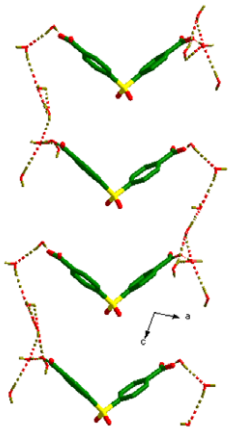


Fig. S1 Viewing of zigzag chain in compound **6**.

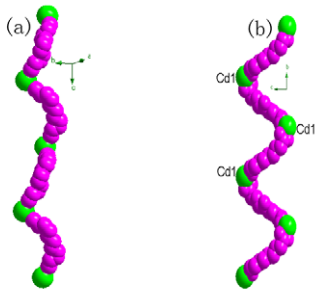


Fig. S2 Viewing of two helical chains in compound **11**.

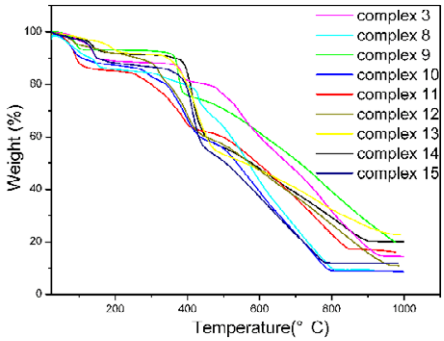


Fig. S3 TG curves of the complexes.

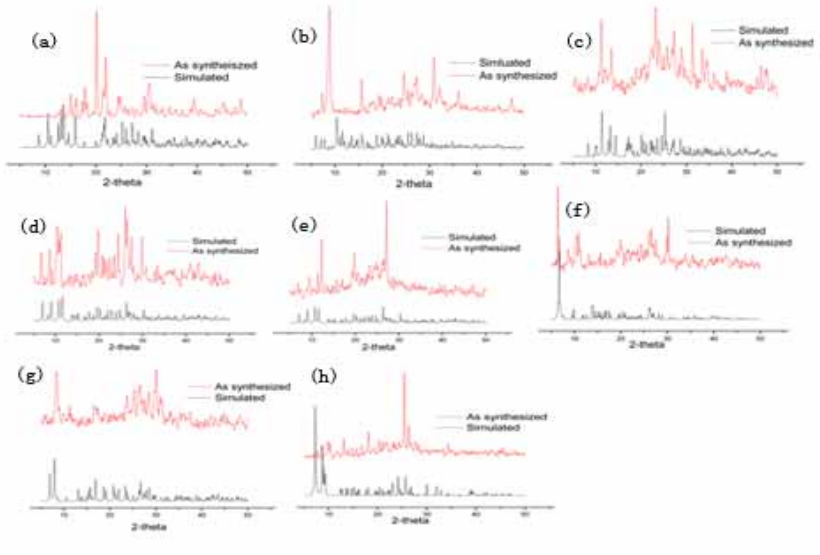
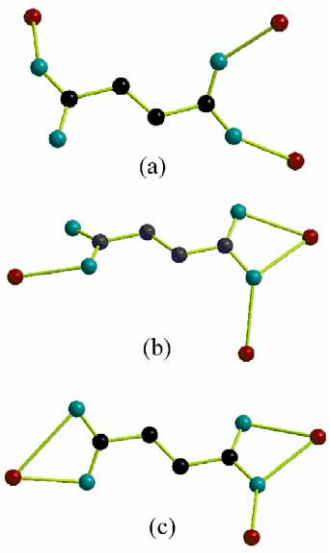
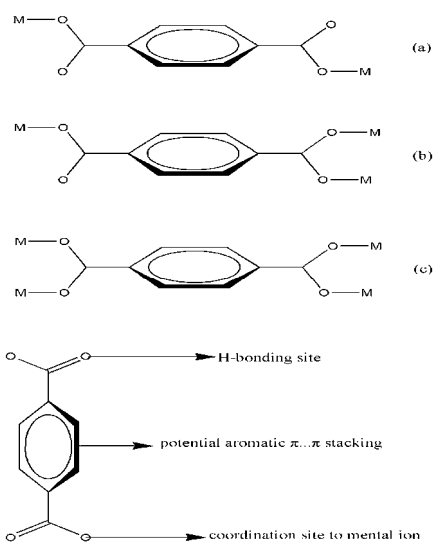


Fig.4S (a) Comparison of XRPD patterns of the simulated pattern from the single-crystal structure determination, the as-synthesized product in compound **4**. (b) in compound **6**. (c) in compound **7**. (d) in compound **9**. (e) in compound **10**. (f) in compound **12**. (g) in compound **13**. (h) in compound **14.**



Scheme S1 The different coordinative modes of fum ligand in **8**, **9** and **10**.



Scheme S2. The different coordinative modes of 1,4-BDC ligand in **13**-**15**.

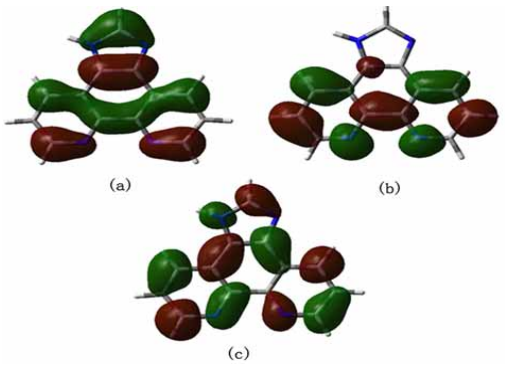


Fig. S5 Sketch of the main molecular orbital involved in the dominant dipole-allowed transition for IP, obtained at the B3LYP/6-31G* level of approximation.

Table S1. Selected bond distances (Å) and angles (°)

Complex **2**			
Zn(1)−O(4)	2.101(3)	Zn(1)−O(5)	2.095(2)
Zn(1)−O(6)	2.135(3)	Zn(1)−N(1)	2.131(3)
Zn(1)−N(2)	2.152(3)	Zn(1)−O(3)#1	2.099(2)
O(4) −Zn(1)−O(5)	92.39(10)	O(4) −Zn(1)−O(6)	173.70(10)
O(5)−Zn(1)−N(1)	171.74(10)	O(5)−Zn(1)−N(2)	94.15(10)
O(3)#1−Zn(1)−N(2)	168.61(10)		

Symmetry codes: #1: 2-x,1/2+y,1/2-z.

Complex **3**

Mn(1)−O(1)	2.185(3)	Mn(1)−O(2)	2.194(3)
Mn(1)−O(3)	2.140(3)	Mn(1)−N(1)	2.247(4)
Mn(1)−N(2)	2.261(4)	Mn(1)−O(6)#1	2.152(3)
O(1)−Mn(1)−O(2)	94.08(13)	O(1)−Mn(1)−O(3)	174.25(13)
O(2)−Mn(1)−N(1)	168.73(13)	O(2)−Mn(1)−N(2)	95.41(13)
O(2)−Mn(1)−O(6)#1	97.66(12)	O(3)−Mn(1)−N(1)	88.43(14)
O(3)−Mn(1)−N(2)	96.05(13)	O(3)−Mn(1)−O(6)#1	91.84(12)

Symmetry codes: #1: 1-x,1/2+y,1/2-z ;

Complex **4**

Zn(1)−O(1)	2.076(2)	Zn(1)−O(2)	2.173(3)
Zn(1)−O(3)	2.090(3)	Zn(1)−O(4)	2.092(2)
Zn(1)−N(1)	2.151(3)	Zn(1)−N(4)	2.148(3)
O(1)−Zn(1)−O(2)	85.40(10)	O(1)−Zn(1)−O(3)	86.89(10)
O(1)−Zn(1)−O(4)	98.65(9)	O(1)−Zn(1)−N(1)	167.16(10)
O(1)−Zn(1)−N(4)	93.45(10)	O(2)−Zn(1)−O(3)	172.07(10)
O(4)−Zn(1)−N(1)	92.47(10)	O(4)−Zn(1)−N(4)	163.24(11)

Complex **5**

Co(1)−O(1)	2.100(2)	Co(1)−O(2)	2.067(2)
Co(1)−O(3)	2.147(2)	Co(1)−O(4)	2.097(2)
Co(1)−N(1)	2.130(2)	Co(1)−N(2)	2.140(2)
O(1)−Co(1)−O(2)	87.22(9)	O(1)−Co(1)−O(3)	84.86(8)
O(2)−Co(1)−O(4)	92.80(10)	O(1)−Co(1)−N(2)	167.69(9)
O(1)−Co(1)−N(1)	93.87(9)	O(2)−Co(1)−O(3)	171.96(8)

Complex **6**

Mn(1)−O(2)	2.127(4)	Mn(1)−O(5)	2.157(4)
Mn(1)−N(1)	2.270(5)	Mn(1)−N(2)	2.251(5)
Mn(1)−N(5)	2.251(5)	Mn(1)−N(6)	2.294(5)
Mn(2)−O(1)	2.102(4)	Mn(2)−O(6)	2.198(4)
Mn(2)−N(9)	2.289(5)	Mn(2)−N(10)	2.265(5)
Mn(2)−N(13)	2.287(5)	Mn(2)−N(14)	2.263(5)
O(2)−Mn(1)−N(2)	94.91(18)	O(2)−Mn(1)−N(5)	86.39(15)
O(2)−Mn(1)−N(6)	92.04(17)	O(5)−Mn(1)−N(1)	86.98(16)
O(5)−Mn(1)−N(2)	105.51(16)	O(5)−Mn(1)−N(5)	89.93(16)
O(5)−Mn(1)−N(6)	160.71(16)	N(1)−Mn(1)−N(2)	73.43(19)
O(6)−Mn(2)−N(13)	160.63(16)	O(1)−Mn(2)−N(10)	161.02(15)
N(14)−Mn(2)−N(13)	103.19(16)	N(14)−Mn(2)−N(9)	152.46(18)

Complex **7**

Mn(1)−O(1W)	2.146(2)	Mn(1)−N(1)	2.230(3)
Mn(1)−N(2)	2.280(3)	Mn(1)−O(1W)#1	2.146(2)
Mn(1)−N(1)#1	2.230(3)	Mn(1)−N(2)#1	2.280(3)
Mn(2)−O(3)	2.237(2)	Mn(2)−N(3)	2.167(2)
Mn(2)−O(1)#1	2.233(2)	Mn(2)−O(3)#1	2.237(2)

Mn(2)−N(3)#1	2.167(2)	Mn(2)−O(1)	2.233(2)	
O(1W)−Mn(1)−N(2)#1	162.97(9)	N(1)−Mn(1)−N(2)	73.05(9)	
N(1)−Mn(1)−N(1)#1	159.55(14)	O(1W)#1−Mn(1)−N(2)	162.97(9)	
N(1)#1−Mn(1)−N(2)	94.78(9)	N(2)−Mn(1)−N(2)#1	108.16(10)	
N(1)#1−Mn(1)−N(2)#1	73.05(9)	N(3)−Mn(2)−N(3)#2	173.76(14)	
O(3) −Mn(2)−O(3)#2	104.47(13)	N(3)−Mn(2)−O(3) #2	111.95(9)	

Symmetry codes: #1: -x,y,1/2-z ; #2: 1-x,y,1/2-z

Complex **8**

Mn(1)−O(1)	2.216(3)	Mn(1)−O(2)	2.113(4)
Mn(1)−N(1)	2.338(4)	Mn(1)−N(2)	2.294(4)
Mn(1)−O(4)#1	2.173(4)	Mn(1)−O(3)#2	2.106(3)
O(1)−Mn(1)−N(2)	88.39(13)	O(1)−Mn(1)−O(4)#1	174.53(13)
O(1)−Mn(1)−O(3)#2	92.12(14)	O(2)−Mn(1)−N(1)	159.25(14)
O(2)−Mn(1)−N(2)	89.00(14)	O(2)−Mn(1)− O(4)#1	85.58(13)
O(2)−Mn(1)−O(3)#2	110.59(15)	N(1)−Mn(1)−N(2)	71.03(14)

Symmetry codes: #1: 1+x,y,z ; #2: 1-x,-y,-z ;

Complex **9**

Cd(1)−O(1)	2.262(4)	Cd(1)−O(3)	2.271(5)
Cd(1)−O(4)	2.580(6)	Cd(1)−N(1)	2.363(5)
Cd(1)−N(2)	2.332(5)	Cd(1)−O(11)#1	2.309(4)
Cd(2)−O(6)	2.339(5)	Cd(2)−O(11)	2.342(4)
Cd(2)−N(5)	2.288(6)	Cd(2)−O(6)#2	2.339(5)
Cd(2)−O(11)#2	2.342(4)	Cd(2)−N(5)#2	2.286(6)
O(1)−Cd(1)−O(3)	125.1(2)	O(1)−Cd(1)−O(4)	175.95(19)
N(1)−Cd(1)−N(2)	71.1 (2)	O(11)#1−Cd(1)−N(1)	161.40(17)
O(11)#1−Cd(1)−N(2)	90.42(18)	O(6)−Cd(2)−O(11)	55.69(15)
O(6)−Cd(2)−N(5)	88.64(18)	O(6)−Cd(2)−O(6)#2	170.9(2)

Symmetry codes: #1: 1-x,y,3/2-z. #2: -x,y,3/2-z

Complex **10**

Zn(1)−O(1)	2.345(8)	Zn(1)−O(6)	2.251(9)
Zn(1)−N(1)	2.310(6)	Zn(1)−N(2)	2.322(6)
Zn(1)−O(3)#1	2.272(9)	Zn(2)−O(1)	2.299(8)
Zn(2)−O(2)	2.317(8)	Zn(2)−N(5)	2.306(11)
O(3)#1−Zn(1)−O(6)	125.7(4)	N(1)−Zn(1)−N(2)	71.6(3)
O(1)−Zn(2)−N(5)	143.2(4)	O(1)−Zn(2)−O(2)#2	119.0(3)
N(5)#2−Zn(2)−O(2)	97.8(4)	O(2)−Zn(2)−O(2)#2	173.2(4)

Symmetry codes: #1: 1-x,y,1/2-z. #2: 2-x,y,1/2-z

Complex **11**

Cd(1)−O(5)	2.438(5)	Cd(1)−O(6)	2.315(6)
Cd(1)−O(11)	2.284(6)	Cd(1)−N(1)	2.315(6)
Cd(1)−N(2)	2.301(6)	Cd(1)−O(2)#3	2.245(5)
Cd(2)−O(4)	2.256(5)	Cd(2)−N(3)	2.367(6)

Cd(2)−N(4)	2.342(6)	Cd(2)−O(12)#1	2.291(5)	
Cd(2)−O(9)#2	2.234(5)			
O(6)−Cd(1)−N(1)	132.6(2)	O(6)−Cd(1)−N(2)	97.81(19)	
O(2)#3−Cd(1)−O(6)	110.8(2)	O(11)−Cd(1)−N(1)	137.9(2)	
O(4)−Cd(2)−N(4)	160.4(2)	O(4)−Cd(2)−O(12)#1	88.56(19)	
O(4)−Cd(2)−O(9)#2	103.4(2)	N(3)−Cd(2)−N(4)	70.3(2)	
O(12)#1−Cd(2)−N(3)	91.71(19)	O(9)#2−Cd(2)−N(3)	164.0(2)	

Symmetry codes: #1: 2-x,1-y,-z； #2: x,1-y,-1/2+z ； #3: 3/2-x,1/2+y,1/2-z

Complex **12**

Zn(1)−O(4)	2.196(13)	Zn(1)−O(11)	2.295(14)
Zn(1)−N(5)	2.358(15)	Zn(1)−O(8)#1	2.355(13)
Zn(1)−O(9)#1	2.410(12)	Zn(2)−O(1)	2.239(11)
Zn(2)−O(10)	2.320(12)	Zn(2)−N(1)	2.390(13)
Zn(2)−N(2)	2.358(19)	Zn(2)−O(6)#2	2.249(11)
Zn(1)−N(6)	2.337(15)	O(4)−Zn(1)−N(5)	149.2(6)
O(4)−Zn(1)−O(8)#1	111.7(5)	O(4)−Zn(1)−O(9)#1	85.5(5)
O(1)−Zn(2)−O(10)	80.6(4)	O(1)−Zn(2)−N(1)	161.2(5)
O(6)#2−Zn(2)−N(2)	160.2(6)	O(6)#2−Zn(2)−O(1)	104.6(5)

Symmetry codes: #1: 3/2-x,1/2+y,1/2-z ; #2: x,-y,-1/2+z.

Complex **13**

Cd(1)−O(1)	2.025(9)	Cd(1)−O(2W)	2.084(8)
Cd(1)−N(1)	2.173(10)	Cd(1)−N(2)	2.098(10)
Cd(1)−O(3)#1	2.112(9)		
O(1)−Cd(1)−N(2)	152.5(4)	O(2W)−Cd(1)−O(3)#1	91.3(4)
O(2W)−Cd(1)−N(2)	92.7(3)	O(2W)−Cd(1)−N(1)	170.4(4)

Symmetry codes: #1: 1/2-x,1/2+y,1-z.

Complex **14**

Mn(1)−O(1)	2.345(9)	Mn(1)−O(2)	2.467(9)
Mn(1)−O(1W)	2.209(11)	Mn(1)−N(1)	2.256(12)
Mn(1)−N(2)	2.322(13)	Mn(1)−O(3)#1	2.466(10)
Mn(1)−O(4)#1	2.283(9)		
O(1W)−Mn(1)−N(1)	168.0(4)	O(1)−Mn(1)−O(3)	139.8(4)
O(2)−Mn(1)−N(2)	85.0(3)	O(4)−Mn(1)−N(2)#1	132.2(3)
O(2)−Mn(1)−O(4)#1	141.1(4)	O(2)−Mn(1)−O(3)	163.9(4)

Symmetry codes: #1: -1/2+x,1/2-y,-1/2+z .

Complex **15**

Zn(1)−O(1)	2.040(4)	Zn(1)−O(3)	2.055(5)
Zn(1)−N(1)#1	2.119(5)	Zn(1)−N(2)#1	2.123(6)
Zn(1)−O(2)#2	2.028(4)	Zn(2)−O(4)	1.974(5)
Zn(2)−O(5)	1.924(5)	Zn(2)−O(7)	1.925(5)
Zn(2)−N(3)	2.013(5)		
O(1)−Zn(1)−O(3)	85.88(19)	O(1)−Zn(1)−N(1)#1	151.16(19)
O(1)−Zn(1)−N(2)#1	98.7(2)	O(1)−Zn(1)−O(2)#2	103.30(17)

O(3)−Zn(1)−N(1)#1	94.3(2)	O(3)−Zn(1)−N(2)#1	170.0(2)	
O(4)−Zn(2)−O(5)	101.5(2)	O(5)−Zn(2)−O(7)	134.8(2)	

Symmetry codes: #1: 1+x,y,z； #2: 2-x,2-y,1-z.

Table S2. Hydrogen Bond Parameters in the Crystal Structures of compounds

Compounds	**D–H···A**	**D···A**(Å)	**H···A** (Å)	**D–H···A**(deg)
1	O4–H4WA···O1[a]	2.683(7)	2.15	123.00
	O5–H5WB···N1[b]	2.731(6)	1.91	176.00
	O7–H4WA···O3[a]	2.682(6)	1.91	156.00
	N4–H4···O6[a]	2.761(7)	1.83(6)	159(5)
	O9–H9W···O2[d]	2.745(6)	1.93	170.00
	O6–H6WB···10[e]	2.723(10)	1.96(5)	152(7)
	O7–H7WB···O2[d]	2.876(7)	2.05(3)	171(4)
	O10–H11A···O1[f]	2.862(9)	2.24(14)	131(15)
	[a] –1+x,y,z; [b] 1–x,–y,1–z; [c] –x,1–y,1–z; [d] 1–x,1–y,–z; [e] x,1+y,–1+z; [f] 1–x,1–y,1–z.			
3	O1–H1B···N4[a]	2.739(5)	1.942(4)	159(5)
	O1–H1C···O5[b]	2.745(4)	2.01(6)	146(6)
	O1–H2B···O6[c]	2.946(5)	2.15(3)	159.00
	N3–H3A···O4[d]	2.782(5)	1.93	168.00
	[a] –x, 2–y,–z; [b]1–x, 1/2+y,1/2–z; [c] x,1+y,z; [d]–1+x,y,z.			
4	O1–H2C···N2[a]	1.980(4)	2.00(5)	163(6)
	N3–H3···O5[b]	2.878(4)	2.04	164.00
	O3–H3B···O6[c]	2.686(4)	1.93(4)	152(4)
	O3–H3C···O7[d]	2.634(4)	1.79	170(5)
	O7–H7B···O5[c]	2.804(4)	1.98(3)	162(4)
	O7–H7C···O6[e]	2.836(4)	1.99(2)	174(4)
	[a] 2–x,–y,–z; [b]1+x,1/2–y,[c]1–x,1–y,–z; [d] x,–1+y,z; [e] x,3/2–y,1/2+z; [f] 1+x,1/2–y,1/2+z			
5	O3–H2B···N3[a]	2.806(3)	2.03	154(4)
	O2–H3B···O7[b]	2.636(4)	1.82(3)	173(4)
	O3–H3C···O6[c]	2.693(3)	1.96(4)	149(4)
	N4–H4A···O5[d]	2.878(3)	2.09(3)	164(3)
	O7–H7B···O6[e]	2.829(4)	2.01(3)	174(5)
	O7–H7C···O5[c]	2.800(3)	2.021(18)	167(3)
	[a] 1–x,–y,–z; [b] x,–1+y,z; [c] –x,1–y,–z; [d]1+x,1/2–y,1/2+z; [e] x,3/2–y,1/2+z			
6	N4–H4c···O7[a]	2.733(7)	1.93	154.00
	N8–H8A···O13[b]	2.949(7)	2.09	175.00
	N11–H11B···O10[a]	2.681(7)	1.90	151.00
	N15–H15A···O15[c]	2.808(7)	2.02	152.00
	O5–H5A···O3	2.698(5)	1.89	157.00
	O6–H6A···O4	2.697(6)	1.9000	160.00
	O5–H5B···O7[d]	2.649(6)	1.82	176.00
	O15–H15D···N7[b]	2.756(7)	2.1600	124.00

	[a] –1/2+x,1/2–y,–1/2+z; [b] -x,1-y,1-z; [c] 1/2-x,-1/2+y,1/2-z;			
	[d] 1/2-x,1/2+y,1/2-z.			
7	O1W–H1W···O1W [a]	2.710(3)	1.86(3)	173(3)
	O2W–H4W···O1W [b]	2.969(4)	2.15(3)	164(3)
	N5–H5A···O2 [c]	2.751(4)	1.92(2)	167(4)
	O3W–H5W···N4[d]	2.834(4)	1.95(3)	169(3)
	O3W–H6W···O3 [a]	2.828(4)	1.98(3)	174(3)
	O2W–H6W···O4 [a]	2.710(3)	1.86(3)	173(3)
	[a] 1–x,y,1/2–z; [b] 1/2–x,1/2+y,1/2–z; [c] x,–y,1/2+z;			
	[d] 1/2+x,1/2–y,–1/2+z.			
8	O1–H1B···N4[a]	2.793(7)	2.06(8)	150(7)
	O1–H1C···O6[b]	2.771(8)	1.98(5)	161(5)
	O6–H6W···O2[c]	3.028(7)	2.37(15)	138(12)
	O6–H6W···O4[d]	2.856(7)	2.19(14)	138(16)
	N3–H3B···O4[e]	3.266(6)	2.56	140.00
	N3–H3B···O5[e]	2.801(7)	1.97	163.00
	O9–H9···O5[e]	3.293(7)	2.42	158.00
	[a] 2–x,–y,1–z; [b] x,–1+y,z; [c] 1–x,1–y,–z; [d] –x,1–y,–z; [e]1–x,1–y,1–z			
9	O1W–H2W…N6[a]	2.774(8)	1.96	160.00
	N4–H4…O3W [b]	2.932(7)	2.10	164.00
	N6–H6…O1W [c]	2.774(8)	1.92	171.00
	[a]1+x,1+y,z; [b]1/2+x,1/2–y,1/2+z; [c] –1+x,–1+y,z.			
10	O1W–H1A···O6[a]	2.685(2)	1.91	178.71
	O3W–H3D···N4[a]	2.742(6)	1.96	179.36
	N6–H6···O2W [b]	2.794(5)	1.94	170.71
	[a] x,y,1+z; [b]1+x,y,z.			
11	N5–H5A···O1[a]	2.835(9)	1.98	173.39
	N7–H7A···O16[b]	2.760(3)	1.90	173.73
	O11–H11A···O6[c]	2.732(8)	1.93	179.63
	O11–H11B···O8[d]	2.744(8)	1.94	179.48
	O12–H12A···O1[e]	2.847(8)	2.05	179.36
	O15–H15B···O2[d]	2.891(6)	2.16	151.42
	[a] 1/2+x,3/2–y,–1/2+z; [b] x,1+y,–1+z; [c] 3/2–x,3/2–y,–z;			
	[d] 3/2–x,1/2+y,1/2–z; [e] x,1–y,–1/2+z.			
12	N4–H4A···O3[a]	2.85(2)	1.99	174.00
	N8–H8A···O12[b]	2.86(2)	2.01	179.00
	O10–H10C···O3[c]	2.856(18)	2.06	179.00
	O10–H10D···O6[d]	2.696(17)	1.90	179.00
	O11–H11D···O8[e]	2.683(19)	1.88	179.00
	O12–H12C···O2[a]	2.75(2)	1.95	178.00
	O12–H12D···N8[f]	2.87(3)	2.53	107.00
	O12–H12D···O5[g]	2.83(2)	2.40	115.00
	O13–H13C···O14[h]	2.88(5)	2.08	179.00
	O13–H13D···O13[i]	2.30(5)	1.75	123.00

		[a] –1/2+x,1/2+y,z; [b] 1+x,–1+y,z; [c] 1–x,–y,–z; [d] 1–x,y,1/2–z;			
		[e] x,–y,–1/2+z; [f] –1+x,1+y,z; [g] –1/2+x,1/2–y,–1/2+z;			
		[h] 1+x,y,z; [i] 2–x,y,1/2–z; [i] 1/2+x,–1/2–y,–1/2+z			
	13	O2W–H2C···O2	2.607(7)	1.90	147.65
		O2W–H2D···O3[a]	2.747(10)	1.95	179.63
		N4–H4A···O4[b]	2.720(11)	1.86	173.20
		O1W–H1C···N3[c]	2.91(2)	2.08	173.96
		[a] x,y,1+z; [b] -1/2+x,1/2-y,-z; [c] -1/2+x,1/2-y,-z.			
	14	N4–H4A···O2[a]	2.646(18)	1.84	156.00
		O11–H11C···O4[b]	2.760(17)	2.16	131.00
		O12–H12D···N3[c]	2.93(2)	2.13	177.00
		[a] –x,–y,–z; [b]–x,y,1/2–z; [c]1/2–x,1/2–y,–z			
	15	O1W–H1W···O6[a]	2.970(11)	2.128	175.79
		N4–H4···O1W[b]	2.845(11)	2.02	161.71
		O3W–H6W···O2W[c]	2.663(19)	2.20	112.72
		[a] 2–x,1–y,2–z; [b] x,1+y,z;[c] 2–x,1–y,1–z.			

Table S3 Main calculated optical transitions for IP

Band	Excitation energy	f[a]	Transition character [b]	Transition feature
1	3.87	0.0091	HOMO→LUMO (0.85582)	π →π*
2	4.02	0.0000	HOMO-2→LUMO (0.91409)	π →π*
3	4.15	0.0330	HOMO-1→LUMO (0.28047) HOMO→LUMO+1 (0.65181)	π →π*

[a] Oscillator strengths.

[b] The proportion of the main transition are given in parenthesis.