Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Variations in the structural composition of pyrazole-3,5-dicarboxylato Cu(II) complexes with 1,2-di(4-pyridyl)ethane synthesized under different conditions

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Table S1. The selected bond lengths (Å) and angles (°) for complexes **1-6**.

Complex **1**[a]			
Cu1—N3	1.932(2)	O1—Cu1—O5	102.13(6)
Cu1—N1	1.942(2)	N3—Cu1—O9	103.42(7)
Cu1—O1	2.002(2)	N1—Cu1—O9	107.20(7)
Cu1—O5	2.020(2)	O1—Cu1—O9	91.04(7)
Cu1—O9	2.265 (2)	O5—Cu1—O9	89.83(7)
Cu2—N2	1.925(2)	N2—Cu2—N4	93.90(7)
Cu2—N4	1.931(2)	N2—Cu2—O7	165.83(8)
Cu2—O7	1.981 (2)	N4—Cu2—O7	80.71(7)
Cu2—O3	2.008(2)	N2—Cu2—O3	80.24(7)
Cu2—O10	2.300(2)	N4—Cu2—O3	162.24(8)
N3—Cu1—N1	93.53(7)	O7—Cu2—O3	100.96(6)
N3—Cu1—O1	165.44(7)	N2—Cu2—O10	98.85(7)
N1—Cu1—O1	80.31(7)	N4—Cu2—O10	108.58(7)
N3—Cu1—O5	79.96(7)	O7—Cu2—O10	95.30(7)
N1—Cu1—O5	162.82(7)	O3—Cu2—O10	88.95(7)
Complex **2**[b]			
Cu1—N1	1.934(3)	O1—Cu1—O5	104.39(11)
Cu1—N3	1.935(3)	N1—Cu1—O14	105.56(14)
Cu1—O1	2.043(3)	N3—Cu1—O14	102.99(14)
Cu1—O5	2.053(3)	O1—Cu1—O14	93.06(13)
Cu1—O14	2.165(4)	O5—Cu1—O14	91.06(13)
Cu2—N4	1.922(3)	N4—Cu2—N2	91.96(13)
Cu2—N2	1.929(3)	N4—Cu2—O3	165.48(13)
Cu2—O3	1.991(3	N2—Cu2—O3	80.52(12)
Cu2—O7	2.018(3)	N4—Cu2—O7	80.86(12)
Cu2—O13	2.303(3)	N2—Cu2—O7	161.84(14)
N1—Cu1—N3	92.70(13)	O3—Cu2—O7	102.56(11)
N1—Cu1—O1	79.29(12)	N4—Cu2—O13	104.85(12)
N3—Cu1—O1	163.54(14)	N2—Cu2—O13	108.12(12)
N1—Cu1—O5	162.87(13	O3—Cu2—O13	89.35(11)
N3—Cu1—O5	79.26(12)	O7—Cu2—O13	89.88(10)
Complex **3**[c]			
Cu1—N3	1.970(3)	N1—Cu1—O5	98.83(13)
Cu1—N1	1.981(3)	O1—Cu1—O5	159.95(14)
Cu1—O1	2.001(3)	N3—Cu1—O6	102.51(14)
Cu1—O5	2.003(3)	N1—Cu1—O6	93.45(14)
Cu1—O6	2.214(3)	O1—Cu1—O6	110.05(14)
Cu2—$O3^{i}$	1.934(3)	O5—Cu1—O6	89.94(14)
Cu2—O3	1.934(3)	$O3^{i}$—Cu2—O3	180.000
Cu2—$N2^{i}$	1.973(3)	$O3^{i}$—Cu2—$N2^{i}$	82.99(13)
Cu2—N2	1.973(3)	O3—Cu2—$N2^{i}$	97.01(13)
N3—Cu1—N1	162.76(14)	$O3^{i}$—Cu2—N2	97.01(13)
N3—Cu1—O1	86.37(13)	O3—Cu2—N2	82.99(13)
N1—Cu1—O1	82.01(12)	$N2^{i}$—Cu2—N2	180.00(13)
N3—Cu1—O5	87.80(13)		

Table S1. The selected bond lengths (Å) and angles (°) for complexes **1-6** (Cont.).

Complex **4**[d]			
Cu1—N1	1.923(3)	N3—Cu1—N6	108.22(13)
Cu1—N3	1.935(3)	O5—Cu1—N6	93.60(11)
Cu1—O5	1.990(3)	O1—Cu1—N6	77.52(11)
Cu1—O1	2.050(3)	N1—Cu1—O13	92.75(12)
Cu1—O13	2.703(4)	N3—Cu1—O13	96.50(12)
Cu1—N6	2.641(3)	O5—Cu1—O13	81.59(11)
Cu2—N4	1.916(3)	O1—Cu1—O13	78.95(10)
Cu2—N2	1.916(3)	N6—Cu1—O13	153.62(9)
Cu2—O7	1.995(3)	N4—Cu2—N2	94.40(13)
Cu2—O3	1.997(3	N4—Cu2—O7	80.41(12)
Cu2—O7^{i}	2.417(3)	N2—Cu2—O7	170.60(13)
N1—Cu1—N3	94.12(13)	N4—Cu2—O3	166.02(13)
N1—Cu1—O5	171.15(13)	N2—Cu2—O3	80.36(11)
N3—Cu1—O5	79.86(12)	O7—Cu2—O3	102.87(11)
N1—Cu1—O1	79.31(11)	N4—Cu2—O7^{i}	103.62(12)
N3—Cu1—O1	171.74(12)	N2—Cu2—O7^{i}	106.11(12)
O5—Cu1—O1	106.06(10)	O7—Cu2—O7^{i}	82.83(11)
N1—Cu1—N6	94.45(12)	O3—Cu2—O7^{i}	90.3(1)
Complex **5**[e]			
Cu1—N3	1.920(3)	N3—Cu1—O1	166.76(13)
Cu1—N1	1.935(3)	N1—Cu1—O1	80.13(12)
Cu1—O1	2.002(3)	N3—Cu1—O5	80.28(11)
Cu1—O5	2.004(3)	N1—Cu1—O5	168.09(12)
Cu1—N9	2.330(3)	O1—Cu1—O5	104.85(11)
Cu2—N4	1.922(3)	N3—Cu1—N9	93.78(13)
Cu2—N2	1.934(3)	N1—Cu1—N9	90.99(12)
Cu2—O7	2.018(3)	O1—Cu1—N9	97.38(12)
Cu2—O3	2.056(3)	O5—Cu1—N9	98.96(12)
Cu2—N11	2.325(3)	N4—Cu2—N2	92.92(12)
Cu3—N5	1.925(3)	N4—Cu2—O7	80.01(11)
Cu3—N7	1.936(3)	N2—Cu2—O7	166.54(13)
Cu3—O13	2.010(3)	N4—Cu2—O3	166.93(13)
Cu3—O9	2.018(3)	N2—Cu2—O3	78.92(11)
Cu3—N12	2.251(3)	O7—Cu2—O3	105.79(11)
Cu4—N6	1.921(3)	N4—Cu2—N11	102.83(13)
Cu4—N8	1.929(3)	N2—Cu2—N11	102.67(12)
Cu4—O11	2.022(3)	O7—Cu2—N11	90.13(11)
Cu4—O15	2.063(3)	O3—Cu2—N11	89.01(11)
Cu4—N10	2.213(3)	N5—Cu3—N7	92.28(13)
N3—Cu1—N1	92.62(12)	N5—Cu3—O13	162.97(14)
N7—Cu3—O13	79.80(12)	N6—Cu4—O11	79.96(12)
N5—Cu3—O9	79.71(11)	N8—Cu4—O11	161.73(13)
N7—Cu3—O9	162.13(14)	N6—Cu4—O15	164.16(13)
O13—Cu3—O9	103.42(11)	N8—Cu4—O15	78.79(12)
N5—Cu3—N12	98.77(14)	O11—Cu4—O15	104.21(11)
N7—Cu3—N12	97.33(14)	N6—Cu4—N10	102.60(14)
O13—Cu3—N12	97.20(12)	N8—Cu4—N10	101.54(13)

Table S1. The selected bond lengths (Å) and angles (°) for complexes **1-6** (Cont.).

Complex **5**[e]			
O9—Cu3—N12	99.65(12)	O11—Cu4—N10	96.37(12)
N6—Cu4—N8	92.59(13)	O15—Cu4—N10	92.21(12)
Complex **6**[f]			
Cu1—N1	1.912(6)	O5—Cu1—O1	102.5(2)
Cu1—N3	1.931(6)	O5—Cu1—O1^{i}	84.5(2)
Cu1—O1	2.016(5)	O1—Cu1—O1^{i}	81.0(2)
Cu1—O5	1.982(5)	N3—Cu1—O1^{i}	110.3(2)
Cu1—O1^{i}	2.452(5)	N1—Cu1—O1^{i}	109.5(2)
Cu2—N4	1.922(6)	N2—Cu2—N4	93.9(3)
Cu2—N2	1.920(6)	N2—Cu2—O3	81.2(2)
Cu2—O7	2.037(5)	N4—Cu2—O3	165.7(2)
Cu2—O3	1.976(5)	N2—Cu2—O7	163.9(2)
Cu2—O2^{ii}	2.279(5)	N4—Cu2—O7	78.7(2)
N1—Cu1—N3	93.8(3)	O3—Cu2—O7	102.5(2)
N1—Cu1—O5	165.9(2)	N2—Cu2—O2^{i}	104.3(2)
N3—Cu1—O5	80.9(2)	N4—Cu2—O2^{i}	99.2(2)
N1—Cu1—O1	80.4(2)	O3—Cu2—O2^{i}	95.1(2)
N3—Cu1—O1	168.6(2)	O7—Cu2—O2^{i}	91.00(19)

[c]Symmetry codes for **3**: (i) -x, 1-y, 1-z; (ii) 2-x, 1-y, 2-z. [d]For **4**: (i) 1-x, 1-y, 1-z; (ii) 1+x, y, z. [f]For **6**: (i) 1-x, 1-y, 1-z; (ii) -1+x, y, z.

Table S2. Intermolecular hydrogen bond length/Å angles/° in complexes **1-6**.

Complex **1**[a]				
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
O9−H1···O4^{i}	0.85	1.95	2.782(2)	167
O9−H2···O16^{ii}	0.84	2.01	2.809(3)	156
O10−H4···O6^{iii}	0.85	1.99	2.843(3)	175
N5−H5···O4^{iv}	0.86	1.97	2.829(3)	174
N6−H6···O6^{v}	0.86	1.97	2.820(3)	171
O10−H7···O12	0.84	2.18	2.896(3)	143
O11−H23···O2	0.85	1.87	2.717(3)	175
O11−H24···O12^{vi}	0.85	2.06	2.898(3)	168
O12−H25···O13	0.85	1.91	2.725(3)	162
O12−H26···O14^{i}	0.85	1.93	2.766(3)	169
O13−H27···O7	0.84	1.99	2.781(3)	156
O13−H28···O11^{vii}	0.85	2.11	2.919(3)	160
O14−H29···O2^{viii}	0.84	2.12	2.813(3)	140
O14−H30···O8^{v}	0.84	1.89	2.713(3)	166
O15−H31···O1^{v}	0.84	2.02	2.797(3)	153
O15−H32···O14^{iv}	0.84	1.98	2.806(3)	168
O16−H33···O11^{iii}	0.85	1.99	2.833(3)	173
O16−H34···O15	0.85	1.89	2.711(3)	164
C11−H11···O3^{iv}	0.93	2.43	3.025(3)	122
C19−H19···O16^{i}	0.93	2.58	3.467(3)	160
C22−H22···O5^{v}	0.93	2.52	3.082(3)	120

Table S2. Intermolecular hydrogen bond length/Å angles/° in complexes **1-6** (Cont.).

Complex **2**[b]				
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
O13−H1···O6^{i}	0.83	2.02	2.846(4)	170
O13−H2···O2^{ii}	0.83	2.02	2.808(4)	159
O14−H4···O8^{i}	0.82	2.00	2.722(5)	146
N5−H5···O8	0.86	1.81	2.663(5)	173
N6−H6···O3^{iii}	0.86	2.11	2.841(7)	142
N6−H6···O4^{iii}	0.86	2.09	2.888(6)	154
O14−H7···O4^{ii}	0.83	1.87	2.688(5)	166
O9−H9A···O2^{iv}	0.86	2.03	2.841(5)	156
O9−H9B···O12^{v}	0.86	2.14	2.809(7)	135
O10−H10A···O6^{i}	0.86	2.00	2.818(7)	159
O10−H10B···O9^{vi}	0.86	2.16	2.830(7)	134
O11−H11A···O10^{vii}	0.86	2.15	2.789(7)	131
O11−H11B···O5^{viii}	0.86	2.06	2.820(5)	146
O12−H12A···O1^{viii}	0.86	2.03	2.816(6)	153
O12−H12B···O11	0.86	2.07	2.811(7)	143
C15−H15···O14^{i}	0.93	2.56	3.333(6)	140
C21−H21···O11^{ix}	0.93	2.55	3.452(8)	165
Complex **3**[c]				
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
O5−H2···O1^{i}	0.85	2.23	3.048(5)	163
O6−H4···O4^{ii}	0.86	2.04	2.857(5)	160
O6−H5···O2^{iii}	0.85	2.16	2.939(5)	153
C6−H6···O4^{ii}	0.93	2.48	3.385(5)	163
C10−H10···O4^{iv}	0.93	2.38	3.297(5)	168
Complex **4**[d]				
D−H···A	D−H···A	D−H···A	D−H···A	D−H···A
O13−H1···O6^{i}	0.86	1.99	2.843(4)	171
O13−H2···O2^{ii}	0.86	1.90	2.724(5)	161
O14−H4···O9^{i}	0.86	1.96	2.754(6)	155
N5−H5···O14^{iii}	0.86	1.86	2.692(6)	162
O14−H6···O5^{iv}	0.85	1.88	2.625(6)	146
N7−H7···O1^{ii}	0.86	2.19	2.920(7)	142
N7−H7···O2^{ii}	0.86	2.10	2.887(8)	151
N8−H8A···O3^{v}	0.86	1.89	2.747(6)	171
O10−H10···O13^{iii}	0.82	1.80	2.605(5)	167
C3−H3···O6^{vi}	0.93	2.47	3.390(4)	173
C8−H8···O4^{vii}	0.93	2.54	3.398(5)	153
C16−H16···O10^{iv}	0.93	2.47	3.337(9)	155
C20−H20···O14^{viii}	0.93	2.58	3.297(10)	134
C21−H21A···O14^{vi}	0.97	2.48	3.387(12)	155
Complex **5**[e]				
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
N13−H13A···O9^{i}	1.01	2.53	3.286(5)	132
N13−H13A···O10^{i}	1.01	1.83	2.787(6)	158
N13−H13B···O5^{ii}	0.95	2.43	3.230	142

Table S2. Intermolecular hydrogen bond length/Å angles/° in complexes **1**-**6** (Cont.).

Complex **5**[e]				
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
N13−H13B···O6[ii]	0.95	1.97	2.836	151
N14−H14A···O14[iii]	0.92	1.99	2.843	153
N14−H14B···O1	1.04	2.36	3.120	130
N14−H14B···O2	1.04	1.97	2.885	145
N15−H15A···O12[iv]	0.90	1.87	2.734(5)	160
N15−H15B···O8[v]	0.95	1.80	2.728	165
N16−H16A···O15[iii]	0.94	1.87	2.791	166
N16−H16B···O3[vi]	0.91	1.92	2.808	168
C22−H22···O16[i]	0.93	2.40	3.320(5)	168
C31−H31···O2[vii]	0.93	2.50	3.380(7)	158
C34−H34···O4[viii]	0.93	2.44	3.201(6)	139
C36−H36···O6[ix]	0.93	2.52	3.257(5)	136
C45−H45A···O16[x]	0.96	2.30	3.233(8)	164
C45−H45C···O4[xi]	0.96	2.43	3.368(7)	166
C46−H46A···O3[xi]	0.96	2.52	3.414(7)	154
C46−H46C···O15[x]	0.96	2.52	3.404(8)	154
C47−H47A···O12[xii]	0.96	2.57	3.463(6)	154
C49−H49A···O10[i]	0.96	2.60	3.495(6)	155
C49−H49C···O6[ii]	0.96	2.50	3.418(6)	160
C50−H50C···O9[i]	0.96	2.57	3.513(5)	167
Complex **6**[f]				
D−H···A	d(D−H)/Å	d(H···A)/Å	d(D···A)/Å	<(DHA)/°
N5−H5···O7[i]	0.86	1.80	2.641(9)	165
N6−H6···O6[ii]	0.86	1.91	2.761(8)	173
C8−H8···O6[iii]	0.93	2.55	3.476(9)	171
C12−H12···O4[iv]	0.93	2.60	3.424(10)	149
C14−H14···O8[v]	0.93	2.48	3.380(10)	164
C16−H16B···O4 [iv]	0.97	2.56	3.346(10)	138
C18−H18···O8[vi]	0.93	2.21	3.136(10)	174
C21−H21···O2[vii]	0.93	2.39	3.271(9)	158

[a]Symmetry codes for **1**: (i) x, 0.5-y, 0.5+z; (ii) x, y, 1+z; (iii) x, 0.5-y, -0.5+z; (iv) 1+x, y, z; (v) x, y, -1+z; (vi) 1-x, 0.5+y, 1.5-z; (vii) -1+x, y, z; (viii) 1-x, 1-y, 1-z. [b]For **2**: (i) -x, 1-y, 1-z; (ii) 1-x, 2-y, 1-z; (iii) 2-x, 1-y, 2-z; (iv) x, -1+y, z; (v) 1-x, 1-y, -z; (vi) 1-x, 1-y, 1-z; (vii) x, y, -1+z; (viii) 1+x, y, z; (ix) 2-x, 1-y, 1-z. [c]For **3**: (i) 1-x, -0.5+y, 1.5-z; (ii) 1+x, y, z; (iii) x, 1.5-y, -0.5+z; (iv) -x, -0.5+y, 1.5-z. [d]For **4**: (i) 2-x,2-y,2-z; (ii) 2-x,1-y,2-z; (iii) 1+x,y,z; (iv) -1+x,y,z; (v) -x,-y,1-z; (vi) x,-1+y,z; (vii) x,1+y,z; (viii) 1-x,1-y,2-z. [e]For **5**: (i) 1+x, y, z; (ii) 1-x, 1-y, 1-z; (iii) -x, 1-y, 1-z; (iv) 1-x, -y, 1-z; (v) 1+x,y,-1+z; (vi) x, 1+y, -1+z; (vii) -1+x, y, z; (viii) 1-x, -y, 2-z; (ix) -x, 1-y, 2-z; (x) -x, -y, 1-z; (xi) x, y, -1+z; (xii) 1+x,1+y,z. [f]For **6**: (i) 1+x, y, z; (ii) -1+x, 0.5-y, 0.5+z; (iii) -x, -y, 1-z; (iv) -x, -0.5+y, 1.5-z; (v) -x, 0.5+y, 1.5-z; (vi) -1-x, 0.5+y, 1.5-z; (vii) 1-x, -0.5+y, 1.5-z.

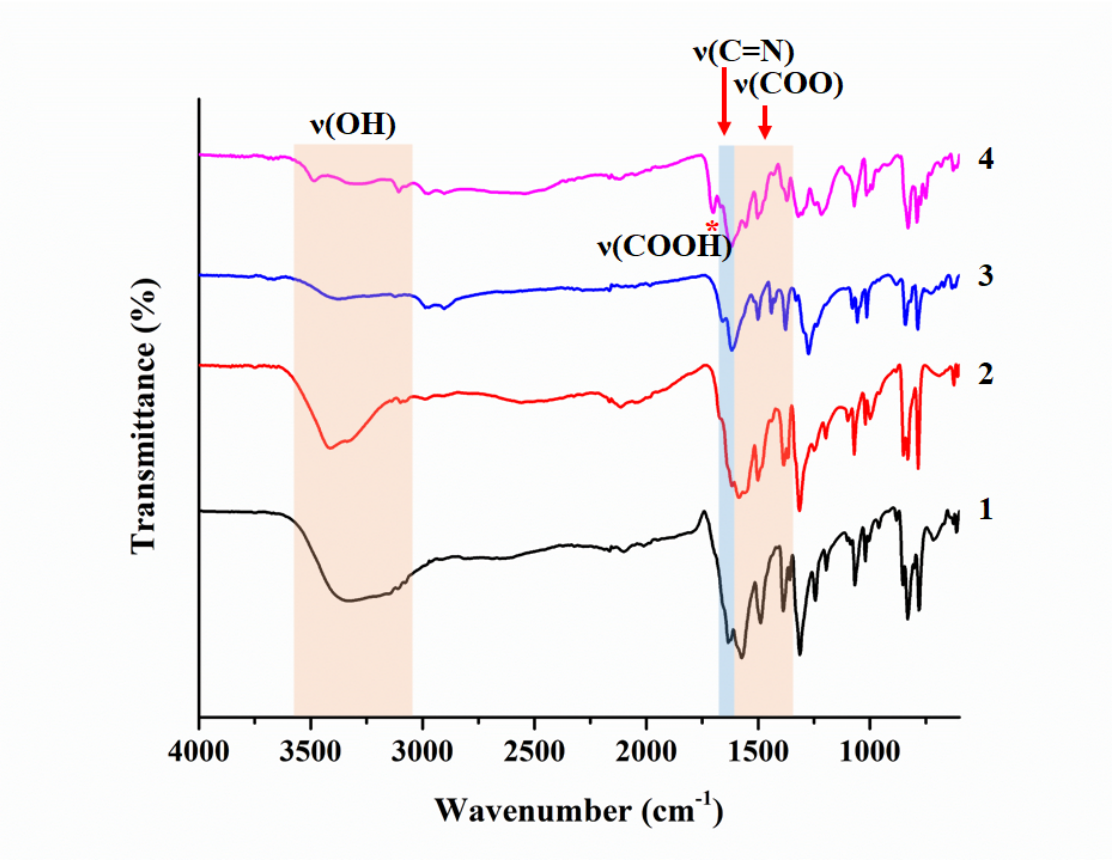

Figure S1. IR spectra of **1**-**4**.

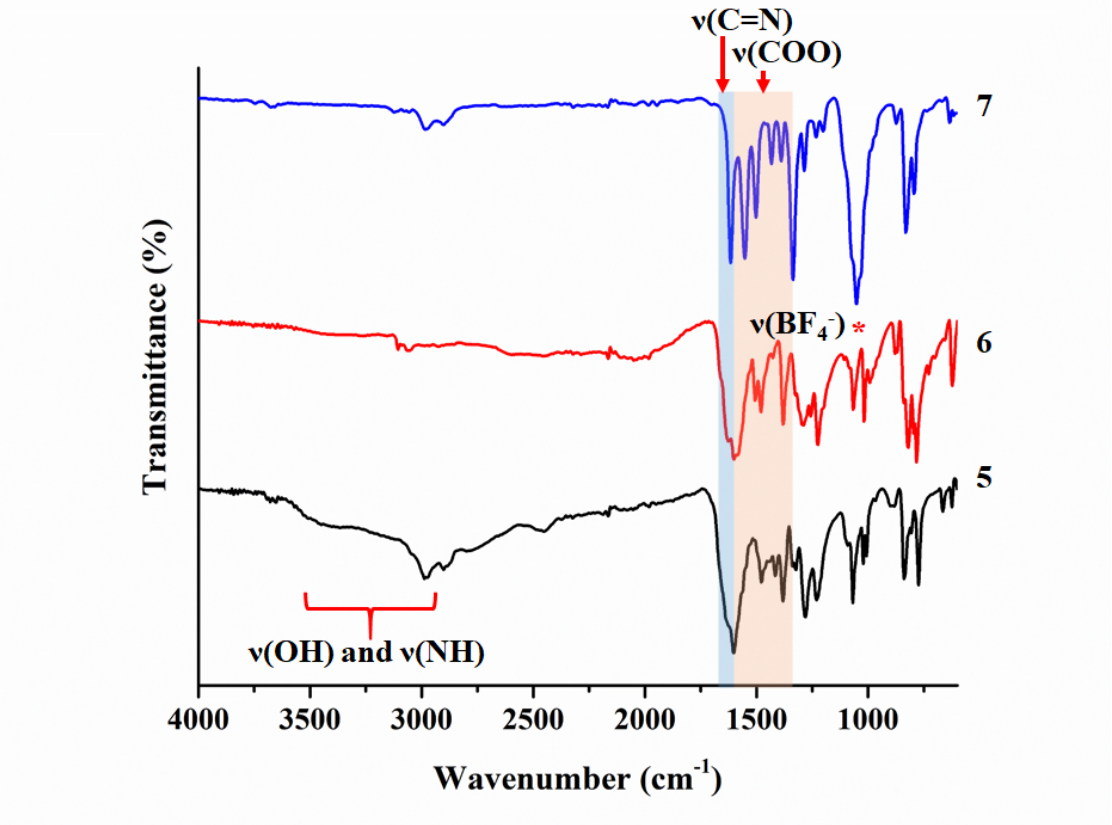

Figure S2. IR spectra of **5**-**7**.

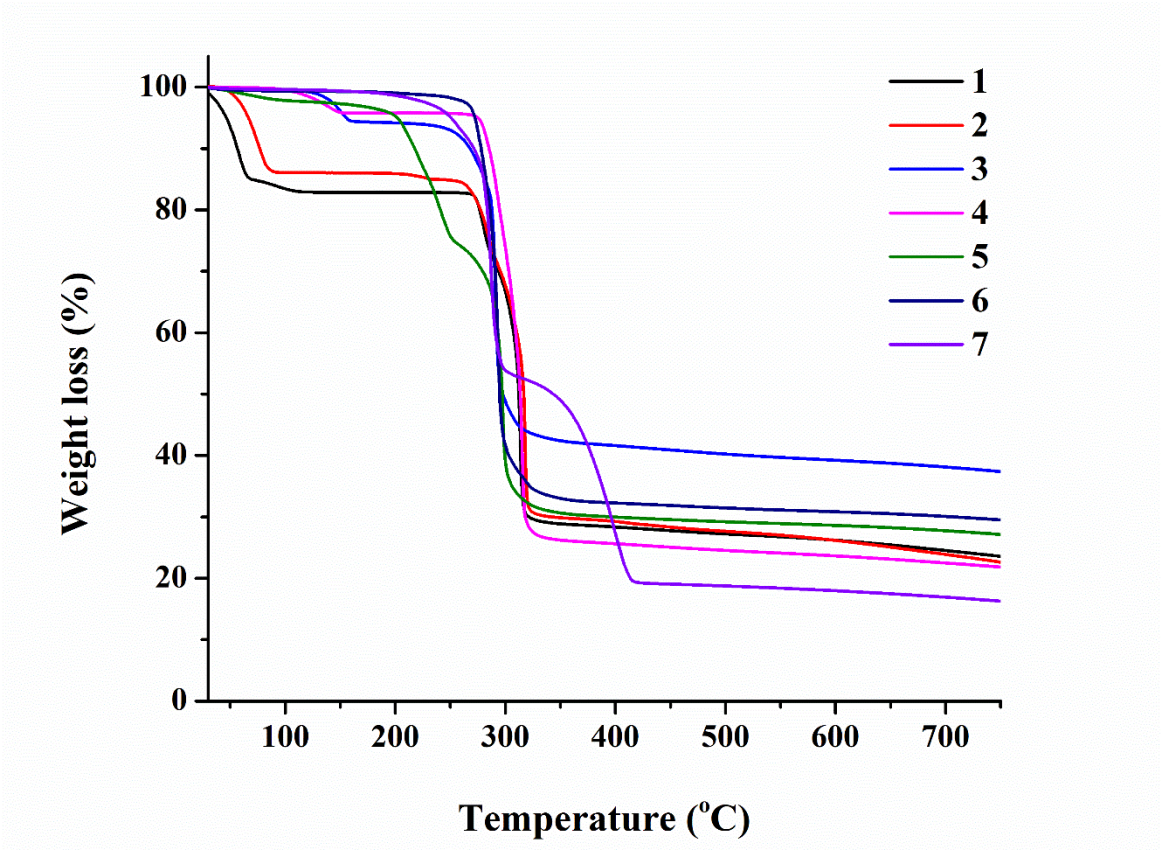

Figure S3. TG curves of **1**-**7**.

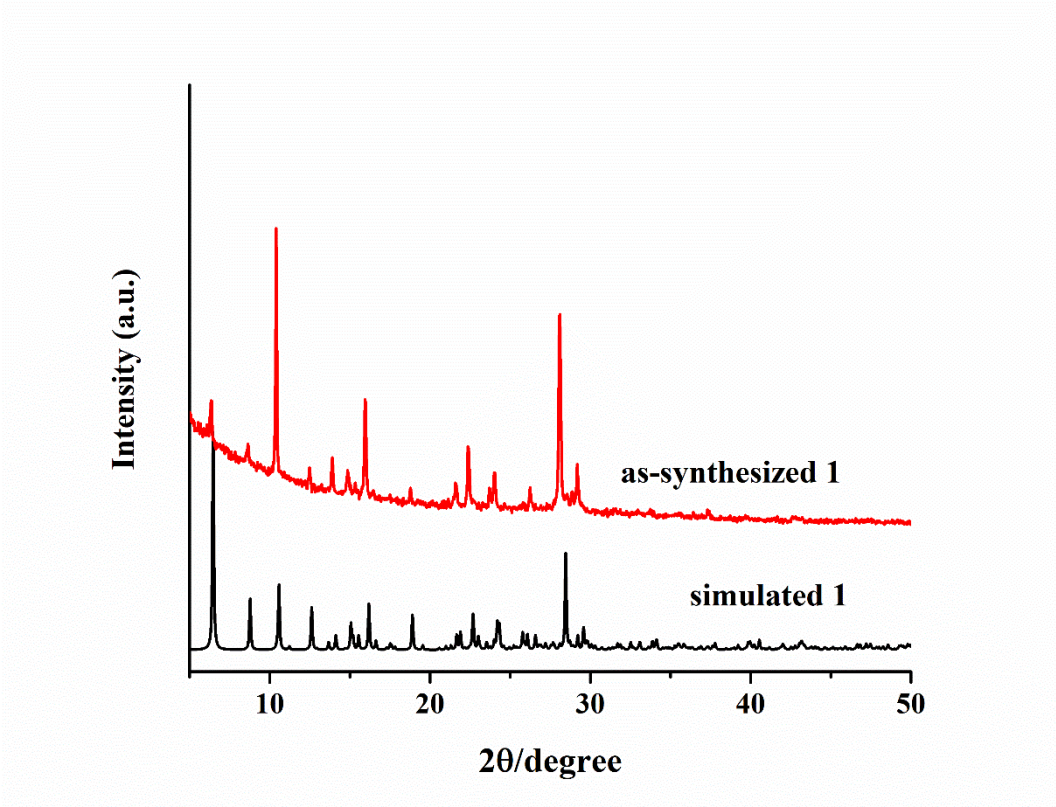

Figure S4. PXRD patterns of simulated from single-crystal XRD data and as-synthesized of **1**.

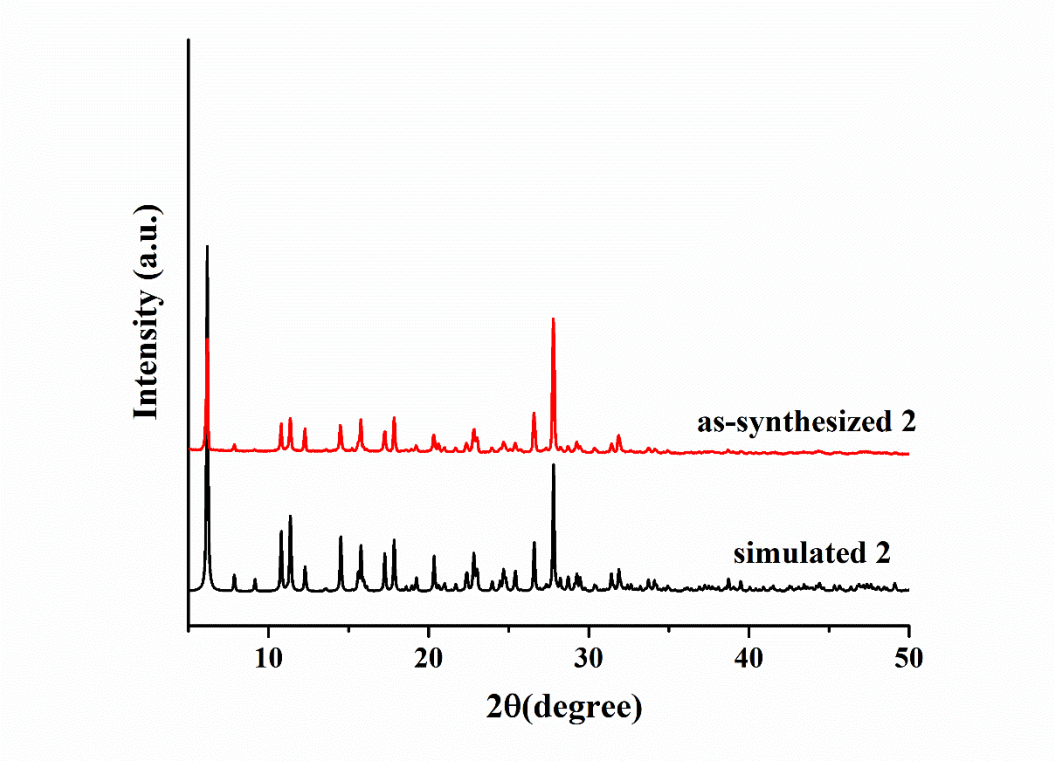

Figure S5. PXRD patterns of simulated from single-crystal XRD data and as-synthesized of **2**.

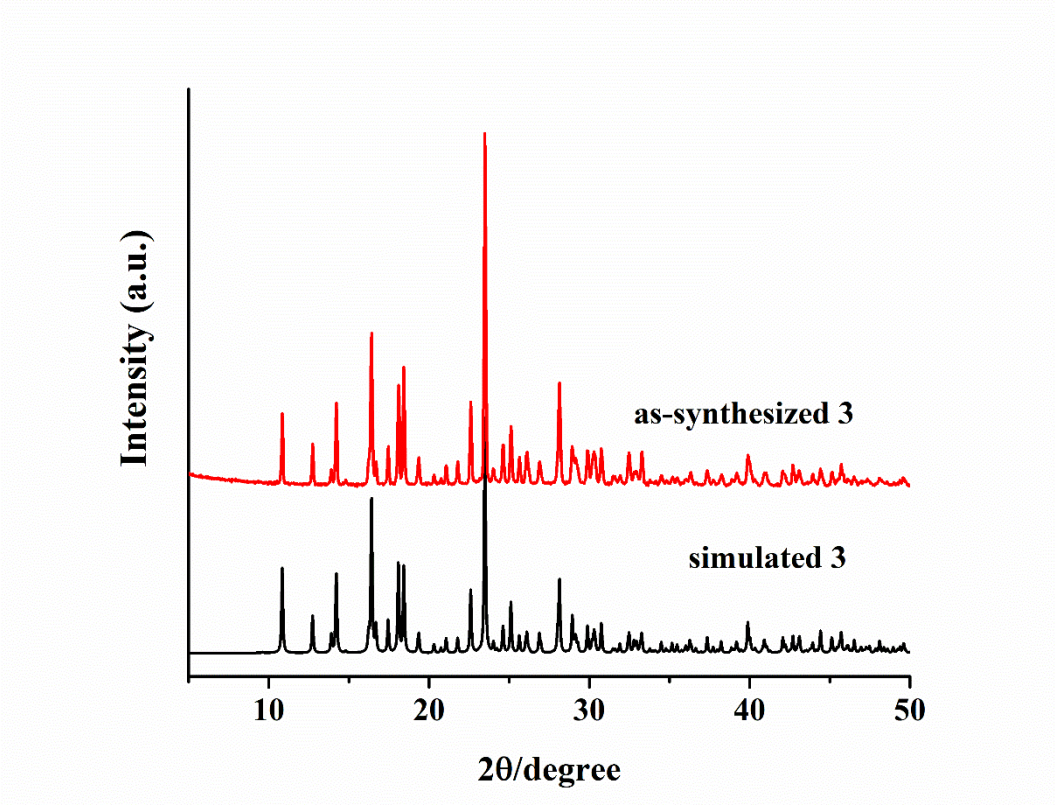

Figure S6. PXRD patterns of simulated from single-crystal XRD data and as-synthesized of **3**.

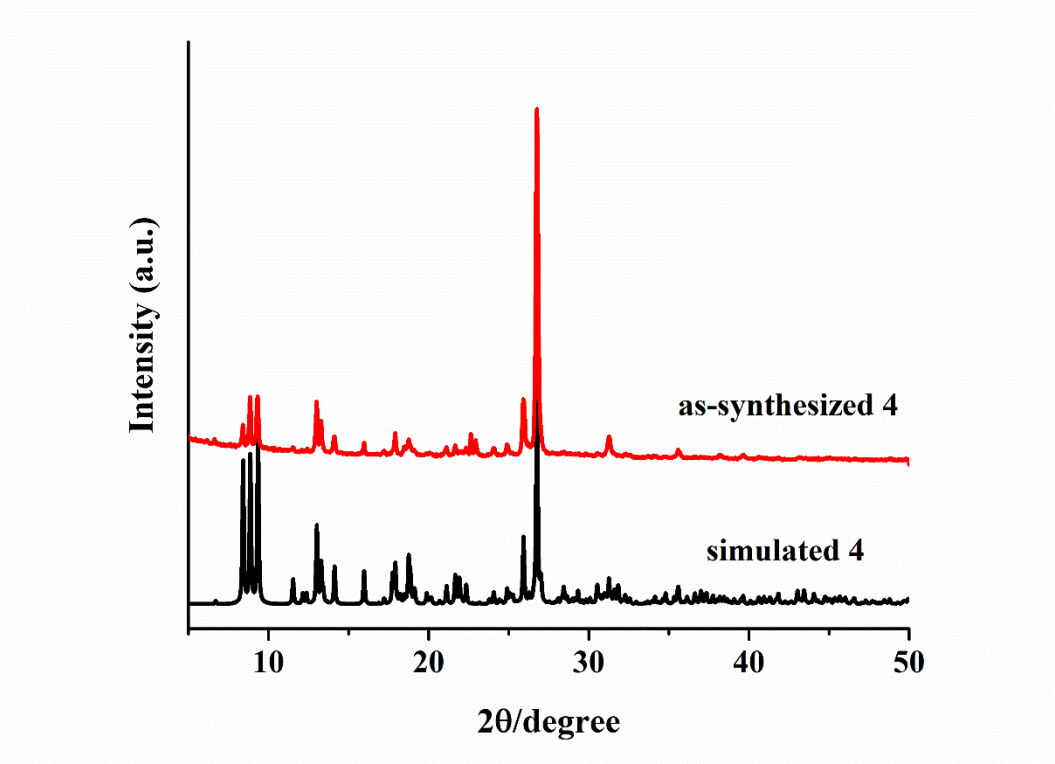

Figure S7. PXRD patterns of simulated from single-crystal XRD data and as-synthesized of **4**.

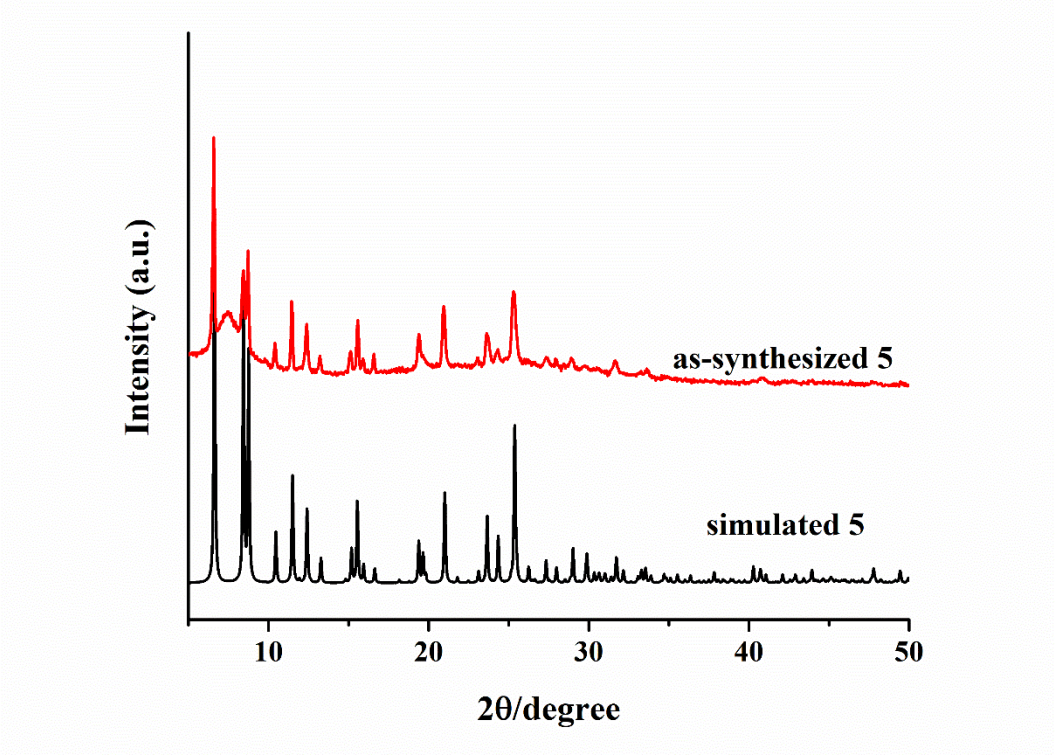

Figure S8. PXRD patterns of simulated from single-crystal XRD data and as-synthesized of **5**.

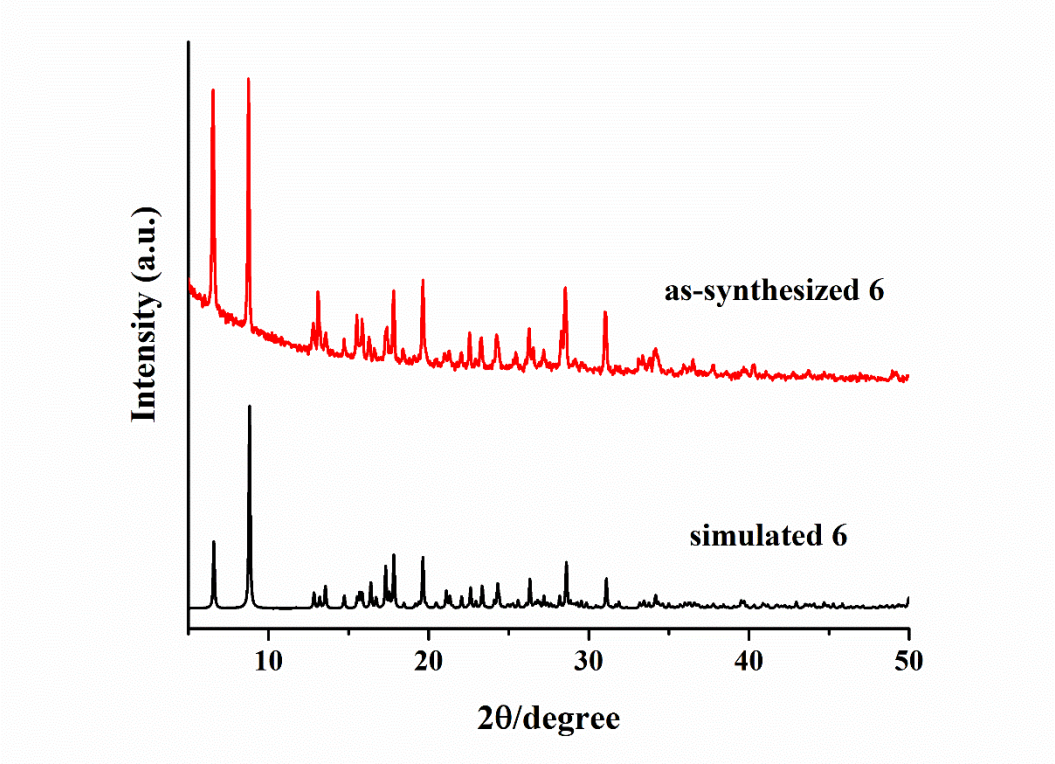

Figure S9. PXRD patterns of simulated from single-crystal XRD data and as-synthesized of **6**.

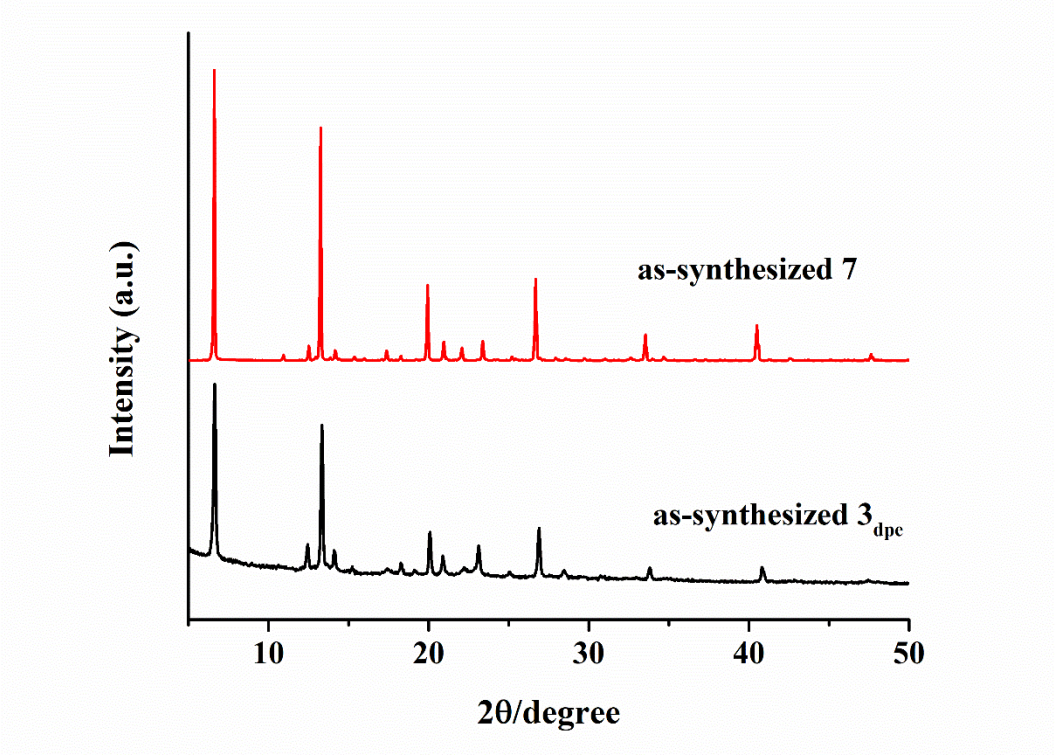

Figure S10. PXRD patterns of simulated from single-crystal XRD data of $\mathbf{3}_{\mathbf{dpe}}$[1] and as-synthesized of **7**.

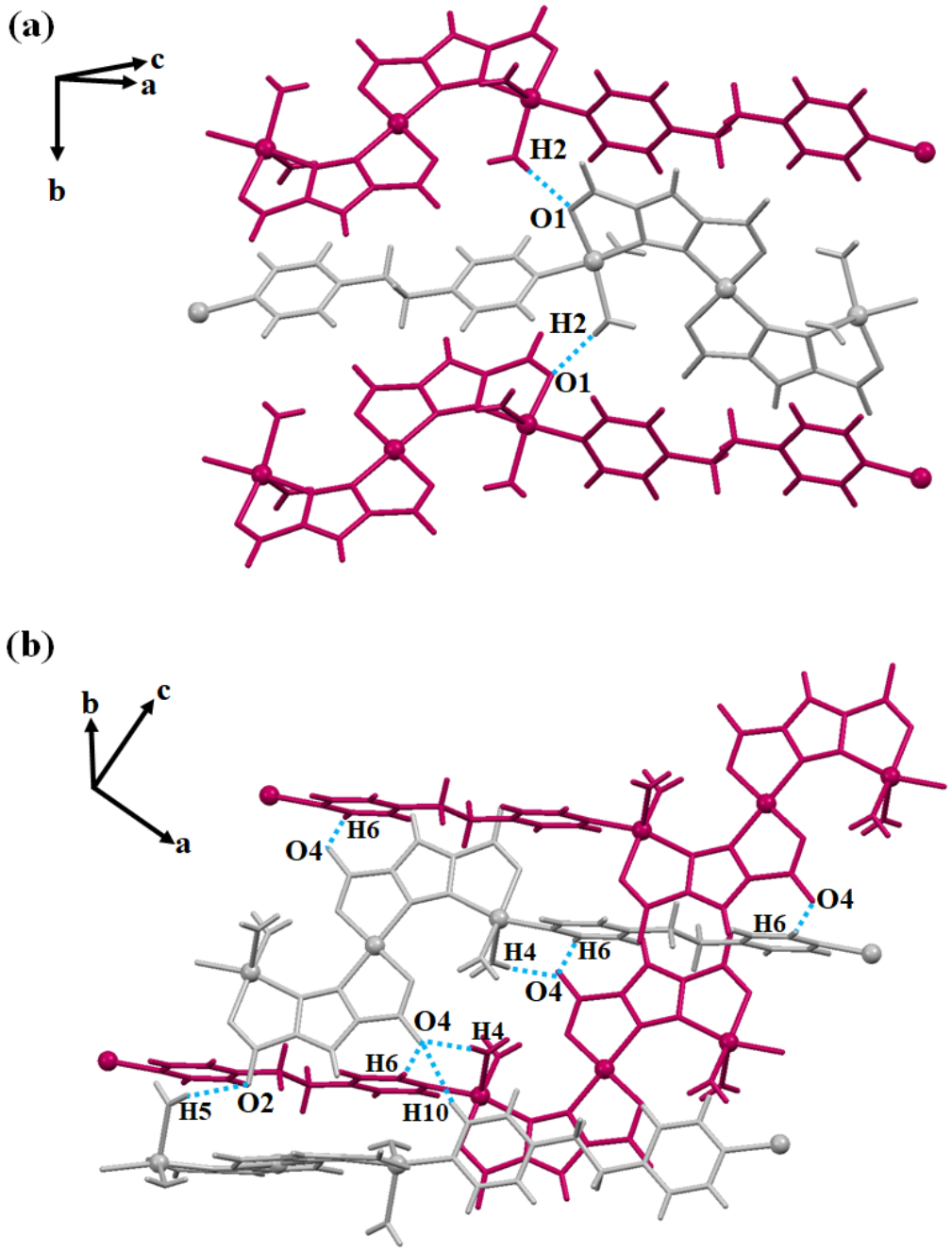

Figure S11. 3D supramolecular structure of **3** built by various interchain hydrogen bonding interactions.

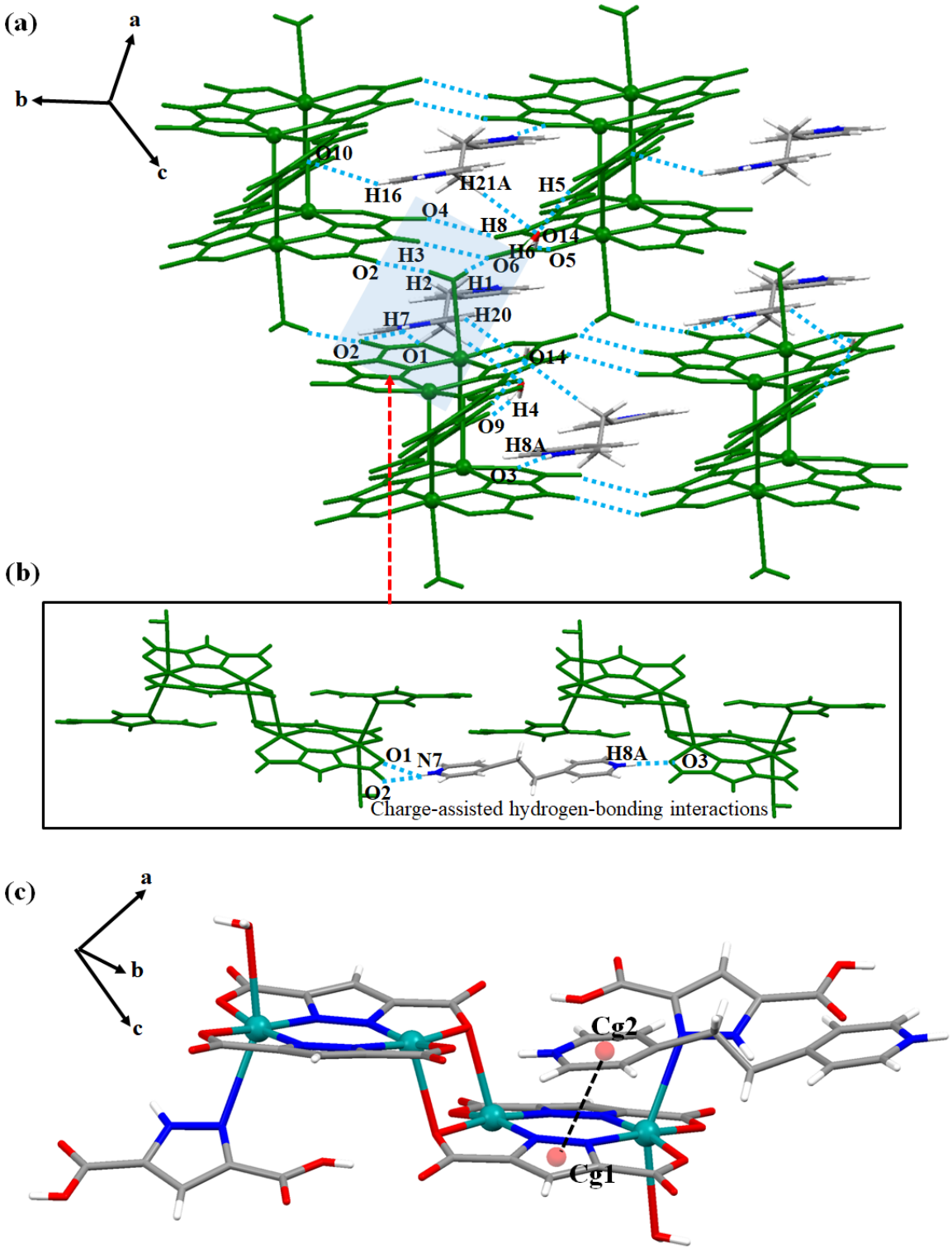

Figure S12. (a) 3D packing diagram of **4** built by hydrogen bonding interactions (b) the charge-assisted hydrogen-bonding interactions between anionic Cu(II) tetramer and H_2bpa^{2+} and (c) π-π stacking interactions.

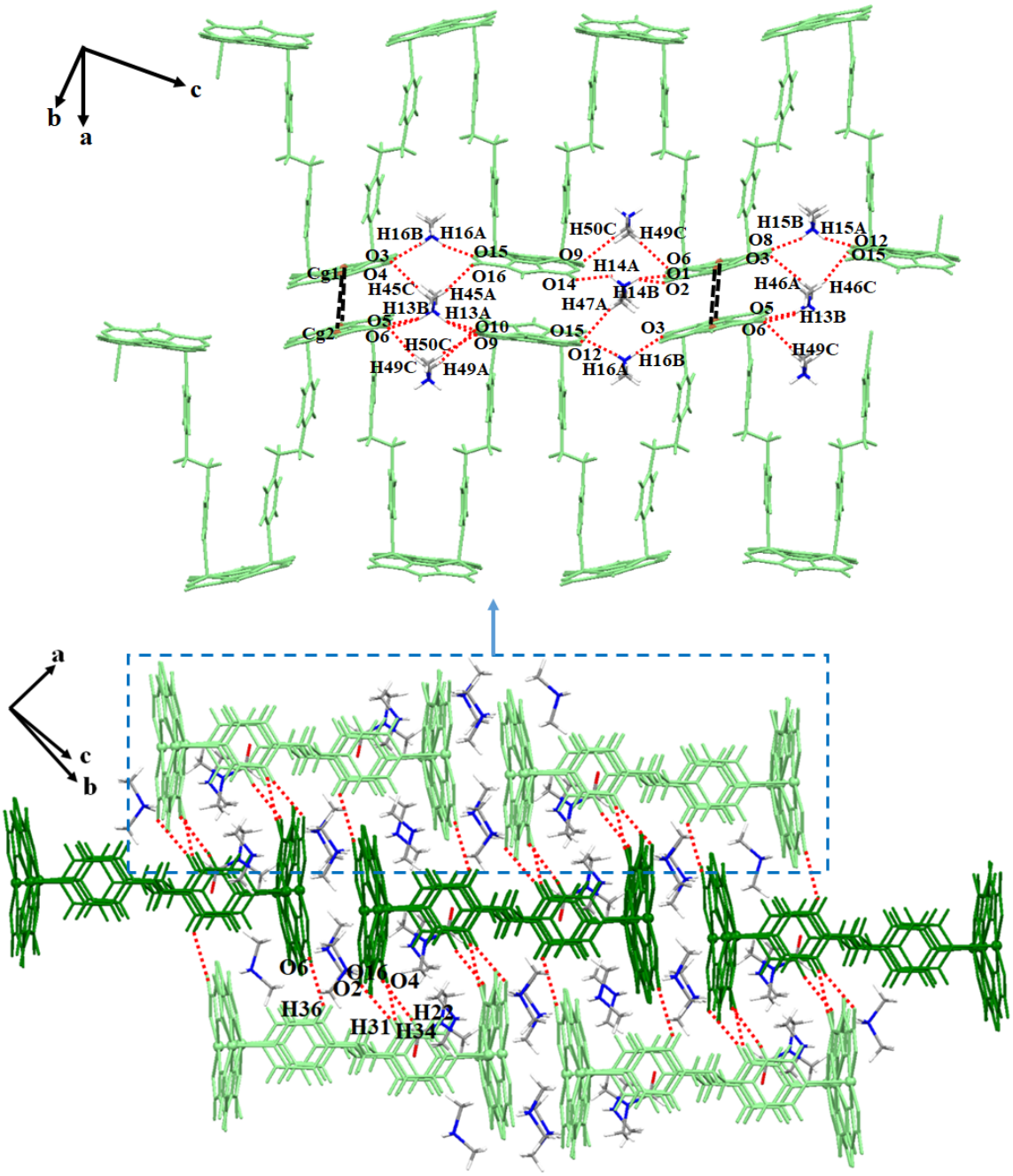

Figure S13. 3D supramolecular structure of **5** built by various interchain hydrogen bonding interactions and π-π stacking interactions.

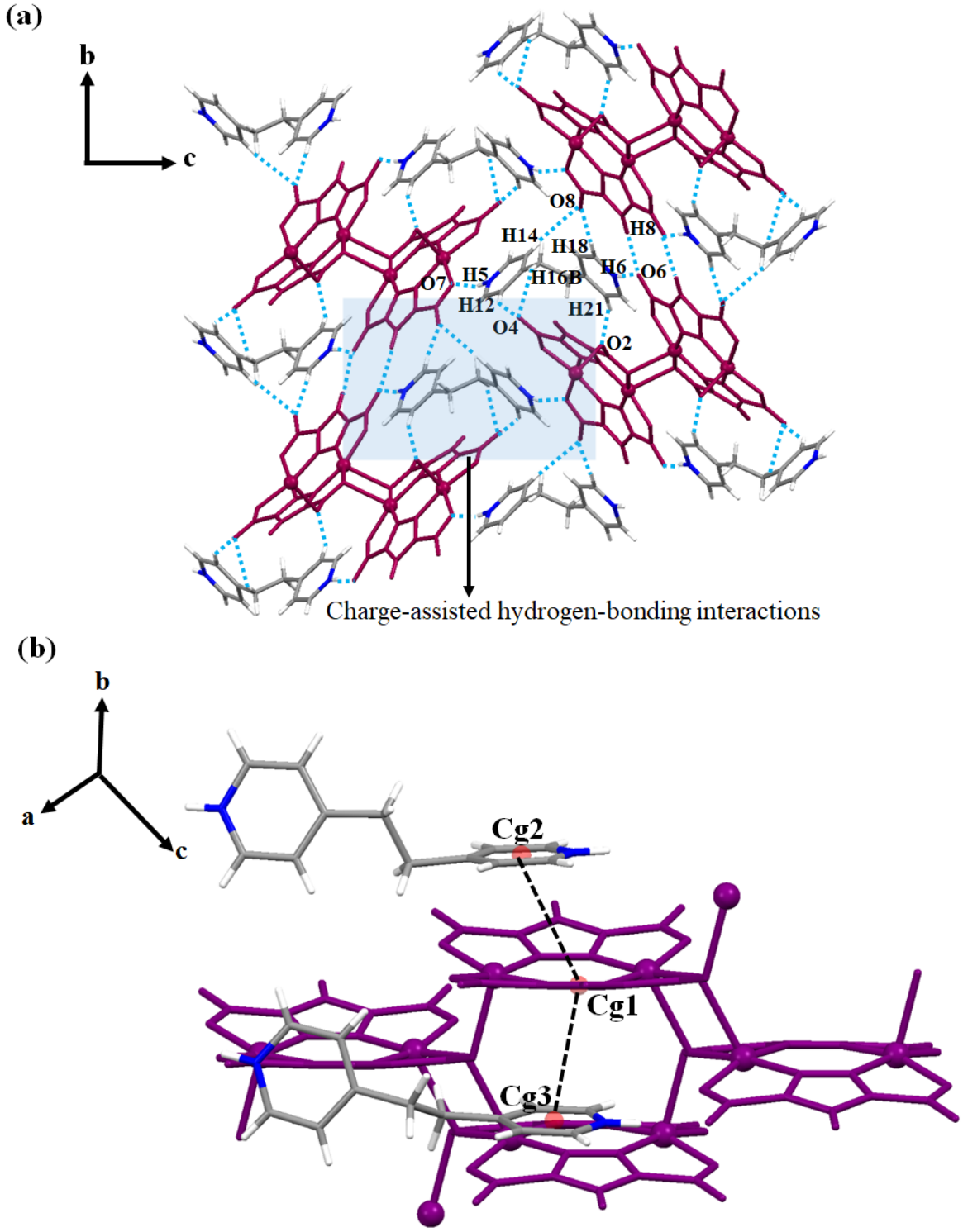

Figure S14. 3D supramolecular structure of **6** built by various interchain hydrogen bonding interactions and π-π stacking interactions.

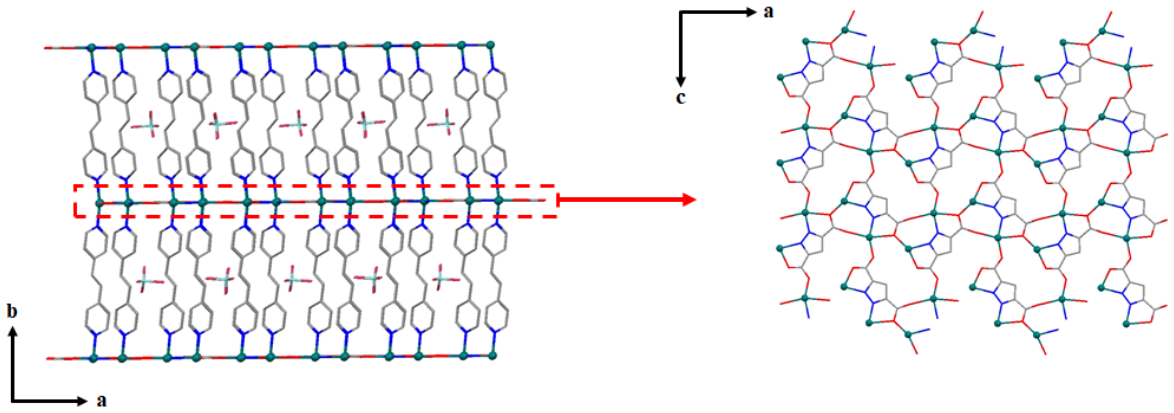

Figure S15. A cationic 3D pillar-layer coordination framework stabilized by lattice BF_4^- anion of **7**.(F. Klongdee, J. Boonmak and S. Youngme, *Dalton Trans.*, 2017, **46**, 4806-4815.)

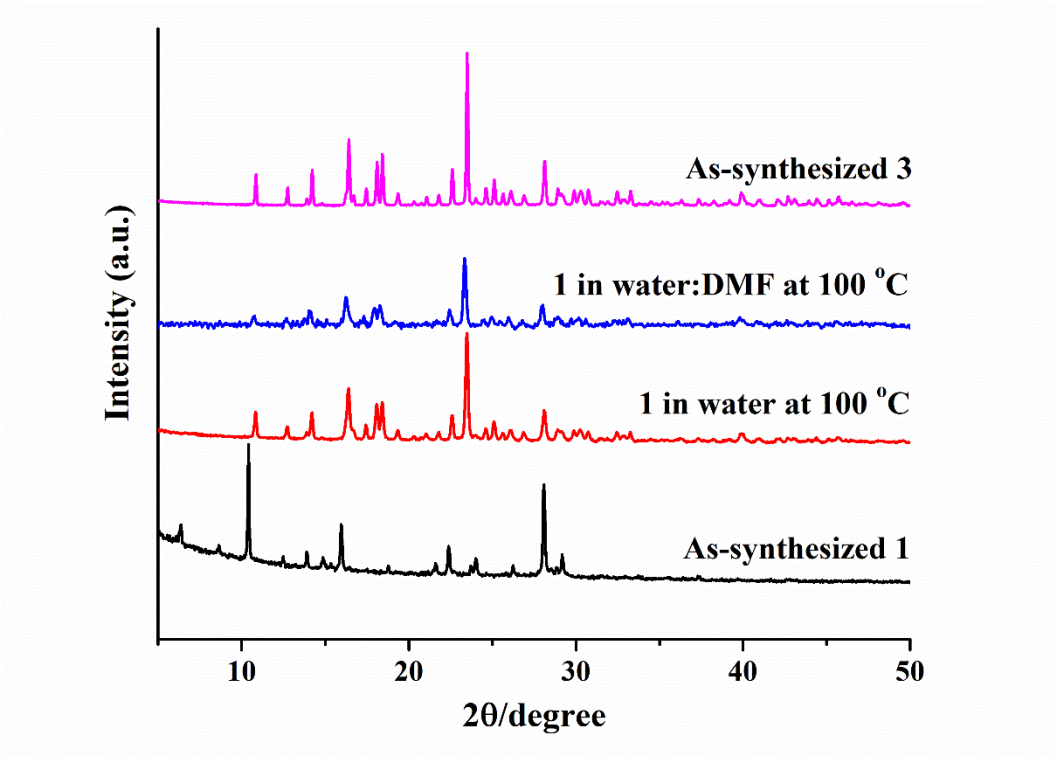

Figure S16. PXRD patterns of structural transformation of **1** in water and water:DMF media at 100 °C.

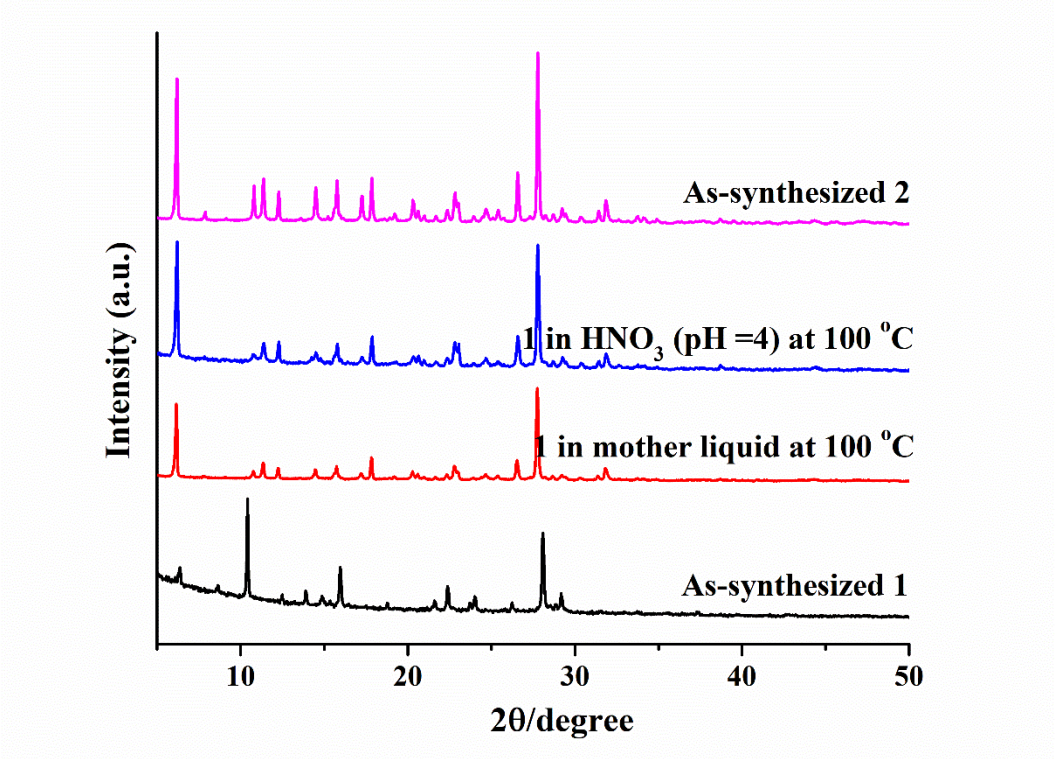

Figure S17. PXRD patterns of structural transformation of **1** in mother liquid and aqueous solution of HNO_3 (pH = 4) at 100 °C.

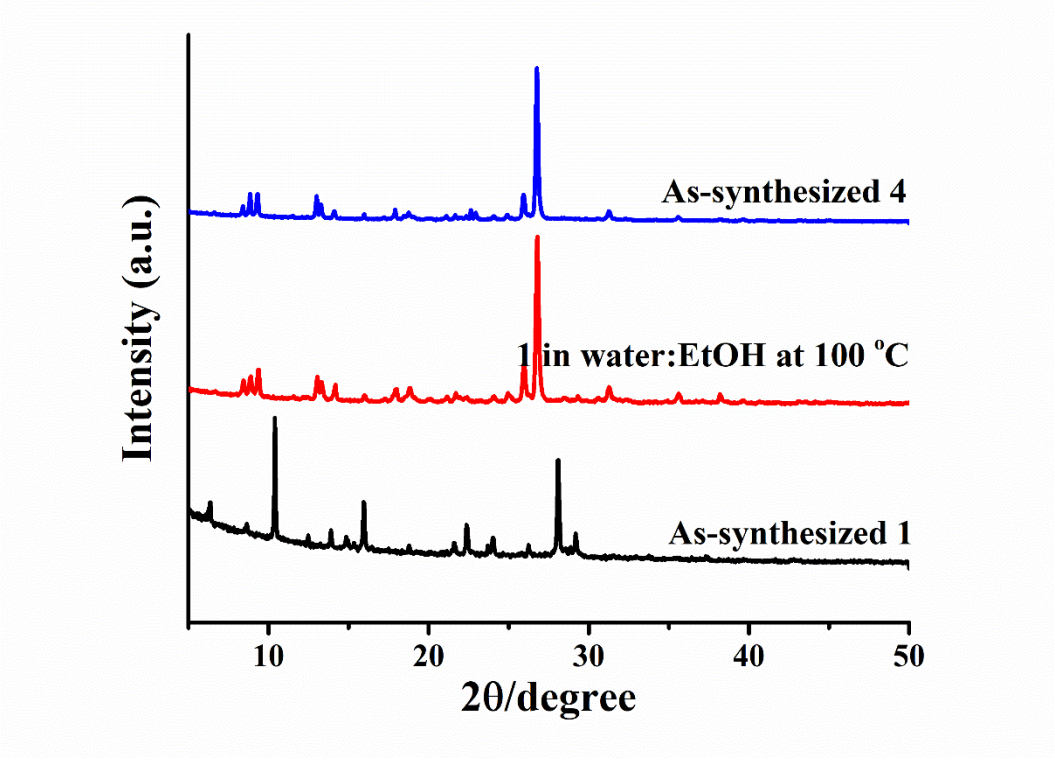

Figure S18. PXRD patterns of structural transformation of **1** in water:EtOH media at 100 °C.

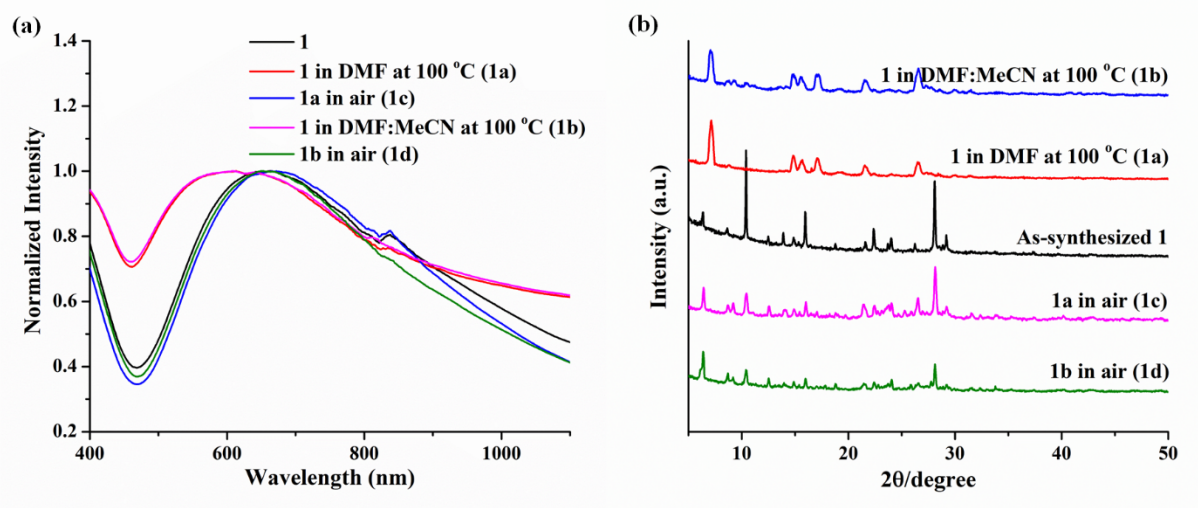

Figure S19. (a) The UV-vis diffuse reflectance spectra and (b) PXRD patterns of **1a**-**1d**.

Table S3. Dimensionality of complexes **1**-**7** and the connectivity of pzdc.

Complex	Dimensionality of structure	connectivity of pzdc
$[Cu_2(pzdc)_2(H_2O)_2](H_2bpa)(H_2O)_6]$ **(1)**	0D	μ_2-pzdc
$[Cu_2(pzdc)_2(H_2O)_2](H_2bpa)(H_2O)_4]$ **(2)**	0D	μ_2-pzdc
$[Cu_3(pzdc)_2(H_2O)_4(bpa)]_n$ **(3)**	1D	μ_2-pzdc
$[Cu_4(pzdc)_4(H_3pzdc)_2(H_2O)_2](H_2bpa)_2(H_2O)_2$ **(4)**	0D	μ_3-pzdc
$\{[Cu_4(pzdc)_4(bpa)_2](DMF)(NH_2(CH_3)_2)_4\}_n$ **(5)**	1D	μ_2-pzdc
$\{[Cu_2(pzdc)_2](H_2bpa)\}_n$ **(6)**	1D	μ_4-pzdc
$\{[Cu_2(pzdc)(bpa)_2](BF_4)\}_n$ **(7)**	3D	μ_5-pzdc

Table S4. The pH values of mother liquids for **1**-**7** at room temperature and 100 °C.

solvents in mother liquid of complex	pH value	
	room temperature	100 °C
complex **1** (water)	~4	-
complex **2** (water)	~4	~4
complex **3** (water:DMF (4.5:4.5))	~4	~5
complex **4** (water:EtOH (4.5:4.5))	~4	~4
complex **5** (DMF)	~3	~6
complex **6** (DMF:MeCN (6:3))	~3	~6
complex **7** (EtOH or MeCN)	~2/~3	~2