Supporting Information

Structures and properties of coordination polymers involving asymmetric biphenyl-3,2′,5′-tricarboxylate†

Jie Zhao,[a] Li-Qiong Xie,[a] Ying-Ming Ma,[a] Ai-Ju Zhou,[a] Wen Dong,[a] Jing Wang*[a], Yan-Cong Chen[b] and Ming-Liang Tong[b]

[a] *Guangzhou Key Laboratory for Environmentally Functional Materials and Technology, School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, P. R. China. Fax: 86 02039366908; Tel: 86 02039366908; E-mail: wangjgzhu@163.com*

[b] *State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, P. R. China*

Experimental Section:

Computational details

A full geometry optimization of the electronic ground state of biphenyl-3,2′,5′-tricarboxylic acid (H_3bptc), was obtained from crystal structure at DFT level using the Becke three-parameter Lee–Yang–Parr(B3-LYP) exchange-correlation functional with the 6-31G(d,p) basis sets. Subsequently, the stable configuration of the complex substance was confirmed by the vibrational frequency analysis, in which no imaginary frequency was found for the configuration at the energy minima. Lastly, starting from the optimized structure, the potential energy surface was explored at the DFT B3-LYP/6-31G(d,p) level of theory along rotations around the most significant dihedral angle. The scan was obtained with 36+1 steps of 10 degrees. Gaussian 09 computational package was used for all these calculations.

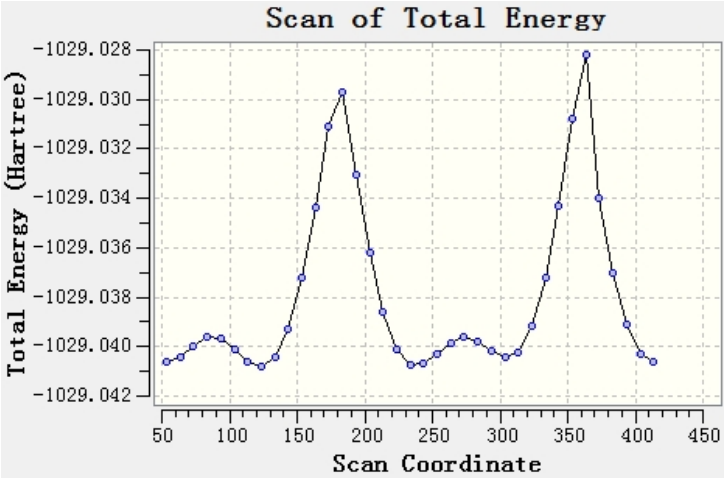


Fig S1. Relationship of the energy and dihedral angle between the two phenyl rings in free H_3bptc.

Table S1. The energy and dihedral angles of the ligand in compounds **1-4** and free H_3bptc.

Compound	**1**	**2**	**3**	**4**	**H_3bptc**
Dihedral angle	47.3º	56.6º	42.2º	35.4º	53.5º
$E_{tot.}$(a.u.)	-1029.0405	-1029.0406	-1029.0402	-1029.0394	-1029.0408
ΔE(kJ.mol^{-1})	0.788	0.525	1.575	3.676	0

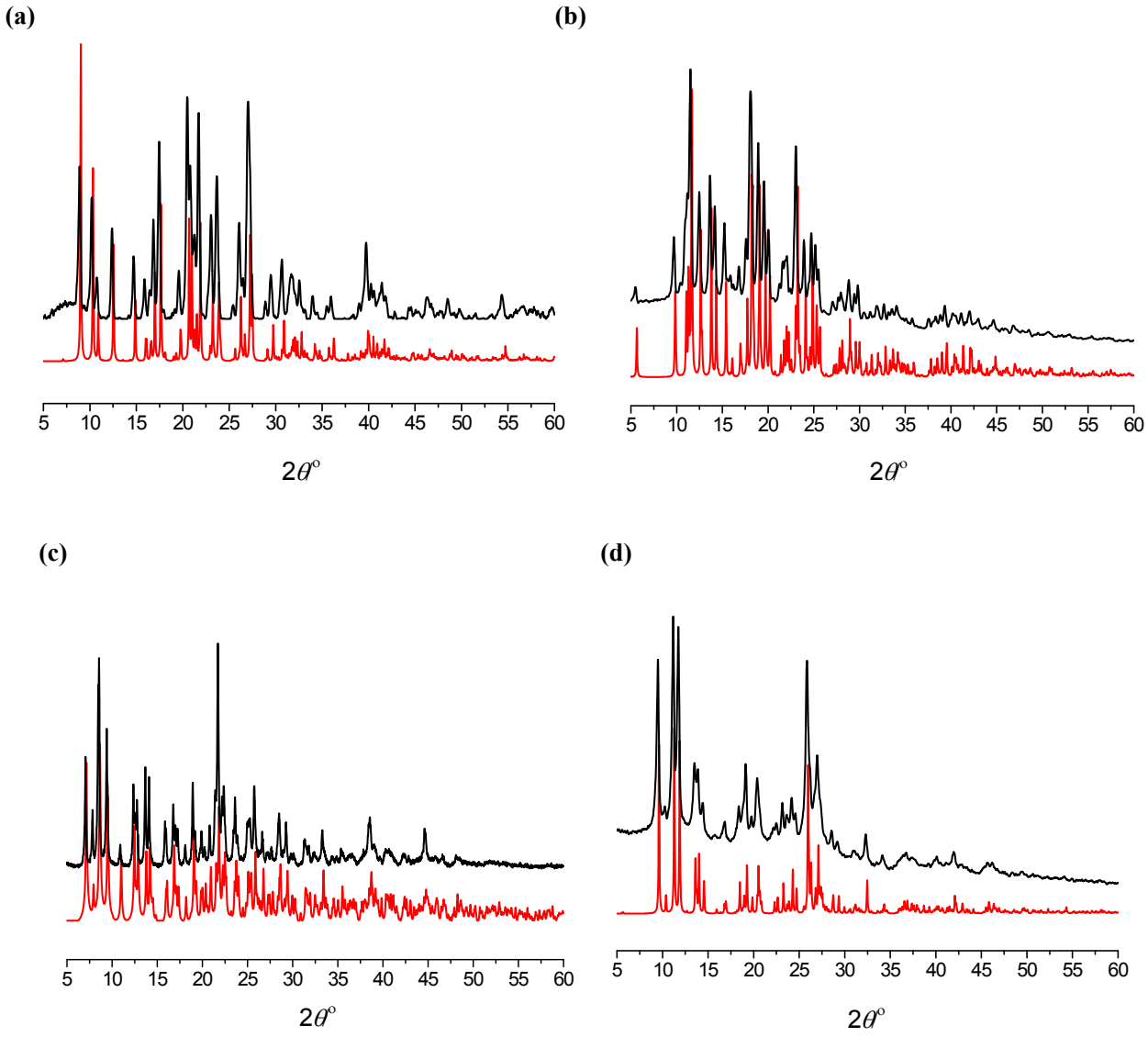
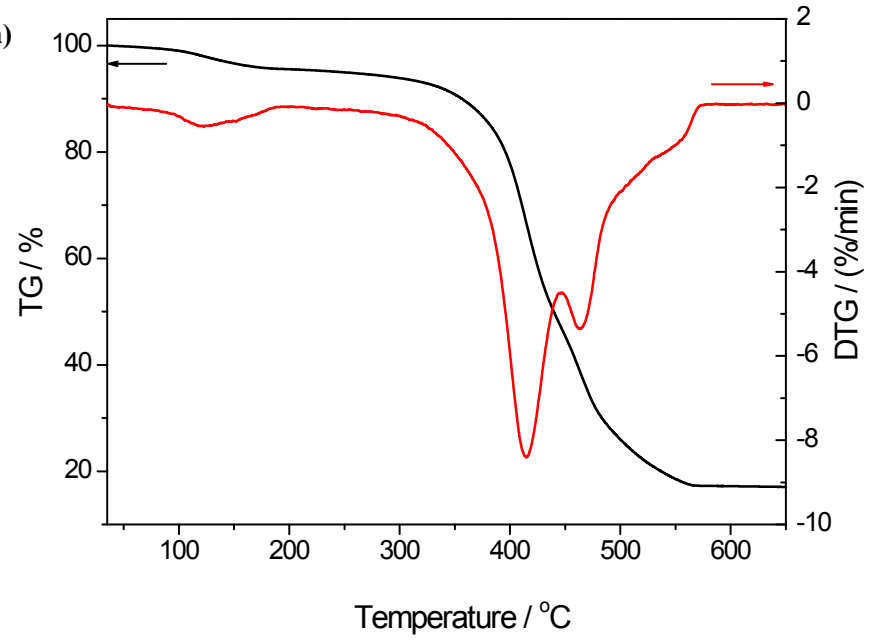
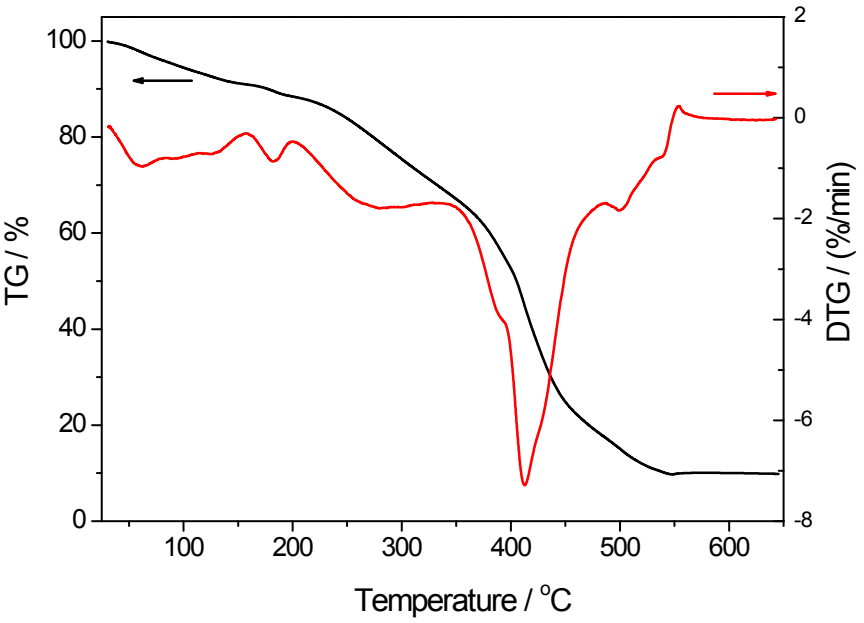


Fig. S2 Simulated (red) and experimental (black) XRPD patterns for compounds **1**(a), **2**(b), **3**(c) and **4**(d).

(a)


100
80
60
40
20
TG / %
2
0
-2
-4
-6
-8
-10
DTG / (%/min)
100
200
300
400
500
600
Temperature / °C

(b)


100
80
60
40
20
0
TG / %
2
0
-2
-4
-6
-8
DTG / (%/min)
100
200
300
400
500
600
Temperature / °C

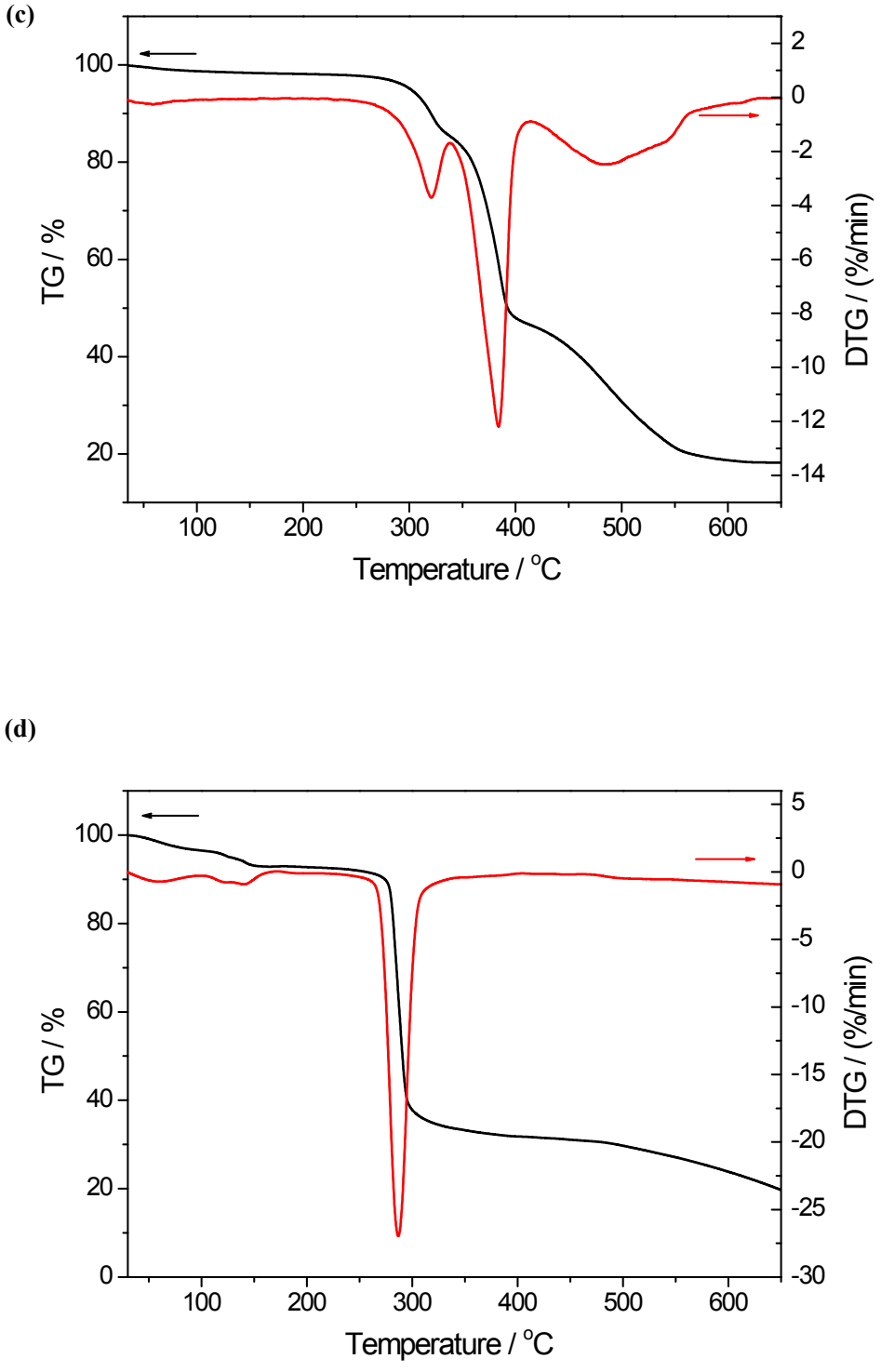
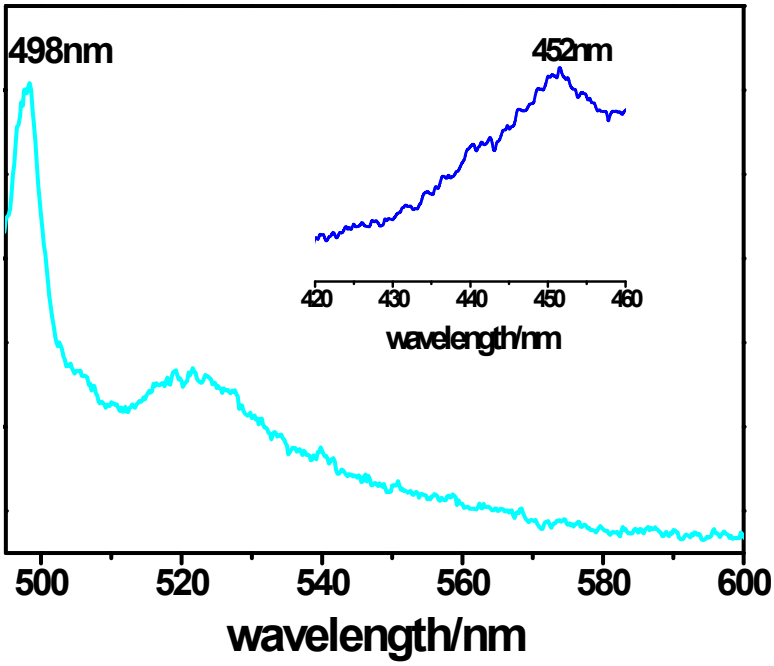
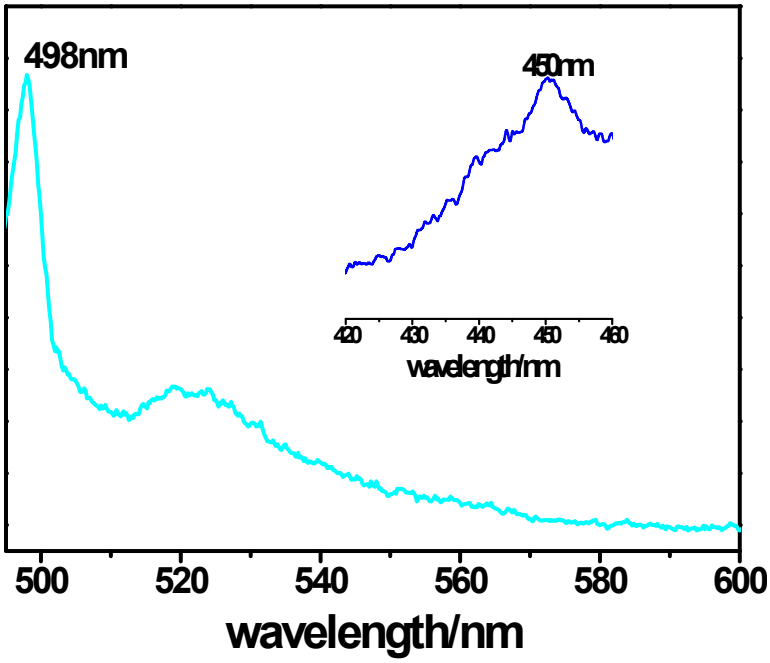


Fig. S3 Thermal gravimetric analyses (TGA) curves for compounds **1**(a), **2**(b), **3**(c) and **4**(d).


498nm
452nm
420
430
440
450
460
wavelength/nm
500
520
540
560
580
600
wavelength/nm


498nm
450nm
420
430
440
450
460
wavelength/nm
500
520
540
560
580
600
wavelength/nm

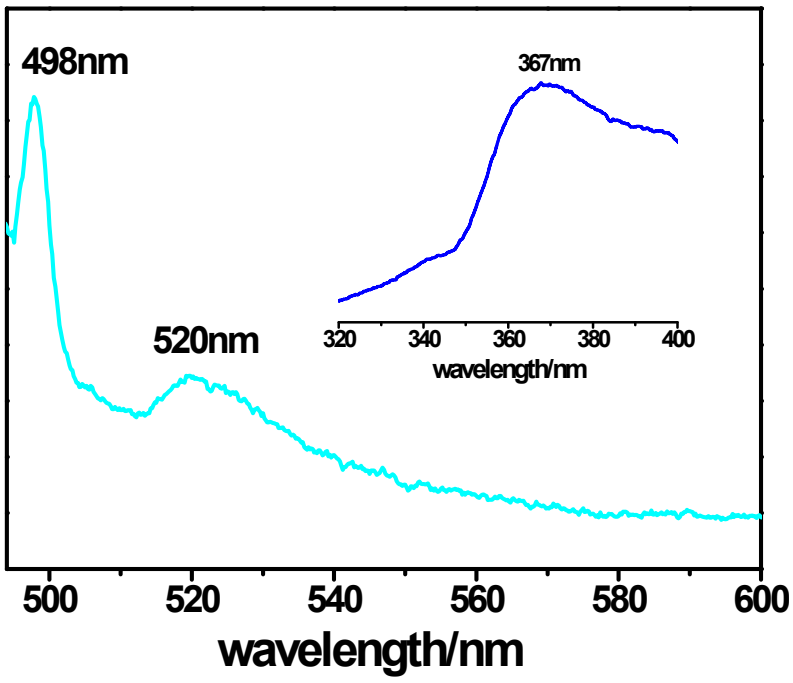


Fig. S4 (a) The excitation (insert) and emission spectra for compounds **1**(a), **2**(b) and **4**(d) in solid state at room temperature.

Table S2. Selected bond lengths (Å) and angles (°) for compounds **1-4**.

Compound **1**			
Mn(1)-O(4*a*)	2.1383(15)	Mn(2)-O(2)	2.1505(13)
Mn(1)-O(6*b*)	2.1600(14)	Mn(2)-O(2*d*)	2.1505(13)
Mn(1)-O(1)	2.1651(14)	Mn(2)-O(5*b*)	2.2055(13)
Mn(1)-N(1)	2.2691(15)	Mn(2)-O(5*e*)	2.2055(13)
Mn(1)-N(2*c*)	2.2740(15)	Mn(2)-N(3)	2.2701(14)
Mn(1)-O(1W)	2.2767(17)	Mn(2)-N(3*d*)	2.2701(14)
O(4*a*)-Mn(1)-O(6*b*)	95.47(6)	O(2)-Mn(2)-O(2*d*)	180
O(4*a*)-Mn(1)-O(1)	169.15(6)	O(2)-Mn(2)-O(5*b*)	90.93(5)
O(6*b*)-Mn(1)-O(1)	93.63(5)	O(2*d*)-Mn(2)-O(5*b*)	89.07(5)
O(4*a*)-Mn(1)-N(1)	88.80(6)	O(2)-Mn(2)-O(5*e*)	89.07(5)
O(6*b*)-Mn(1)-N(1)	88.14(6)	O(2*d*)-Mn(2)-O(5*e*)	90.93(5)
O(1)-Mn(1)-N(1)	85.60(5)	O(5*b*)-Mn(2)-O(5*e*)	180
O(4*a*)-Mn(1)-N(2*c*)	93.79(6)	O(2)-Mn(2)-N(3)	83.28(5)
O(6*b*)-Mn(1)-N(2*c*)	94.05(6)	O(2*d*)-Mn(2)-N(3)	96.72(5)
O(1)-Mn(1)-N(2*c*)	91.45(5)	O(5*b*)-Mn(2)-N(3)	89.49(5)
N(1)-Mn(1)-N(2*c*)	176.43(6)	O(5*e*)-Mn(2)-N(3)	90.51(5)
O(4*a*)-Mn(1)-O(1W)	78.62(7)	O(2)-Mn(2)-N(3*d*)	96.72(5)
O(6*b*)-Mn(1)-O(1W)	171.77(6)	O(2*d*)-Mn(2)-N(3*d*)	83.28(5)
O(1)-Mn(1)-O(1W)	91.71(6)	O(5*b*)-Mn(2)-N(3*d*)	90.51(5)
N(1)-Mn(1)-O(1W)	86.02(6)	O(*5e*)-Mn(2)-N(3*d*)	89.49(5)
N(2*c*)-Mn(1)-O(1W)	92.07(6)	N(3)-Mn(2)-N(3*d*)	180

Compound **2**			
Ni(1)-N(3)	2.0596(18)	Ni(1)-O(2W)	2.0908(17)
Ni(1)-O(2)	2.0597(15)	Ni(1)-O(1W)	2.0921(18)
Ni(1)-O(3*a*)	2.0634(15)	Ni(1)-N(1)	2.0943(19)
N(3)-Ni(1)-O(2)	93.80(7)	O(3*a*)-Ni(1)-O(1W)	87.47(7)
N(3)-Ni(1)-O(3*a*)	92.02(7)	O(2W)-Ni(1)-O(1W)	89.90(8)
O(2)-Ni(1)-O(3*a*)	173.53(6)	N(3)-Ni(1)-N(1)	91.71(7)
N(3)-Ni(1)-O(2W)	178.23(7)	O(2)-Ni(1)-N(1)	87.64(7)
O(2)-Ni(1)-O(2W)	85.91(7)	O(3*a*)-Ni(1)-N(1)	95.02(7)
O(3*a*)-Ni(1)-O(2W)	88.36(7)	O(2W)-Ni(1)-N(1)	86.53(7)
N(3)-Ni(1)-O(1W)	91.84(8)	O(1W)-Ni(1)-N(1)	175.59(7)
O(2)-Ni(1)-O(1W)	89.52(7)		

Compound **3**			
Cd(1)-O(2*a*)	2.246(2)	Cd(1)-N(1)	2.331(3)
Cd(1)-O(1)	2.270(3)	Cd(1)-N(2)	2.359(3)
Cd(1)-N(3)	2.298(3)	Cd(1)-N(4)	2.432(3)
O(2*a*)-Cd(1)-O(1)	93.58(10)	N(3)-Cd(1)-N(2)	98.64(12)
O(2*a*)-Cd(1)-N(3)	108.31(12)	N(1)-Cd(1)-N(2)	71.24(12)
O(1)-Cd(1)-N(3)	99.14(11)	O(2*a*)-Cd(1)-N(4)	168.99(11)
O(2*a*)-Cd(1)-N(1)	94.00(17)	O(1)-Cd(1)-N(4)	97.39(10)
O(1)-Cd(1)-N(1)	90.49(11)	N(3)-Cd(1)-N(4)	70.91(12)
N(3)-Cd(1)-N(1)	154.93(12)	N(1)-Cd(1)-N(4)	84.99(12)
O(2*a*)-Cd(1)-N(2)	85.46(10)	N(2)-Cd(1)-N(4)	83.83(11)
O(1)-Cd(1)-N(2)	161.55(11)		

Compound **4**			
Cu(1)-O(2)	1.9115(13)	Cu(1)-N(1)	2.0089(16)
Cu(1)-O(4*a*)	1.9904(13)	Cu(1)-O(1W)	2.2187(15)
Cu(1)-N(2)	1.9929(16)		
O(2)-Cu(1)-O(4*a*)	97.21(6)	N(2)-Cu(1)-N(1)	80.27(7)
O(2)-Cu(1)-N(2)	168.38(6)	O(2)-Cu(1)-O(1W)	93.21(6)
O(4*a*)-Cu(1)-N(2)	89.50(6)	O(4*a*)-Cu(1)-O(1W)	85.29(6)
O(2)-Cu(1)-N(1)	89.64(6)	N(2)-Cu(1)-O(1W)	96.79(7)
O(4*a*)-Cu(1)-N(1)	153.60(6)	N(1)-Cu(1)-O(1W)	119.89(6)

Symmetry code: *a*) x-1/2,-y+1/2,z+1/2; *b*) x-1,y,z ; *c*) x,y,z-1; *d*) -x,-y,-z; *e*) -x+1,-y,-z for **1**; *a*) x+1,y-1,z for **2**; *a*) -x+1/2,-y+3/2,-z+1 for **3**; *a*) -x+2,-y+1,-z+1for **4**.

Table S3. Selected Hydrogen bond lengths (Å) and angles (º) for compounds **2** and **4**.

D-H···A	d(D-H)	D(H···A)	d(D···A)	<(D-H···A)
Compound **2**				
O(5)-H(5O)...O(4*a*)	0.85(3)	1.83(3)	2.664(3)	166(5)
O(1W)-H(1WA)...O(3W*b*)	0.85(2)	1.99(2)	2.831(4)	172(3)
O(1W)-H(1WB)...O(1)	0.85(3)	1.89(3)	2.699(3)	158(3)
O(2W)-H(2WA)...O(4*c*)	0.85	1.90	2.675(3)	151
O(2W)-H(2WB)...O(3W*b*)	0.85	2.30	3.137(3)	166
O(3W)-H(3WA)...O(1*d*)	0.85(2)	1.92(2)	2.767(3)	170(3)
O(3W)-H(3WB)...N(2*e*)	0.85(3)	2.13(3)	2.977(4)	171(4)

Compound **4**				
O(5)-H(5O)...O(2W*a*)	0.851(16)	1.802(18)	2.638(3)	167(4)
O(1W)-H(1WA)...O(1)	0.85(2)	1.95(2)	2.778(2)	166(2)
O(1W)-H(1WB)...O(3*b*)	0.852(18)	1.948(18)	2.798(2)	175(2)
O(2W)-H(2WA)...O(6*c*)	0.84(3)	2.15(3)	2.950(3)	161(3)
O(2W)-H(2WA)...O(4*d*)	0.84(3)	2.24(3)	3.023(2)	157(4)

Symmetry codes: *a*) -x,-y+2,-z+2; *b*) x,y,z+1; *c*) x+1,y-1,z; *d*) -x+1,-y+1,-z+2; *e*) -x+1,-y+1,-z+1 for **2**; *a*) -x+2, -y+1, -z+1; *b*) -x+1,-y+1,-z+1; *c*) x,y+1,z+1; *d*) x,y,z+1 for **4**.