

Figure S1. Conformational isomers of the bpa ligand in compound **4**.

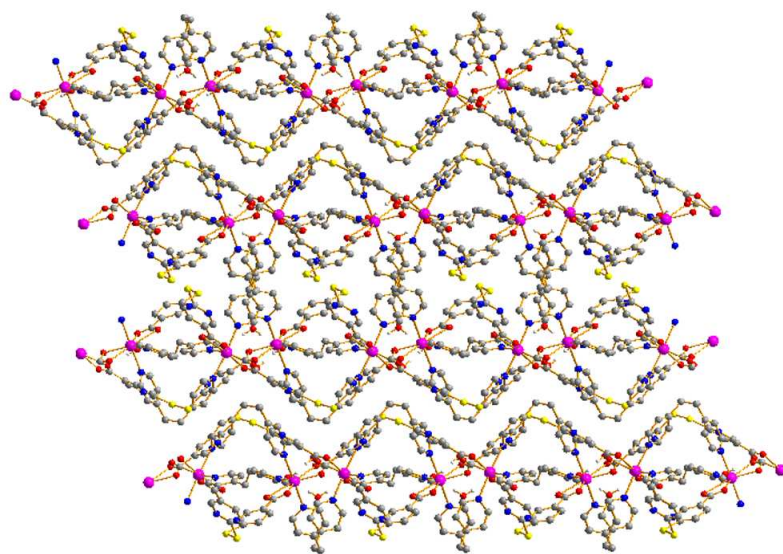


Figure S2. The alternating stack of 2D chiral layers with a sequence of ABAB in **4**.

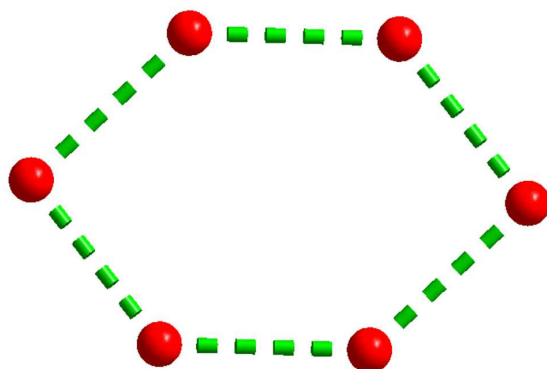


Figure S3. The hexamer with planar conformation through the strong hydrogen bonds in **5**.

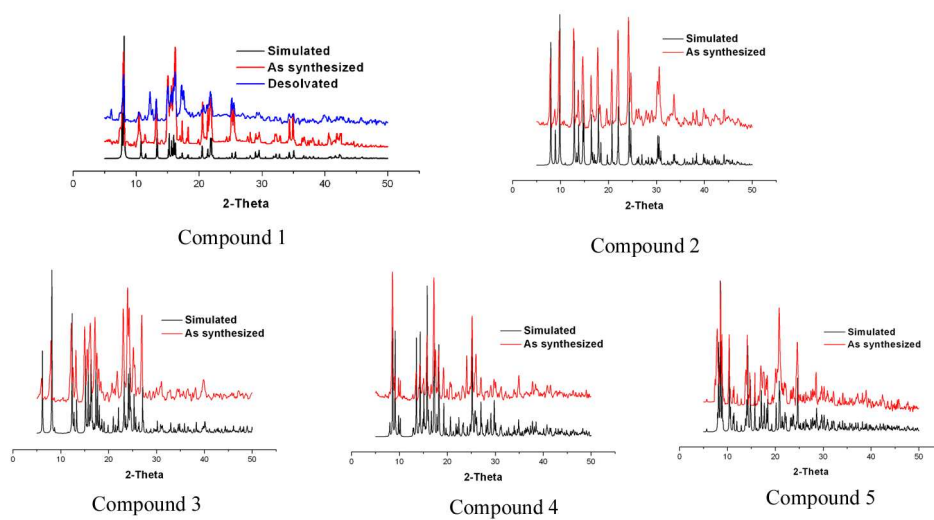


Figure S4. Comparison of XRPD patterns of the simulated pattern and the as-synthesized in compound **1–5** and the desolvated product in **1**.

Table S1 Selected bond lengths [Å] and angles [°] for complexes **1–5**.

Complex 1					
Zn(1)–O(1) ^a	2.017(6)	Zn(1)–O(4)	2.019(5)	Zn(1)–O(2) ^b	2.027(7)
Zn(1)–O(3) ^c	2.064(5)	Zn(1)–N(1) ^d	2.080(5)		
O(1) ^a –Zn(1)–O(4) ^a	89.0(3)	O(1) ^a –Zn(1)–O(2) ^b	157.9(2)	O(4)–Zn(1)–O(2) ^b	89.9(2)
O(1) ^a –Zn(1)–O(3) ^c	87.0(3)	O(4)–Zn(1)–O(3) ^c	157.95(19)	O(2) ^b –Zn(1)–O(3) ^c	85.8(2)
O(1) ^a –Zn(1)–N(1) ^d	99.9(2)	O(4)–Zn(1)–N(1) ^d	107.6(2)	O(2) ^b –Zn(1)–N(1) ^d	101.5(2)
O(3) ^c –Zn(1)–N(1) ^d	94.5(2)				
Complex 2					
Zn(1)–O(1)	2.028(9)	Zn(1)–O(2) ^a	2.035(9)	Zn(1)–O(4) ^b	2.049(9)
Zn(1)–O(3) ^c	2.135(9)	Zn(1)–N(3)	2.030(11)		
O(1)–Zn(1)–N(3)	100.5(4)	O(1)–Zn(1)–O(2) ^a	159.8(4)	N(3)–Zn(1)–O(2) ^a	98.6(4)
O(1)–Zn(1)–O(4) ^b	90.0(4)	N(3)–Zn(1)–O(4) ^b	106.9(5)	O(2) ^a –Zn(1)–O(4) ^b	90.5(4)
O(1)–Zn(1)–O(3) ^c	84.9(4)	N(3)–Zn(1)–O(3) ^c	94.0(5)	O(2) ^a –Zn(1)–O(3) ^c	87.5(4)
O(4) ^b –Zn(1)–O(3) ^c	159.0(4)				
Complex 3					
Zn(1)–O(1) ^a	1.941(3)	Zn(1)–N(1) ^b	2.030(4)	Zn(1)–N(2)	2.055(4)
Zn(1)–O(3)	2.058(5)	Zn(1)–O(4)	2.417(6)		
O(1) ^a –Zn(1)–N(1) ^b	120.14(17)	O(1) ^a –Zn(1)–N(2)	105.02(16)	N(1) ^b –Zn(1)–N(2)	100.41(18)
O(1) ^a –Zn(1)–O(3)	99.26(18)	N(1) ^b –Zn(1)–O(3)	91.9(2)	N(2)–Zn(1)–O(3)	142.0(2)
O(1) ^a –Zn(1)–O(4)	113.9(2)	N(1) ^b –Zn(1)–O(4)	120.4(2)	N(2)–Zn(1)–O(4)	87.99(19)
O(3)–Zn(1)–O(4)	55.2(2)				
Complex 4					
Cd(1)–O(4) ^a	2.353(6)	Cd(1)–N(1)	2.366(8)	Cd(1)–N(2)	2.365(6)
Cd(1)–N(3) ^b	2.370(7)	Cd(1)–O(2)	2.386(6)	Cd(1)–O(1)	2.494(6)
Cd(1)–O(3) ^a	2.573(7)				
O(4) ^a –Cd(1)–N(1)	91.7(2)	O(4) ^a –Cd(1)–N(2)	131.3(2)	N(1)–Cd(1)–N(2)	86.6(2)
O(4) ^a –Cd(1)–N(3) ^b	92.9(2)	N(1)–Cd(1)–N(3) ^b	174.1(2)	N(2)–Cd(1)–N(3) ^b	87.6(2)
O(4) ^a –Cd(1)–O(2)	91.8(2)	N(1)–Cd(1)–O(2)	92.1(2)	N(2)–Cd(1)–O(2)	136.9(2)
N(3) ^b –Cd(1)–O(2)	91.4(2)	O(4) ^a –Cd(1)–O(1)	145.8(2)	N(1)–Cd(1)–O(1)	91.6(2)
N(2)–Cd(1)–O(1)	82.8(2)	N(3) ^b –Cd(1)–O(1)	86.6(2)	O(2)–Cd(1)–O(1)	54.09(19)
O(4) ^a –Cd(1)–O(3) ^a	53.4(2)	N(1)–Cd(1)–O(3) ^a	84.9(2)	N(2)–Cd(1)–O(3) ^a	78.0(2)
N(3) ^b –Cd(1)–O(3) ^a	95.0(2)	O(2)–Cd(1)–O(3) ^a	144.8(2)	O(1)–Cd(1)–O(3) ^a	160.7(2)
Complex 5					

Cd(1)–O(4) ^a	2.208(3)	Cd(1)–O(7) ^b	2.244(2)	Cd(1)–O(2)	2.272(3)
Cd(1)–N(5)	2.282(3) ^v	Cd(1)–O(5)	2.290(2)	Cd(1)–O(9)	2.372(2)
Cd(2)–O(1)	2.237(3)	Cd(2)–O(3) ^a	2.285(3)	Cd(2)–O(10)	2.298(3)
Cd(2)–O(11)	2.317(3)	Cd(2)–N(6) ^c	2.323(3)	Cd(2)–O(9)	2.365(2)
O(4) ^a –Cu(1)–O(7) ^b	172.12(12)	O(4) ^a –Cd(1)–O(2)	80.35(12)	O(7) ^b –Cd(1)–O(2)	92.62(11)
O(4) ^a –Cd(1)–N(5)	92.25(11)	O(7) ^b –Cd(1)–N(5)	85.48(9)	O(2)–Cd(1)–N(5)	100.30(11)
O(4) ^a –Cd(1)–O(5)	92.08(12)	O(7) ^b –Cd(1)–O(5)	95.40(10)	O(2)–Cd(1)–O(5)	168.58(10)
N(5)–Cd(1)–O(5)	88.45(10)	O(4) ^a –Cd(1)–O(9)	99.45(10)	O(7) ^b –Cd(1)–O(9)	83.84(8)
O(2)–Cd(1)–O(9)	88.78(10)	N(5)–Cd(1)–O(9)	166.28(9)	O(5)–Cd(1)–O(9)	84.02(8)
O(1)–Cd(2)–O(3) ^a	93.41(12)	O(1)–Cd(2)–O(10)	94.59(11)		
O(3) ^a –Cd(2)–O(10)		82.69(11)	O(1)–Cd(2)–O(11)		175.86(11)
O(3) ^a –Cd(2)–O(11)		85.15(12)	O(10)–Cd(2)–O(11)		89.09(12)
O(1)–Cd(2)–N(6) ^c		87.98(10)	O(3) ^a –Cd(2)–N(6) ^c		172.34(11)
O(10)–Cd(2)–N(6) ^c		89.69(10)	O(11)–Cd(2)–N(6) ^c		93.96(12)
O(1)–Cd(2)–O(9)		95.80(9)	O(3) ^a –Cd(2)–O(9)		101.77(11)
O(10)–Cd(2)–O(9)		168.42(10)	O(11)–Cd(2)–O(9)		80.72(10)
N(6) ^c –Cd(2)–O(9)		85.56(9)			

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

For 2: ^a -x+1,-y+1,-z+1; ^b x-1,y,z+1; ^c -x+2,-y+1,-z.

For 3: ^a x,y,z+1; ^b x,y-1,z;

For 4: ^a -x+1,y-1,-z+1/2 z; ^b -x+1/2,y-1/2,-z+1/2.

For 5: ^a x,-y+3/2,z-1/2; ^b -x+2,-y,-z+2; ^c x-1,y,z.

Table S2 Hydrogen-bonding geometries for compound **5**.

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A (°)
Complex 5				
O(10)–H(10C)···O(13)#1	0.82	2.01	2.813(4)	166
O(10)–H(10D)···O(6)#2	0.82	1.91	2.727(4)	176
O(11)–H(11C)···O(12)	0.82	1.89	2.672(5)	159
O(11)–H(11D)···O(15)#1	0.82	2.39	3.140(5)	152
O(12)–H(12C)···O(1)#3	0.82	2.33	3.017(5)	142
O(12)–H(12D)···N(3)#4	0.82	2.06	2.857(5)	165
O(13)–H(13C)···O(14)#1	0.82	2.03	2.815(5)	159
O(13)–H(13D)···N(1)#5	0.82	2.10	2.883(5)	160
O(14)–H(14C)···O(15)	0.82	2.15	2.847(6)	142

O(14)–H(14D)···O(8)#6	0.82	2.00	2.819(4)	174
O(15)–H(15C)···O(11)#1	0.82	2.60	3.140(5)	125
O(15)–H(15D)···O(13)	0.82	1.99	2.775(6)	160

For **5**: #1 1-x, 1-y, 1-z, #2 1-x, 1/2+y, 3/2-z, #3 1-x, -1/2+y, 3/2-z, #4 1-x, 1/2+y, 3/2-z, #5, x, 3/2-y, -1/2+z, #6 -1+x, 1/2-y, -1/2+z.

Table S3 S–S bond lengths [Å] and C–S–S–C torsion angles [°], the dihedral angles of the two pyridyl rings [°] in the cpds²⁻ ligands.

Complexes	S–S distance (Å)	C–S–S–C torsion angle(°)	Dihedral angle of the two pyridyl rings (°)
1	2.041	80.96	84.93
2	2.030	86.23	86.33
3	2.020	92.69	85.77
4	1.963	101.89	67.89
5	2.026	83.18	75.28
	2.034	87.68	69.58