. Li, J.H. Yu, *Chem. Commun.*, 2013, **49**, 4995.



Scheme S1 The possible formation routes of $tmpip^{2+}$ from *apy* amine.

Table S2 Reactant liquors for mass spectrum determination in **4**

Sequence	H_2O [mL]	Methanol [mL]	*Apy* [g]	H_3PO_4 [mL]	$BeSO_4{\cdot}4H_2O$ [g]	Temp [°C]	Time [days]
I	1.00	5.00	0.18	0.26	0	160	4
II	1.00	5.00	0.18	0.26	0.18	160	5

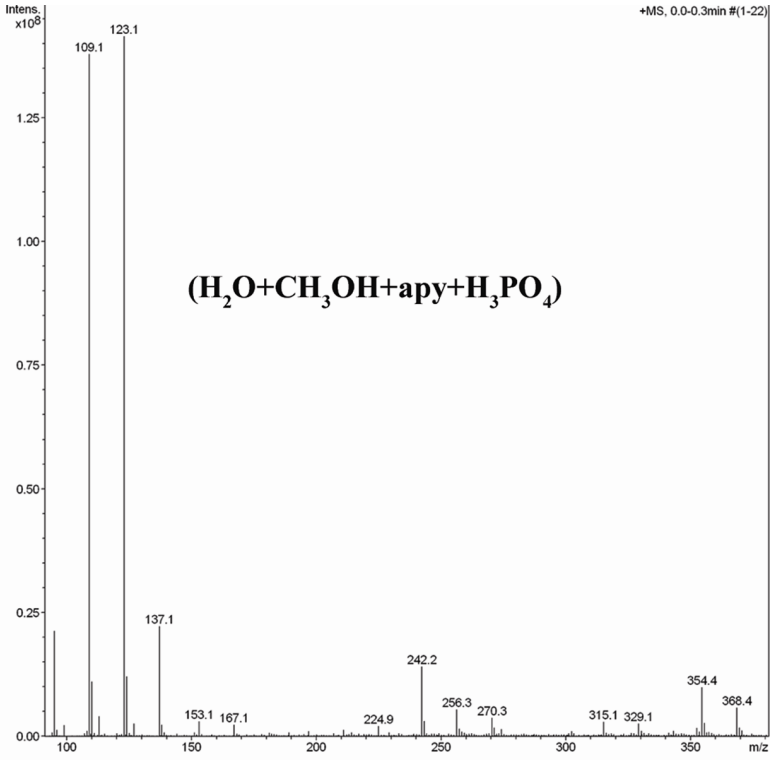


Figure S1. The mass spectrum of reactant liquor of **I**.

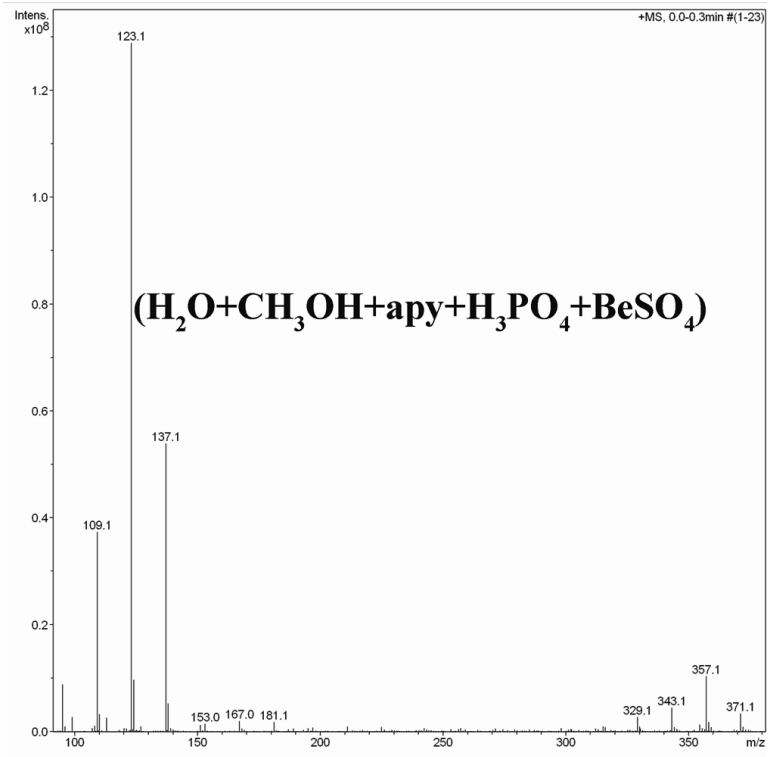


Figure S2. The mass spectrum of reactant liquor of **II**.

Table S3 Selected bond lengths (Å) and bond angels (°) for **1**-**4**

Compound **1**			
Be(1)-O(5)	1.606(3)	O(4)-P(1)-O(2)	105.98(9)
Be(1)-O(3)#1	1.617(3)	P(1)-O(4)	1.5319(17)
Be(1)-O(7)#2	1.630(3)	P(1)-O(2)	1.5747(17)
Be(1)-O(4)	1.642(3)	P(2)-O(5)	1.5132(17)
P(1)-O(3)	1.5118(17)	P(2)-O(7)	1.5192(17)
P(1)-O(1)	1.5158(17)	P(2)-O(8)	1.5271(17)
O(5)-Be(1)-O(3)#1	109.4(2)	P(2)-O(6)	1.5629(17)
O(5)-Be(1)-O(7)#2	116.1(2)	O(5)-P(2)-O(7)	112.30(10)
O(3)#1-Be(1)-O(7)#2	107.21(18)	O(5)-P(2)-O(8)	108.74(10)
O(5)-Be(1)-O(4)	111.17(18)	O(7)-P(2)-O(8)	108.79(10)
O(3)#1-Be(1)-O(4)	109.67(19)	O(5)-P(2)-O(6)	109.72(10)
O(7)#2-Be(1)-O(4)	102.99(19)	O(7)-P(2)-O(6)	108.35(10)
O(3)-P(1)-O(1)	111.00(10)	O(8)-P(2)-O(6)	108.87(10)
O(3)-P(1)-O(4)	112.71(9)	P(1)-O(3)-Be(1)#1	137.46(15)
O(1)-P(1)-O(4)	112.60(10)	P(1)-O(4)-Be(1)	130.02(15)
O(3)-P(1)-O(2)	105.89(10)	P(2)-O(5)-Be(1)	145.46(16)
O(1)-P(1)-O(2)	108.20(10)	P(2)-O(7)-Be(1)#2	137.38(16)
Compound **2**			
Be(1)-O(13)	1.612(5)	P(1)-O(4)	1.528(2)
Be(1)-O(8)	1.629(5)	P(1)-O(3)	1.595(2)
Be(1)-O(9)	1.631(5)	P(2)-O(6)	1.508(2)
Be(1)-O(1)	1.645(5)	P(2)-O(5)	1.512(2)
Be(2)-O(5)	1.596(5)	P(2)-O(8)	1.513(2)
Be(2)-O(14)#1	1.625(5)	P(2)-O(7)	1.599(2)
Be(2)-O(10)#2	1.627(5)	P(3)-O(13)	1.495(3)
Be(2)-O(4)	1.671(5)	P(3)-O(16)	1.517(2)
Be(3)-O(6)#3	1.613(5)	P(3)-O(14)	1.522(2)
Be(3)-O(12)#4	1.621(5)	P(3)-O(15)	1.603(3)
Be(3)-O(16)	1.623(5)	P(4)-O(9)	1.516(2)
Be(3)-O(2)#4	1.656(5)	P(4)-O(12)	1.518(2)
P(1)-O(1)	1.504(3)	P(4)-O(10)	1.527(2)
P(1)-O(2)	1.525(2)	P(4)-O(11)	1.592(2)
O(13)-Be(1)-O(8)	109.1(3)	O(6)-P(2)-O(7)	107.43(14)
O(13)-Be(1)-O(9)	109.1(3)	O(5)-P(2)-O(7)	104.83(15)
O(8)-Be(1)-O(9)	110.4(3)	O(8)-P(2)-O(7)	104.64(14)
O(13)-Be(1)-O(1)	105.9(3)	O(13)-P(3)-O(16)	111.43(14)

O(8)-Be(1)-O(1)	108.9(3)	O(13)-P(3)-O(14)	111.26(14)
O(9)-Be(1)-O(1)	113.3(3)	O(16)-P(3)-O(14)	113.16(15)
O(5)-Be(2)-O(14)#1	108.7(3)	O(13)-P(3)-O(15)	106.21(16)
O(5)-Be(2)-O(10)#2	113.3(3)	O(16)-P(3)-O(15)	106.80(14)
O(14)#1-Be(2)-O(10)#2	109.4(3)	O(14)-P(3)-O(15)	107.55(14)
O(5)-Be(2)-O(4)	112.4(3)	O(9)-P(4)-O(12)	112.42(14)
O(14)#1-Be(2)-O(4)	106.6(3)	O(9)-P(4)-O(10)	111.48(14)
O(10)#2-Be(2)-O(4)	106.1(3)	O(12)-P(4)-O(10)	114.52(15)
O(6)#3-Be(3)-O(12)#4	110.8(3)	O(9)-P(4)-O(11)	109.98(15)
O(6)#3-Be(3)-O(16)	107.5(3)	O(12)-P(4)-O(11)	106.72(15)
O(12)#4-Be(3)-O(16)	109.5(3)	O(10)-P(4)-O(11)	100.93(13)
O(6)#3-Be(3)-O(2)#4	106.6(3)	P(1)-O(1)-Be(1)	143.0(2)
O(12)#4-Be(3)-O(2)#4	113.7(3)	P(1)-O(2)-Be(3)#1	134.2(2)
O(16)-Be(3)-O(2)#4	108.5(3)	P(1)-O(4)-Be(2)	131.9(2)
O(1)-P(1)-O(2)	113.37(14)	P(2)-O(5)-Be(2)	150.6(2)
O(1)-P(1)-O(4)	114.08(14)	P(2)-O(6)-Be(3)#5	151.6(2)
O(2)-P(1)-O(4)	112.03(14)	P(2)-O(8)-Be(1)	141.1(2)
O(1)-P(1)-O(3)	102.99(15)	P(4)-O(9)-Be(1)	131.0(2)
O(2)-P(1)-O(3)	107.03(13)	P(4)-O(10)-Be(2)#6	144.8(2)
O(4)-P(1)-O(3)	106.41(13)	P(4)-O(12)-Be(3)#1	138.3(2)
O(6)-P(2)-O(5)	115.22(15)	P(3)-O(13)-Be(1)	170.9(3)
O(6)-P(2)-O(8)	110.84(15)	P(3)-O(14)-Be(2)#4	130.1(2)
O(5)-P(2)-O(8)	112.96(15)	P(3)-O(16)-Be(3)	137.4(2)

Compound **3**

Be(1)-O(10)#1	1.611(4)	P(2)-O(1)	1.503(2)
Be(1)-O(2)	1.620(4)	P(2)-O(7)	1.503(2)
Be(1)-O(1)	1.629(4)	P(2)-O(3)	1.540(2)
Be(1)-O(14)#2	1.633(4)	P(2)-O(4)	1.574(2)
Be(2)-O(8)	1.602(4)	P(3)-O(10)	1.497(2)
Be(2)-O(13)	1.617(4)	P(3)-O(9)	1.504(2)
Be(2)-O(9)	1.619(4)	P(3)-O(12)	1.549(2)
Be(2)-O(7)	1.623(4)	P(3)-O(11)	1.567(2)
P(1)-O(2)	1.502(2)	P(4)-O(13)	1.494(2)
P(1)-O(8)	1.504(2)	P(4)-O(14)	1.511(2)
P(1)-O(6)	1.548(2)	P(4)-O(15)	1.543(2)
P(1)-O(5)	1.568(2)	P(4)-O(16)	1.572(2)
O(10)#1-Be(1)-O(2)	110.6(3)	O(7)-P(2)-O(4)	109.22(13)
O(10)#1-Be(1)-O(1)	108.1(2)	O(3)-P(2)-O(4)	106.74(15)

O(2)-Be(1)-O(1)	110.8(2)	O(10)-P(3)-O(9)	110.34(12)
O(10)#1-Be(1)-O(14)#2	109.4(2)	O(10)-P(3)-O(12)	112.37(13)
O(2)-Be(1)-O(14)#2	107.9(2)	O(9)-P(3)-O(12)	108.70(12)
O(1)-Be(1)-O(14)#2	110.1(2)	O(10)-P(3)-O(11)	106.30(13)
O(8)-Be(2)-O(13)	113.7(3)	O(9)-P(3)-O(11)	110.97(13)
O(8)-Be(2)-O(9)	107.1(2)	O(12)-P(3)-O(11)	108.15(14)
O(13)-Be(2)-O(9)	105.3(2)	O(13)-P(4)-O(14)	110.52(12)
O(8)-Be(2)-O(7)	112.0(2)	O(13)-P(4)-O(15)	110.65(12)
O(13)-Be(2)-O(7)	108.8(2)	O(14)-P(4)-O(15)	112.04(13)
O(9)-Be(2)-O(7)	109.8(2)	O(13)-P(4)-O(16)	110.62(13)
O(2)-P(1)-O(8)	114.84(13)	O(14)-P(4)-O(16)	110.13(12)
O(2)-P(1)-O(6)	108.76(12)	O(15)-P(4)-O(16)	102.63(13)
O(8)-P(1)-O(6)	108.15(12)	P(2)-O(1)-Be(1)	137.1(2)
O(2)-P(1)-O(5)	109.10(13)	P(1)-O(2)-Be(1)	140.4(2)
O(8)-P(1)-O(5)	109.58(13)	P(2)-O(7)-Be(2)	134.7(2)
O(6)-P(1)-O(5)	106.05(14)	P(1)-O(8)-Be(2)	148.9(2)
O(1)-P(2)-O(7)	114.93(13)	P(3)-O(9)-Be(2)	139.65(19)
O(1)-P(2)-O(3)	108.11(13)	P(3)-O(10)-Be(1)#3	146.9(2)
O(7)-P(2)-O(3)	109.04(13)	P(4)-O(13)-Be(2)	147.9(2)
O(1)-P(2)-O(4)	108.49(13)	P(4)-O(14)-Be(1)#4	131.96(19)

Compound **4**

Be(1)-O(7)#1	1.604(4)	P(1)-O(3)	1.557(2)
Be(1)-O(1)	1.615(4)	P(1)-O(2)	1.561(2)
Be(1)-O(6)#2	1.620(4)	P(2)-O(7)	1.505(2)
Be(1)-O(12)#3	1.658(4)	P(2)-O(6)	1.519(2)
Be(2)-O(9)	1.589(4)	P(2)-O(5)	1.534(2)
Be(2)-O(4)	1.612(4)	P(2)-O(8)	1.570(2)
Be(2)-O(10)#4	1.625(4)	P(3)-O(9)	1.491(2)
Be(2)-O(5)	1.646(4)	P(3)-O(10)	1.510(2)
P(1)-O(4)	1.491(2)	P(3)-O(12)	1.525(2)
P(1)-O(1)	1.499(2)	P(3)-O(11)	1.576(2)
O(7)#1-Be(1)-O(1)	110.2(2)	O(7)-P(2)-O(5)	111.63(12)
O(7)#1-Be(1)-O(6)#2	112.1(2)	O(6)-P(2)-O(5)	110.69(11)
O(1)-Be(1)-O(6)#2	112.1(2)	O(7)-P(2)-O(8)	108.98(12)
O(7)#1-Be(1)-O(12)#3	111.2(2)	O(6)-P(2)-O(8)	102.86(12)
O(1)-Be(1)-O(12)#3	105.0(2)	O(5)-P(2)-O(8)	109.21(12)
O(6)#2-Be(1)-O(12)#3	105.9(2)	O(9)-P(3)-O(10)	109.01(12)
O(9)-Be(2)-O(4)	111.6(2)	O(9)-P(3)-O(12)	111.40(12)

O(9)-Be(2)-O(10)#4	105.7(2)	O(10)-P(3)-O(12)	113.25(12)
O(4)-Be(2)-O(10)#4	107.4(2)	O(9)-P(3)-O(11)	107.95(13)
O(9)-Be(2)-O(5)	112.3(2)	O(10)-P(3)-O(11)	107.74(12)
O(4)-Be(2)-O(5)	106.8(2)	O(12)-P(3)-O(11)	107.29(12)
O(10)#4-Be(2)-O(5)	113.0(2)	P(1)-O(1)-Be(1)	134.7(2)
O(4)-P(1)-O(1)	111.29(12)	P(1)-O(4)-Be(2)	144.1(2)
O(4)-P(1)-O(3)	111.52(13)	P(2)-O(5)-Be(2)	129.87(18)
O(1)-P(1)-O(3)	110.30(13)	P(2)-O(6)-Be(1)#2	140.63(19)
O(4)-P(1)-O(2)	111.32(13)	P(2)-O(7)-Be(1)#5	138.5(2)
O(1)-P(1)-O(2)	110.24(12)	P(3)-O(9)-Be(2)	162.0(2)
O(3)-P(1)-O(2)	101.80(14)	P(3)-O(10)-Be(2)#6	139.98(19)
O(7)-P(2)-O(6)	113.06(12)	P(3)-O(12)-Be(1)#7	127.19(18)

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

Table S4 Details of hydrogen bonds for **1-4**.

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	(deg)
Compound **1**				
N(2)–H(2A) ···O(7)	0.89	2.19	2.988(3)	148.5
N(2)–H(2B) ···O(8)	0.89	1.82	2.697(3)	167.6
N(2)–H(2C) ···O(4)	0.89	2.12	2.916(3)	148.3
O(2)–H(2E) ···O(8)	0.82	1.75	2.571(2)	177.1
O(6)–H(6C) ···O(1)	0.82	1.66	2.481(2)	175.5
C(1) –H(1A) ···O(8)	0.93	2.33	3.165(5)	150
C(2) –H(2D) ···O(1)	0.93	2.46	3.338(7)	158
C(3) –H(3A) ···O(6)	0.93	2.52	3.370(1)	152
C(5) –H(5A) ···O(3)	0.93	2.22	3.086(1)	154
C(6) –H(4B) ···O(4)	0.97	2.44	3.338(3)	154
C(6) –H(4C) ···O(2)	0.97	2.40	3.169(2)	136
C(7) –H(5A) ···O(5)	0.96	2.56	3.513(7)	173
C(7) –H(5A) ···O(5)	0.96	2.55	3.449(3)	157
Compound **2**				
O(3)–H(3A) ···O(4)	0.82	2.18	2.994(4)	175.6
O(7)–H(7D) ···O(1W)	0.82	1.75	2.571(5)	179.8

O(7)–H(7D) ···O(1W')	0.82	1.90	2.646(2)	151.3
O(11)–H(11A) ···O(7)	0.82	1.94	2.748(2)	170.0
O(15)–H(15A) ···O(5)	0.82	2.28	3.000(4)	147.0
C(7) –H(7A) ···O(6)	0.96	2.52	3.446(1)	163
C(7) –H(7B) ···O(15)	0.96	2.55	3.484(6)	164
C(7) –H(7C) ···O(9)	0.96	2.45	3.372(6)	161
C(8) –H(8B) ···O(14)	0.96	2.49	3.358(8)	150
Compound **3**				
O(4) –H(4A) ···O(12)	0.82	1.90	2.695(3)	163.0
O(5) –H(5A) ···O(15)	0.82	1.87	2.665(3)	164.2
O(11)–H(11A) ···O(6)	0.82	1.91	2.675(3)	155.0
O(12) –H(12A) ···O(15)	0.82	1.66	2.469(3)	168.2
O(16) –H(16A) ···O(3)	0.82	1.96	2.684(3)	146.4
N(2) –H(2A) ··· O(11)	0.89	2.07	2.916(3)	157.9
N(2) –H(2B) ··· O(6)	0.89	2.01	2.883(3)	165.0
N(2) –H(2C) ··· O(10)	0.89	2.25	2.943(3)	134.4
N(2) –H(2C) ··· O(7)	0.89	2.42	3.142(3)	139.1
C(1) –H(1A) ···O(14)	0.97	2.56	3.455(2)	154
C(2) –H(2A) ···O(1)	0.97	2.55	3.398(6)	146
C(2) –H(2D) ···O(1)	0.97	2.32	3.228(3)	156
C(4) –H(4B) ···O(6)	0.97	2.49	3.444(8)	171
C(5) –H(5B) ···O(3)	0.97	2.50	3.445(1)	165
C(5) –H(5C) ···O(3)	0.97	2.42	3.302(4)	151
C(7) –H(7A) ···O(16)	0.96	2.48	3.304(2)	143
C(7) –H(7B) ···O(7)	0.96	2.56	3.385(9)	144
C(7) –H(7B) ···O(13)	0.96	2.59	3.471(4)	153
C(8) –H(8C) ···O(16)	0.96	2.36	3.220(2)	149
Compound **4**				
O(2) –H(2A) ···O(5)	0.82	1.92	2.723(3)	167.5
O(3) –H(3A) ···O(12)	0.82	1.95	2.695(3)	150.7
O(8)–H(8A) ···O(10)	0.82	1.99	2.775(3)	159.1
O(11) –H(11A) ···O(6)	0.82	2.05	2.827(3)	157.6
C(2) –H(2C) ···O(2)	0.97	2.38	3.092(9)	130
C(3) –H(3B) ···O(11)	0.96	2.38	3.332(5)	169
C(4) –H(4C) ···O(7)	0.96	2.49	3.165(1)	128

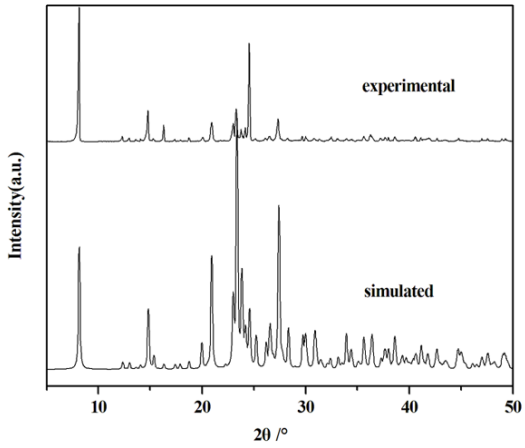


Figure S3. The XRD patters of **1**.

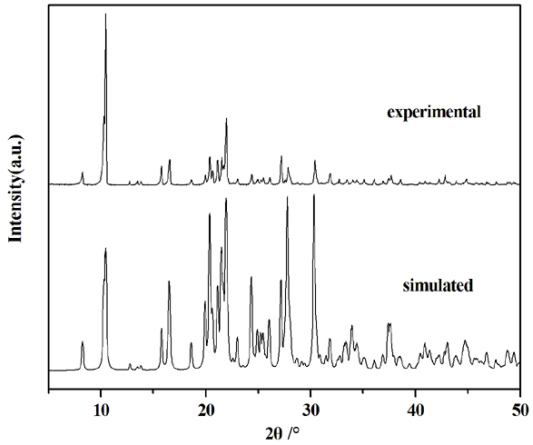


Figure S4. The XRD patters of **2**.

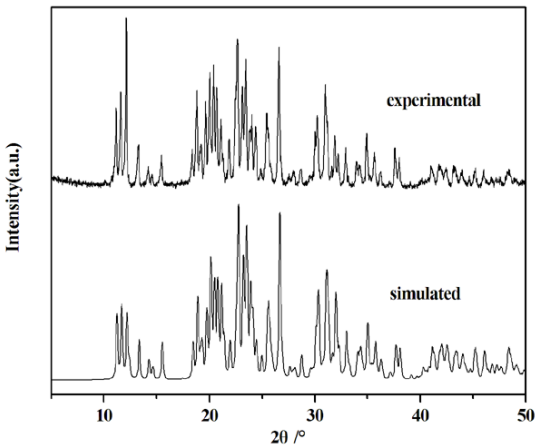


Figure S5. The XRD patters of **3**.

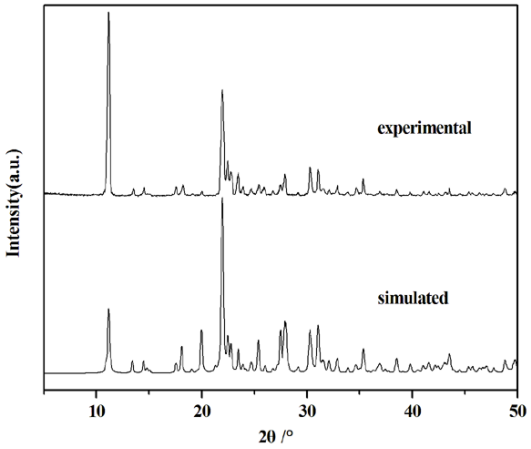


Figure S6. The XRD patters of **4**.

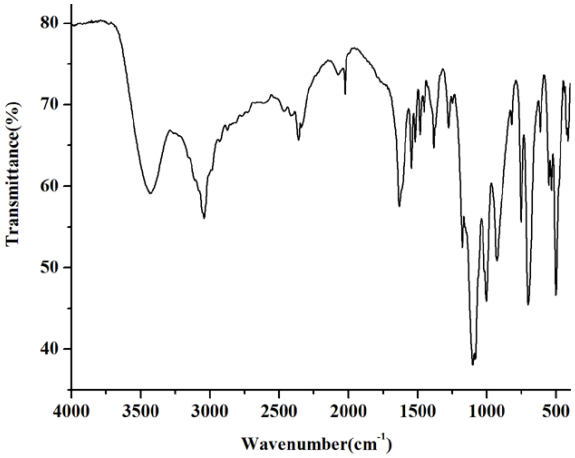


Figure S7. The IR spectrum of **1**.

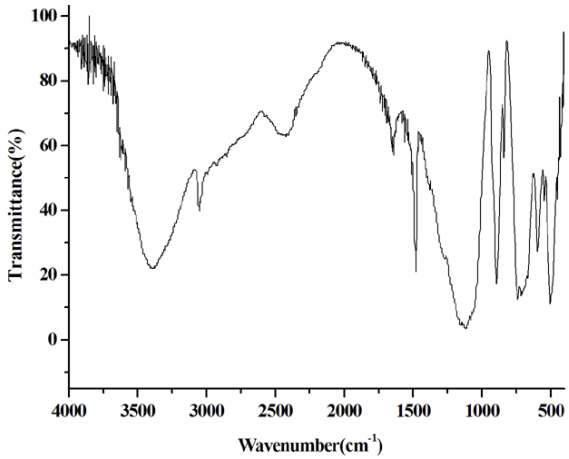


Figure S8. The IR spectrum of **2**.

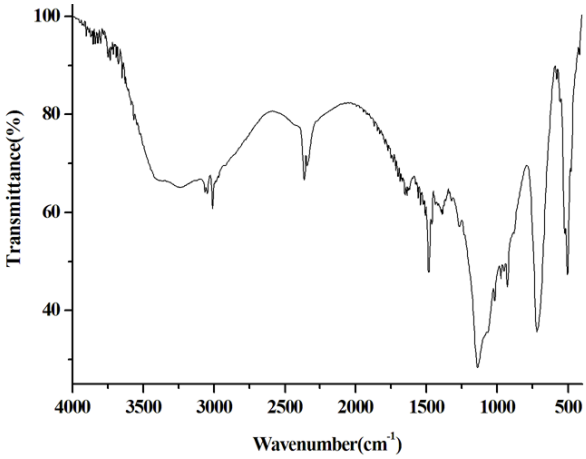


Figure S9. The IR spectrum of **3**.

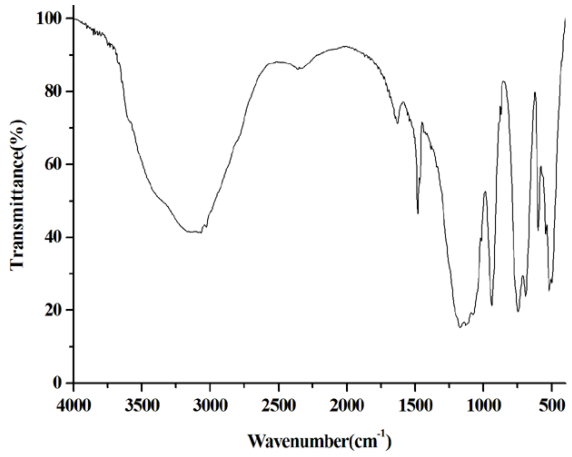


Figure S10. The IR spectrum of **4**.

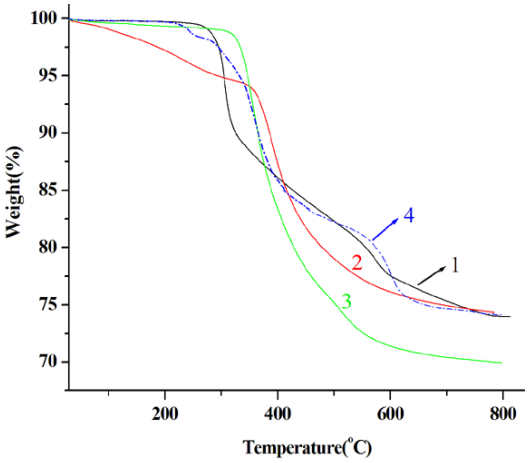


Figure S11. The TG curves of **1**-**4**.