Supporting Information (SI)

Zn^{II} Complexes with a Versatile Multi-topic Tetrazolate-Based Ligand Showing Various Structures: Impact of Reaction Conditions on the Final Product Structures

Tong-Liang Hu, Ying Tao, Ze Chang, and Xian-He Bu*

Department of Chemistry, and Tianjin Key Laboratory of Metal & Molecule-based Material Chemistry, Nankai University, Tianjin 300071, China

To whom correspondence should be addressed. E-mail: buxh@nankai.edu.cn

Synthesis of ligands[1-4]

5,6-Di(pyridine-2-yl)-2,3-dicarbonitrile.

A mixture of 1,2-di(pyridin-2-yl)ethane-1,2-dione (2.12 g, 0.01 mol) and diaminomaleonitrile (DAMN) (2.16 g, 0.02 mol) in 24 ml of water, 36 ml ethanol, and 2 ml of acetic acid were heated and reflux for ca 2 hours, cooled, filtered, and recrystallized from ethanol to give light pale white needle-shaped products with m.p. 173-175 ^{o}C. Yield: 74 %. Anal. Calcd. for $C_{16}H_8N_6$: C, 67.60; H, 2.84; N, 29.56. Found: C, 67.78; H, 2.97; N, 29.23. IR (KBr, cm^{-1}): 3127b, 2360m, 2170w, 1653w, 1588m, 1522w, 1473w, 1437w, 1386s, 1234w, 1199w, 1130w, 1096m, 995m, 793m, 740m, 676w, 624w, 573w, 533w.

2,3-Di(pyridine-2-yl)-5,6-di(1*H*-tetrazol-5-yl)pyrazine (H_2ptp).

5,6-Di(pyridine-2-yl)-2,3-dicarboni- trile (2.84 g, 0.01 mol), NaN_3 (1.30 g, 0.02 mol), $ZnCl_2$ (2.72 g, 0.02 mol) were placed in a 250 ml round flask with ca 100 ml water. The mixture was heated under reflux for ca 48 h. Then NaOH (2.0 g, 0.05 mol) was added to the reaction mixture, refluxing for ca 2 h. After cooled to room temperature and filtered, the filtrate was acidified (to pH~1) with concentrated hydrochloric acid and filtered to give the crude power which was washed with ethanol and water to obtain white power. Yield: 89 %. m.p. 277-279 ^{o}C Anal. Calcd. for $C_{16}H_{10}N_{12}$: C, 51.89; H, 2.72; N, 45.39. Found: C, 51.48; H, 2.90; N, 45.05. IR (KBr, cm^{-1}) 3125b, 2361m, 1586w, 1540w, 1402vs, 1285w, 1183w, 1105m, 1070w, 790s, 747m, 557w, 513w.

References

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3. Demko, Z. P.; Sharpless, K. B. *Org. Lett.* **2001**, *3*, 4091.
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Table S1. Selected bond distances (Å) and angles (deg) for complex **1.**

Zn(1)-O(1)	1.973(3)	Zn(1)-N(5A)	2.009(3)
Zn(1)-N(9)	2.131(3)	Zn(1)-N(1)	2.142(3)
Zn(1)-N(11)	2.177(3)		
O(1)-Zn(1)-N(5A)	111.04(14)	O(1)-Zn(1)-N(9)	113.86(13)
N(5A)-Zn(1)-N(9)	135.05(13)	O(1)-Zn(1)-N(1)	102.58(14)
N(5A)-Zn(1)-N(1)	97.64(13)	N(9)-Zn(1)-N(1)	74.94(12)
O(1)-Zn(1)-N(11)	90.58(15)	N(5A)-Zn(1)-N(11)	103.90(13)
N(9)-Zn(1)-N(11)	73.83(13)	N(1)-Zn(1)-N(11)	148.77(13)

Symmetry code: A -x+1, -y+1, -z

Table S2. Selected bond distances (Å) and angles (deg) for complex **2**.

Zn(1)-N(5A)	2.031(4)	Zn(1)-O(1)	2.115(4)
Zn(1)-N(11)	2.153(4)	Zn(1)-N(4A)	2.159(4)
Zn(1)-N(9)	2.183(4)	Zn(1)-N(1)	2.215(4)
N(5A)-Zn(1)-O(1)	90.83(18)	N(5A)-Zn(1)-N(11)	113.29(16)
O(1)-Zn(1)-N(11)	86.82(17)	N(5A)-Zn(1)-N(4A)	85.73(18)
O(1)-Zn(1)-N(4A)	175.03(18)	N(11)-Zn(1)-N(4A)	97.83(16)
N(5A)-Zn(1)-N(9)	171.23(17)	O(1)-Zn(1)-N(9)	94.58(15)
N(11)-Zn(1)-N(9)	73.96(15)	N(4A)-Zn(1)-N(9)	88.42(16)
N(5A)-Zn(1)-N(1)	99.22(16)	O(1)-Zn(1)-N(1)	88.13(15)
N(11)-Zn(1)-N(1)	147.14(15)	N(4A)-Zn(1)-N(1)	88.87(15)
N(9)-Zn(1)-N(1)	74.11(15)		

Symmetry code: A -x+2, y-1/2, -z+2

Table S3. Selected bond distances (Å) and angles (deg) for complex **3.**

Zn(1)-N(5A)	2.074(3)	Zn(1)-N(11)	2.136(3)
Zn(1)-N(1)	2.148(3)	Zn(1)-N(7B)	2.177(3)
Zn(1)-N(9)	2.228(3)	Zn(1)-N(4A)	2.319(3)
N(5A)-Zn(1)-N(11)	107.28(11)	N(5A)-Zn(1)-N(1)	104.07(11)
N(1)-Zn(1)-N(11)	147.95(10)	N(5A)-Zn(1)-N(7B)	91.24(10)
N(11)-Zn(1)-N(7B)	89.19(10)	N(1)-Zn(1)-N(7B)	96.67(10)
N(5A)-Zn(1)-N(9)	165.58(10)	N(11)-Zn(1)-N(9)	72.60(10)
N(1)-Zn(1)-N(9)	75.38(10)	N(7B)-Zn(1)-N(9)	103.16(10)
N(5A)-Zn(1)-N(4A)	83.73(10)	N(11)-Zn(1)-N(4A)	88.12(9)
N(1)-Zn(1)-N(4A)	88.83(10)	N(7B)-Zn(1)-N(4A)	173.32(10)
N(9)-Zn(1)-N(4A)	81.85(10)		

Symmetry code: A x+1/2, -y+3/2, -z+2 B x, y+1, z

Table S4. Selected bond distances (Å) and angles (deg) for complex **4.**

Zn(1)-N(30)	2.018(5)	Zn(1)-N(5A)	2.033(5)
Zn(1)-N(9)	2.109(5)	Zn(1)-N(1)	2.110(5)
Zn(1)-N(11)	2.193(5)	Zn(2)-N(7B)	2.013(5)
Zn(2)-N(20C)	2.047(5)	Zn(2)-N(13)	2.116(5)
Zn(2)-N(21)	2.135(5)	Zn(2)-N(23)	2.169(5)
Zn(3)-N(32D)	2.018(5)	Zn(3)-N(17)	2.036(5)
Zn(3)-N(25)	2.104(5)	Zn(3)-N(33)	2.105(5)
Zn(3)-N(35)	2.217(5)		
N(30)-Zn(1)-N(5A)	102.6(2)	N(30)-Zn(1)-N(9)	124.89(19)
N(5A)-Zn(1)-N(9)	132.41(18)	N(30)-Zn(1)-N(1)	100.64(19)
N(5A)-Zn(1)-N(1)	100.34(19)	N(9)-Zn(1)-N(1)	76.10(18)
N(30)-Zn(1)-N(11)	96.85(19)	N(5A)-Zn(1)-N(11)	99.78(19)
N(9)-Zn(1)-N(11)	73.57(18)	N(1)-Zn(1)-N(11)	149.66(18)
N(7B)-Zn(2)-N(20C)	111.7(2)	N(7B)-Zn(2)-N(13)	97.5(2)
N(20C)-Zn(2)-N(13)	100.61(18)	N(7B)-Zn(2)-N(21)	116.11(19)
N(20C)-Zn(2)-N(21)	132.11(18)	N(13)-Zn(2)-N(21)	75.56(18)
N(7B)-Zn(2)-N(23)	96.35(19)	N(20C)-Zn(2)-N(23)	99.34(19)
N(13)-Zn(2)-N(23)	149.45(18)	N(21)-Zn(2)-N(23)	73.89(18)
N(32D)-Zn(3)-N(17)	111.17(19)	N(32V)-Zn(3)-N(25)	99.74(19)
N(17)-Zn(3)-N(25)	109.4(2)	N(32V)-Zn(3)-N(33)	118.29(19)
N(17)-Zn(3)-N(33)	128.33(18)	N(25)-Zn(3)-N(33)	76.77(19)
N(32D)-Zn(3)-N(35)	94.12(19)	N(17)-Zn(3)-N(35)	89.68(18)
N(25)-Zn(3)-N(35)	150.1(2)	N(33)-Zn(3)-N(35)	73.33(18)

Symmetry code: A -x+1,-y+1,-z; B x+1,y+1,z+1; C -x+2,-y+3,-z+1; D -x+1,-y+2,-z+1

Table S5. Dihedral angles (deg) between the planes of aromatic heterocycles in ptp^{2-} of complexes **1**-**4**.

Complexes	**1**	**2**	**3**	**4**		
Structures	0-D	1-D	2-D	3-D		
$Tetra^1$-$Tetra^2$	56.1	54.4	61.2	60.8	60.0	76.4
$Pyri^1$-$Pyri^2$	51.8	52.2	54.7	56.4	70.8	82.7
$Tetra^1$-Pyra	14.0	29.3	26.5	7.4	3.4	2.0
$Tetra^2$-Pyra	43.2	38.9	46.0	62.4	60.9	74.4
$Pyri^1$-Pyra	17.6	30.9	26.6	18.5	6.8	14.7
$Pyri^2$-Pyra	35.4	37.6	36.4	58.4	73.9	73.2
Σ(Dih-Ang)	218.1	243.3	251.4	263.9	275.8	323.4

Tetra = tetrazolate ring, Pyri = pyridine ring, Pyra = pyrazine ring, Σ(Dih-Ang) = the sum of all dihedral angles in one ptp^{2-}.

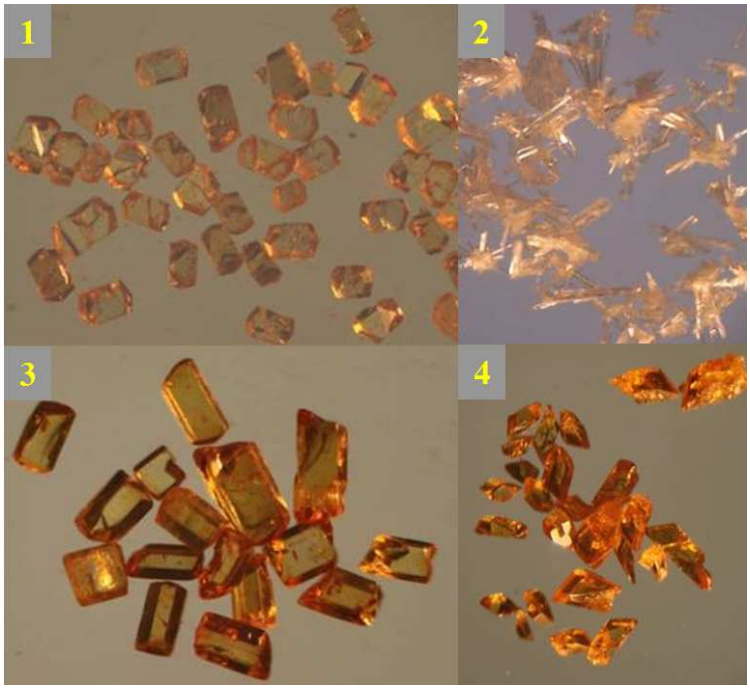

Figure S1 The photos of metal-organic crystalline materials **1**-**4**.

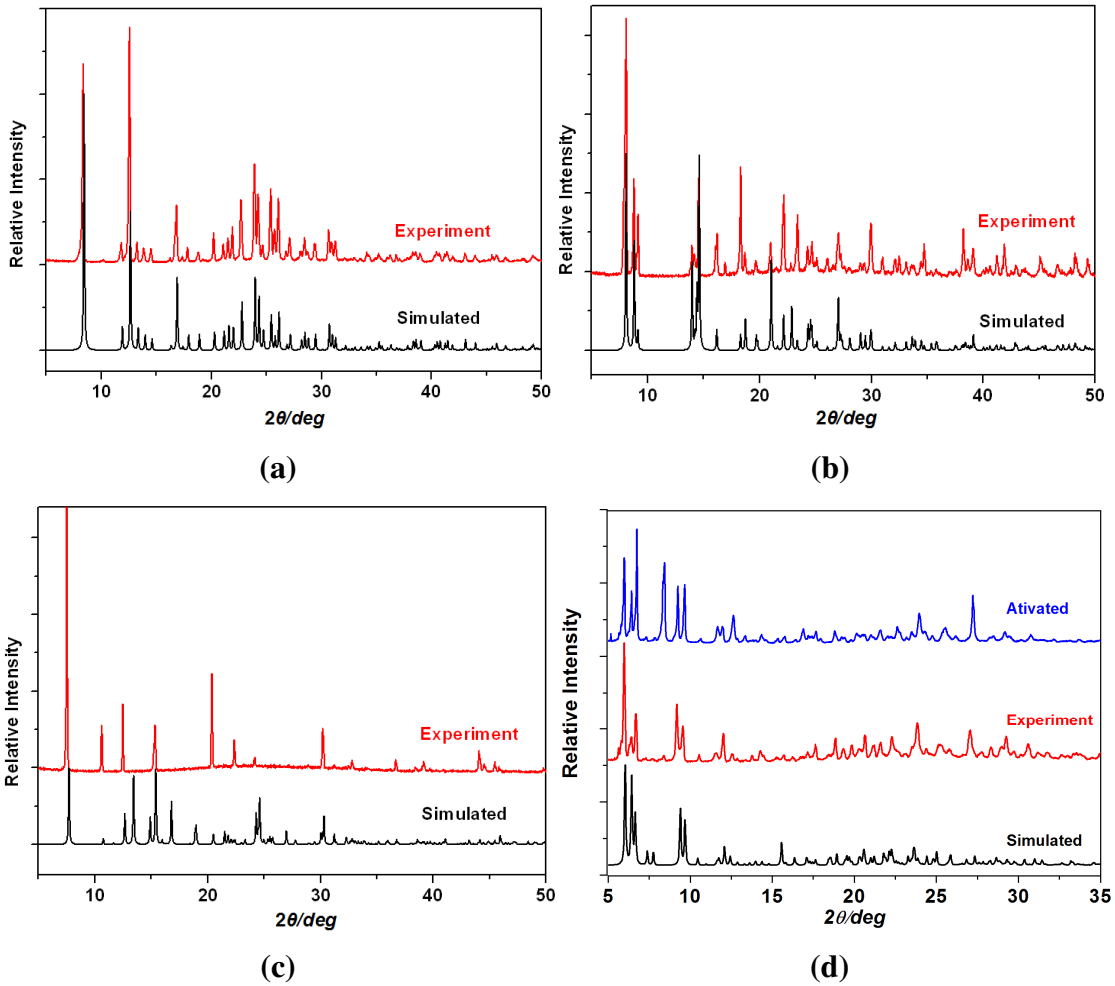

Figure S2 The XRPD patterns: (a) for **1**, (b) for **2**, (c) for **3**, and (d) for **4**.

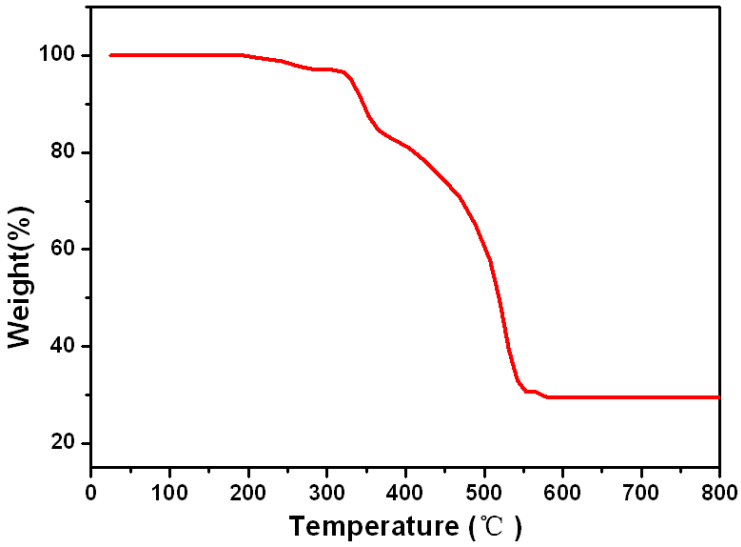

Figure S3 Thermogravimetric analyses (TGA) curve for complex **4**.

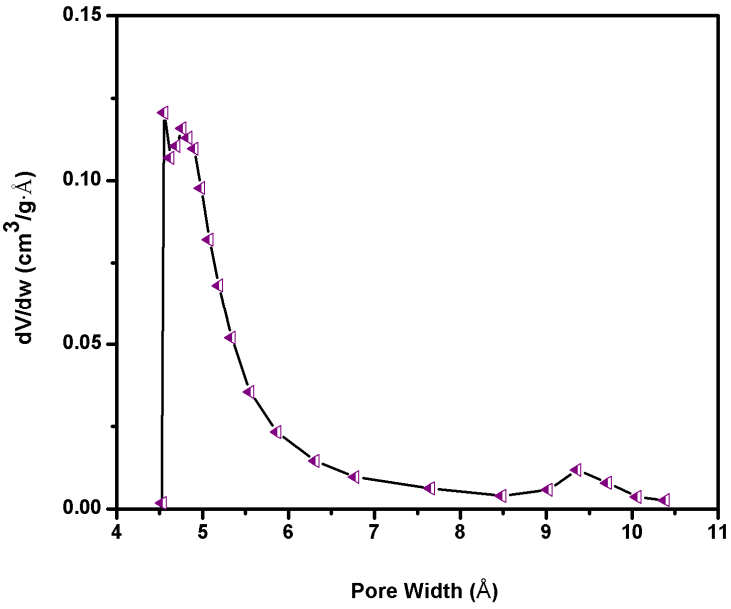

Figure S4 Horvath-Kawazoe pore size distribution plot of **4a**.

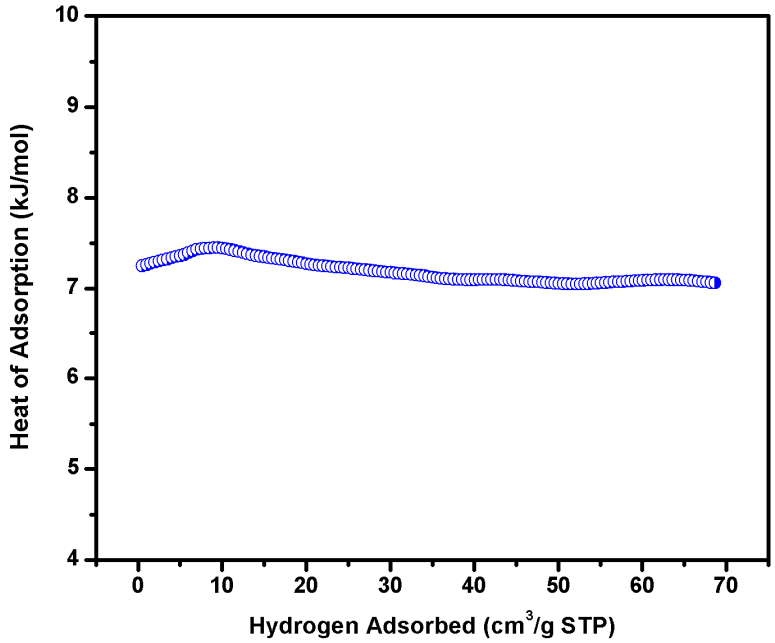

Figure S5 Isosteric heat of H_2 adsorption for **4a**.