pH variation induced construction of a series of entangled frameworks based on bi- and trimetallic Cores as Nodes

Lian-Jie Li, Chao Qin, Xin-Long Wang, Shuang Wang, Liang Zhao,* Guang-Sheng Yang, Hai-Ning Wang, Gang Yuan, Kui-Zhan Shao and Zhong-Min Su*

Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun, 130024, People's Republic of China

*Corresponding author. Tel.: (+86)-431-5099108.

E-mail address: zmsu@nenu.edu.cn

Compound **1** :

IR (KBr pellet, cm^{-1}): 3440.45 (w), 2852.72 (s), 1625.96 (w), 1508.97 (m), 1443.64 (m), 1371.94 (m), 1230.61 (m), 1108.14 (s), 1063.86 (s), 1028.35 (s), 935.28 (s), 818.65 (m), 787.18 (m), 760.67 (m), 717.89 (m), 489.61 (w), 434.07 (w).

Compound **2** :

IR (KBr pellet, cm^{-1}): 3419.33 (m), 2922.07 (s), 2461.64 (s), 1640.16 (w), 1567.67 (m), 1508.99 (w), 1443.37 (w), 383.71 (w), 1229.77 (w), 1106.78 (m), 1041.89 (m), 932.67 (s), 873 (s), 814.51 (m), 760.19 (m), 719.51 (m), 607 (s).

Compound **3** :

IR (KBr pellet, cm^{-1}): 3861 (w) 3744 (w), 2897 (s), 2854(s), 1562 (m), 1508 (m), 1449 (m), 1030 (s), 719 (m), 514 (m), 447 (m).

Compound **4** :

IR (KBr pellet, cm^{-1}): 3897.11 (s), 3648.56 (s), 3619.73 (s), 3860 (s), 1064.33 (m), 939.60 (m), 1739.20 (m), 1286.68 (m), 1113.04 (m), 1564.01 (w), 1645.65 (w), 1513.65 (w), 1678.71 (w), 773.23 (w).

Compound **5** :

IR (KBr pellet, cm^{-1}): 3076.76 (s), 1708.49 (m), 1708.49 (m), 1625.27 (m), 1509.14 (s), 1423.96 s), 1219.55 (w), 1165.45 (m), 1107.12 (m), 1027.74 (m), 934.85 (w), 817.13 (w), 769.17 (w), 710.08 (w), 661.48 (w), 536.69 (w), 481.23 (w), 422.26 (w).

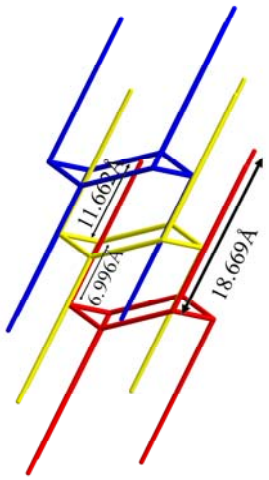

Fig. S1 A schematic illustration of three cyclohexane conformation in the compound **2**.

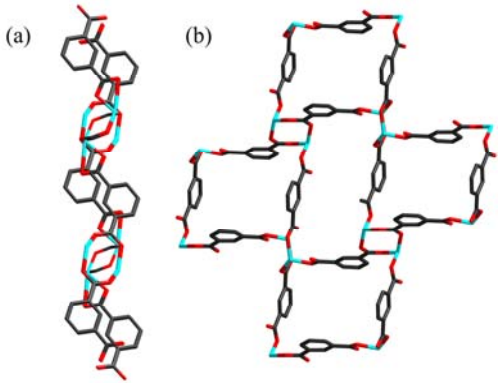

Fig. S2 (a) Side and (b) front views of one Zn^{II}–carboxylate layer with built from paddle-wheel shaped dinuclear Zn units in the bc plane.

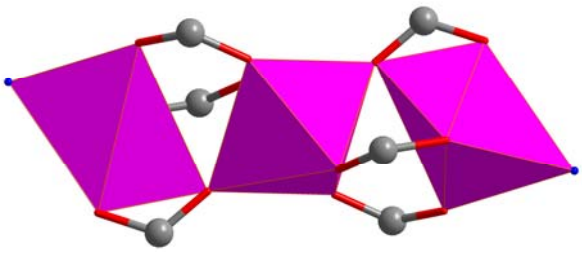

Fig. S3 Schematic representation of inorganic SBU in the compound **4**.

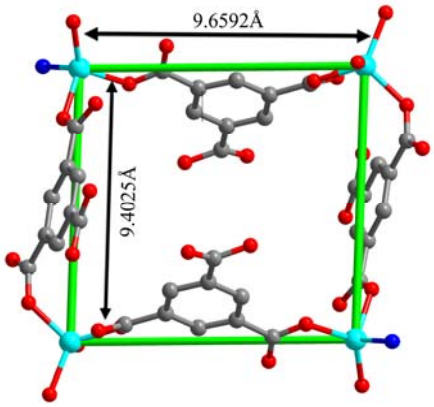

Fig. S4 Schematic view of the squres in the compound **5**

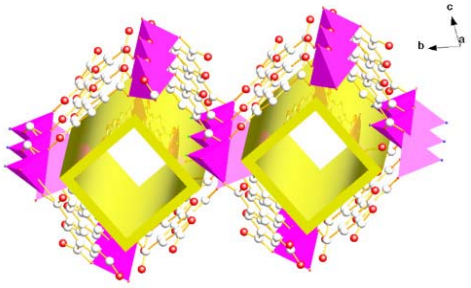

Fig. S5 Schematic representation of the tube structure in the compound **5**.

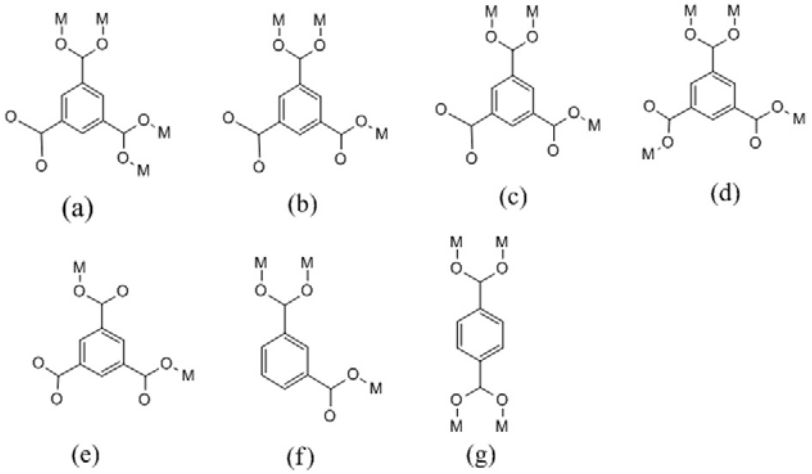

Fig. S6 Coordination modes of aromatic carboxyl ligands in **1-5**

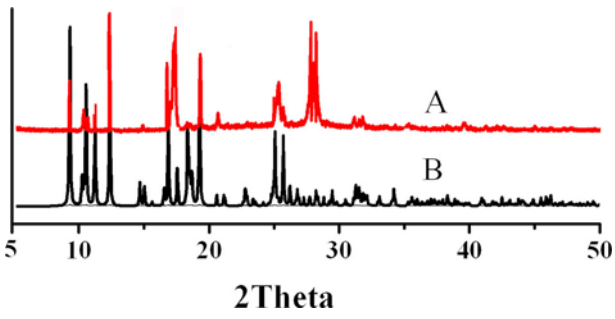

Fig. S7 Simulated and experimental PXRD spectra of **1:** A as-synthesized; B

simulated.

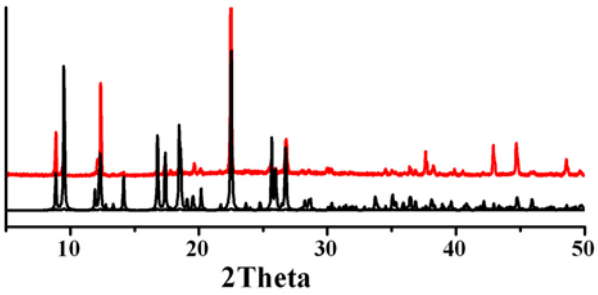

Fig. S8 Simulated and experimental PXRD spectra of **2:** A as-synthesized; B simulated.

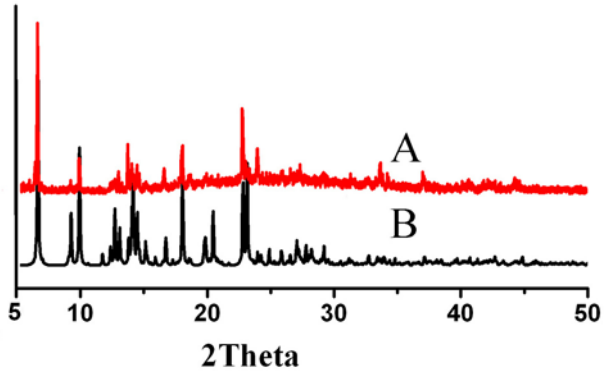

Fig. S9 Simulated and experimental PXRD spectra of **3:** A as-synthesized; B simulated.

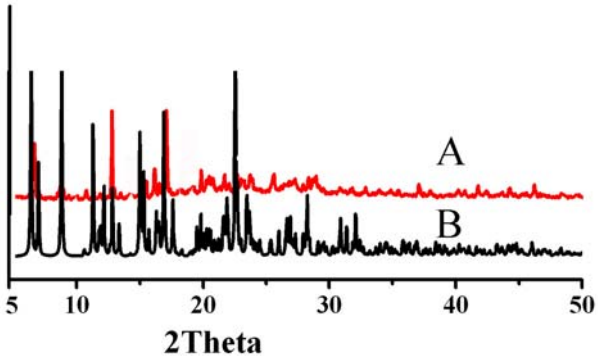

Fig. S10 Simulated and experimental PXRD spectra of **4:** A as-synthesized; B simulated.

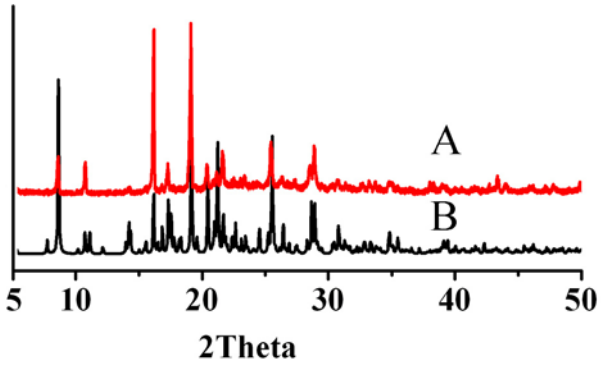

Fig. S11 Simulated and experimental PXRD spectra of **5:** A as-synthesized; B simulated.

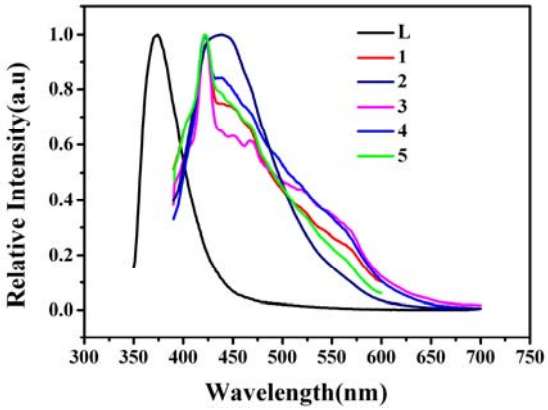

Fig. S12 Emission spectra of compounds **1, 2, 3, 4, 5** and **L** in the solid state at room temperature.

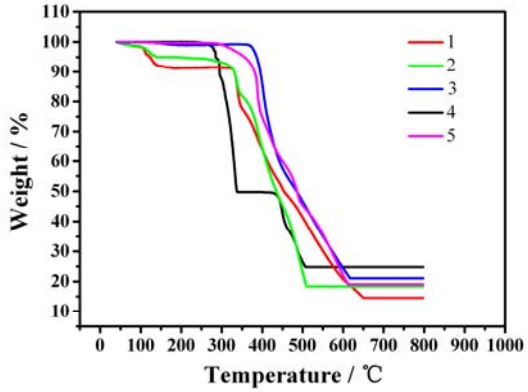

Fig. S13 The TG curves of **1-5**

Table S1 Crystal data and structure refinements for complexes **1-5**.

Complex	**1**	**2**	**3**	**4**	**5**
Formula	$C_{54}H_{42}N_4O_{17}Zn_2$	$C_{36}H_{26}N_2O_{15}Zn_2$	$C_{34}H_{26}N_2O_{11}Zn_2$	$C_{42}H_{28}N_2O_{14}Zn_3$	$C_{36}H_{26}N_2O_{15}Zn_2$
Formula	1149.70	857.37	769.33	980.83	857.37

weight					
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a /Å	26.912(2)	8.359(3)	15.236(1)	10.253(1)	8.538(1)
b /Å	14.301(13)	16.453(12)	13.873(2)	10.665(3)	11.780(2)
c /Å	13.659(3)	25.367(4)	15.344(4)	10.740(1)	17.055(3)
α/°	90.	90	90.	94.601(13)	78.041(2)
β/°	98.357(2)	94.624(3)	109.954(1)	113.788(1)	77.984(4)
γ/°	90	90	90.	110.685(2)	78.729(12)
V/Å^3	5201(3)	3477(2)	3048.54	970.7(8)	1620.4
Z	4	4	1	1	2
$D_{calcd.}$[g cm^{-3}]	1.466	1.634	1.672	1.678	1.757
μ/mm^{-1}	1.000	1.458	1.643	1.914	1.565
F(000)	2352	1736	1560.0	497.07	872
Observed reflection/uniq ue	30392/11709	20935/8174	8663/3279	5913/4307	9855/7185
R_{int}	0.1622	0.0346	0.0317	0.0181	0.0213

Table S2 Selected bond lengths (Å) and angles (˚) for complexes **1-5**[a]

Complex **1**

Zn(2)-N(1)	2.044(12)	Zn(1)-N(3)	2.025(11)
Zn(1)-O(1)	2.036(10)	Zn(2)-O(2)	2.049(11)
Zn(2)-O(3)A	2.107(11)	Zn(1)-O(4) A	2.045(10)
Zn(2)-O(5)	2.024(10)	Zn(1)-O(7)	2.078(11)
Zn(2)-O(8)	2.038(10)	N(3)-Zn(1)-O(6)	95.6(5)
N(3)-Zn(1)-O(1)	102.0(5)	O(6)-Zn(1)-O(1)	161.1(4)
N(3)-Zn(1)-O(4)A	111.7(5)	O(6)-Zn(1)-O(4)A	91.4(5)
O(1)-Zn(1)-O(4)A	88.5(4)	N(3)-Zn(1)-O(7)	94.5(5)
O(6)-Zn(1)-O(7)	85.5(5)	O(1)-Zn(1)-O(7)	86.2(5)

O(7)-Zn(1)-O(4)A	153.7(4)	O(5)-Zn(2)-O(8)	90.5(4)
O(5)-Zn(2)-N(1)	105.9(5)	O(8)-Zn(2)-N(1)	103.2(5)
O(5)-Zn(2)-O(2)	156.3(4)	O(8)-Zn(2)-O(2)	93.1(5)
N(1)-Zn(2)-O(2)	96.1(5)	O(5)-Zn(2)-O(3)A	85.6(5)
O(8)-Zn(2)-O(3)A	161.9(4)	N(1)-Zn(2)-O(3)A	94.8(5)
O(2)-Zn(2)-O(3)A	83.7(5)		
	Complex **2**		
Zn(1)-O(4)A	1.951(3)	Zn(2)-O(6)A	1.945(3)
Zn(1)-N(1)	2.030(3)	Zn(1)-O(3)	1.982(3)
Zn(2)-O(5)	1.966(3)	Zn(2)-O(8)B	2.000(3)
Zn(1)-O(13)	2.076(3)	Zn(2)-O(14)	1.937(3)
Zn(1)-O(4)A	1.951(3)	O(4)A-Zn(1)-O(3)	134.82(12)
O(4)A-Zn(1)-N(1)	116.82(12)	O(3)-Zn(1)-N(1)	105.78(13)
O(4)A-Zn(1)-O(13)	102.00(13)	O(3)-Zn(1)-O(13)	92.97(13)
N(1)-Zn(1)-O(13)	88.65(11)	O(14)-Zn(2)-O(6)A	110.48(15)
O(14)-Zn(2)-O(5)	119.55(13)	O(6)A-Zn(2)-O(5)	96.21(14)
O(14)-Zn(2)-O(8)B	101.85(12)	O(6)A-Zn(2)-O(8)B	101.41(12)
O(5)-Zn(2)-O(8)B	125.19(13)		
	Complex **3**		
Zn(1)-O(2)	1.952(3)	Zn(1)-O(7)A	1.977(2)
Zn(1)-O(3)B	1.976(2)	Zn(1)-N(1)	2.025(3)
O(2)-Zn(1)-O(7)A	108.40(12)	O(2)-Zn(1)-O(3)B	100.05(11)
O(7)A-Zn(1)-O(3)B	122.01(11)	O(2)-Zn(1)-N(1)	132.97(13)
O(7)A-Zn(1)-N(1)	99.41(11)	O(3)B-Zn(1)-N(1)	96.07(11)
	Complex **4**		
Zn(1)-O(2)	2.0738(17)	Zn(1)-O(3)A	2.084(2)
Zn(1)-O(5)	2.150(2)	Zn(2)-O(6)	1.930(2)
Zn(2)-O(1)	1.9342(18)	Zn(2)-O(4)	1.979(2)
Zn(2)-N(1)	2.047(2)	O(2)-Zn(1)-O(2)A	180.00(10)
O(2)-Zn(1)-O(3)A	88.74(7)	O(2)A-Zn(1)-O(3)A	91.26(7)
O(2)-Zn(1)-O(5)	94.90(8)	O(2)A-Zn(1)-O(5)	85.10(8)

O(3)A-Zn(1)-O(5)	91.67(8)	O(3)-Zn(1)-O(5)	88.33(8)
O(2)A-Zn(1)-O(5)A	94.90(8)	O(6)-Zn(2)-O(1)	117.39(9)
O(6)-Zn(2)-O(4)	104.45(9)	O(1)-Zn(2)-O(4)	128.21(9)
O(6)-Zn(2)-N(1)	110.30(9)	O(1)-Zn(2)-N(1)	91.31(8)
O(4)-Zn(2)-N(1)	101.90(9)		
		Complex **5**	
Zn(1)-N(1)	2.046(3)	Zn(1)-O(4)	1.943(3)
Zn(2)-O(7)	1.913(3)	Zn(2)-O(8)	1.952(3)
Zn(1)-O(11)	1.979(2)	Zn(1)-O(14)	1.919(3)
Zn(2)-O(13)	1.945(3)	Zn(2)-O(1W)	1.977(3)
O(14)-Zn(1)-O(4)	124.29(11)	O(14)-Zn(1)-O(11)	114.24(12)
O(4)-Zn(1)-O(11)	101.57(12)	O(14)-Zn(1)-N(1)	110.88(12)
O(4)-Zn(1)-N(1)	100.38(12)	O(11)-Zn(1)-N(1)	102.70(12)
O(7)-Zn(2)-O(13)	104.83(13)	O(7)-Zn(2)-O(8)	114.79(13)
O(13)-Zn(2)-O(8)	103.92(12)	O(7)-Zn(2)-O(1W)	118.43(13)
O(13)-Zn(2)-O(1W)	103.84(13)	O(8)-Zn(2)-O(1W)	109.23(12)

[a]Symmetry transformations used to generate equivalent atoms: for **1**: A, x, 0.5-y, 0.5+z. for **2**: A, -x, 0.5 + y, 1.5-z; B, -x, -y, 1-z. for **3**: A, -1-x, -y, 1-z; B, x, -y, -0.5+z. for **4**: A, -x, 1-y, -z. for **5**: A, 2-x, 1-y, -z.

Table S3 Distances (Å) and Angles (°) of Hydrogen bonds for compound **5**.

D-H…A	d(H…A)	d(D…A)	∠D-H…A
O(1W)-H(A)-O8A	1.87(2)	2.705(4)	175(4)
O(1W)-H(B)-O18B	1.93(3)	2.675(5)	148(5)

Symmetry codes: A, -x, 2-y, 1-z; B, -1+x, y, z.