Supporting Information

Two cationic metal-organic frameworks featuring different cage-to-cage connections: syntheses, crystal structures, photoluminescence and gas sorption properties

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Table S1 Selected Bond Lengths [Å] and Angles [°] for Compound **1**[a].

Compound **1**[a]			
Zn(1)-N(1)#1	1.979(5)	Zn(1)-N(1)#2	1.979(5)
Zn(1)-N(1)	1.979(5)	Zn(1)-N(1)#3	1.979(5)
N(1)#1-Zn(1)-N(1)#2	113.13(19)	N(1)#1-Zn(1)-N(1)	113.13(19)
N(1)#2-Zn(1)-N(1)	102.4(4)	N(1)#1-Zn(1)-N(1)#3	102.4(4)
N(1)#2-Zn(1)-N(1)#3	113.13(19)	N(1)-Zn(1)-N(1)#3	113.13(19)

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

Table S2 Selected Bond Lengths [Å] and Angles [°] for Compound **2**[a].

Compound **2**[a]			
Zn(1)-N(7)	2.019(2)	Zn(1)-N(9)#1	2.029(2)
Zn(1)-N(13)	2.039(2)	Zn(1)-N(1)	2.194(2)
Zn(1)-N(11)#2	2.240(2)	Zn(2)-N(17)#3	1.964(2)
Zn(2)-N(3)#3	1.977(2)	Zn(2)-N(15)	1.982(2)
Zn(2)-N(5)#4	2.004(2)	N(3)-Zn(2)#5	1.977(2)
N(5)-Zn(2)#4	2.004(2)	N(9)-Zn(1)#1	2.029(2)
N(11)-Zn(1)#6	2.240(2)	N(17)-Zn(2)#5	1.964(2)
N(7)-Zn(1)-N(9)#1	122.23(9)	N(7)-Zn(1)-N(13)	127.29(9)
N(9)#1-Zn(1)-N(13)	110.46(9)	N(7)-Zn(1)-N(1)	90.50(9)
N(9)#1-Zn(1)-N(1)	90.85(9)	N(13)-Zn(1)-N(1)	89.78(9)
N(7)-Zn(1)-N(11)#2	89.97(9)	N(9)#1-Zn(1)-N(11)#2	89.14(9)
N(13)-Zn(1)-N(11)#2	89.71(9)	N(1)-Zn(1)-N(11)#2	179.45(9)
N(17)#3-Zn(2)-N(3)#3	116.94(10)	N(17)#3-Zn(2)-N(15)	105.62(10)
N(3)#3-Zn(2)-N(15)	114.62(10)	N(17)#3-Zn(2)-N(5)#4	108.68(10)
N(3)#3-Zn(2)-N(5)#4	102.54(9)	N(15)-Zn(2)-N(5)#4	108.07(10)
C(10)-N(3)-Zn(2)#5	130.15(18)	C(11)-N(3)-Zn(2)#5	122.28(18)
C(13)-N(5)-Zn(2)#4	127.6(2)	C(14)-N(5)-Zn(2)#4	124.68(19)
C(25)-N(9)-Zn(1)#1	126.50(19)	C(26)-N(9)-Zn(1)#1	127.10(18)
C(28)-N(11)-Zn(1)#6	125.46(18)	C(29)-N(11)-Zn(1)#6	127.55(19)
C(43)-N(17)-Zn(2)#5	130.08(19)	C(44)-N(17)-Zn(2)#5	123.42(19)

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

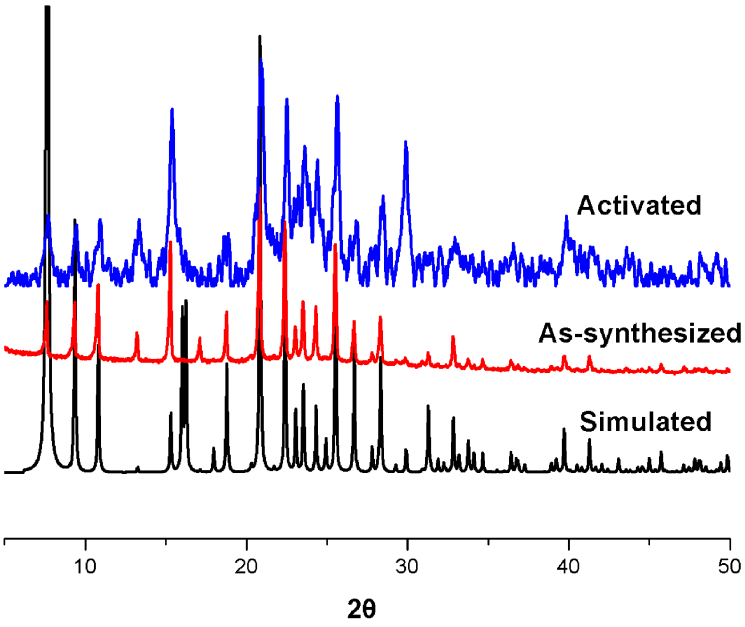

Figure S1 PXRD patterns of simulated from the single-crystal data of compound **1** (black); as-synthesized (red); activated solid (blue).

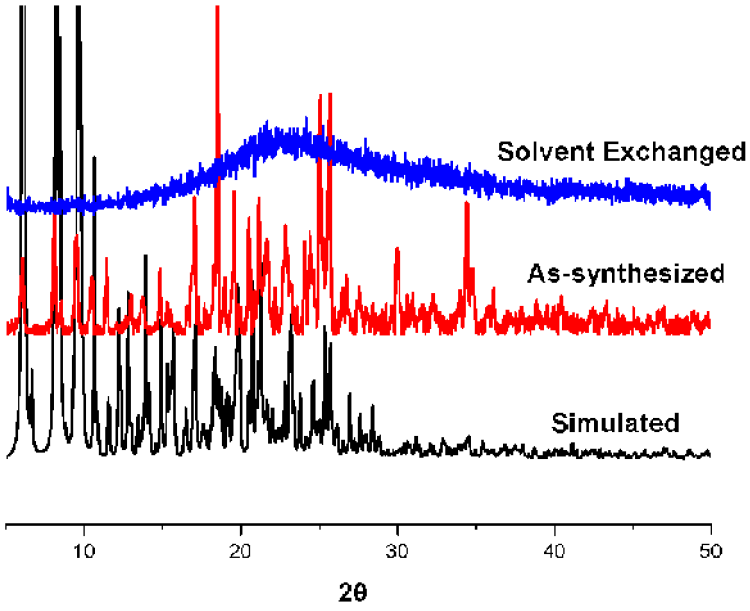

Figure S2 PXRD patterns of simulated from the single-crystal data of compound **2** (black); as-synthesized (red); solvent exchanged solid (blue).

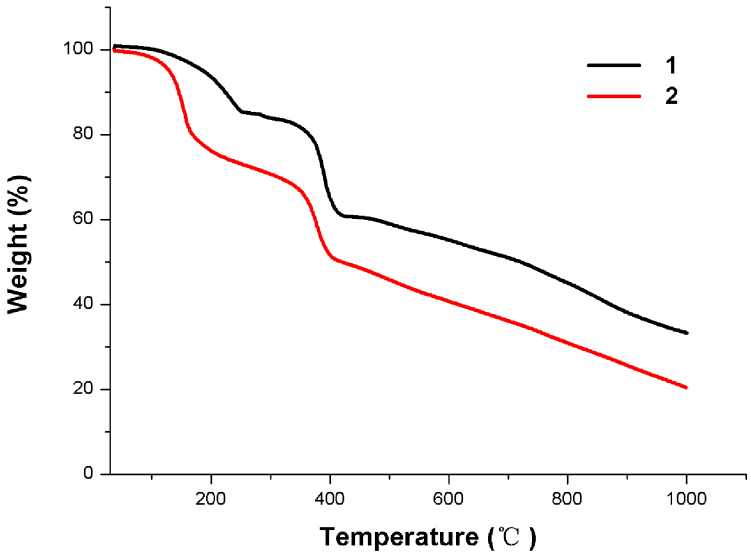

Figure S3 TGA curves for compounds **1** and **2**.

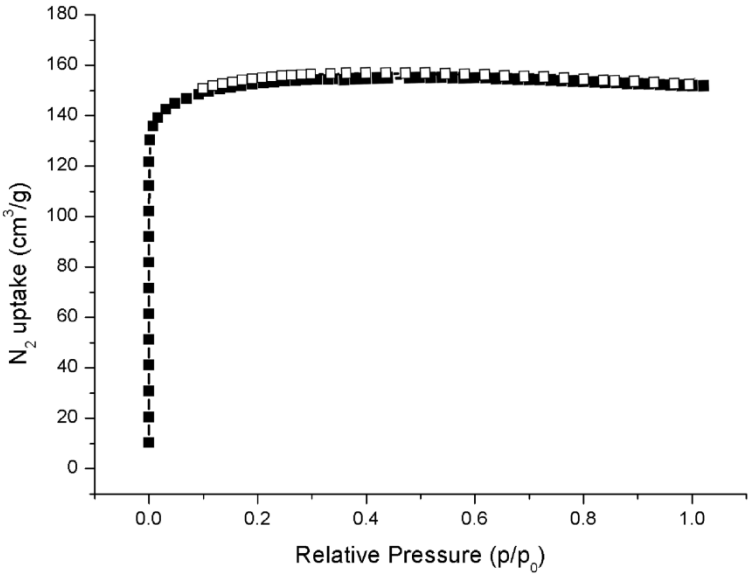

Figure S4 N_2 sorption isotherms of compound **1** at 77K (■, adsorption; □, desorption).

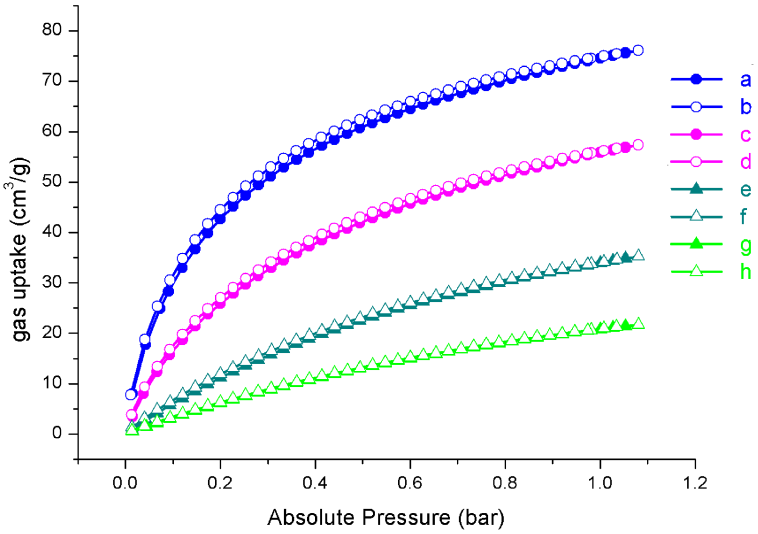

Figure S5 The sorption isotherms of compound **1**: CO_2 adsorption (a) and desorption (b) at 273K; CO_2 adsorption (c) and desorption (d) at 299 K; CH_4 adsorption (e) and desorption (f) at 273 K; CH_4 adsorption (g) and desorption (h) at 299 K.

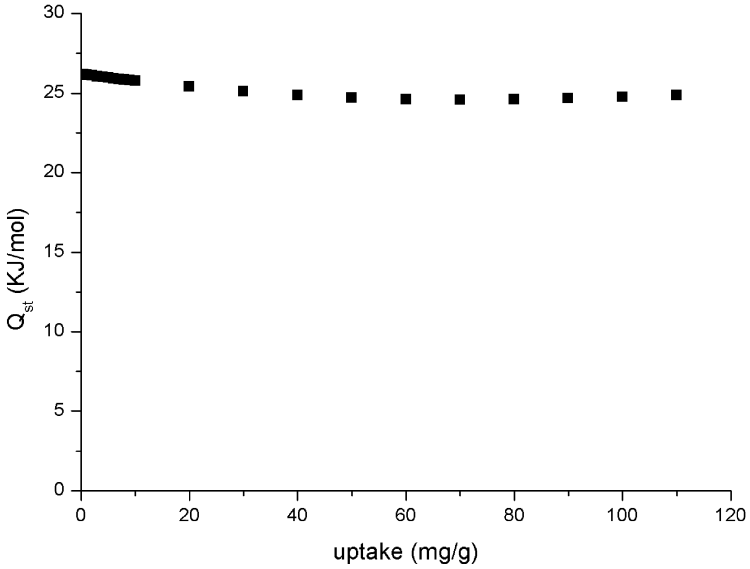

Figure S6 The isosteric heat of adsorption for CO_2 in compound **1**.

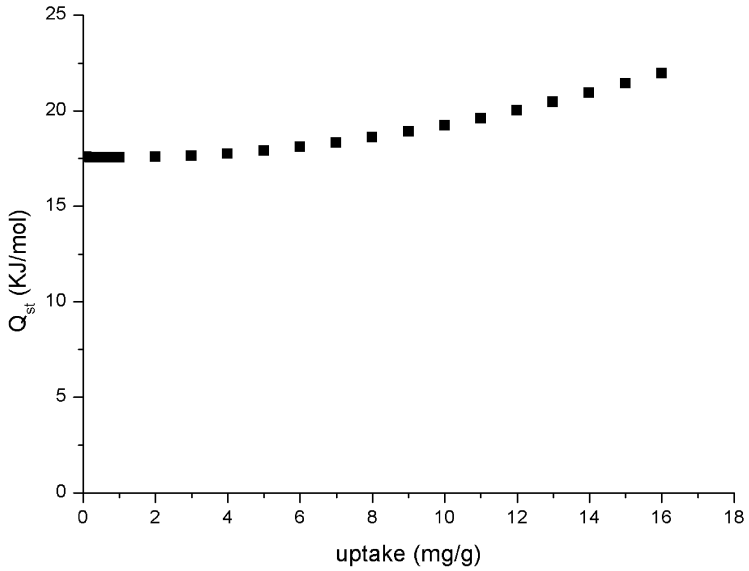

Figure S7 The isosteric heat of adsorption for CH_4 in compound **1**.