crystals

Supplementary Materials: Breathing 3D Frameworks with T-Shaped Connecting Ligand Exhibiting Solvent Induction, Metal Ions Effect and Luminescent Properties

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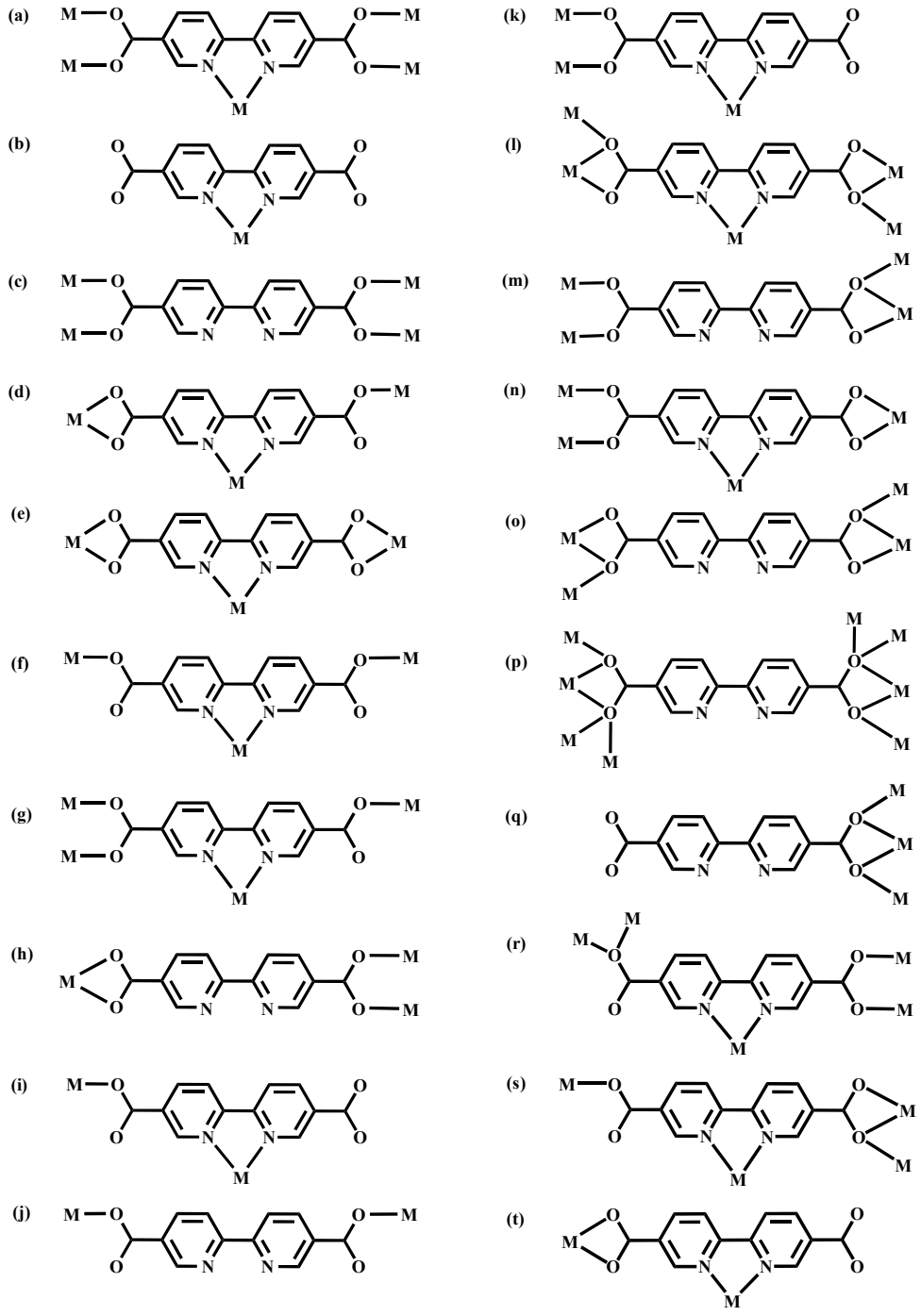


Scheme S1. Coordination modes displayed by H_2bpdc ligand in metal complexes, as retrieved from the Cambridge Structural Database (CSD version 5.38, updated to Feb 2017)

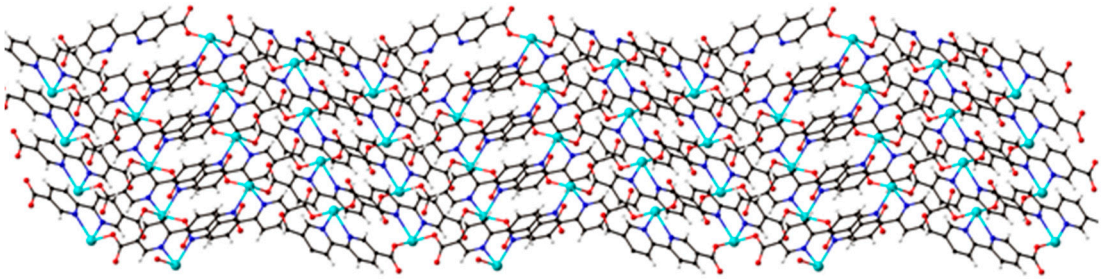
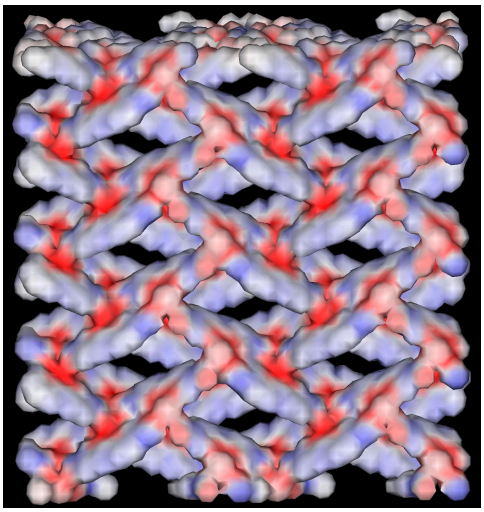
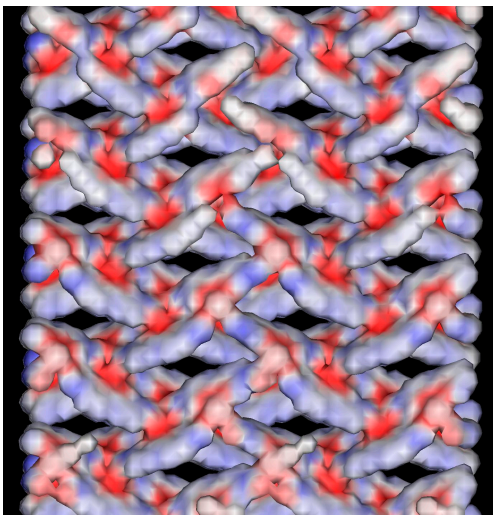


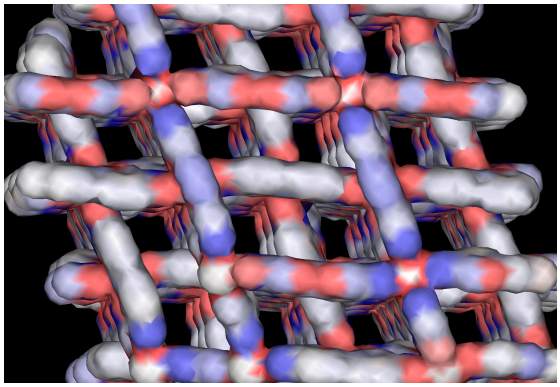
Figure S1. The wavy 2D layer structure of Cd1bpdc(N1,2).



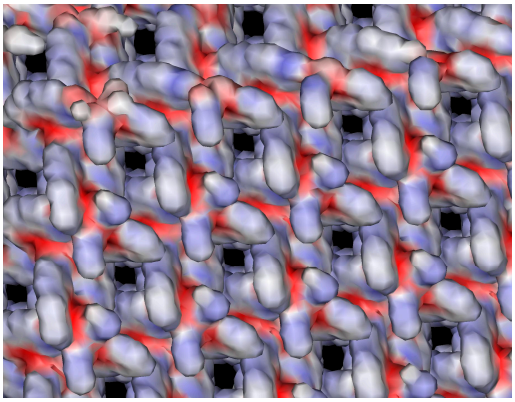
(**a**)



(**b**)



(**c**)



(**d**)

Figure S2. View of the 3D porous structure of **1** from direction on *a*-axis (**a**), *c*-axis (**b**), (101) (**c**) and (111) (**d**).

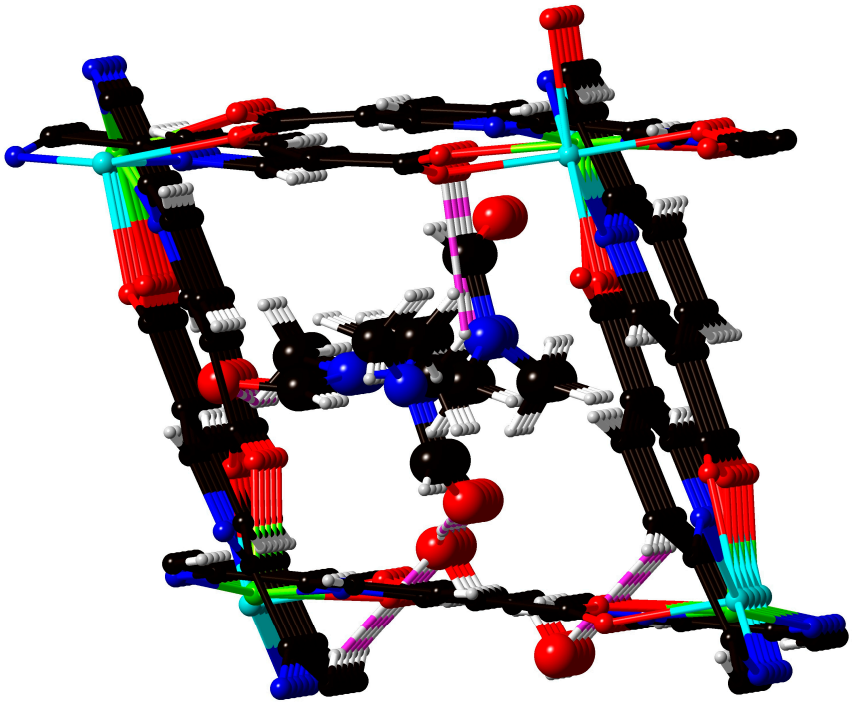


Figure S3. The hydrogen bonding interactions (multi-color bonds) for the DMF and H_2O molecules in complex **1**.

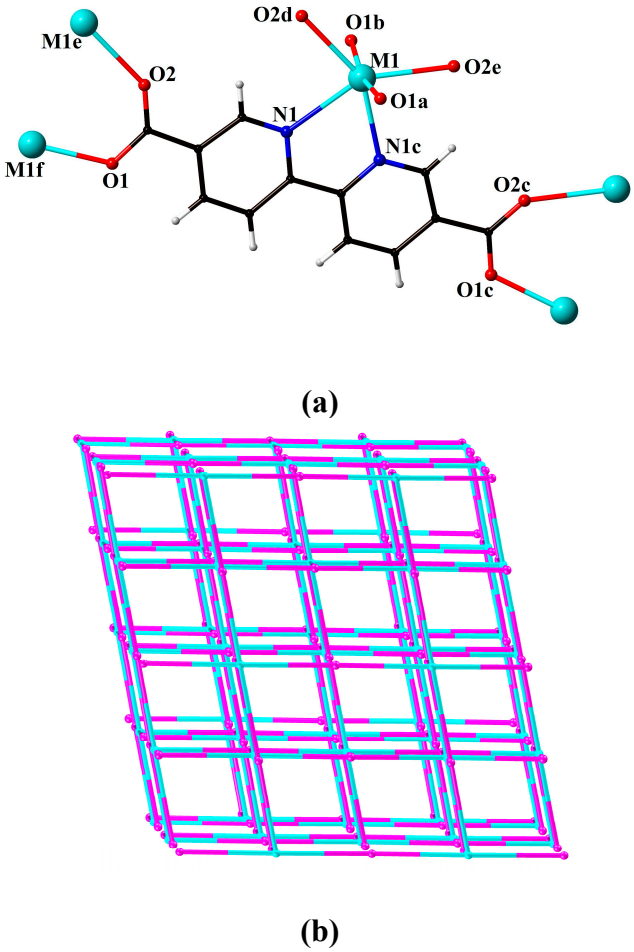
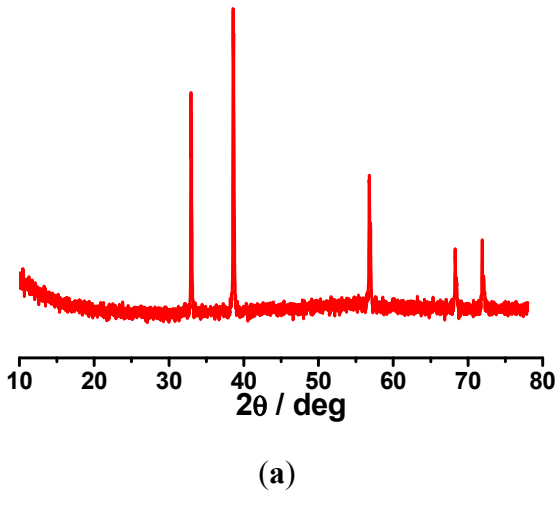
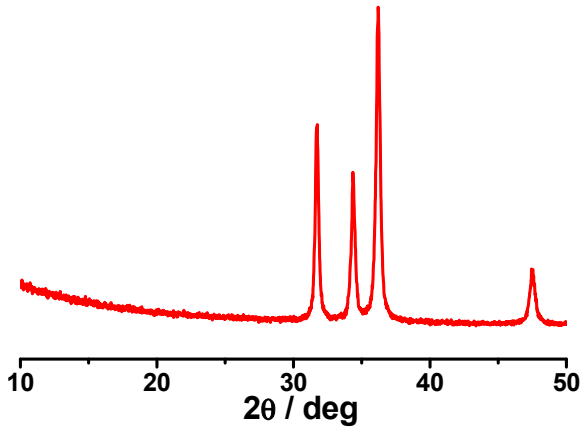


Figure S4 (**a**) The coordination environments of metal atoms and $bpdc^{2-}$ ligand and (**b**) the **ant** topological network for **2** and **3**. (cyan balls and purple balls represent dinuclear units and $bpdc^{2-}$ ligands respectively)





(**b**)

Figure S5. The PXRD patterns for the rest samples of **2** (**a**) and **3** (**b**) after TGA analysis, which corresponded to the patterns of CdO (monteponite, syn) and ZnO (Zincite, syn) respectively.

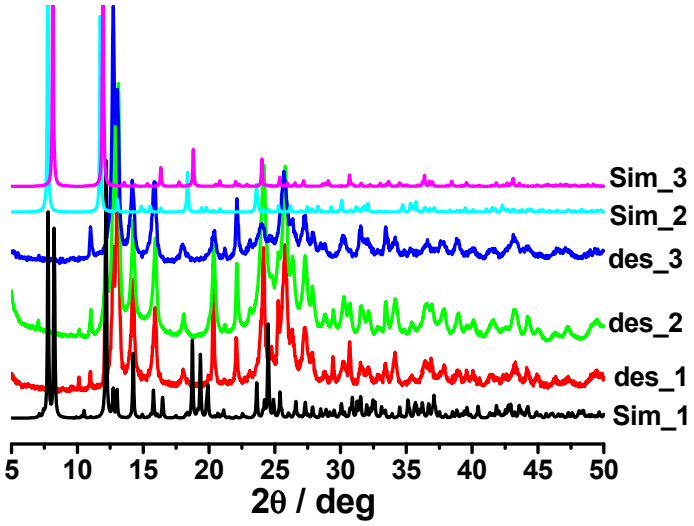


Figure S6. The XPRD patterns for desolvated samples of **1**-**3**.

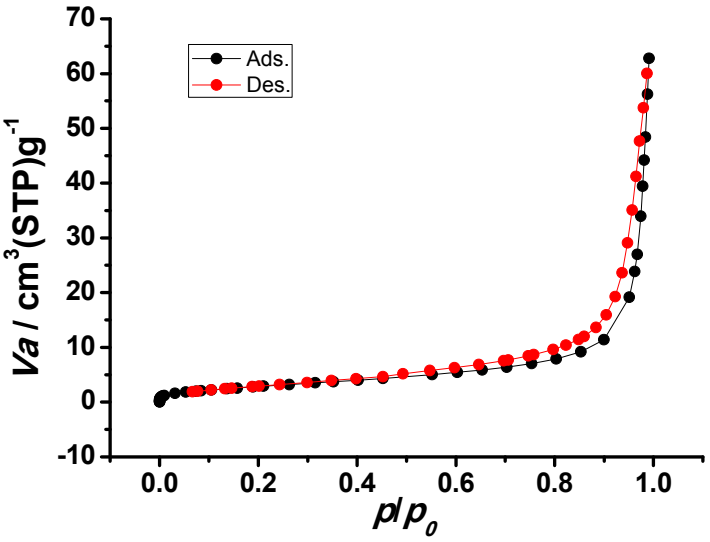


Figure S7. The N2 adsorption data at 77 K of the activated samples of **1**.

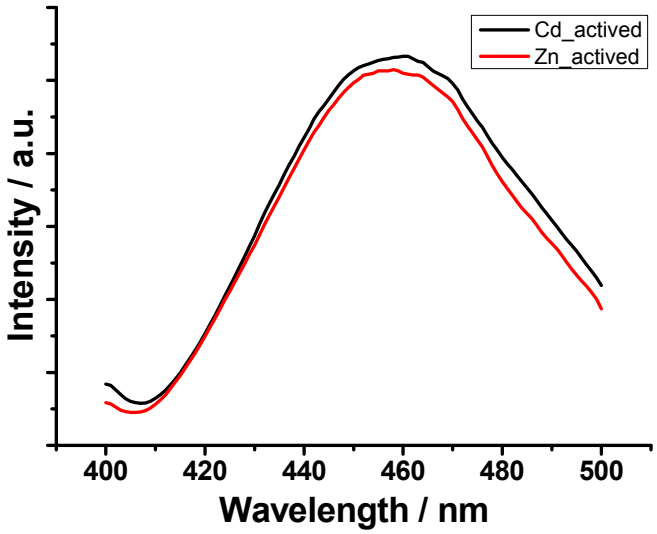


Figure S8 The luminescent properties for active samples of two metal complexes excited at 363 nm.

Table S1. Selected bond lengths (Å) and angles (°) for **1**-**3**.

1			
Cd(1)-O(3a)	2.166(4)	Cd(2)-O(8b)	2.165(4)
Cd(1)-O(5)	2.166(4)	Cd(2)-O(2c)	2.184(4)
Cd(1)-N(1)	2.390(4)	Cd(2)-N(4d)	2.372(4)
Cd(1)-N(2)	2.394(4)	Cd(2)-N(3d)	2.388(4)
Cd(1)-O(7b)	2.414(4)	Cd(2)-O(4a)	2.415(4)
Cd(1)-O(1c)	2.446(4)	Cd(2)-O(6)	2.420(3)
O(3a)-Cd(1)-O(5)	168.42(13)	O(8b)-Cd(2)-O(2c)	169.22(14)
O(3a)-Cd(1)-N(1)	95.90(14)	O(8b)-Cd(2)-N(4d)	91.40(15)
O(5)-Cd(1)-N(1)	92.06(14)	O(2c)-Cd(2)-N(4d)	96.46(14)
O(3a)-Cd(1)-N(2)	90.64(14)	O(8b)-Cd(2)-N(3d)	104.84(15)

O(5)-Cd(1)-N(2)	100.10(14)	O(2c)-Cd(2)-N(3d)	84.93(15)
N(1)-Cd(1)-N(2)	68.70(14)	N(4d)-Cd(2)-N(3d)	68.96(14)
O(3a)-Cd(1)-O(7b)	89.86(14)	O(8b)-Cd(2)-O(4a)	87.43(14)
O(5)-Cd(1)-O(7b)	87.23(14)	O(2c)-Cd(2)-O(4a)	86.43(14)
N(1)-Cd(1)-O(7b)	150.90(13)	N(4d)-Cd(2)-O(4a)	81.73(13)
N(2)-Cd(1)-O(7b)	82.77(13)	N(3d)-Cd(2)-O(4a)	148.20(13)
O(3a)-Cd(1)-O(1c)	88.02(14)	O(8b)-Cd(2)-O(6)	90.64(14)
O(5)-Cd(1)-O(1c)	84.82(13)	O(2c)-Cd(2)-O(6)	86.08(13)
N(1)-Cd(1)-O(1c)	81.71(13)	N(4d)-Cd(2)-O(6)	150.92(13)
N(2)-Cd(1)-O(1c)	150.09(13)	N(3d)-Cd(2)-O(6)	82.50(13)
O(7b)-Cd(1)-O(1c)	127.09(12)	O(4a)-Cd(2)-O(6)	127.34(12)
		2	
Cd(1)-O(1a)	2.171(2)	Cd(1)-N(1c)	2.396(3)
Cd(1)-O(1)	2.171(2)	Cd(1)-O(2d)	2.418(2)
Cd(1)-N(1b)	2.396(3)	Cd(1)-O(2e)	2.418(2)
O(1a)-Cd(1)-O(1)	167.10(13)	N(1b)-Cd(1)-O(2d)	150.48(9)
O(1a)-Cd(1)-N(1b)	92.28(11)	N(1c)-Cd(1)-O(2d)	82.01(8)
O(1)-Cd(1)-N(1b)	98.38(10)	O(1a)-Cd(1)-O(2e)	86.59(11)
O(1a)-Cd(1)-N(1c)	98.38(10)	O(1)-Cd(1)-O(2e)	87.70(11)
O(1)-Cd(1)-N(1c)	92.28(11)	N(1b)-Cd(1)-O(2e)	82.01(8)
N(1b)-Cd(1)-N(1c)	68.77(12)	N(1c)-Cd(1)-O(2e)	150.48(9)
O(1a)-Cd(1)-O(2d)	87.70(11)	O(2d)-Cd(1)-O(2e)	127.41(12)
O(1)-Cd(1)-O(2d)	86.59(11)		
		3	
Zn(1)-O(1a)	1.947(4)	Zn(1)-N(1c)	2.208(4)
Zn(1)-O(1b)	1.947(4)	Zn(1)-O(2d)	2.384(3)
Zn(1)-N(1)	2.208(4)	Zn(1)-O(2e)	2.384(3)
O(1a)-Zn(1)-O(1b)	167.5(2)	N(1)-Zn(1)-O(2d)	157.88(14)
O(1a)-Zn(1)-N(1)	97.57(15)	N(1c)-Zn(1)-O(2d)	83.92(13)
O(1b)-Zn(1)-N(1)	92.38(15)	O(1a)-Zn(1)-O(2e)	86.79(14)
O(1a)-Zn(1)-N(1c)	92.38(15)	O(1b)-Zn(1)-O(2e)	86.80(14)
O(1b)-Zn(1)-N(1c)	97.57(16)	N(1)-Zn(1)-O(2e)	83.91(13)
N(1)-Zn(1)-N(1c)	74.3(2)	N(1c)-Zn(1)-O(2e)	157.87(14)
O(1a)-Zn(1)-O(2d)	86.80(14)	O(2d)-Zn(1)-O(2e)	118.07(17)
O(1b)-Zn(1)-O(2d)	86.79(14)		

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

Table S2. Selected Hydrogen bond lengths (Å) and angles (°) for **1**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...O(9)	0.85	2.04	2.881(7)	171.9
O(1W)-H(1WB)...O(9g)	0.85	2.05	2.896(7)	171.9
C(10)-H(10A)...O(11h)	0.95	2.54	3.056(11)	114.0
C(16)-H(16A)...O(1Wi)	0.95	2.62	3.409(8)	141.0
C(25)-H(25A)...O(2c)	0.95	2.41	3.332(7)	164.3
C(27)-H(27C)...O(5j)	0.98	2.63	3.500(8)	147.4
C(29)-H(29A)...O(10)	0.98	2.28	2.87(2)	117.3
C(30)-H(30C)...O(8k)	0.98	2.58	3.340(14)	134.0
C(32)-H(32C)...O(3l)	0.98	2.66	3.515(14)	146.0

Symmetry codes: c) -x+1, -y+1, -z+1; g) -x, -y+1, -z; h) -x+1, -y+1, -z+2; i) x, y, z+1; j) x, y, z-1; k) x, -y+3/2, z-1/2; l) -x+1, y+1/2, -z+3/2.