

Supporting Information

Syntheses, Structural Evolutions and Properties of Cd(II) Coordination
Polymers Induced by Bis(pyridyl) Ligand with Chelated or Protonated
Spacer and Diverse Counter-anions

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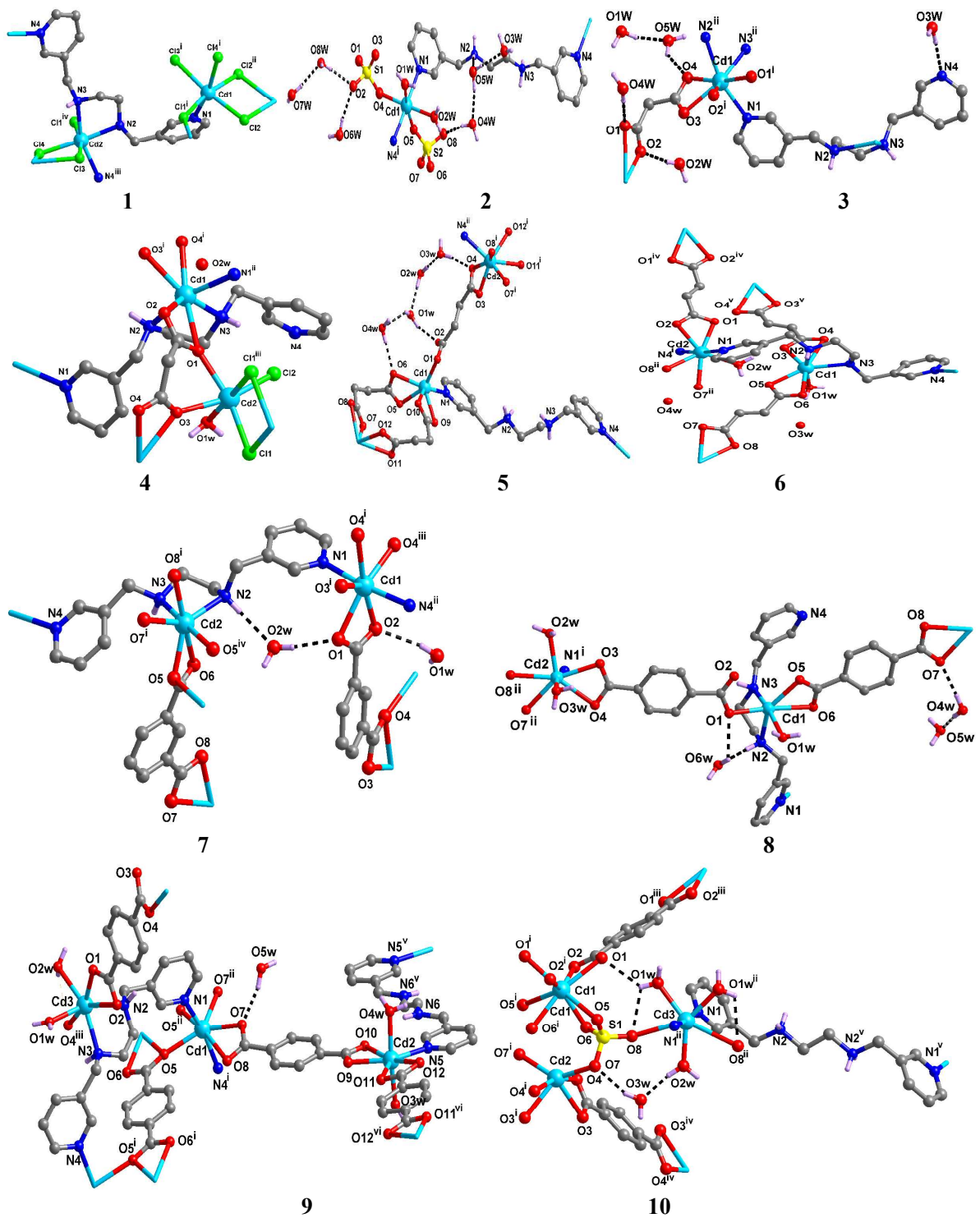


Figure S1 Molecular structures of **1-10** with the hydrogen-bonding interactions denoted as black dashed lines.

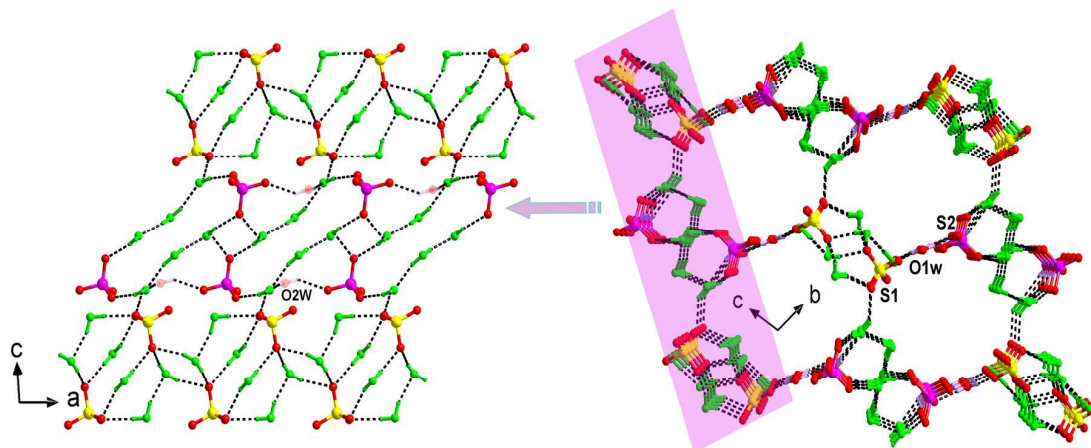


Figure S2 The supramolecular α -Po network of **2** formed by the interconnection of two types of sulfonate-water clusters through lattice O1w and O2w molecules.

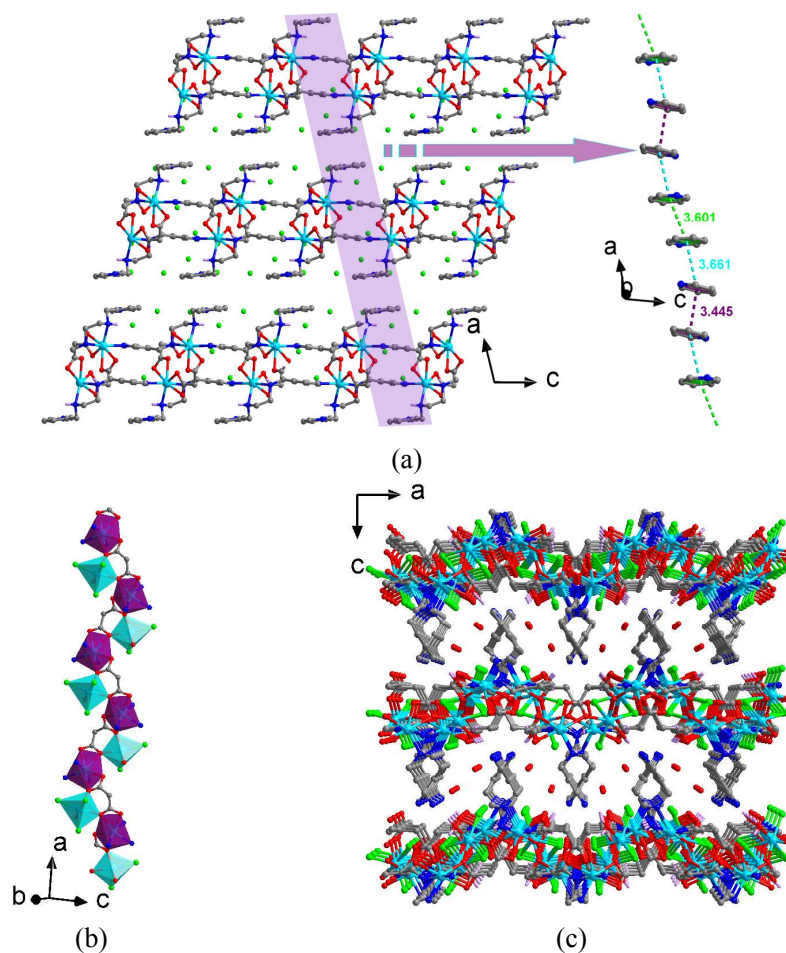


Figure S3 (a) The 3D supramolecular structure of **3** extended by continuous interlamellar and intralamellar $\pi \cdots \pi$ interactions (light purple region). Water molecules were denoted as green balls.

The rod-shape SBU (b) and the 3D supramolecular structure (c) in **4**.

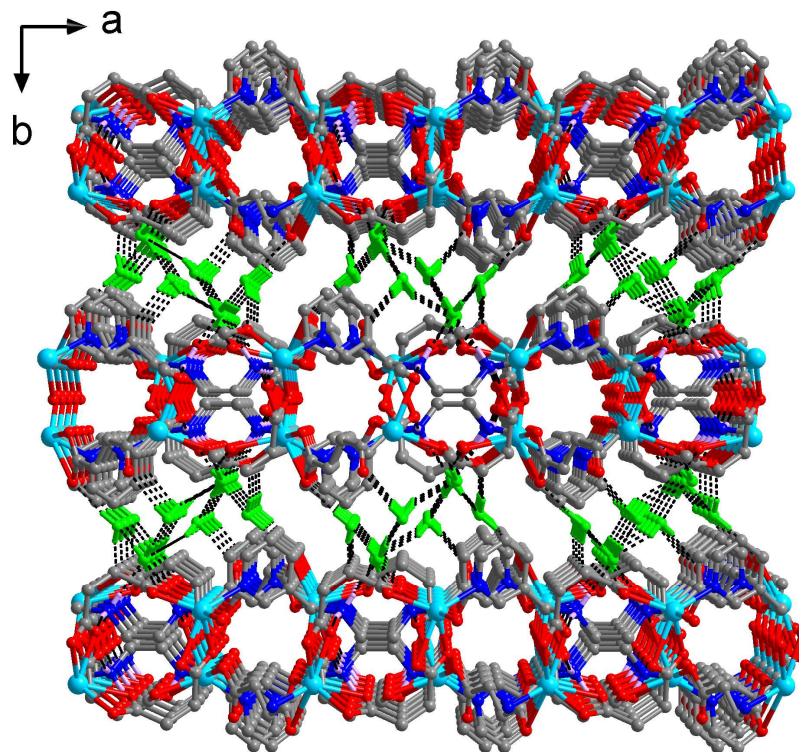


Figure S4 The 3D supramolecular network of **5** formed by O/N-H $\cdots$ O hydrogen bonds linking adjacent layers. Water molecules were denoted as green balls.

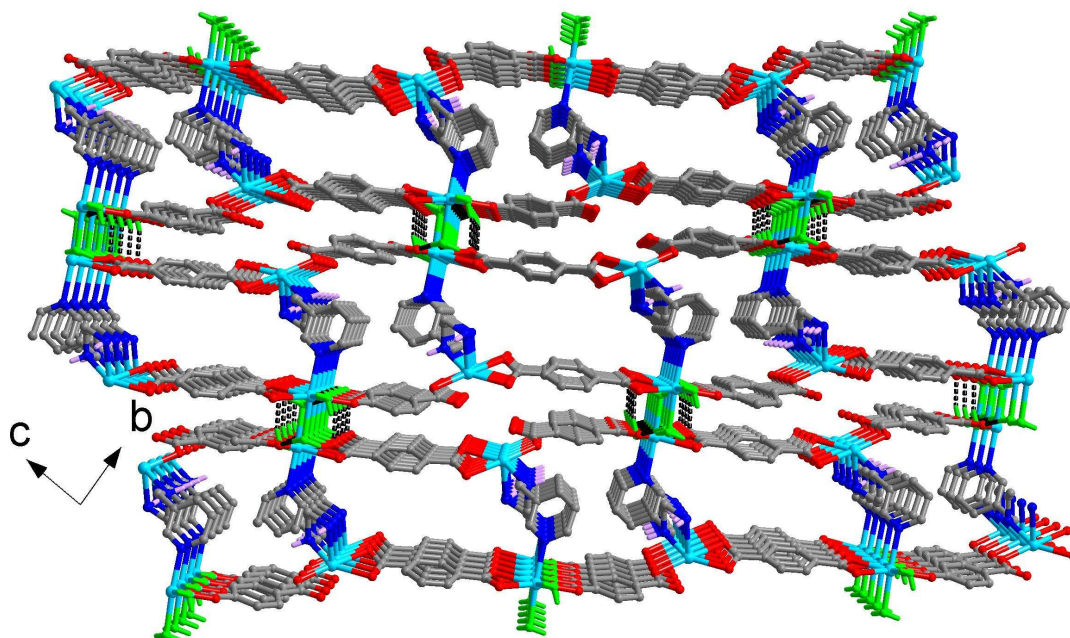


Figure S5 The 3D supramolecular network of **8** formed by the interconnection of two types of layers through O-H $\cdots$ O hydrogen bonds. Water molecules were denoted as green balls.

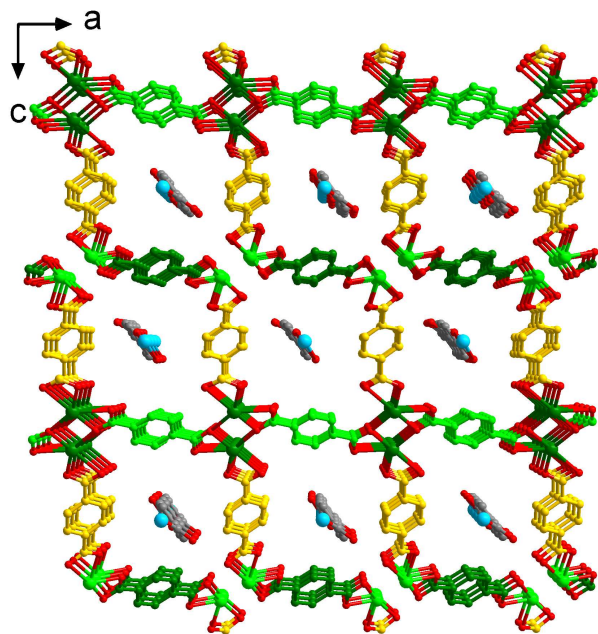


Figure S6 Packing of adjacent layers generated 1D channels that filled by chain structures in **9**.

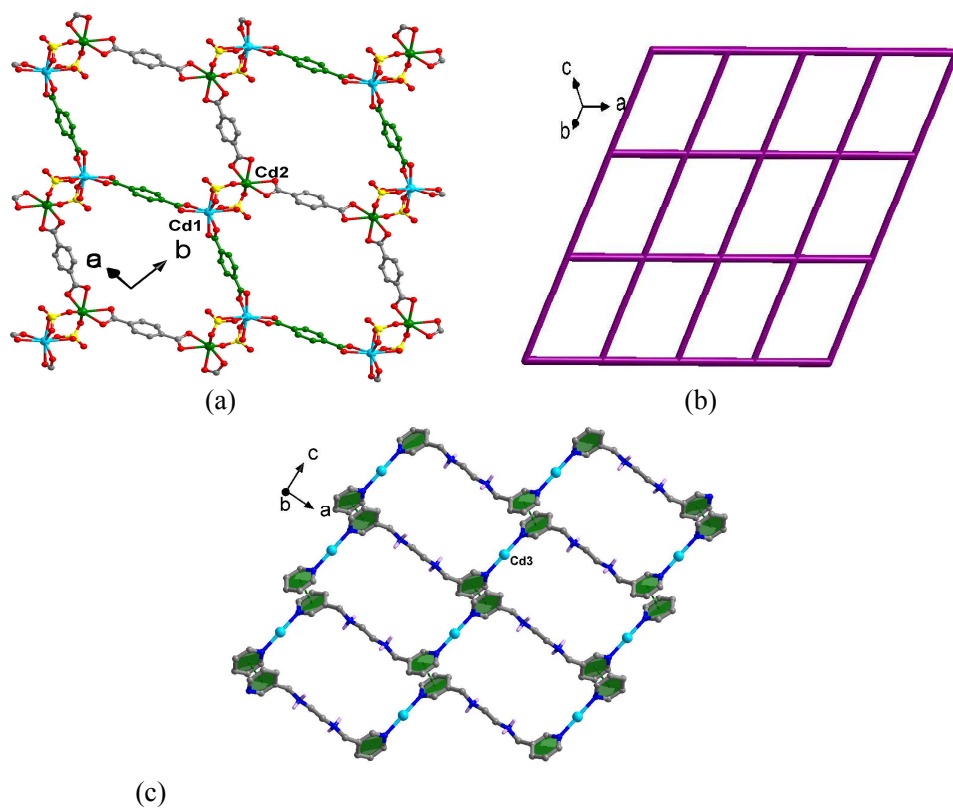


Figure S7 The (4,4) layer structure (a), the **pcu** net (b), and the $\pi \cdots \pi$ interactions between ligands (c) in **10**.

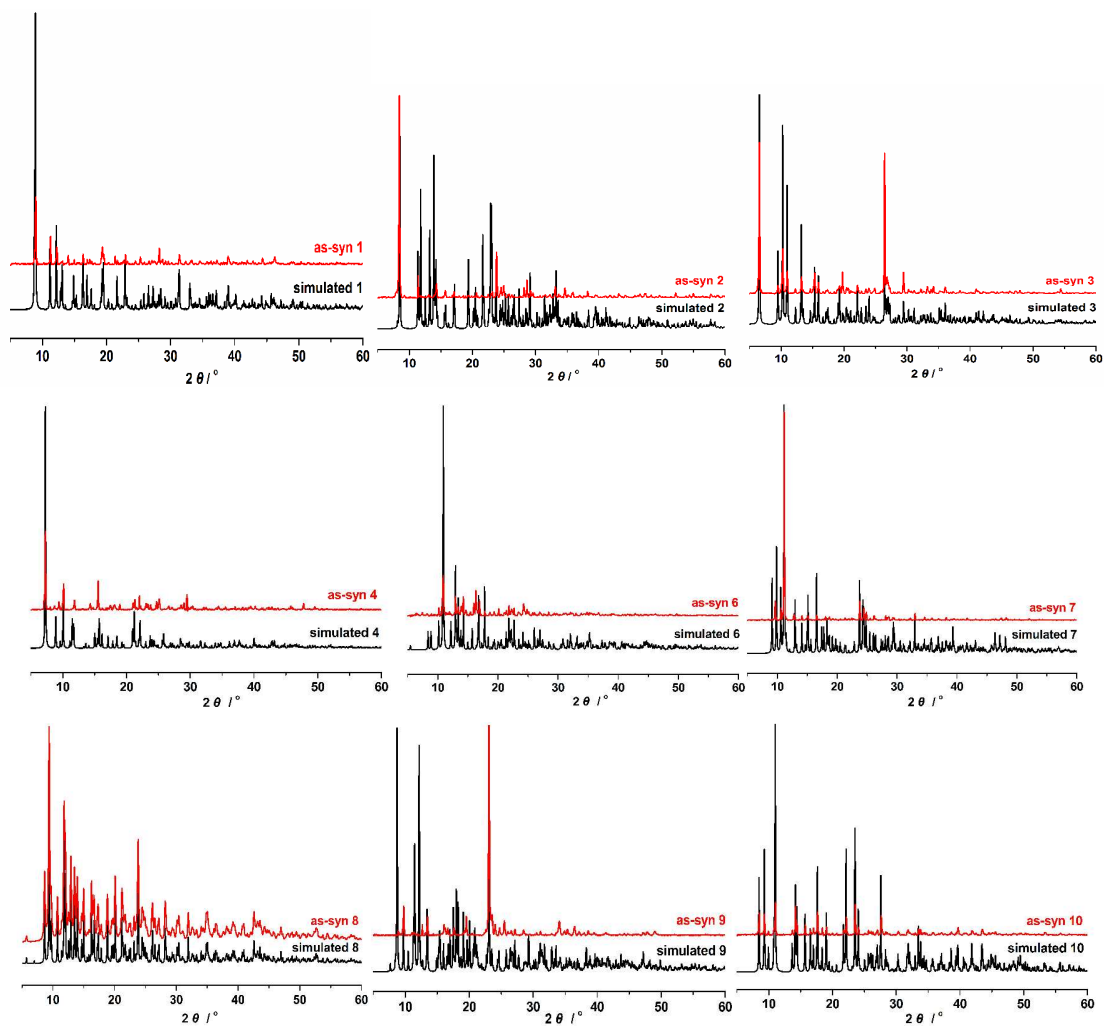


Figure S8. PXRD patterns of complexes **1-4** and **6-10**.

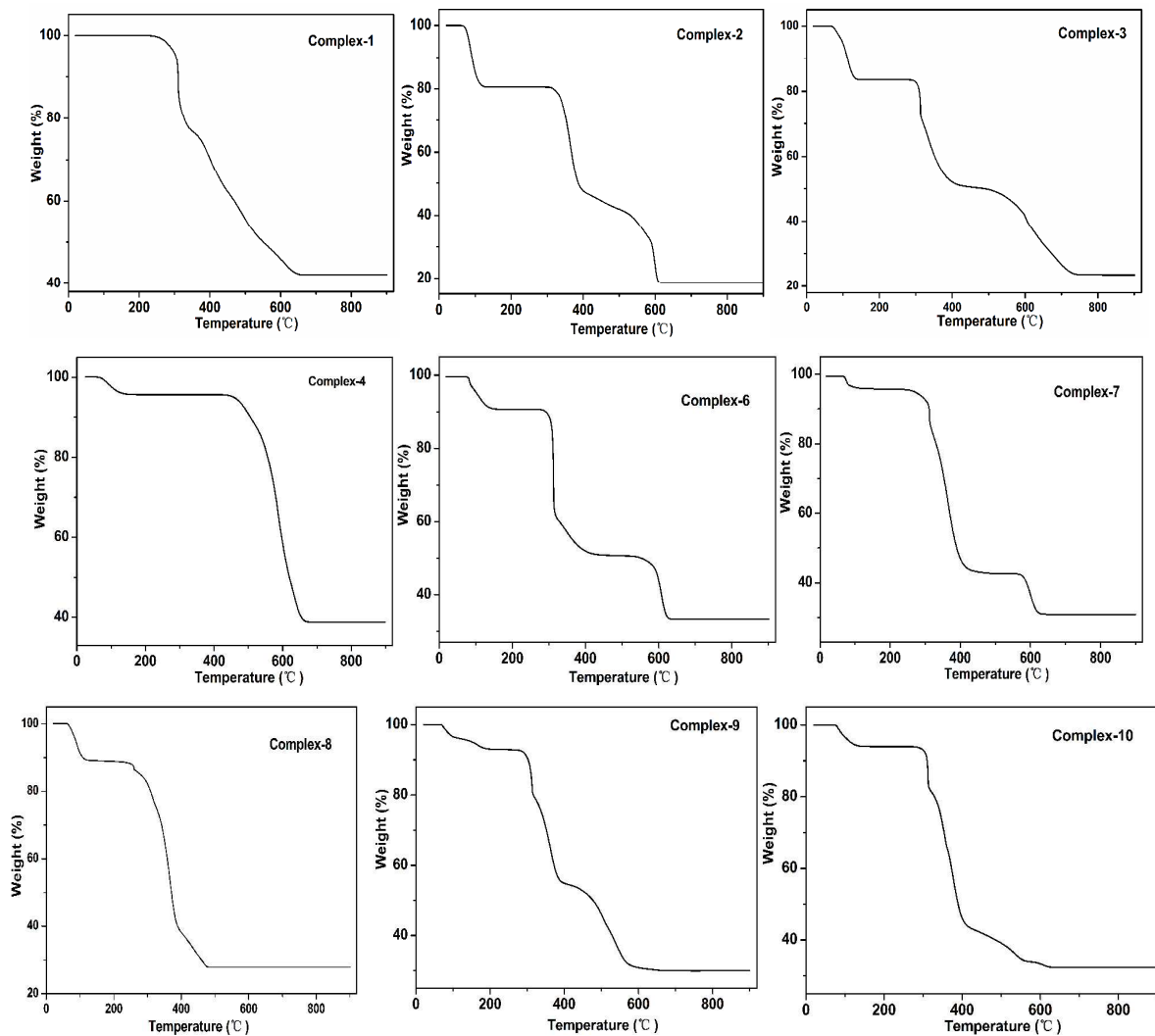


Figure S9 TG curves of complexes1-4 and 6-10.

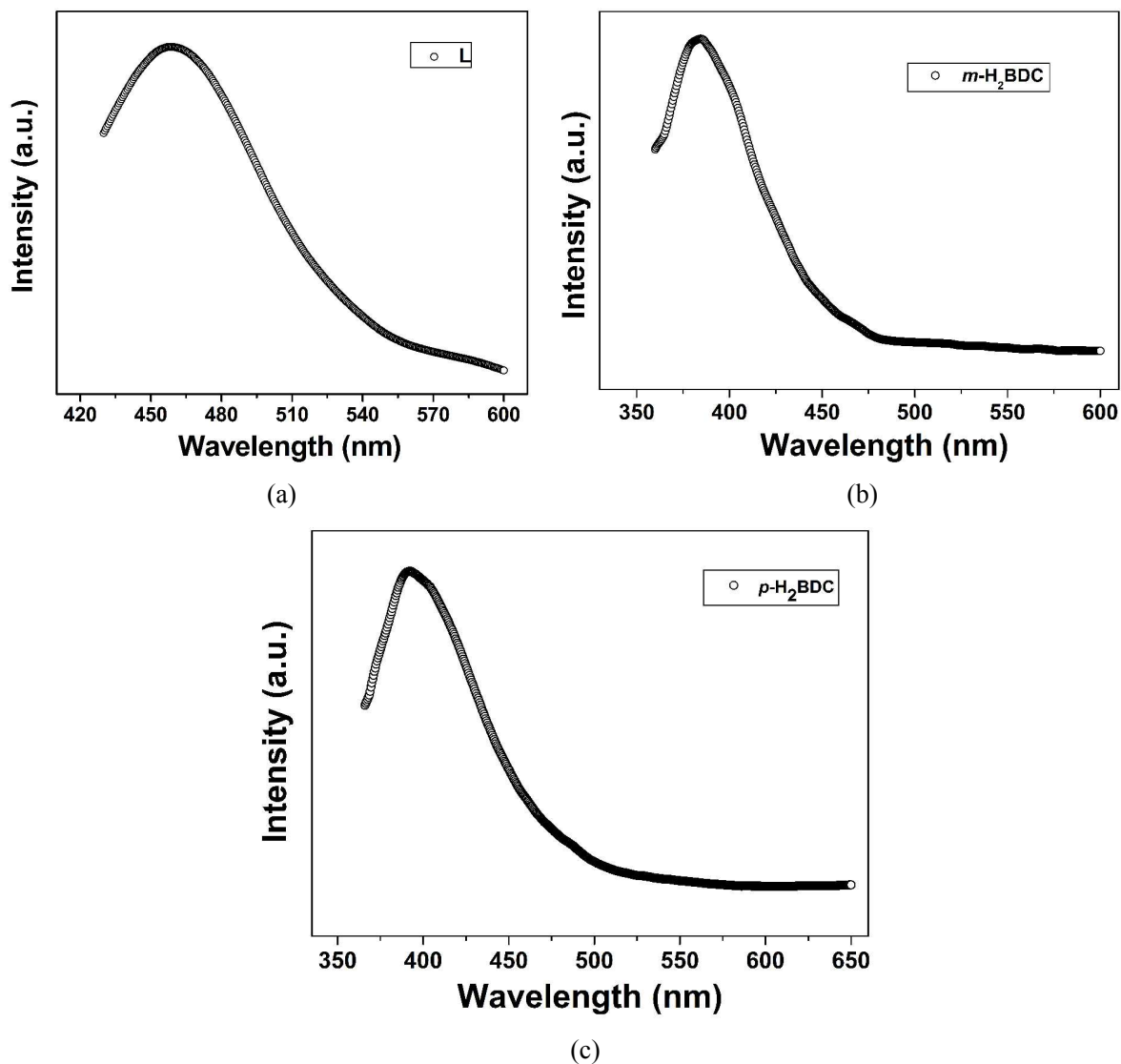


Figure S10 Emission spectra of **L** (a), ***m*-H₂BDC** (b) and ***p*-H₂BDC** (c) in the solid state at room

Table S1. Selected Bond Lengths (Å) for Complexes **1-10^a**

Complex 1			
Cd(1)-N(1)	2.330(4)	Cd(2)-N(4) ^{#3}	2.382(3)
Cd(1)-Cl(4) ^{#1}	2.5882(11)	Cd(2)-N(3)	2.389(4)
Cd(1)-Cl(1)	2.5899(12)	Cd(2)-N(2)	2.398(3)
Cd(1)-Cl(2) ^{#2}	2.6530(11)	Cd(2)-Cl(4)	2.5653(11)
Cd(1)-Cl(2)	2.6912(11)	Cd(2)-Cl(1) ^{#4}	2.6319(12)

Cd(1)-Cl(3) ^{#1}	2.7206(11)	Cd(2)-Cl(3)	2.6847(12)
Cl(1)-Cd(2) ^{#5}	2.6319(12)	Cl(3)-Cd(1) ^{#6}	2.7206(11)
Cl(2)-Cd(1) ^{#2}	2.6530(11)	Cl(4)-Cd(1) ^{#6}	2.5882(11)
Complex 2			
Cd(1)-O(5)	2.293(3)	Cd(1)-O(4)	2.293(3)
Cd(1)-O(1W)	2.298(3)	Cd(1)-N(1)	2.316(3)
Cd(1)-N(4) ^{#1}	2.338(3)	Cd(1)-O(2W)	2.380(3)
Complex 3			
Cd(1)-O(2) ^{#1}	2.318(5)	Cd(1)-N(1)	2.324(5)
Cd(1)-N(3) ^{#2}	2.375(6)	Cd(1)-O(4)	2.396(6)
Cd(1)-N(2) ^{#2}	2.418(6)	Cd(1)-O(3)	2.454(5)
Cd(1)-O(1) ^{#1}	2.691(6)		
Complex 4			
Cd(1)-O(2)	2.296(4)	Cd(2)-O(1W)	2.324(4)
Cd(1)-N(2)	2.388(5)	Cd(2)-O(1)	2.297(4)
Cd(1)-N(1) ^{#2}	2.429(5)	Cd(2)-O(3)	2.361(4)
Cd(1)-O(1)	2.626(4)	Cd(2)-Cl(2)	2.5055(17)
Cd(1)-N(3)	2.325(5)	Cd(2)-Cl(1)	2.5427(15)
Cd(1)-O(4) ^{#1}	2.395(4)	Cd(2)-Cl(1) ^{#3}	2.7110(16)
Cd(1)-O(3) ^{#1}	2.456(4)	Cl(1)-Cd(2) ^{#3}	2.7110(16)
Complex 5			
Cd(1)-O(1)	2.186(4)	Cd(1)-O(9)	2.335(5)
Cd(1)-N(1)	2.342(5)	Cd(1)-O(5)	2.350(5)
Cd(1)-O(6)	2.365(5)	Cd(1)-O(10)	2.499(5)
Cd(2)-O(3)	2.233(5)	Cd(2)-O(12) ^{#1}	2.275(5)
Cd(2)-N(4) ^{#2}	2.358(5)	Cd(2)-O(7) ^{#1}	2.388(5)
Cd(2)-O(8) ^{#1}	2.409(5)	Cd(2)-O(11) ^{#1}	2.500(5)
Cd(2)-O(4)	2.639(5)		
Complex 6			
Cd(1)-O(3)	2.245(4)	Cd(1)-O(5)	2.318(4)
Cd(1)-O(1W)	2.324(5)	Cd(1)-N(3)	2.346(4)
Cd(1)-N(2)	2.356(5)	Cd(1)-O(6)	2.482(5)
Cd(1)-O(4)	2.825(3)	Cd(2)-O(7) ^{#2}	2.526(4)
Cd(2)-N(1)	2.309(5)	Cd(2)-O(2W)	2.343(4)
Cd(2)-N(4) ^{#1}	2.347(4)	Cd(2)-O(8) ^{#2}	2.349(4)

Cd(2)-O(1)	2.377(4)	Cd(2)-O(2)	2.426(4)
Complex 7			
Cd(1)-N(1)	2.317(3)	Cd(1)-O(3) ^{#1}	2.318(3)
Cd(1)-N(4) ^{#2}	2.330(3)	Cd(1)-O(4) ^{#3}	2.334(3)
Cd(1)-O(1)	2.392(3)	Cd(1)-O(2)	2.411(3)
Cd(1)-O(4) ^{#1}	2.643(3)	Cd(2)-O(5)	2.267(3)
Cd(2)-N(2)	2.290(3)	Cd(2)-O(7) ^{#1}	2.346(3)
Cd(2)-O(8) ^{#1}	2.399(3)	Cd(2)-N(3)	2.416(3)
Cd(2)-O(5) ^{#4}	2.458(3)	Cd(2)-O(6)	
Complex 8			
Cd(1)-O(1)	2.214(5)	Cd(2)-O(3W)	2.344(4)
Cd(1)-O(5)	2.306(4)	Cd(2)-N(1) ^{#1}	2.353(5)
Cd(1)-O(1W)	2.314(5)	Cd(2)-O(3)	2.370(4)
Cd(1)-N(3)	2.347(8)	Cd(2)-O(8) ^{#2}	2.389(4)
Cd(1)-N(2)	2.360(6)	Cd(2)-O(7) ^{#2}	2.402(4)
Cd(1)-O(6)	2.467(4)	Cd(2)-O(4)	2.429(4)
Cd(2)-O(2W)	2.340(4)		
Complex 9			
Cd(1)-O(7)	2.239(6)	Cd(1)-N(1)	2.310(8)
Cd(1)-N(4) ^{#1}	2.319(8)	Cd(1)-O(5)	2.341(6)
Cd(1)-O(6) ^{#2}	2.431(7)	Cd(1)-O(5) ^{#2}	2.441(6)
Cd(1)-O(8)	2.784(6)	Cd(2)-O(10)	2.717(6)
Cd(2)-O(11)	2.266(6)	Cd(2)-N(5)	2.292(7)
Cd(2)-O(9)	2.302(6)	Cd(2)-O(3W)	2.323(7)
Cd(2)-O(4W)	2.340(7)	Cd(2)-O(12)	2.641(6)
Cd(3)-O(1)	2.229(8)	Cd(3)-O(1W)	2.345(7)
Cd(3)-N(3)	2.359(9)	Cd(3)-O(2W)	2.370(8)
Cd(3)-N(2)	2.385(8)	Cd(3)-O(4) ^{#3}	2.410(7)
Cd(3)-O(2)	2.839(8)		
Complex 10			
Cd(1)-O(2) ^{#1}	2.246(4)	Cd(1)-O(2)	2.246(4)
Cd(1)-O(6)	2.387(4)	Cd(1)-O(6) ^{#1}	2.387(4)
Cd(1)-O(1) ^{#1}	2.509(4)	Cd(1)-O(1)	2.509(4)
Cd(1)-O(5)	2.637(4)	Cd(1)-O(5) ^{#1}	2.637(4)
Cd(2)-O(7) ^{#1}	2.309(4)	Cd(2)-O(7)	2.309(4)

Cd(2)-O(4)	2.326(4)	Cd(2)-O(4) ^{#1}	2.326(4)
Cd(2)-O(3)	2.483(4)	Cd(2)-O(3) ^{#1}	2.483(4)
Cd(3)-O(2W)	2.208(6)	Cd(3)-N(1) ^{#2}	2.282(4)
Cd(3)-N(1)	2.282(4)	Cd(3)-O(1W)	2.303(5)
Cd(3)-O(1W) ^{#2}	2.303(5)	Cd(3)-O(8)	2.842(2)
Cd(3)-O(8) ^{#2}	2.842(2)		

^aSymmetry codes: For **1**, #1: -x+1, y-1/2, -z+3/2; #2: -x+2, -y+1, -z+2; #3: x, -y+3/2, z+1/2; #4 x-1, y, z; #5: x+1, y, z; #6: -x+1, y+1/2, -z+3/2. For **2**, #1: x, y, z+1. For **3**, #1: -x+2, y+1/2, -z+3/2; #2: x, -y+3/2, z+1/2. For **4**, #1: x-1/2, -y+1/2, -z+1; #2: -x+1/2, y+1/2, z; #3 -x+1,-y+1,-z+1. For **5**, #1: x-1, -y+3/2, z+1/2; #2 x+1, y, z+1. For **6**, #1: x-1, y-1, z; #2: -x, -y+1, -z+1. For **7**, #1: x, y+1, z; #2: x+1/2, -y+3/2, z+1/2; #3: -x+1, -y+1, -z+1; #4: -x+1/2, -y+3/2, -z+1. For **8**, #1: -x+1, -y, -z+1; #2: x+1, y-1, z+1. For **9**, #1: -x+1, -y+2, -z+1; #2: -x, -y+2, -z+1; #3: x, y+1, z. For **10**, #1: -x, y, -z+1/2; #2: -x+1, y, -z+1/2.

Table S2. Hydrogen Bond Parameters for Complexes **1-10^a**

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Complex 1				
N(2)-H(2N)...Cl(2) ^{#4}	0.86(4)	2.727(15)	3.569(4)	168(4)
N(3)-H(3N)...Cl(2) ^{#8}	0.86(4)	2.62(2)	3.410(4)	154(4)
Complex 2				
O(1W)-H(1W1)...O(7W) ^{#3}	0.85(5)	1.988(15)	2.826(5)	169(5)
O(1W)-H(1W2)...O(7) ^{#4}	0.85(5)	1.882(12)	2.723(5)	172(5)
O(2W)-H(2W1)...O(7) ^{#4}	0.85(4)	1.96(3)	2.723(4)	148(5)
O(2W)-H(2W2)...O(3W) ^{#5}	0.85(6)	2.16(2)	2.987(6)	163(5)
O(3W)-H(3W1)...O(1) ^{#6}	0.85(6)	2.00(5)	2.764(6)	149(10)
O(3W)-H(3W2)...O(6) ^{#5}	0.85(6)	1.913(13)	2.763(6)	175(9)
O(4W)-H(4W1)...O(8) ^{#7}	0.85(6)	2.31(9)	2.837(6)	120(8)
O(4W)-H(4W2)...O(8)	0.85(6)	2.05(3)	2.871(6)	162(9)
O(5W)-H(5W1)...O(3W)	0.85(8)	2.03(2)	2.869(8)	166(7)
O(5W)-H(5W2)...O(4W)	0.85(7)	1.95(2)	2.757(7)	157(6)
O(6W)-H(6W2)...O(1) ^{#8}	0.85(6)	2.12(2)	2.926(6)	159(5)
O(6W)-H(6W1)...O(2)	0.85(5)	1.929(14)	2.757(5)	165(4)
O(7W)-H(7W1)...O(8W)	0.85(5)	1.947(14)	2.781(5)	166(5)
O(7W)-H(7W2)...O(4) ^{#8}	0.85(4)	2.018(14)	2.863(4)	172(6)

O(8W)-H(8W1)...O(2)	0.85(5)	2.009(19)	2.836(5)	164(5)
O(8W)-H(8W2)...O(2) ^{#3}	0.85(6)	2.06(2)	2.878(6)	160(6)
N(2)-H(2N1)...O(3) ^{#6}	0.86(4)	2.26(3)	2.910(4)	133(3)
N(2)-H(2N1)...O(7W) ^{#2}	0.86(5)	2.23(2)	2.918(5)	136(3)
N(2)-H(2N2)...O(5W)	0.86(5)	1.884(13)	2.725(5)	165(4)
N(3)-H(3N2)...O(6) ^{#7}	0.86(4)	1.916(15)	2.763(4)	168(4)
N(3)-H(3N2)...O(6) ^{#7}	0.86(4)	1.916(15)	2.763(4)	168(4)
N(3)-H(3N2)...O(7) ^{#7}	0.86(5)	2.61(3)	3.226(5)	130(3)
Complex 3				
O(1W)-H(1W1)...O(4W) ^{#5}	0.85	2.04	2.868(14)	166.5
O(1W)-H(1W2)...O(5W)	0.85	1.96	2.795(14)	166.1
O(2W)-H(2W1)...O(2)	0.85	1.92	2.759(12)	170.8
O(2W)-H(2W2)...O(4W) ^{#3}	0.85	1.89	2.728(14)	169.3
O(3W)-H(3W1)...N(4)	0.85	1.92	2.767(14)	171.4
O(3W)-H(3W2)...O(2W) ^{#4}	0.85	1.87	2.714(16)	171.6
O(4W)-H(4W1)...O(1)	0.85	1.87	2.722(12)	179.1
O(4W)-H(4W2)...O(1) ^{#5}	0.85	2.52	3.367(12)	179.1
O(5W)-H(5W1)...O(4)	0.85	1.97	2.711(13)	144.5
N(2)-H(2N)...O(3) ^{#6}	0.86(8)	2.504(19)	3.351(8)	170(7)
N(3)-H(3N)...O(1W) ^{#7}	0.86(1)	2.28(6)	2.973(1)	138(8)
Complex 4				
O(1W)-H(1W1)...O(2) ^{#4}	0.85(6)	1.882(17)	2.722(6)	171(7)
O(1W)-H(1W2)...N(4) ^{#6}	0.85(9)	2.05(3)	2.867(9)	162(8)
N(2)-H(2N)...Cl(2) ^{#5}	0.86(5)	2.76(4)	3.495(5)	144(6)
N(2)-H(2N)...Cl(1) ^{#1}	0.86(5)	2.97(5)	3.601(5)	132(6)
N(3)-H(3N)...Cl(2)	0.86(6)	2.72(4)	3.499(6)	151(7)
Complex 5				
O(1W)-H(1W1)...O(2)	0.85(1)	2.01(7)	2.783(1)	151(13)
O(1W)-H(1W2)...O(4W)	0.85(2)	2.22(12)	2.874(2)	134(15)
O(2W)-H(2W1)...O(3W)	0.85(8)	1.85(2)	2.665(8)	162(7)
O(2W)-H(2W2)...O(1W)	0.85(9)	1.84(3)	2.664(9)	163(6)
O(3W)-H(3W1)...O(4)	0.85(8)	1.93(3)	2.743(8)	161(10)
O(3W)-H(3W2)...O(12) ^{#5}	0.85(7)	1.881(15)	2.728(7)	174(9)
O(4W)-H(4W1)...O(6)	0.85(8)	1.98(3)	2.815(8)	169(14)
O(4W)-H(4W2)...O(11) ^{#6}	0.845(8)	2.30(11)	2.923(8)	130(12)

N(2)-H(2N1)...O(7) ^{#7}	0.86(6)	1.792(17)	2.648(6)	169(7)
N(2)-H(2N2)...O(2W) ^{#8}	0.86(7)	1.965(14)	2.823(7)	170(5)
N(3)-H(3N1)...O(2W) ^{#8}	0.86(7)	1.926(16)	2.773(7)	170(5)
N(3)-H(3N2)...O(10) ^{#9}	0.86(6)	1.895(14)	2.737(6)	169(5)
Complex 6				
O(1W)-H(1W1)...O(2) ^{#6}	0.85(6)	1.856(19)	2.696(6)	170(8)
O(1W)-H(1W2)...O(3W)	0.85(1)	1.96(3)	2.783(1)	163(7)
O(2W)-H(2W1)...O(3)	0.85(5)	1.889(17)	2.729(5)	170(6)
O(2W)-H(2W2)...O(5)	0.85(6)	2.47(5)	3.075(6)	129(5)
O(2W)-H(2W2)...O(7) ^{#2}	0.85(6)	2.58(6)	2.986(6)	110(5)
N(2)-H(2N)...O(4W)	0.86(2)	2.40(5)	3.104(2)	140(6)
N(3)-H(3N)...O(4)	0.86(6)	2.30(5)	2.955(6)	133(6)
Complex 7				
O(1W)-H(1W1)...O(2)	0.85(6)	2.14(3)	2.959(6)	158(6)
O(1W)-H(1W2)...O(2) ^{#3}	0.85(6)	2.42(6)	3.071(6)	133(7)
O(2W)-H(2W1)...O(7) ^{#7}	0.85(5)	1.963(15)	2.806(5)	172(7)
O(2W)-H(2W2)...O(1)	0.85(5)	2.092(16)	2.926(5)	168(6)
N(2)-H(2N)...O(2W)	0.86(5)	2.169(19)	2.986(5)	159(4)
Complex 8				
O(1W)-H(1W1)...O(2) ^{#4}	0.85	2.14	2.951(9)	160.2
O(1W)-H(1W2)...O(5) ^{#4}	0.85	1.92	2.733(7)	158.5
O(2W)-H(2W1)...O(8) ^{#5}	0.85	1.97	2.754(7)	152.1
O(2W)-H(2W2)...O(3W) ^{#6}	0.85	2.14	2.924(5)	153.3
O(3W)-H(3W1)...O(4W) ^{#4}	0.85(6)	1.89(2)	2.718(6)	163(5)
O(3W)-H(3W2)...O(4) ^{#7}	0.85(6)	1.896(18)	2.730(6)	166(5)
O(4W)-H(4W1)...O(7)	0.85(6)	1.989(16)	2.834(7)	173(8)
O(4W)-H(4W2)...O(5W)	0.85(6)	1.914(16)	2.757(9)	174(9)
O(5W)-H(5W1)...O(6) ^{#8}	0.85(6)	2.40(15)	2.757(10)	106(12)
O(5W)-H(5W2)...N(4) ^{#9}	0.85(6)	2.01(6)	2.784(12)	152(11)
O(6W)-H(6W1)...O(3) ^{#9}	0.85(6)	1.98(3)	2.818(7)	166(11)
O(6W)-H(6W2)...O(1)	0.85(6)	2.40(9)	2.849(10)	113(8)
N(2)-H(2N)...O(6W)	0.86(8)	2.16(3)	2.988(8)	161(8)
Complex 9				
O(1W)-H(1W1)...O(11) ^{#7}	0.85(1)	2.01(8)	2.751(1)	145(12)
O(1W)-H(1W2)...O(9) ^{#7}	0.85(1)	2.07(7)	2.806(1)	145(11)

O(2W)-H(2W1)...O(3) ^{#3}	0.85(1)	1.77(3)	2.613(1)	172(14)
O(2W)-H(2W1)...O(4) ^{#3}	0.85(1)	2.43(10)	3.015(1)	126(10)
O(2W)-H(2W2)...O(10) ^{#8}	0.85(1)	2.27(8)	3.005(1)	145(12)
O(3W)-H(3W1)...N(6) ^{#9}	0.85	2.20	2.79(3)	126.7
O(3W)-H(3W1)...N(6) ^{#9}	0.85	2.38	2.91(3)	120.1
O(3W)-H(3W2)...O(10) ^{#9}	0.85	2.04	2.888(10)	172.1
O(4W)-H(4W1)...O(12) ^{#10}	0.85(1)	1.99(4)	2.816(1)	163(12)
O(4W)-H(4W2)...O(3) ^{#11}	0.85(9)	1.90(2)	2.750(9)	177(12)
O(5W)-H(5W1)...O(7)	0.85(1)	1.97(8)	2.775(1)	157(20)
O(5W)-H(5W2)...O(2) ^{#8}	0.85(2)	2.53(16)	3.133(2)	128(17)
N(2)-H(2N)...O(5W) ^{#8}	0.86(2)	2.21(5)	3.026(2)	159(12)
N(3)-H(3N)...O(4) ^{#3}	0.86(1)	2.49(13)	2.954(1)	115(11)
N(6)-H(6)...O(3W) ^{#9}	0.86	2.38	2.91(3)	120.0
N(6')-H(6')...O(3W) ^{#9}	0.86	2.29	2.79(3)	117.4
N(6')-H(6')...O(2W) ^{#8}	0.86	2.53	3.11(2)	125.1

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O(1W)-H(1W1)...O(3) ^{#6}	0.85(6)	1.890(14)	2.736(6)	175(8)
O(1W)-H(1W2)...O(8)	0.85(6)	2.48(6)	2.935(6)	114(5)
O(1W)-H(1W2)...O(1)	0.85(7)	2.43(6)	3.055(7)	131(6)
O(2W)-H(2W)...O(3W) ^{#2}	0.85(7)	1.858(16)	2.700(7)	173(9)
O(3W)-H(3W1)...O(1) ^{#7}	0.85(7)	2.063(13)	2.912(7)	177(9)
O(3W)-H(3W2)...O(7)	0.85(7)	2.10(3)	2.917(7)	162(8)
N(2)-H(2N1)...O(4) ^{#8}	0.86(6)	1.979(17)	2.827(6)	168(6)
N(2)-H(2N2)...O(5) ^{#2}	0.86(6)	1.956(14)	2.807(6)	170(5)

^aSymmetry codes: For **1**, #4: x-1, y, z; #8: x-1, -y+3/2, z-1/2. For **2**, #2: x, y, z-1; #3: -x-1, -y-1, -z+2; #4: x-1, y, z; #5: -x-1, -y, -z+1; #6: -x-1, -y-1, -z+1; #7: -x, -y, -z+1; #8: -x, -y-1, -z+2. For **3**, #3: -x+2, y-1/2, -z+3/2; #4: x, -y+3/2, z-1/2; #5: -x+2, -y+1, -z+2; #6: -x+2, -y+1, -z+1; #7: x, y, z-1. For **4**, #1: x-1/2, -y+1/2, -z+1; #4: x+1/2, -y+1/2, -z+1; #5: -x+1/2, y-1/2, z; #6: -x+1, y, -z+1/2. For **5**, #5: -x+2, y-1/2, -z+3/2; #6: x, -y+3/2, z+1/2; #7: x-1, y, z; #8: -x+1, -y+1, -z+1; #9: x-1, -y+3/2, z-1/2. For **6**, #2: -x, -y+1, -z+1; #6: x, y+1, z. For **7**, #3: -x+1, -y+1, -z+1; #7: -x+1/2, -y+1/2, -z+1. For **8**, #4: -x+1, -y, -z; #5: -x+2, -y, -z; #6: -x+3, -y-1, -z+1; #7: -x+2, -y-1, -z+1; #8: -x, -y+1, -z; #9: x-1, y, z. For **9**, #3: x, y+1, z; #7: -x+1, -y+1, -z+1; #8: -x, -y+1, -z+1; #9: -x, -y+1, -z+2; #10: -x, -y, -z+2; #11: -x, -y, -z+1. For **10**, #2: -x+1, y, -z+1/2; #6: -x+1/2, y-1/2, -z+1/2; #7: -x+1/2, y+1/2, -z+1/2; #8: -x+1, -y+1, -z+1.