Supporting Information

Thiocyanate-induced conformational transformation of a flexible fluconazole ligand in Cd(II) coordination polymers

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Table S1. Crystal data and structure refinements

	1	2	3	4	5	6
Empirical formula	$C_{26}H_{28}CdCl_2F_4N_{12}O_{12}$	$C_{39}H_{37}CdF_6N_{20}O_{9.5}$	$C_{27}H_{24}CdClF_4N_{13}O_6S$	$C_{27}H_{24}CdF_4N_{14}O_5S$	$C_{27}H_{24}CdClF_4N_{13}O_2S$	$C_{28}H_{28}CdF_4N_{14}O_4S_2$
Formula weight	959.90	1164.29	882.50	845.06	818.50	877.16
T [K]	293(2)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	P-1	P-1	P-1	P-1	P-1	P2(1)/c
a [Å]	8.0708(6)	10.816(3)	10.6019(9)	10.693(6)	10.418(7)	8.965(6)
b [Å]	10.1838(7)	15.076(4)	12.0311(11)	12.064(7)	11.828(8)	12.605(9)
c [Å]	11.5445(8)	15.098(4)	14.5296(12)	14.206(8)	14.374(9)	17.485(14)
α [°]	89.5510(10)	79.599(4)	87.735(2)	87.859(7)	89.593(9)	
β [°]	86.1850(10)	89.568(4)	77.347(2)	77.101(7)	71.405(9)	114.149(14)
γ [°]	67.5610(10)	89.695(4)	75.328(2)	74.224(7)	77.472(8)	
Volume (Å³)	874.92(11)	2421.4(12)	1749.1(3)	1718.7(17)	1635.0(19)	1803(2)
Z	1	2	2	2	2	2
D_{calc} (g·cm⁻³)	1.822	1.597	1.676	1.633	1.663	1.616
μ (mm⁻¹)	0.878	0.550	0.843	0.777	0.886	0.798
Collected/ Unique	4791 / 3047	13250 / 8480	9151 / 6269	9464 / 6081	8897 / 5774	8696 / 3215
(R$_{int}$)	(0.014)	(0.018)	(0.031)	(0.015)	(0.037)	(0.151)
GOF on F²	1.05	1.09	1.02	1.05	1.00	0.95
R$_1$/wR$_2$ [I>2σ(I)]	0.0297/0.0825	0.0327/0.0862	0.0513/ 0.1140	0.0317/0.0822	0.0502/0.145	0.0880/ 0.2108
Max/min ρ [e Å⁻³]	0.61/-0.75	0.68/-0.61	0.45/ -0.57	0.50/-0.42	1.48/-0.85	0.75/-1.01

Table S2. Selected bond lengths (Å) and angles (°)

1

Cd(1)–O(2)	2.320(2)	Cd(1)–N(1)	2.339(2)	Cd(1)–N(6)#1	2.321(2)
O(2)–Cd(1)–N(6)#1	89.43(8)	O(2)–Cd(1)–N(6)#2	90.57(8)	O(2)#3–Cd(1)–N(1)	89.83(9)
O(2)–Cd(1)–N(1)	90.17(9)	N(6)#1–Cd(1)–N(1)	90.16(8)	N(6)#2–Cd(1)–N(1)	89.84(8)

2

Cd(1)–N(1)	2.453(2)	Cd(1)–N(6)#2	2.363(2)	Cd(1)–N(7)	2.323(2)
Cd(1)–N(12) #4	2.383(2)	Cd(1)–N(13)	2.310(2)	Cd(1)–O(5)	2.419(3)
N(13)–Cd(1)–N(7)	178.05(8)	N(13)–Cd(1)–N(6)#2	90.87(8)	N(7)–Cd(1)–N(6)#2	91.01(8)
N(13)–Cd(1)–N(12)#4	89.38(8)	N(7)–Cd(1)–N(12)#4	88.68(8)	N(6)#2–Cd(1)–N(12)#4	169.22(8)
N(13)–Cd(1)–O(5)	87.09(9)	N(7)–Cd(1)–O(5)	92.58(9)	N(6)#2–Cd(1)–O(5)	115.70(9)
N(12)#3–Cd(1)–O(5)	75.07(8)	N(13)–Cd(1)–N(1)	90.61(8)	N(7)–Cd(1)–N(1)	89.00(8)
N(6)#2–Cd(1)–N(1)	85.90(8)	N(12)#3–Cd(1)–N(1)	83.33(7)	O(5)–Cd(1)–N(1)	158.30(9)

3

Cd(1)–N(1)	2.380(5)	Cd(1)–N(6)#7	2.348(5)	Cd(1)–N(7)	2.384(4)
Cd(1)–N(12)#6	2.341(4)	Cd(1)–N(13)#5	2.291(6)	Cd(1)–S(1)	2.686(2)
N(13)#5–Cd(1)–N(12)#6	92.41(18)	N(13)#5–Cd(1)–N(6)#7	88.45(18)	N(12)#6–Cd(1)–N(6)#7	177.37(16)
N(13)#5–Cd(1)–N(1)	84.18(16)	N(12)#6–Cd(1)–N(1)	88.95(16)	N(6)#7–Cd(1)–N(1)	88.67(16)
N(13)#5–Cd(1)–N(7)	171.02(16)	N(12)#6–Cd(1)–N(7)	85.05(15)	N(6)#7–Cd(1)–N(7)	93.73(16)
N(1)–Cd(1)–N(7)	87.17(15)	N(13)#5–Cd(1)–S(1)	100.86(12)	N(12)#6–Cd(1)–S(1)	89.72(12)
N(6)#7–Cd(1)–S(1)	92.56(12)	N(1)–Cd(1)–S(1)	174.84(11)	N(7)–Cd(1)–S(1)	87.75(12)
N(13)–C(27)–S(1)	178.1(6)				

4

Cd(1)–N(1)	2.337(3)	Cd(1)–N(6)#8	2.384(3)	Cd(1)–N(7)	2.380(3)
Cd(1)–N(12)#6	2.329(3)	Cd(1)–N(13)	2.296(4)	Cd(1)–S(1)#4	2.7005(17)
N(13)–Cd(1)–N(12)#6	91.80(12)	N(13)–Cd(1)–N(1)	90.48(12)	N(12)#6–Cd(1)–N(1)	177.10(10)
N(13)–Cd(1)–N(7)	172.15(9)	N(12)#6–Cd(1)–N(7)	85.44(9)	N(1)–Cd(1)–N(7)	92.07(9)
N(13)–Cd(1)–N(6)#8	83.24(9)	N(12)#6–Cd(1)–N(6)#8	88.66(9)	N(1)–Cd(1)–N(6)#8	89.82(9)
N(7)–Cd(1)–N(6)#8	89.34(8)	N(13)–Cd(1)–S(1)#4	100.54(6)	N(12)#6–Cd(1)–S(1)#4	89.69(6)
N(1)–Cd(1)–S(1)#4	91.67(6)	N(7)–Cd(1)–S(1)#4	86.81(6)	N(6)#8–Cd(1)–S(1)#4	175.92(7)
N(13)–C(27)–S(1)	178.5(3)				

5

Cd(1)–N(1)	2.355(5)	Cd(1)–N(6)#9	2.402(4)	Cd(1)–N(7)	2.388(5)
Cd(1)–N(12)#4	2.350(5)	Cd(1)–Cl(1)	2.611(2)	Cd(1)–Cl(1)#10	2.656(2)
N(12)#4–Cd(1)–N(1)	169.35(15)	N(12)#4–Cd(1)–N(7)	81.29(15)	N(1)–Cd(1)–N(7)	88.07(15)
N(12)#4–Cd(1)–N(6)#9	90.56(15)	N(1)–Cd(1)–N(6)#9	88.59(14)	N(7)–Cd(1)–N(6)#9	87.09(15)
N(12)#4–Cd(1)–Cl(1)	91.08(12)	N(1)–Cd(1)–Cl(1)	91.00(9)	N(7)–Cd(1)–Cl(1)	99.62(11)
N(6)#9–Cd(1)–Cl(1)	173.26(10)	N(12)#4–Cd(1)–Cl(1)#10	92.75(11)	N(1)–Cd(1)–Cl(1)#10	97.81(11)
N(7)–Cd(1)–Cl(1)#10	171.53(11)	N(6)#9–Cd(1)–Cl(1)#10	86.96(10)	Cl(1)–Cd(1)–Cl(1)#10	86.43(4)
Cd(1)–Cl(1)–Cd(1)#10	93.57(4)				

6

Cd(1)–N(1)	2.321(10)	Cd(1)–N(6)#11	2.312(8)	Cd(1)–N(7)	2.231(11)
N(7)–Cd(1)–N(6)#11	89.0(3)	N(7)–Cd(1)–N(6)#12	91.0(3)	N(7)–Cd(1)–N(1)	89.3(4)

N(7)#7–Cd(1)–N(1)	90.8(4)	N(6)#11–Cd(1)–N(1)	91.5(3)	N(6)#12–Cd(1)–N(1)	88.5(3)
N(7)–C(14)–S(1)	174.6(14)				

Symmetry code: #1 -x+1,-y,-z; #2 -x+1,-y+1,-z; #3 -x+1,-y,-z; #4 x+1,y,z; #5 -x,-y+2,-z+1; #6 x-1,y,z; #7 -x+1,-y+1,-z+1; #8 -x+1,-y,-z+1; #9 -x+1,-y+2,-z+1; #10 -x+2,-y+1,-z+1; #11 x+1,-y+1/2,z+1/2; #12 -x,y+1/2,-z+1/2.

Table S3. Selected hydrogen bonding interaction

	D–H⋯A	d(D–H)/ Å	d(H⋯A)/ Å	d(D⋯A)/ Å	∠DHA / °
1	O(1)–H(1)⋯O(5)	0.82	2.59	3.265(6)	140
	O(2)–H(2A)⋯O(6)#1	0.85	1.97	2.818(4)	172
	O(2)–H(2B)⋯N(5)#2	0.85	2.11	2.952(4)	169
	C(2)– H(2)⋯O(3)#3	0.93	2.53	3.417(5)	159
	C(5)– H(5A)⋯O(4)	0.97	2.46	3.291(5)	143
	C(6)–H(6)⋯ O(3)#4	0.93	2.34	3.268(4)	172
	C(7)– H(7)⋯O(6)	0.93	2.53	3.449(5)	170
2	O(1)–H(1W)⋯O(7)#1	0.82	2.01	2.822(3)	170
	O(2)–H(2W)⋯O(7)	0.82	2.08	2.820(3)	150
	O(3)–H(3W)⋯F(4)#5	0.82	2.41	2.990(3)	128
	O(10)–H(10A)⋯N(14)#6	0.96	2.37	3.214(7)	147
	C(2)–H(2)⋯ O(9)#1	0.93	2.47	3.288(4)	147
	C(19)–H(19)⋯O(8)	0.93	2.30	3.182(4)	157
	C(29)–H(29A)⋯F(6)#7	0.97	2.34	3.267(4)	161
	C(29)–H(29B)⋯F(1)#8	0.97	2.44	3.312(4)	149
	C(1)–H(1A)⋯O(6)#9	0.93	2.60	3.373(4)	140
	C(1)–H(1A)⋯O(5)#9	0.93	2.69	3.411(4)	134
	C(14)–H(14)⋯O(6)#9	0.93	2.62	3.439(4)	148
3	O(1)–H(1W)⋯O(5)	0.82	2.21	2.969(7)	155
	O(2)–H(2W)⋯O(5)#10	0.82	2.37	3.057(7)	142
	O(2)–H(2W)⋯O(6)#10	0.82	2.53	3.319(9)	162
	C(3)–H(3B)⋯O(4)#10	0.93	2.66	3.591(7)	163
	C(3)–H(3A)⋯F(1)	0.97	2.27	2.927(6)	124
	C(18)–H(18B)⋯F(2)#11	0.97	2.48	3.190(8)	130
4	O(2)–H(2W)⋯O(3)	0.82	2.02	2.757(4)	150
	C(6)–H(6)⋯O(5)	0.93	2.42	3.233(5)	145
	C(18)–H(18A)⋯O(4)	0.97	2.64	3.482(5)	146
	C(16)–H(16A)⋯O(3)	0.97	2.61	3.351(5)	134
	C(5)–H(5B)⋯F(4)	0.97	2.35	2.966(4)	121
	C(16)–H(16A)⋯F(1)	0.97	2.44	3.054(4)	120
	C(16)–H(16B)⋯N(11)	0.97	2.51	3.152(6)	124
	C(18)–H(18A)⋯F(3)#12	0.97	2.49	3.366(6)	150
	C(19)–H(19)⋯F(3)	0.93	2.44	3.155(5)	133
5	O(2)–H(2W)⋯N(13)	0.82	1.99	2.772(12)	159
	C(14)–H(14)⋯F(2)#13	0.93	2.53	3.289(8)	139
	C(15)–H(15)⋯N(2)#10	0.93	2.43	3.323(7)	160
	C(25)–H(25)⋯N(13)	0.93	2.38	3.155(12)	141
6	O(1)–H(1C)⋯N(2)	0.83	2.16	2.882(7)	145
	O(1W)–H(1WB)⋯S(1)#10	0.97	2.57	3.422(6)	146
	C(1)–H(1)⋯O(1W)#10	0.93	2.26	3.183(7)	169

Smmetry code: #1 1-x,1-y,-z; #2 -x,1-y,-z; #3 -1+x,y,z; #4 -1+x,1+y,z; #5 x,y,-1+z; #6 -1+x,y,1+z; #7 2-x,1-y,-1-z; #8 2-x,1-y,-z; #9 2-x, -y, -z; #10 1-x,1-y,1-z; #11 2-x,1-y,-z; #12 1+x,y,-1+z; #13 x,y,1+z

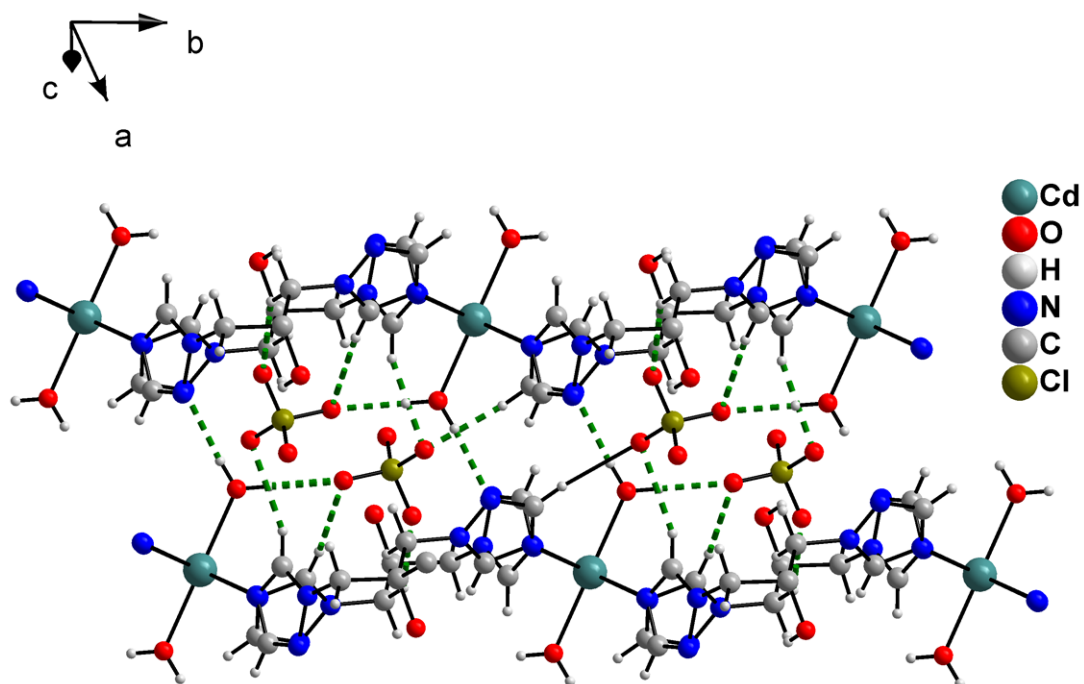**Fig. S1.** The ClO$_4^-$ anions are fixed between the 1-D chain through hydrogen bonds in **1**.

Figure S2. (a) Coordination geometry of **2**, (b) 1D ladder-like structure of **2**.
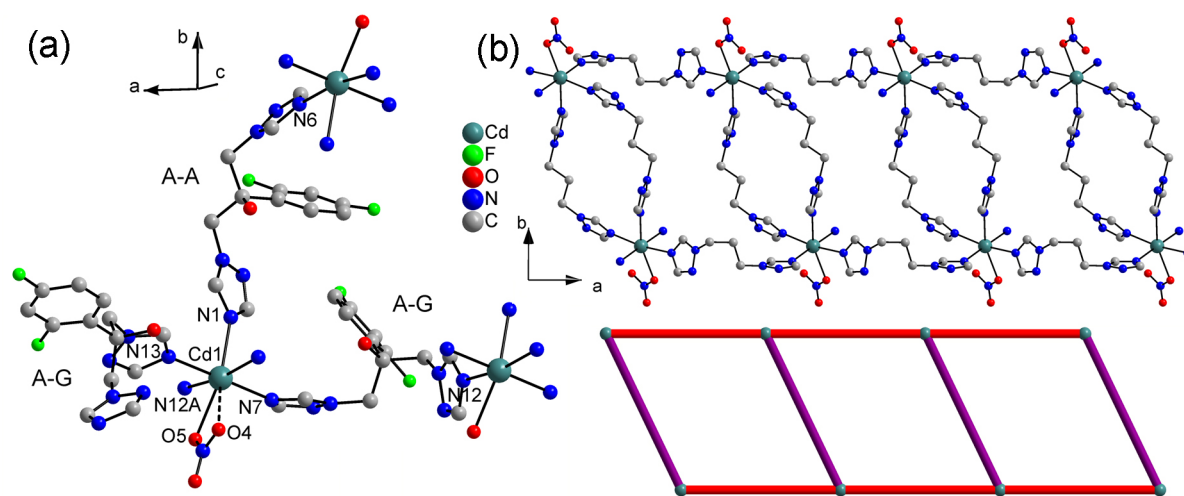
Fig. S3 (a) The ClO_4^- anions are fixed between the layers in **3** through hydrogen bonds, (b)

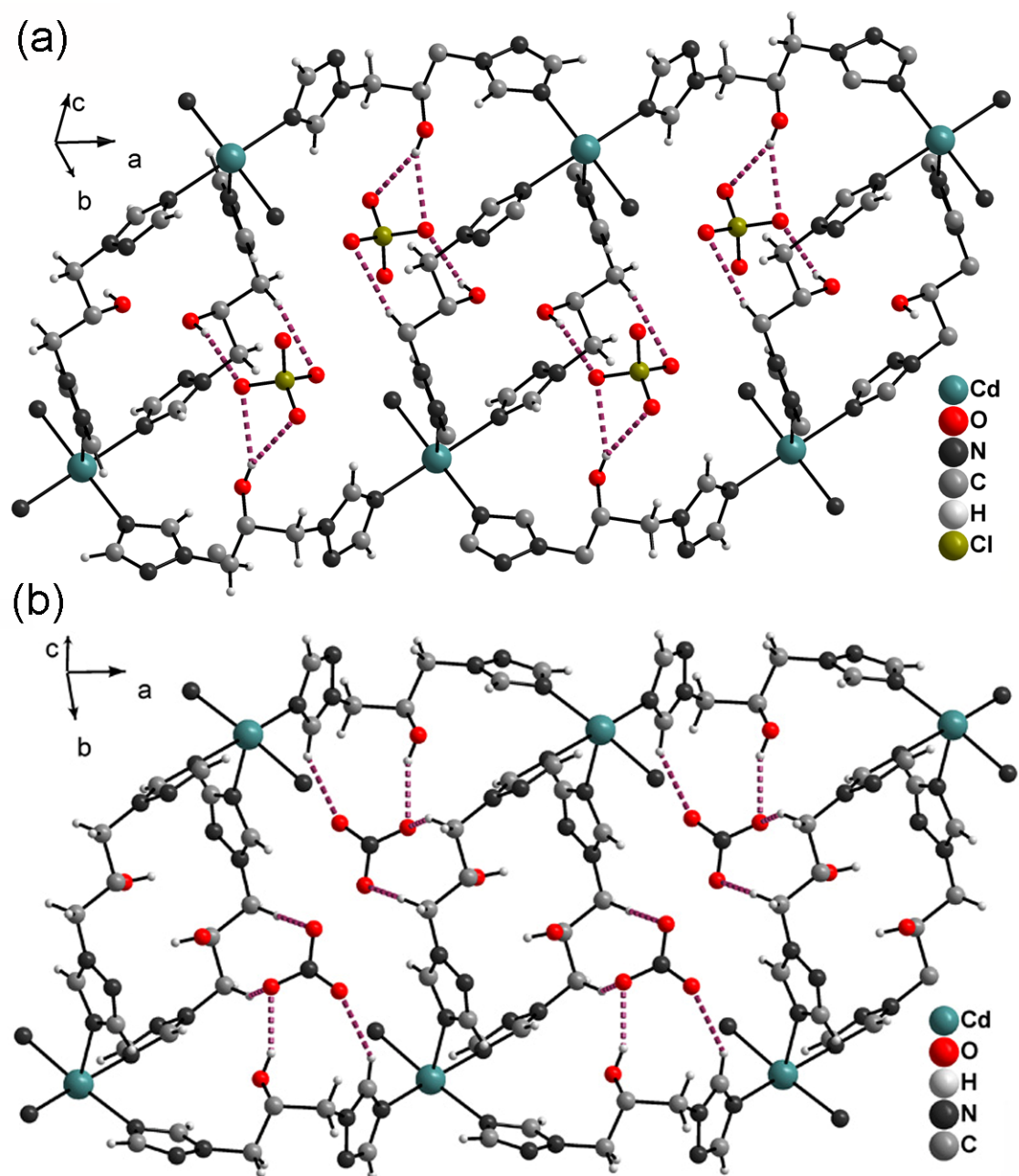The NO_3^- anions are fixed between the layers in **4** through hydrogen bonds
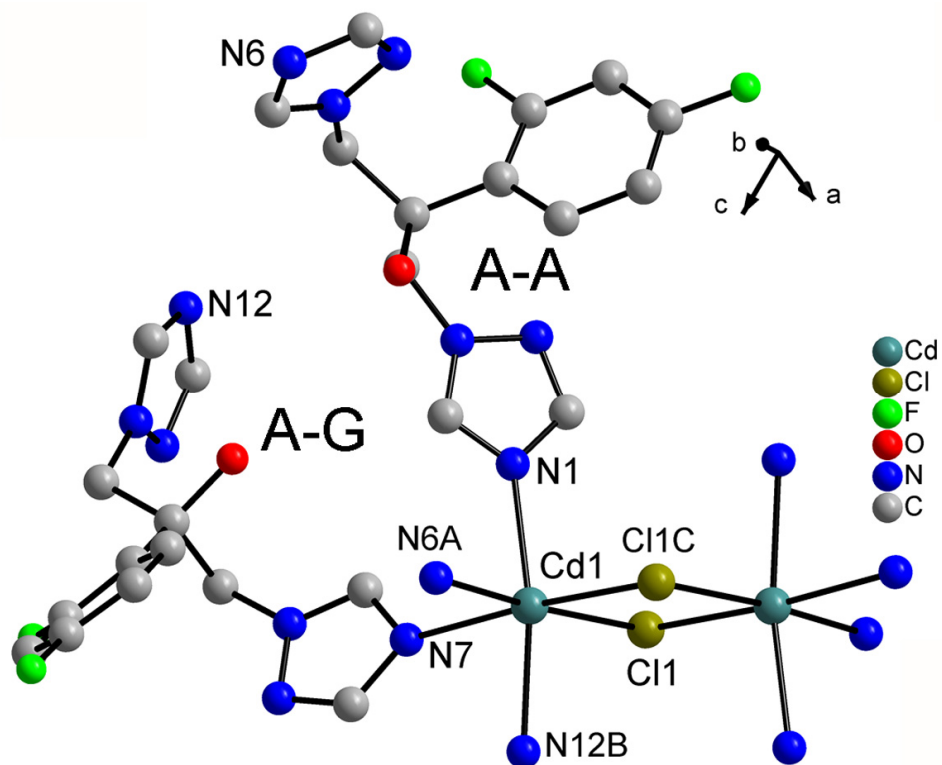
Figure S4. Coordination geometry of **5.**
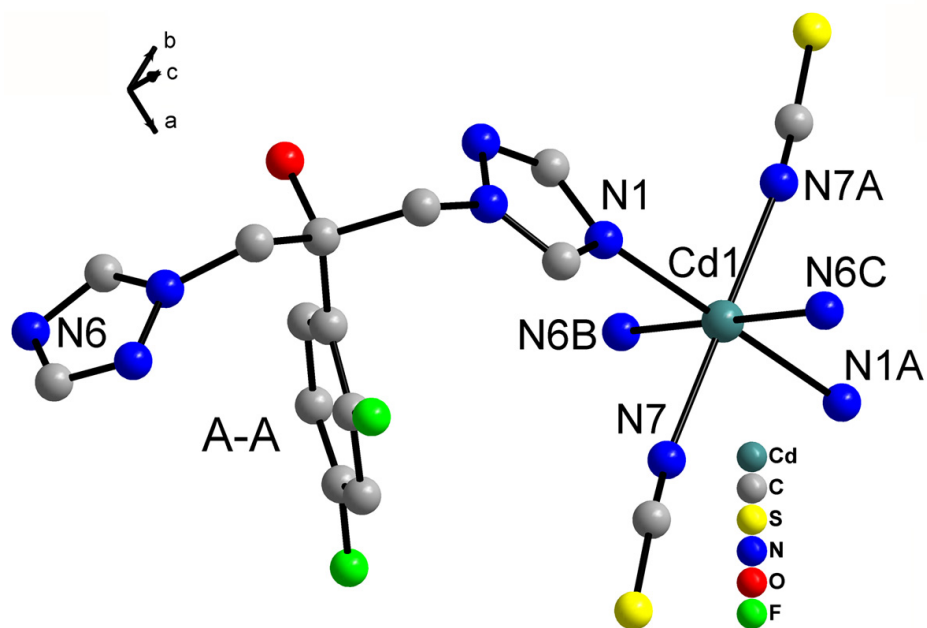
Figure S5. Coordination geometry of **6**.

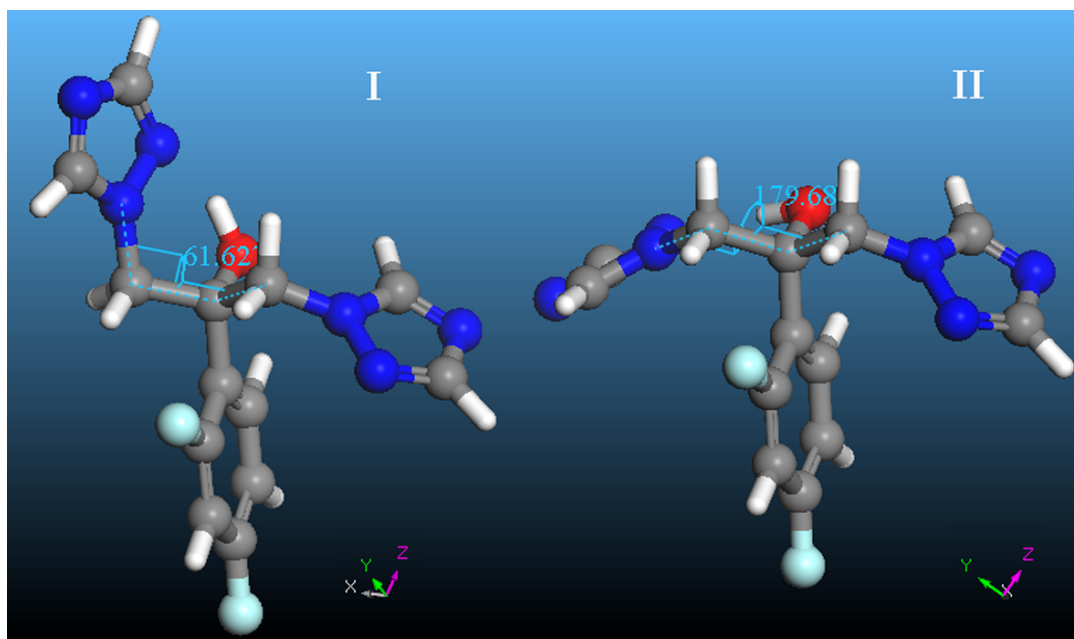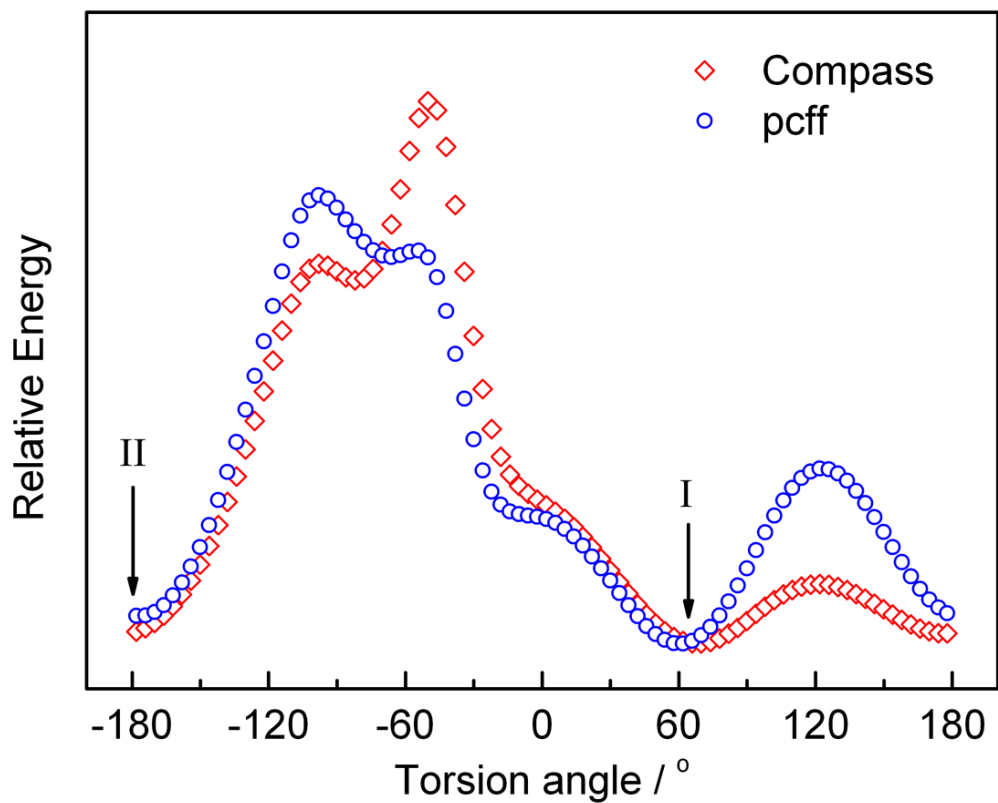**Figure S6.** PXRD and simulated spectra from crystal data for polymers **3**, **4**, **5** and **6**

Fig. S7 The energy related conformation transformation in the range of -180~180° calculated

by *Conformation Tools* in *Material Studio* 4.3

NOTE: The structure of HFlu in this calculation was obtained directly from CIF data of free HFlu ligand

and then geometry optimized by *Dmol³* program (Functional: BLYP; Basis set: DNP, all calculation quality set to be fine). The optimized structure showed no imaginary frequency. The conformational calculation was then carried out with *Conformers* program (Forcefield: Compass or pcff. All calculation quality set to be ultra-fine). Only gauche form to anti form transformation process was taken in consideration and the motion groups were kept rigid. The results of the two stable conformers **I** and **II** were then geometry optimized.

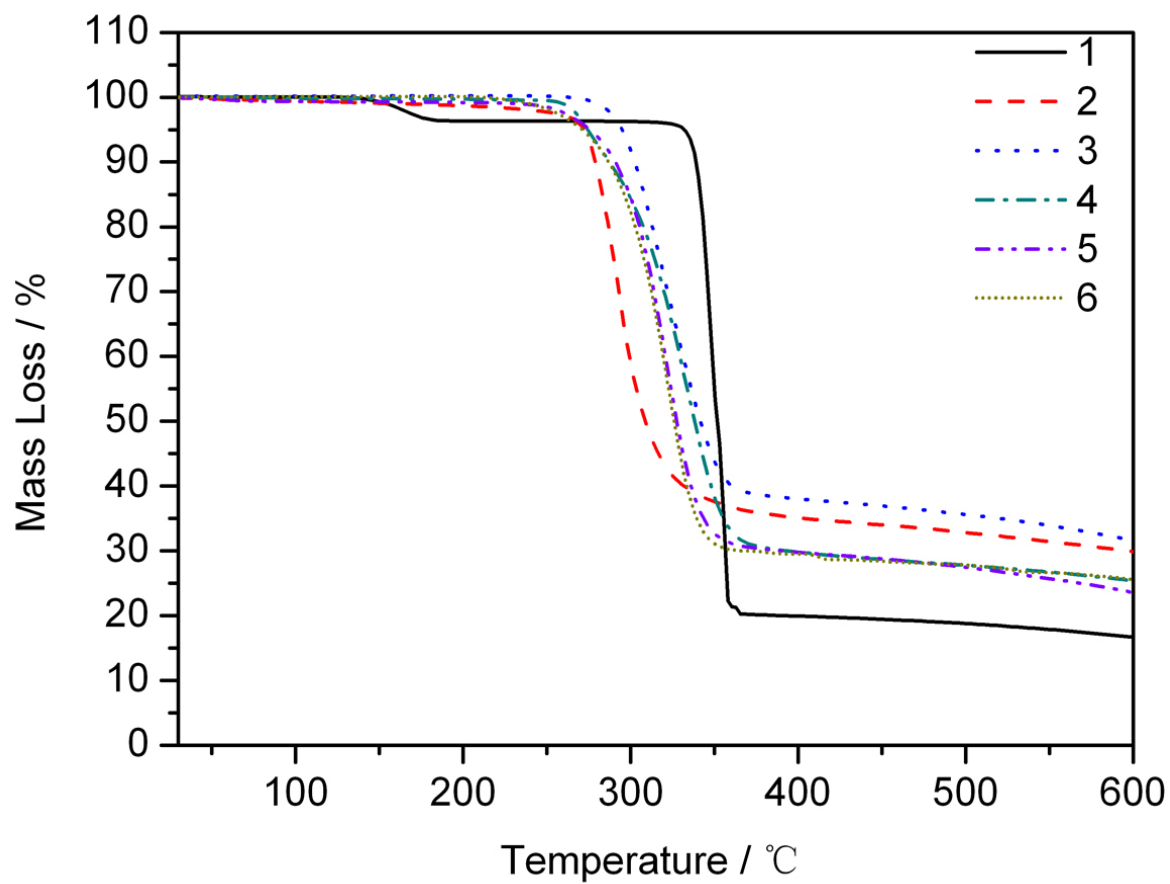**Figure S8.** TGA analyses for coordination polymers **1-6**

Figure S9. The emission spectra of coordination polymers **1-6** excited by 261 nm.