Electronic Supplementary Material (ESI) for CrystEngComm

A series of coordination polymers constructed by a flexible tetracarboxylic acid: synthesis, structural diversity and luminescent properties

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Table S1 Selected bond lengths (Å) and angles (deg) for compounds H_4L, and **1-10**

H_4L					
O(1)-C(23)	1.271(3)	O(2)-C(23)	1.265(2)	O(6)-C16(3)	1.261(3)
O(3)-C(24)	1.273(3)	O(8)-C(15)	1.267(3)	O(4)-C(24)	1.253(3)
O(7)-C(15)	1.273(2)				
Complex **1**					
N(4)#3 -Cu(1)	2.008(3)	N(6)#4-Cu(1)	2.028(3)	N(4)#1-Cu(1)-N(5)	115.19(13)
N(4)#1-Cu(1)-N(6)#2	104.68(12)	N(5)-Cu(1)-N(6)#2	113.12(10)	N(4)#1-Cu(1)-N(3)	112.50(12)
N(5)-Cu(1)-N(3)	101.28(12)	N(6)#2-Cu(1)-N(3)	110.26(12)		
Symmetry code: #1 -x+1/2, -y+1/2, z+1/2; #2 x-1/2, -y , z+1/2; #3 x-1/2, -y+1, z-1/2 ; #4 x+1/2, -y, z-1/2					
Complex **2**					
Cd(1)-O(4)#1	2.308(3)	Cd(1)-O(3)#2	2.333(3)	Cd(1)-N(2)	2.339(4)
Cd(1)-O(1)	2.355(3)	Cd(1)-N(1)	2.381(4)	Cd(1)-O(2)	2.466(3)
O(4)#1-Cd(1)-O(3)#2	102.22(13)	O(4)#1-Cd(1)-N(2)	135.16(12)	O(3)#2-Cd(1)-N(2)	84.67(11)
O(4)#1-Cd(1)-O(1)	82.78(12)	O(3)#2-Cd(1)-O(1)	107.23(13)	N(2)-Cd(1)-O(1)	137.96(12)
O(4)#1-Cd(1)-N(1)	88.41(14)	O(3)#2-Cd(1)-N(1)	151.67(12)	N(2)-Cd(1)-N(1)	69.75(13)
O(1)-Cd(1)-N(1)	100.07(14)	O(4)#1-Cd(1)-O(2)	136.72(10)	O(3)#2-Cd(1)-O(2)	90.93(12)
N(2)-Cd(1)-O(2)	86.53(12)	O(1)-Cd(1)-O(2)	53.96(11)	N(1)-Cd(1)-O(2)	99.20(13)
Symmetry code: #1 x-1,y,z; #2 -x+1,y,-z+1/2; #3 x+1,y,z; #4 -x+1,-y,-z; #5 -x,-y+1,-z+2					
Complex **3**					
Cd(1)-O(1W)	2.301(9)	Cd(1)-O(2W)	2.306(8)	Cd(1)-O(3W)	2.338(8)
Cd(1)-O(1)	2.371(6)	Cd(1)-O(4)#1	2.376(6)	Cd(1)-O(2)	2.414(7)
Cd(1)-O(3)#1	2.440(7)				
O(1W)-Cd(1)-O(2W)	83.6(4)	O(1W)-Cd(1)-O(3W)	171.4(3)	O(2W)-Cd(1)-O(3W)	91.4(4)
O(1W)-Cd(1)-O(1)	101.8(3)	O(2W)-Cd(1)-O(1)	138.1(3)	O(3W)-Cd(1)-O(1)	86.6(3)
O(1W)-Cd(1)-O(4)#1	88.3(3)	O(2W)-Cd(1)-O(4)#1	138.7(3)	O(3W)-Cd(1)-O(4)#1	90.9(3)
O(1)-Cd(1)-O(4)#1	83.2(2)	O(1W)-Cd(1)-O(2)	90.0(3)	O(2W)-Cd(1)-O(2)	83.8(3)
O(3W)-Cd(1)-O(2)	96.4(3)	O(1)-Cd(1)-O(2)	55.0(2)	O(4)#1-Cd(1)-O(2)	136.8(2)
O(1W)-Cd(1)-O(3)#1	87.6(3)	O(2W)-Cd(1)-O(3)#1	85.0(3)	O(3W)-Cd(1)-O(3)#1	85.0(3)
O(1)-Cd(1)-O(3)#1	136.3(2)	O(4)#1-Cd(1)-O(3)#1	54.2(2)	O(2)-Cd(1)-O(3)#1	168.8(2)
Symmetry code: #1 -x+1/2,y-1/2,-z+1/2; #2 -x+1,-y+1,-z; #3 -x+1/2,y+1/2,-z+1/2					
Complex **4**					

Mn(1)-O(4)#2	2.271(4)	Mn(1)-O(3) #1	2.367(4)	Mn(1)-O(3W)	2.176(4)
Mn(1)-O(2W)	2.195(5)	Mn(1)-O(1W)	2.201(4)	Mn(1)-O(2)	2.241(4)
Mn(1)-O(1)	2.396(4)				
O(3W)-Mn(1)-O(2W)	172.13(17)	O(3W)-Mn(1)-O(1W)	85.28(16)	O(2W)-Mn(1)-O(1W)	90.14(18)
O(3W)-Mn(1)-O(2)	88.60(15)	O(2W)-Mn(1)-O(2)	91.20(18)	O(1W)-Mn(1)-O(2)	142.80(15)
O(3W)-Mn(1)-O(4)#2	101.58(15)	O(2W)-Mn(1)-O(4)#2	86.15(17)	O(1W)-Mn(1)-O(4)#2	136.06(16)
O(2)-Mn(1)-O(4)#2	81.10(14)	O(3W)-Mn(1)-O(3)#2	88.99(16)	O(2W)-Mn(1)-O(3)#2	96.64(19)
O(1W)-Mn(1)-O(3)#2	81.17(15)	O(2)-Mn(1)-O(3)#2	135.45(14)	O(4)#2-Mn(1)-O(3)#2	55.95(14)
O(3W)-Mn(1)-O(1)	87.82(17)	O(2W)-Mn(1)-O(1)	85.54(19)	O(1W)-Mn(1)-O(1)	86.89(15)
O(2)-Mn(1)-O(1)	56.19(13)	O(4)#2-Mn(1)-O(1)	136.19(13)	O(3)#2-Mn(1)-O(1)	167.85(13)
Symmetry code: #1 -x+1/2,y+1/2,-z+3/2; #2 -x+1/2,y-1/2,-z+3/2; #3 -x+1,-y,-z+2					
Complex **5**					
Co(1)-O(4) #1	2.372(5)	Co(1)-O(3) #1	2.275(4)	Co(1)-O(2W)	2.177(4)
Co(1)-O(1W)	2.189(5)	Co(1)-O(3W)	2.210(4)	Co(1)-O(1)	2.247(4)
Co(1)-O(2)	2.398(4)				
O(2W)-Co(1)-O(1W)	172.08(17)	O(2W)-Co(1)-O(3W)	84.94(16)	O(1W)-Co(1)-O(3W)	90.38(18)
O(2W)-Co(1)-O(1)	88.76(15)	O(1W)-Co(1)-O(1)	91.11(18)	O(3W)-Co(1)-O(1)	142.66(15)
O(2W)-Co(1)-O(3)#3	101.27(16)	O(1W)-Co(1)-O(3)#3	86.52(17)	O(3W)-Co(1)-O(3)#3	136.24(17)
O(1)-Co(1)-O(3)#3	81.08(14)	O(2W)-Co(1)-O(4)#3	89.26(16)	O(1W)-Co(1)-O(4)#3	96.3(2)
O(3W)-Co(1)-O(4)#3	81.07(16)	O(1)-Co(1)-O(4)#3	135.70(15)	O(3)#3-Co(1)-O(4)#3	56.04(15)
O(2W)-Co(1)-O(2)	87.68(17)	O(1W)-Co(1)-O(2)	85.7(2)	O(3W)-Co(1)-O(2)	86.81(15)
O(1)-Co(1)-O(2)	56.14(13)	O(3)#3-Co(1)-O(2)	136.24(14)	O(4)#3-Co(1)-O(2)	167.71(14)
Symmetry code: #1 -x+1/2,y+1/2,-z+1/2; #2 -x+1,-y,-z; #3 -x+1/2,y-1/2,-z+1/2					
Complex **6**					
Zn(1)-O(1)#2	1.970(3)	Zn(1)–O(4)	1.986(3)	Zn(1) –N(2)	2.058(3)
Zn(1) –N(3)	2.105(3)				
O(4)-Zn(1)-O(1)#2	104.71(12)	N(3)-Zn(1)-O(4)	130.69(12)	N(3)-Zn(1)-N(2)	79.65(12)
N(2)-Zn(1)-O(1)#2	120.58(12)	N(3)-Zn(1)-O(1)#2	109.18(12)	N(2)-Zn(1)-O(4)	112.04(11)
Complex **7**					
Zn(1)-O(3) #1	1.938(3)	Zn(1)-O(1)	1.938(3)	Zn(1)-N(1)	2.077(4)
Zn(1)-N(2)	2.054(4)				
O(3)#2-Zn(1)-O(1)	105.73(14)	O(3)#2-Zn(1)-N(2)	122.21(13)	O(1)-Zn(1)-N(2)	113.40(13)
O(3)#2-Zn(1)-N(1)	107.22(15)	O(1)-Zn(1)-N(1)	127.96(15)	N(2)-Zn(1)-N(1)	80.25(18)
Symmetry code: #1 x,-y,z+1/2; #2 x,-y,z-1/2; #3 -x+1/2,-y-1/2,-z, #4 -x,y,-z+1/2					
Complex **8**					
O(1W)-Ni(1)	2.049(4)	N(1)-Ni(1)	2.066(5)	N(2)-Ni(1)	2.030(5)
Ni(1)-O(1)	2.045(4)	Ni(1)-O(3)#3	2.082(4)	Ni(1)-O(4)#3	2.122(4)
O(3)#1-Ni(1)	2.082(4)	O(4)-Ni(1)#1	2.122(4)	N(2)-Ni(1)-O(1)	98.11(19)
N(2)-Ni(1)-O(1W)	97.05(19)	O(1)-Ni(1)-O(1W)	92.78(16)	N(2)-Ni(1)-N(1)	79.8(2)
O(1)-Ni(1)-N(1)	177.45(19)	O(1W)-Ni(1)-N(1)	88.96(18)	N(2)-Ni(1)-O(3)#3	162.91(18)
O(1)-Ni(1)-O(3)#3	90.84(16)	O(1W)-Ni(1)-O(3)#3	97.02(17)	N(1)-Ni(1)-O(3)#3	90.79(19)
N(2)-Ni(1)-O(4)#3	102.56(17)	O(1)-Ni(1)-O(4)#3	89.91(15)	O(1W)-Ni(1)-O(4)#3	159.62(17)
N(1)-Ni(1)-O(4)#3	89.10(18)	O(3)#3-Ni(1)-O(4)#3	62.73(15)		
Symmetry code: #1 x,-y+1,z-1/2; #2 -x+1/2,-y+1/2,-z+1; #3 x,-y+1,z+1/2					

Complex **9**					
Cu(1)-O(4)#1	1.959(19)	Cu(1)-O(1)	1.977(2)	Cu(1)-N(1)	2.028(2)
Cu(1)-N(2)	2.070(2)	Cu(1)-O(1W)	2.296(2)		
O(4)#1-Cu(1)-O(1)	97.28(9)	O(4)#1-Cu(1)-N(1)	170.89(9)	O(1)-Cu(1)-N(1)	91.84(10)
O(4)#1-Cu(1)-N(2)	90.98(9)	O(1)-Cu(1)-N(2)	155.28(9)	O(1)-Cu(1)-N(2)	155.28(9)
N(1)-Cu(1)-N(2)	80.67(10)	O(4)#1-Cu(1)-O(1W)	92.06(9)	O(1)-Cu(1)-O(1W)	97.78(9)
N(1)-Cu(1)-O(1W)	86.65(10)	N(2)-Cu(1)-O(1W)	105.19(9)		
Symmetry code: #1 -x+1,y-1/2,-z+3/2; #2 -x+1,y+1/2,-z+3/2; #3 -x+1,-y+1,-z+2					
Complex **10**					
O(4)-Zn(1)	2.001 (3)	O(1) -Zn(1)	2.009(3)	OW-Zn(1)	2.053(3)
N(3)-Zn(1)	2.150(3)	N(2)-Zn(1)	2.200(4)	O(4)-Zn(1)-O(1)	103.76(12)
O(4)-Zn(1)-OW	102.19(13)	O(1)-Zn(1)-OW	97.17(15)	O(4)-Zn(1)-N(3)	146.22(12)
O(1)-Zn(1)-N(3)	90.59(12)	OW-Zn(1)-N(3)	106.18(13)	O(4)-Zn(1)-N(2)	88.46(13)
O(1)-Zn(1)-N(2)	166.20(12)	OW-Zn(1)-N(2)	86.29(15)	N(3)-Zn(1)-N(2)	75.62(13)

Table S2 Selected hydrogen bonds (Å) of copmounds H_4**L** and **1-10**

D −H ···A	D−H (Å)	H··· A (Å)	D··· A (Å)	DHA (deg)	Symmetry code
H_4L					
N1-H1···O1	0.894	2.540	3.269	139.09	[x+1, -y+3/2, z-1/2]
N2-H2···O7	0.874	2.527	3.310	149.49	[x-1, -y+3/2, z+1/2]
O1-H1C···O5	0.815	1.834	2.649	177.56	[-x+1, -y+1, -z+1]
O6-H6A···O2	0.818	1.786	2.602	174.02	[-x+1, -y+1, -z+1]
O8-H8···O4	0.819	1.783	2.593	169.65	[-x+2, -y+1, -z]
O3-H3A···O7	0.822	1.798	2.618	175.87	[-x+2, -y+1, -z]
Complex **1**					
O4-H4··· O7	0.82	1.85	2.657(4)	169.0	[x-1/2, -y+1, z-1/2]
O5-H5···O8	0.82	1.85	2.619(4)	156.0	[x+1/2, -y+1, z+1/2]
Complex **2**					
O2W-H2WB···N3	0.868	2.371	3.112	143.37	[x, y, z+1]
O2W-H2WA···O4	0.871	2.223	3.067	163.32	[-x+1, -y+1, -z+1]
Complex **3**					
O1W-H1WA···O4	0.835	2.336	2.758	111.88	[-x+1/2, -y+1/2, -z]
O1W-H1WA···O1	0.835	2.574	3.384	163.69	[x, -y, z-1/2]
O2W-H2WB···O1	0.838	2.062	2.860	159.07	[x, -y, z-1/2]
O3W-H3WB···O2	0.820	1.956	2.765	169.00	[x, -y, z+1/2]
O4W-H4WB···O3	0.836	2.208	2.881	137.53	
Complex **4**					
N1-H1A···O6W	0.860	2.540	3.388	168.94	[-x+1/2, -y+1/2, -z+2]
O1W-H1WB···O4	0.831	1.959	2.783	171.59	[-x+1/2, -y+1/2, -z+1]
O3W-H3WA···O2	0.836	1.894	2.720	169.58	[x, -y, z-1/2]
O1W-H1WA···O5W	0.833	2.096	2.739	133.80	
O2W-H2WA···O3	0.805	1.938	2.740	174.22	[-x+1/2, -y+1/2, -z+2]
O3W-H3WB···O4W	0.835	2.099	2.896	159.64	

O4W-H4WB···O1	0.841	1.962	2.769	160.39	[-x+1/2, -y+1/2, -z+1]
O4W-H4WA···O5W	0.848	2.186	2.620	111.68	[-x+1/2, -y+1/2, -z+1]
O4W-H4WA···O1	0.848	2.504	3.058	123.83	
O2W-H2WB···O6W	0.800	2.315	3.064	156.07	
Complex **5**					
O1W-H1WA···O5W	0.892	2.446	2.985	119.32	
O3W-H3WA···O6W	0.893	2.031	2.735	134.77	
O2W-H2WB···O4W	0.892	2.186	2.913	138.27	[-x+1/2, -y+1/2, -z+1]
O3W-H3WB···O3	0.881	2.003	2.787	147.67	[-x+1/2, -y+1/2, -z+1]
O2W-H2WA···O1	0.900	1.935	2.718	144.43	[x, -y, z+1/2]
O1W-H1WB···O4	0.889	1.974	2.741	143.58	[-x+1/2, -y+1/2, -z]
O4W-H4WB···N1	0.814	2.239	2.975	150.58	[-x+1/2, -y+1/2, -z]
O4W-H4WA···O2	0.821	2.367	3.055	141.72	[-x+1/2, -y+1/2, -z+1]
Complex **6**					
N1-H1···O4	0.925	2.218	2.993	140.83	[-x+1/2, y-1/2, -z+1/2]
Complex **7**					
N3-H3B···O1	0.860	2.160	2.930	148.84	[-x+1/2, y-1/2, -z+1/2]
Complex **8**					
N3-H3···O1	0.860	2.327	3.186	177.45	[-x+1/2, y-1/2, -z+1/2]
O1W-H1WB···O2	0.860	1.849	2.562	139.09	
O1W-H1WA···O3W	0.829	2.312	2.953	134.44	[x, -y+1, z-1/2]
Complex **9**					
O1W-H1WB…O3	0.85	2.36	2.966(3)	128	[1-x, -0.5+y, 1.5-z]
O1W-H1WB…O1	0.85	2.41	3.042(4)	132	[-x, 1-y, 1-z]
O1W-H1WA…O3	0.85	2.21	2.904(4)	139	[-1+x, 1.5-y, -0.5+z]
N3-H3A...O2	0.86	2.26	2.936(3)	136.0	[x, -y+3/2, z+1/2]
N3-H3A...N1	0.86	2.59	3.198(3)	129.0	[x, -y+3/2, z+1/2]
Complex **10**					
N1-H13...O3	0.89(4)	2.02(4)	2.886(5)	164(4)	[-0.5+x, 0.5-y, -0.5+z]
OW-HWB...O2	0.91(6)	1.76(6)	2.671(5)	172(6)	[-0.5+x, 0.5-y, 0.5+z]
OW-HWB...O4	0.72(5)	2.25(4)	2.808(5)	135(4)	[-x, -y, -z]

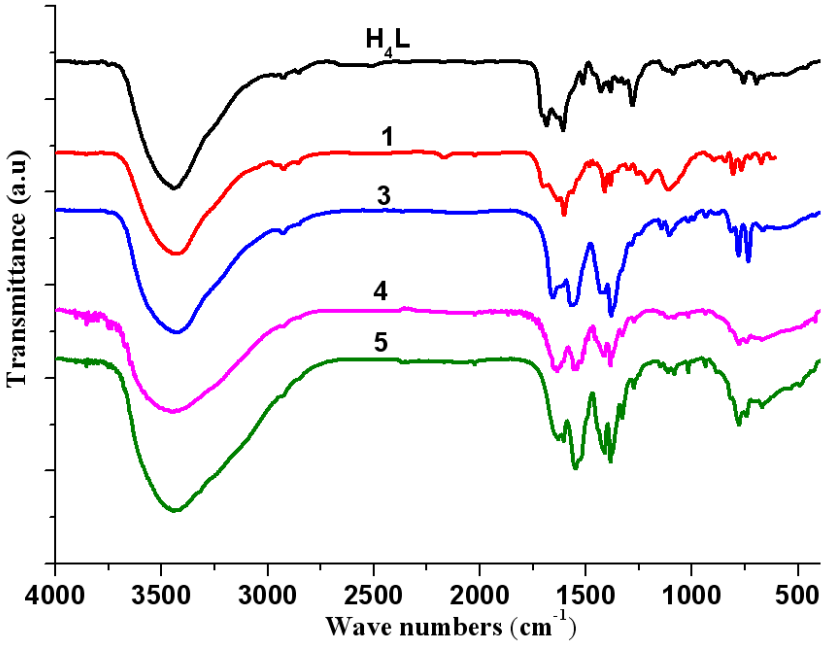

Fig. S1 IR spectra of compounds H_4L, **1**, **3**, **4** and **5**

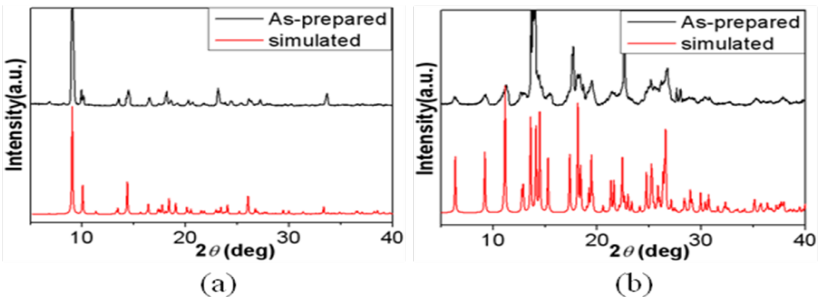

Fig. S2 Comparison of XRPD patterns for complexes **3** (a) and **6** (b).

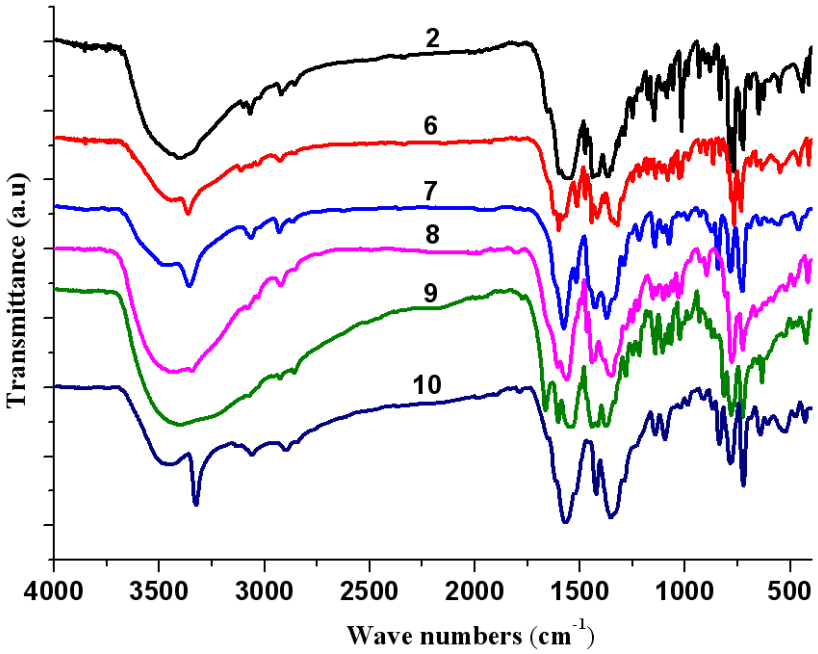

Fig. S3 IR spectra of compound **2**, **6**, **7**, **8**, **9** and**10**.

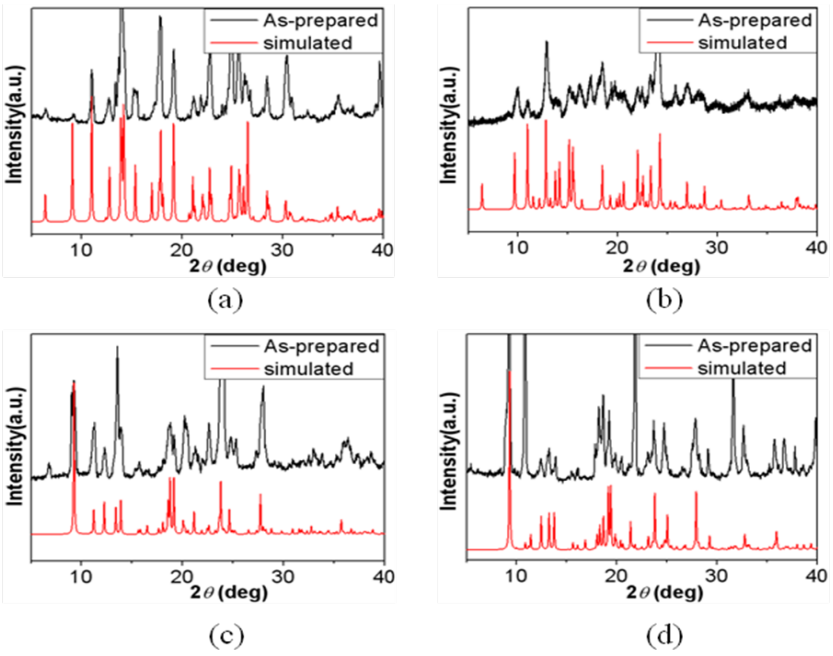

Fig. S4 Comparison of XRPD patterns for complexes **7** (a), **8** (b), **9** (c) and **10** (d).

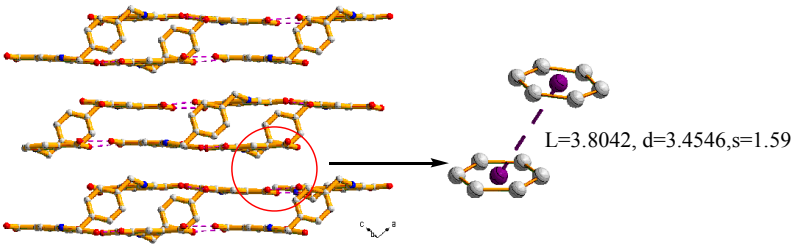

Fig. S5 The 2D supramolecular structure of H_4L formed by π⋯π stacking interactions

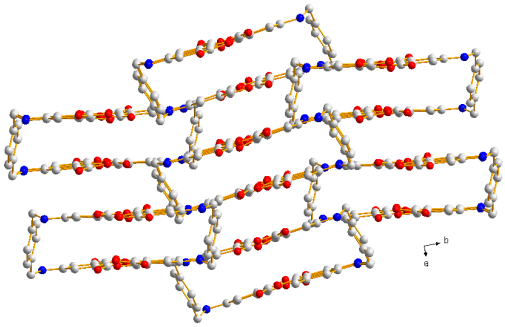

Fig. S6 The 3D supramolecular structure of H_4L formed by strong hydrogen-bonds between layers.

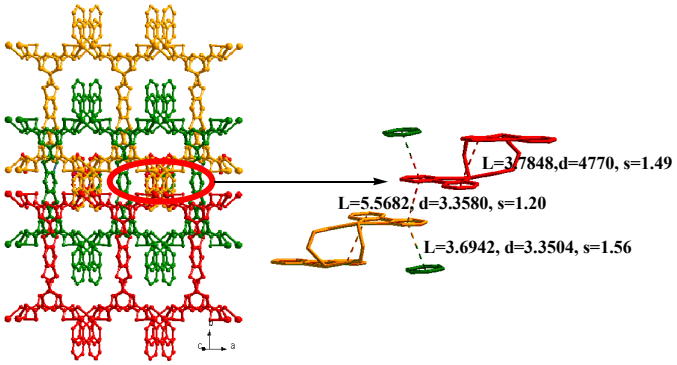

Fig. S7 Packing of three 2D layers of complex **2** to generate a 3D supramolecular framework by π⋯π stacking (different layers denoted in different colors).

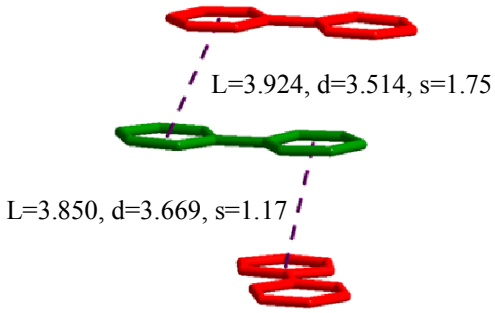

Fig. S8 The 3D supramolecular structure of **6** by interlayer π⋯π stacking (different layers denoted in different colors).

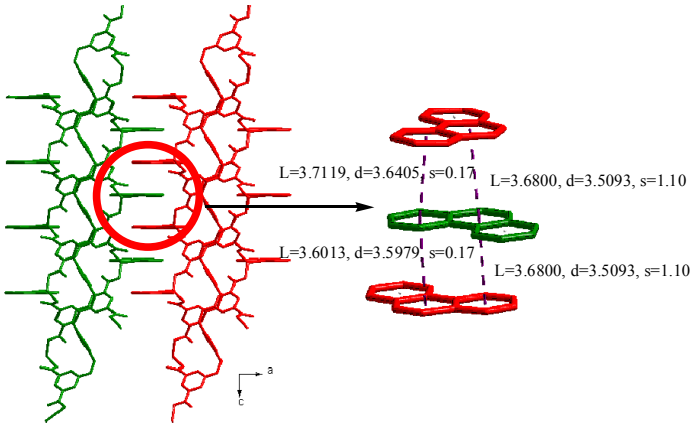

Fig. S9 The 3D supramolecular structure of 7 by interlayer π···π stacking (different layers denoted in different colors).

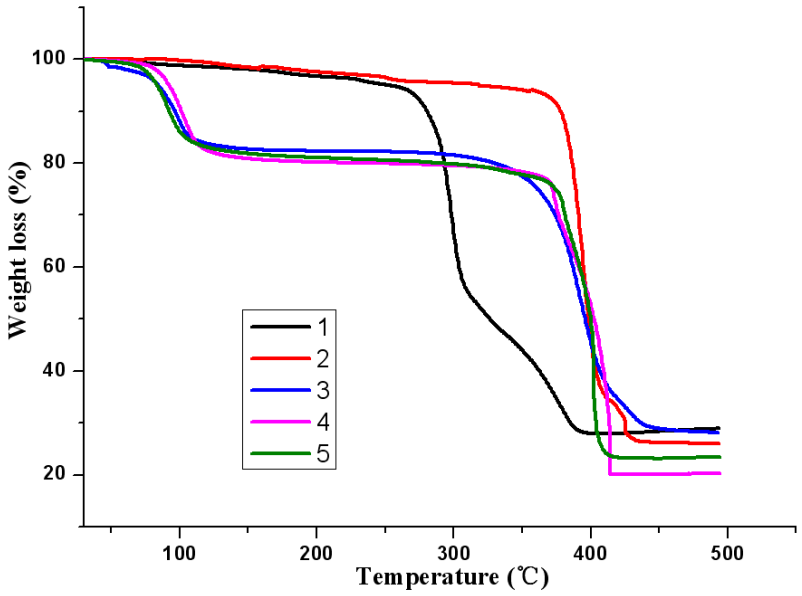

Fig. S10 TGA curves for complexes **1-5**.

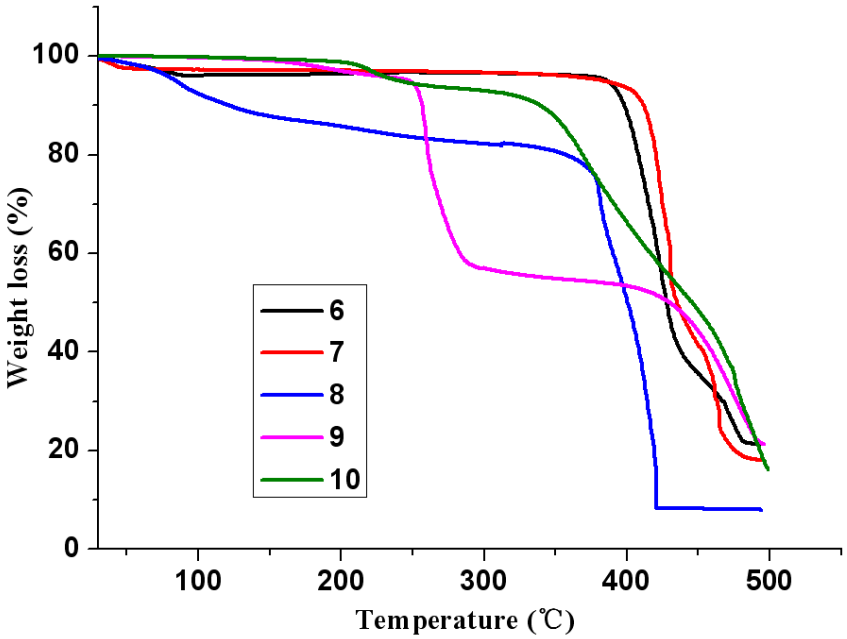

Fig. S11 TGA curves for complexes **6-10**.

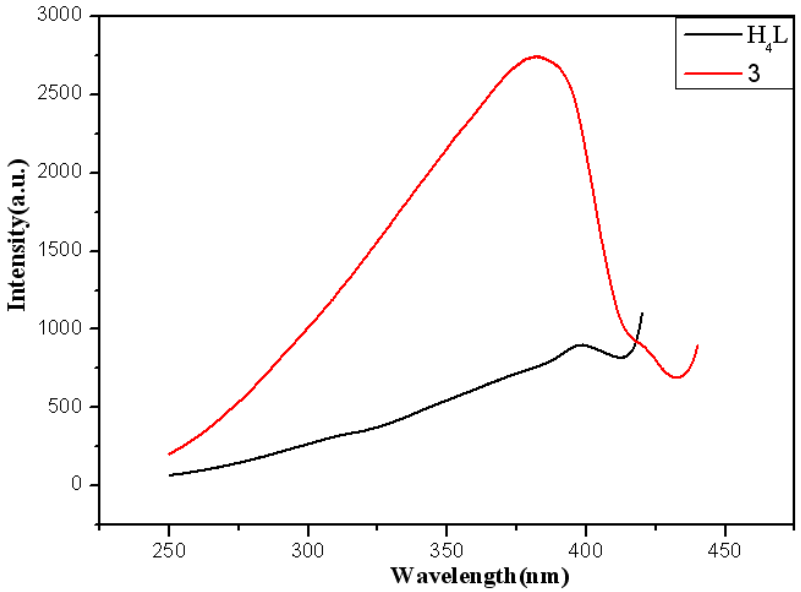

Fig. S12 The excitation spectra of H_4L and **3**

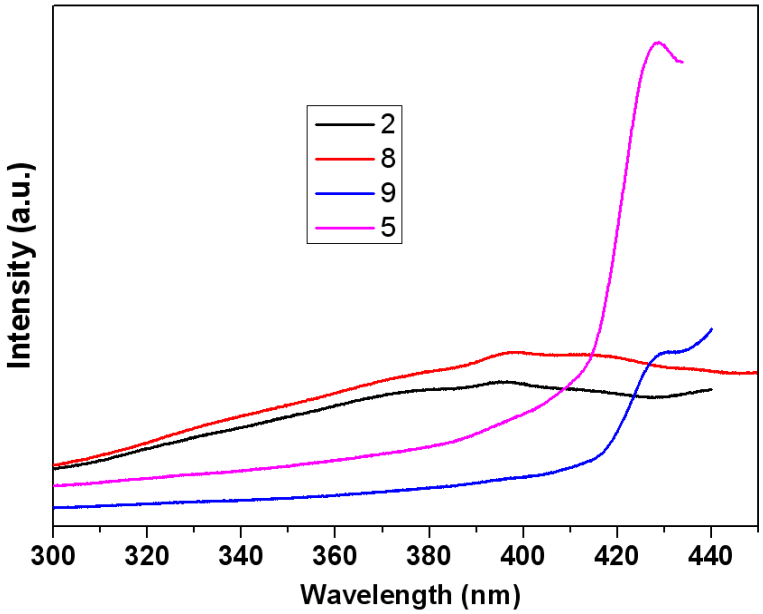

Fig. S13 The excitation spectra of complexes **2**, 5, **8** and **9**