Supplementary Material (ESI) for CrystEngComm

Synthesis, Crystal Structures and Properties of Four Topologies Based on 2,3,5,6-Tetramethyl-1,4-Benzenedicarboxylic Acid and Bipyridine Ligands

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Electronic Supplementary Information

I. Structures about complexes

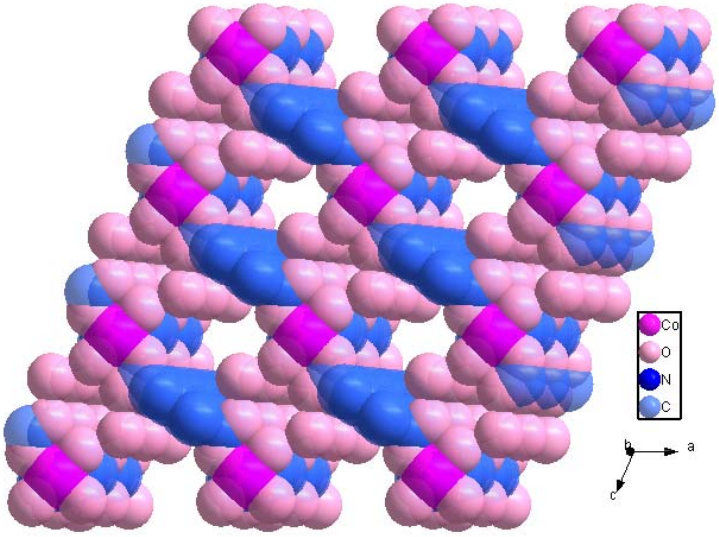

Fig. S1 Packing Structure of complex **2** in single net with channels along *b* axis.

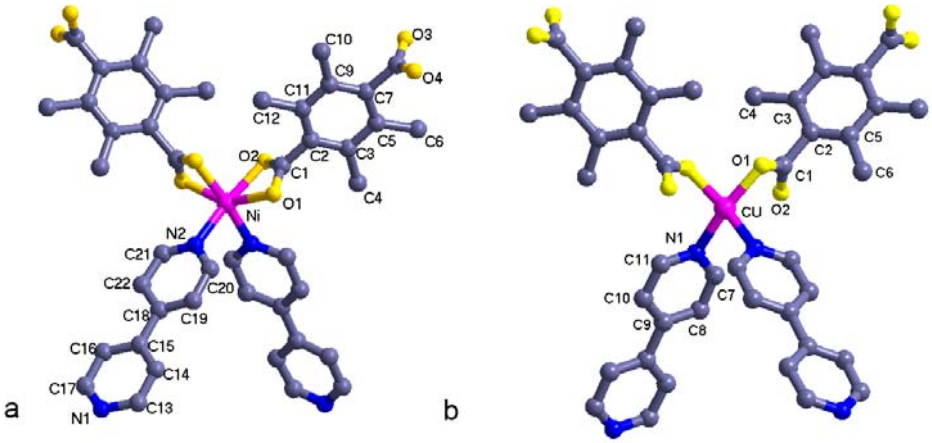

Fig. S2 The slight difference of coordination environment between **3** and **4**.

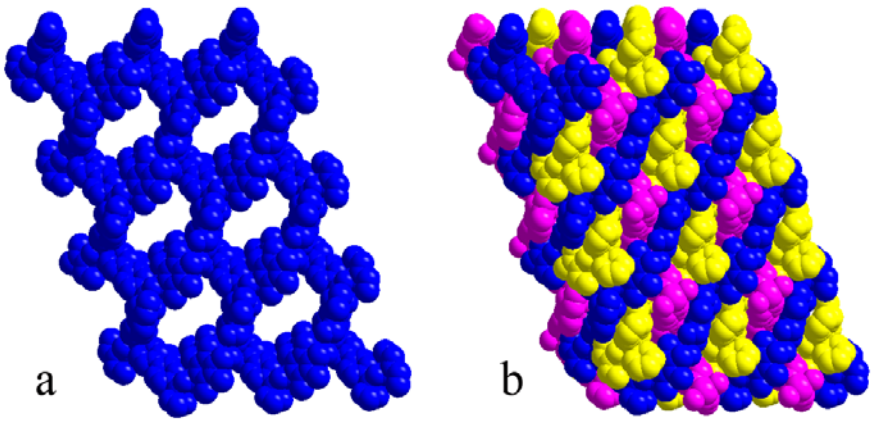

Fig. S3 Structure of complex **3** (a) single net with channels (b) three-fold interpenetrating packing shown in different color.

II. Gas sorption properties

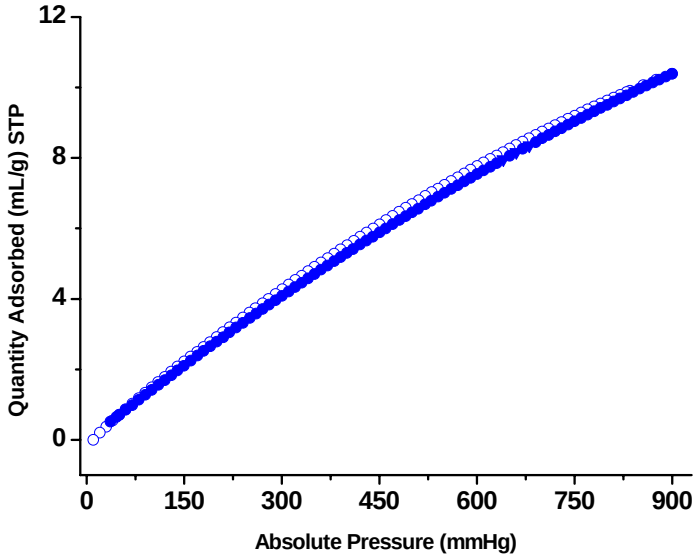

Fig. S4 The CH_4 sorption isotherm of complex **5** at 273K.

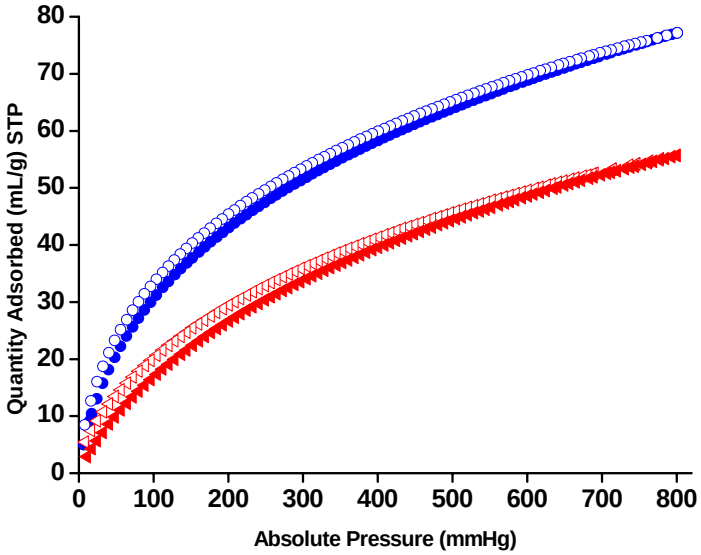

Fig. S5 The H_2 sorption isotherm of complex **5:** blue, at 77 K; red, at 87K.

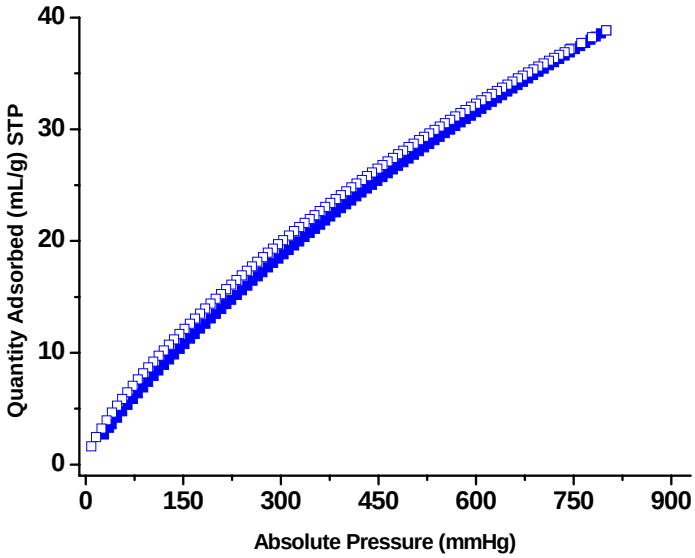

Fig. S6 The CO_2 sorption isotherm of complex **5** at 273 K.

III. Thermal gravity analysis

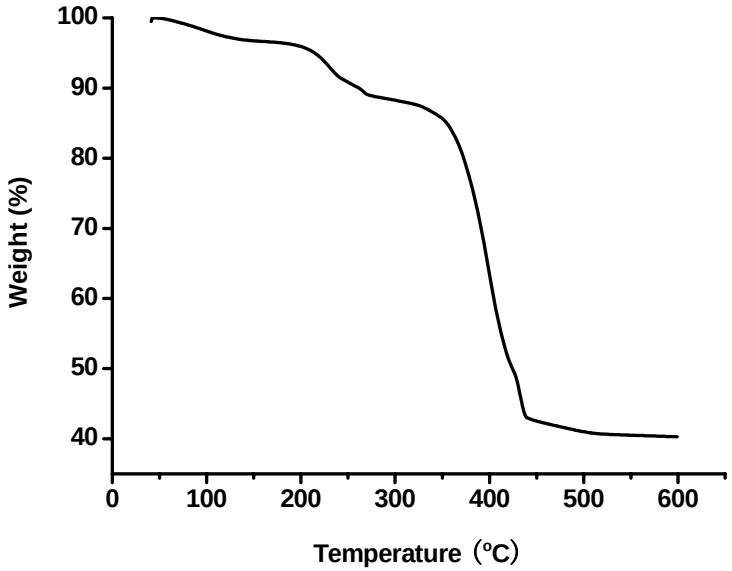

Fig. S7 TGA of complex **1**.

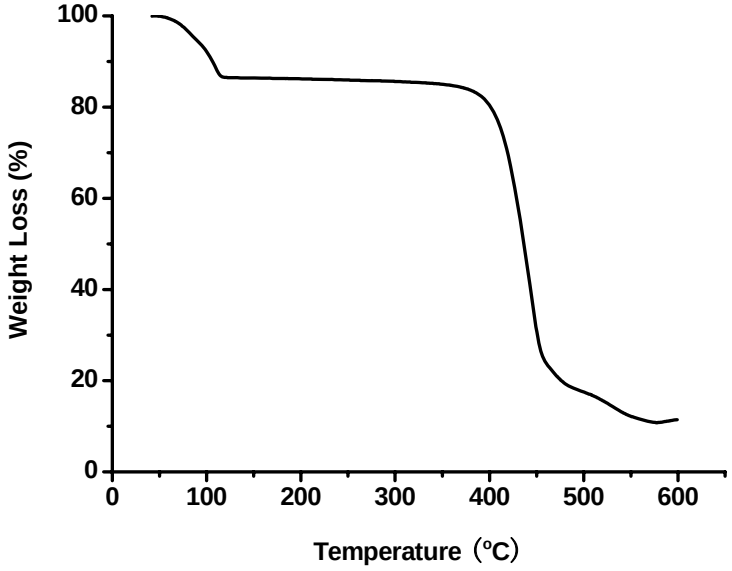

Fig. S8 TGA of complex **2**.

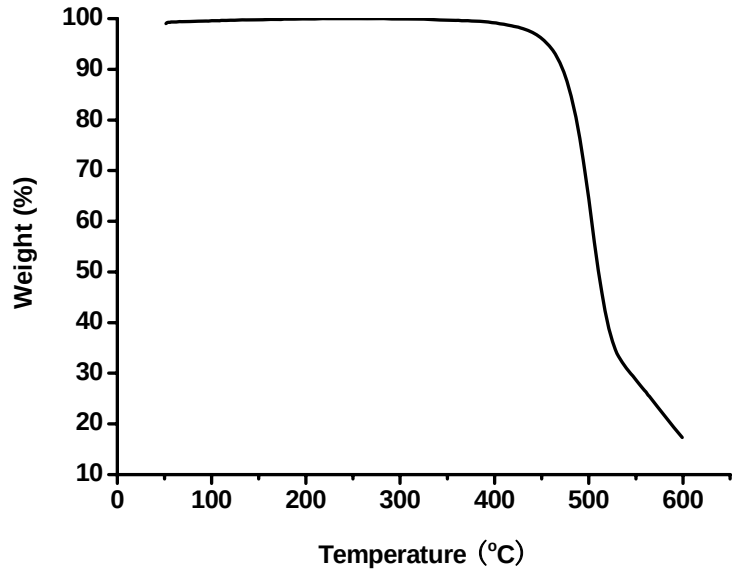

Fig. S9 TGA of complex **3**.

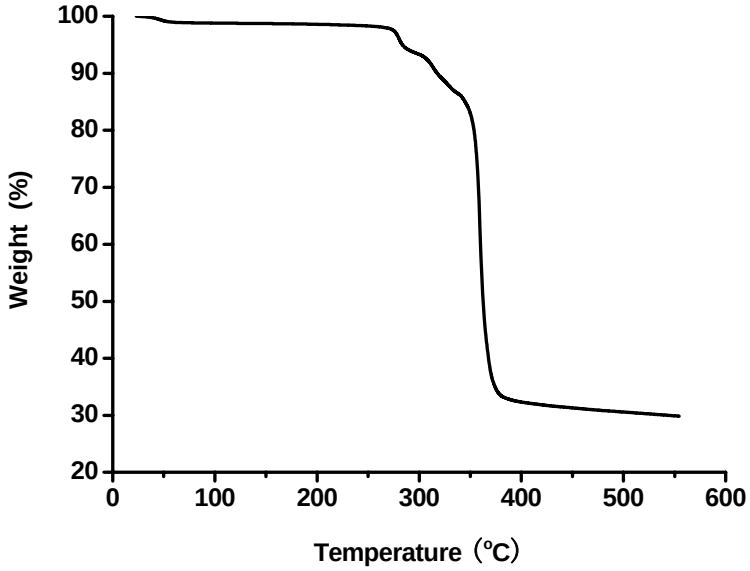

Fig. S10 TGA of complex **4**.

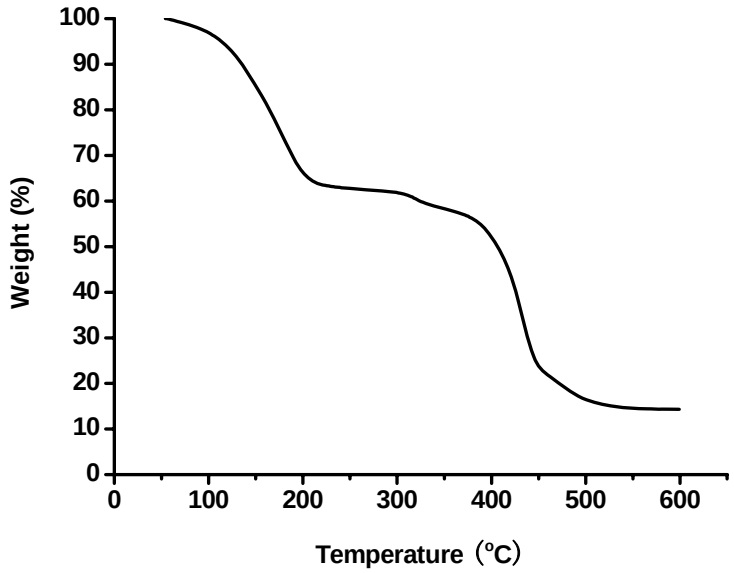

Fig. S11 TGA of complex **5**.

IV. Powder x-ray diffraction analysis about complex 5

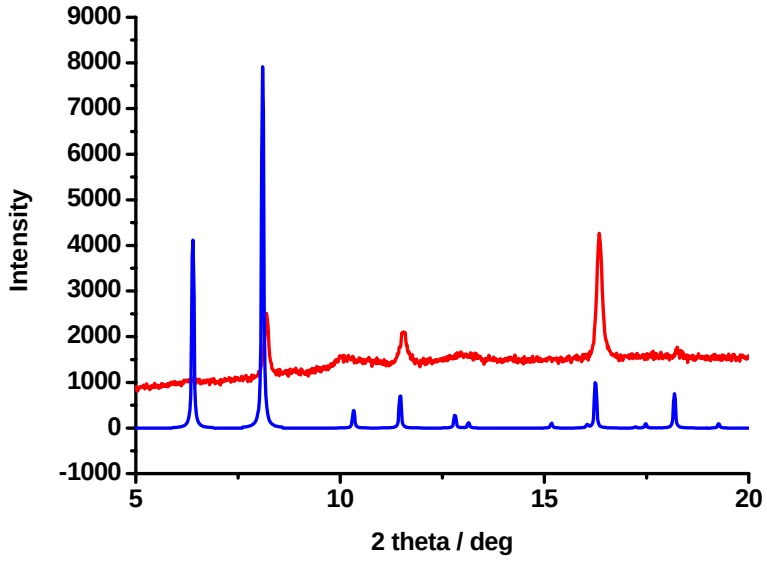

Fig. S12 PXRD of complex **5**: blue, **5**-simulated; red, **5** after gas-sorption measurement.

V. The details of crystallographic data and selected bond parameters for complexes 1-5

Table S1. Crystal Data Collection and Structure Refinement for 1−5.

	1	2	3	4	5
empirical formula	$C_{22}H_{24}CdN_2O_6$	$C_{22}H_{22}CoN_2O_8$	$C_{22}H_{20}Ni\ N_2O_4$	$C_{22}H_{20}Cu\ N_2O_4$	$C_{21}H_{24}CoNO_5$
formula weight	524.83	501.35	435.11	439.94	429.34
temp (K)	273(2)	293(2)	293(2)	293(2)	293(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	tetragonal
space group	*P2(1)/n*	*C2/m*	*C2/c*	*C2/c*	*I4/mcm*
a (Å)	7.7773(6)	11.578(4)	14.1443(10)	14.2254(8)	15.4168(7)
b (Å)	17.6806(13)	11.488(4)	10.5695(7)	10.6516(6)	15.4168(7)
c (Å)	16.5160(13)	9.342(3)	13.5488(9)	13.6134(8)	27.623(2)
α(deg)	90	90	90	90	90
β(deg)	97.3930(10)	113.459(6)	109.7910(10)	110.3700(10)	90
γ(deg)	90	90	90	90	90
V (Å^3)	2252.2(3)	1139.9(7)	1905.9(2)	1933.75(19)	6565.4(6)
Z	4	2	4	4	8
ρcalc (g/cm^3)	1.548	1.461	1.516	1.511	0.869
F(000)	1064	525	904	908	1792
data/restraints/params	5009/0/292	1331/0/87	2149/0/132	1988/0/132	2042/0/71
GOF on *F*2	0.979	0.991	1.006	1.066	1.110
final *R* indices [*I* > 2*ó*(*I*)]	R1 = 0.0772, wR2 = 0.1018	R1 = 0.0494, wR2 = 0.1240	R1 = 0.0371, wR2 = 0.0941	R1 = 0.0314, wR2 = 0.0834	R1 = 0.0932, wR2 = 0.2538

Table S2. The Selected Bond Lengths (Å) and Angles (deg) of Complexes 1−5.

	1
Cd1 O2 2.255(3)	Cd1 O3 2.343(3)
Cd1 O4 2.293(2)	Cd1 O1 2.346(3)
Cd1 N1 2.304(3)	Cd1 N2 2.357(3)
O2 Cd1 O4 88.35(12)	O3 Cd1 O1 55.90(10)
O2 Cd1 N1 103.83(13)	O2 Cd1 N2 95.66(13)
O4 Cd1 N1 90.21(11)	O4 Cd1 N2 160.74(11)
O2 Cd1 O3 150.36(12)	N1 Cd1 N2 70.53(12)
O4 Cd1 O3 87.61(9)	O3 Cd1 N2 97.75(11)
N1 Cd1 O3 105.54(11)	O1 Cd1 N2 92.80(11)
O2 Cd1 O1 97.22(12)	N1 Cd1 O1 154.14(12)
O4 Cd1 O1 105.40(10)	
	2
Co O3 2.125(3)	Co N 2.168(3)
Co O1 2.134(2)	O3 Co O1 91.68(11)
O3 Co N 90.000(1)	O1 Co N 90.000(1)

O3 Co O1 88.32(11)	
	3
Ni N1 2.0608(17)	Ni O1 2.1396(14)
Ni O2 2.0870(14)	N1 Ni O2 169.59(7)
N1 Ni O1 94.61(6)	N1 Ni O1 107.10(6)
O2 Ni O1 62.50(6)	N1 Ni O2 94.24(6)
	4
Cu O1 1.9707(14)	Cu N1 2.0094(16)
O1 Cu O1 88.66(9)	N1 Cu N1 87.54(9)
O1 Cu N1 164.37(6)	O1 Cu N1 94.02(7)
	5
Co1 N1 2.027(6)	Co1 O1 2.033(2)
N1 Co1 O1 97.43(7)	N1 Co1 O1 97.43(7)
O1 Co1 O1 165.15(14)	O1 Co1 O1 89.043(18)

VI. Heat adsorption calculation

Isosteric analysis of adsorption isotherms collected at various temperatures allows an estimation of the coverage-dependent isosteric heat of adsorption (Q_{st}), where the behavior of this function is determined by the relative magnitudes of the adsorbent-adsorbate and adsorbate-adsorbate interactions. [1]

Hydrogen adsorption isotherms were collected using a volumetric technique at 77, 87 K for complex **5**. The samples were synthesized, activated, and outgassed according to the optimal procedures described above and yielded surface areas and pore volumes (measured by N_2 adsorption at 77 K) comparable to those determined by the gravimetric method. The data are shown in Figure S5. The data were converted to gravimetric units by the factor 9.0 mg H_2 per 100 cm^3 at STP.

To extract the coverage-dependent isosteric heat of adsorption, the data were modeled with a virial-type expression composed of parameters a_i and b_i that are independent of temperature[2]:

$$\ln P = \ln N + \frac{1}{T}\sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

where P is pressure, N is the amount adsorbed (or uptake), T is temperature, and m and n determine the number of terms required to adequately describe the isotherm.

The isosteric heat of adsorption is calculated according to:

$$Q_{st} = -R\sum_{i=0}^{m} a_i N^i \qquad (2)$$

where R is the universal gas constant.

References

1 J. L. C. Rowsell, O. M. Yaghi, *J. Am. Chem. Soc.,* 2006, **128**, 1304.

2 L. Czepirski, J. Jagiello, *Chem. Eng. Sci.* 1989, **44**, 797.