Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Tuning photoelectric response of pyrene-based coordination polymers by optimizing charge transfer

Wenjuan Xu,[a] Yupei Sun,[a] Xiangru Meng,[a] Wenjing Zhang[a] and Hongwei Hou*[a]

[a]The College of Chemistry, Green Catalysis Centre, Zhengzhou University,

Zhengzhou, Henan, 450001, P. R. China

Author for correspondence:

Prof. Hongwei Hou, E-mail: houhongw@zzu.edu.cn.

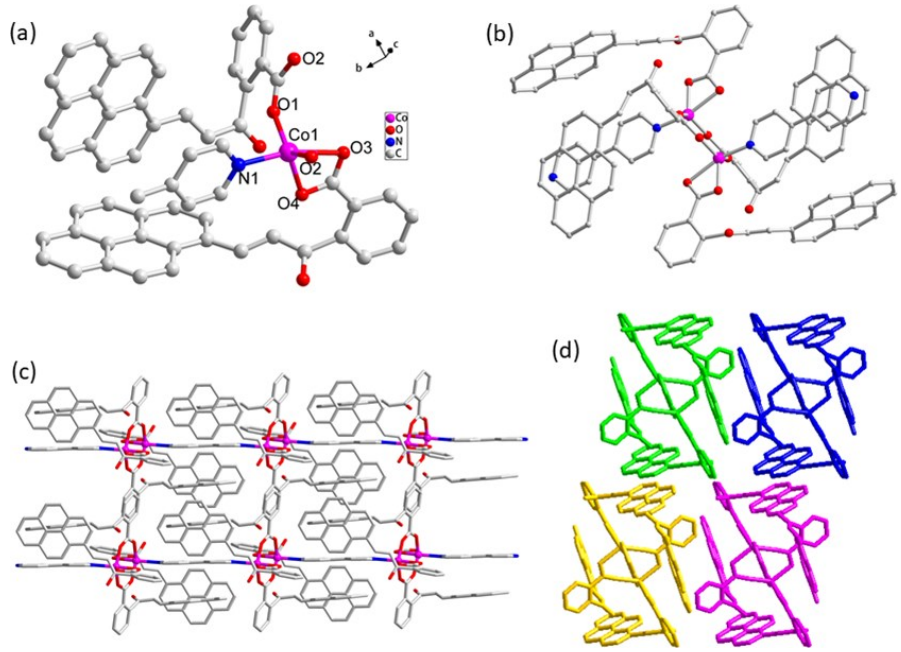

Figure S1. (a) View of the local coordination environment of Co atoms in **1**. (b) the dinuclear $[Co_2(COO)_4]$ secondary building unit in **1**. (c) The 2D layer through π-π stacking between the pyrene of L from different chains. (d) The single structure of **1** viewed down the b axis.

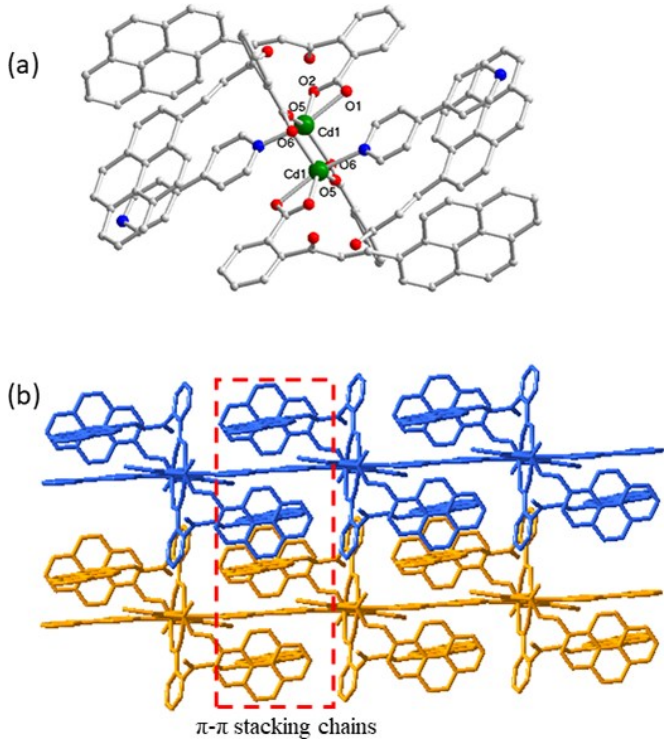

Figure S2. (a)The dinuclear $[Cd_2(COO)_4]$ secondary building unit in **2**. (c) The 2D plane through the π-π stacking between two adjacent chains in **2**.

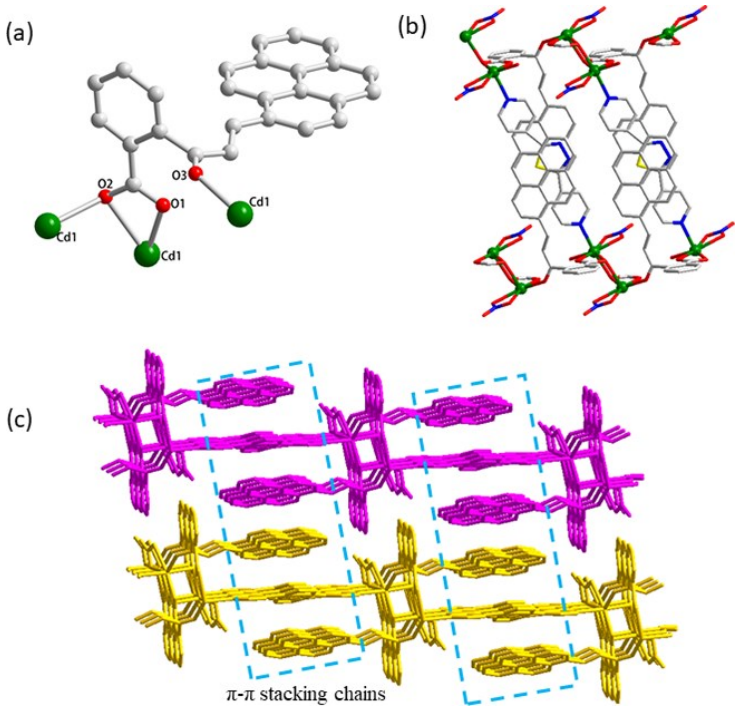

Figure S3. (a) View of the local coordination environment of L in **3**. (b) The link model of the dinuclear $[Cd_2(COO)_2(NO_3)_2]$ secondary building unit in **3**. (c) View of 3D supramolecular framework of **3**, which shows a staggered overlap between 2D zig-zag layers.

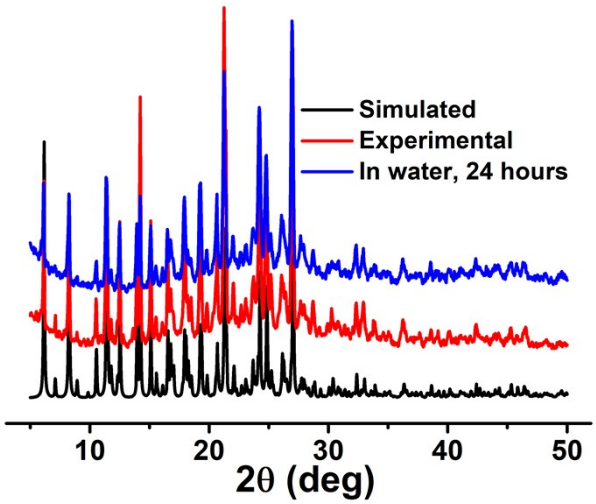

Figure S4. PXRD patterns of **1**; the simulated, experimental and after soaking in water for 24 h.

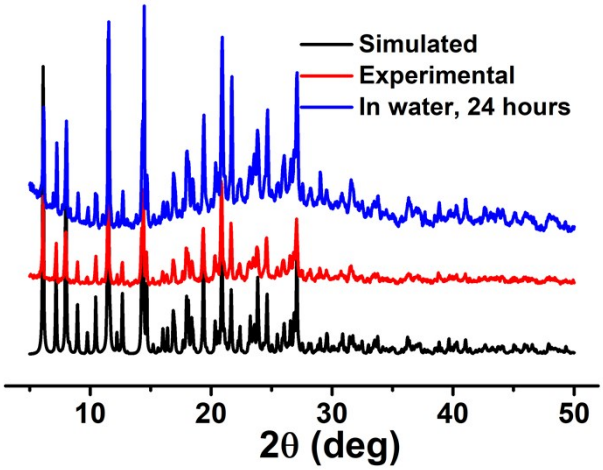

Figure S5. PXRD patterns of **2**; the simulated, experimental and after soaking in water for 24 h.

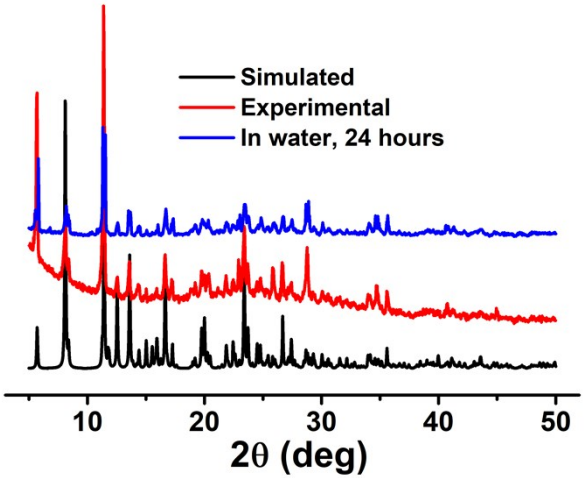

Figure S6. PXRD patterns of **3**; the simulated, experimental and after soaking in water for 24 h.

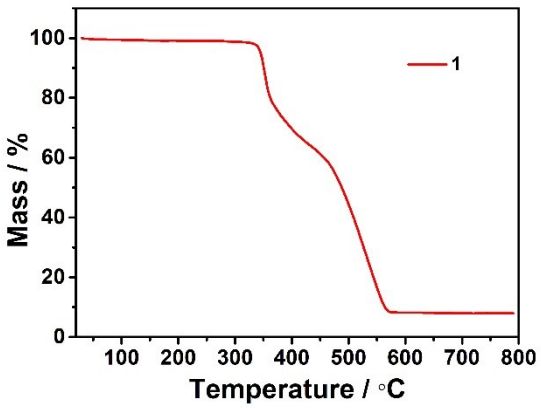

Figure S7. Thermogravimetric curve of **1**.

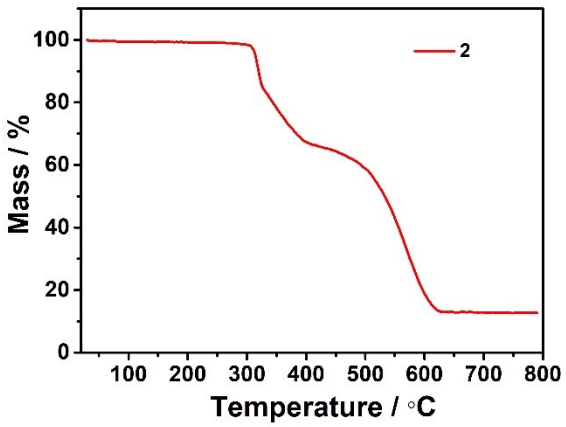

Figure S8. Thermogravimetric curve of **2**.

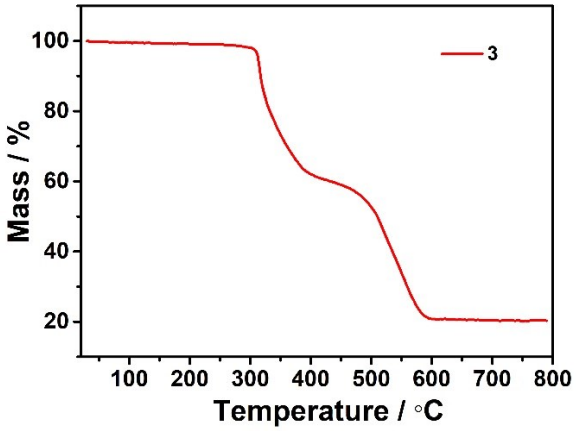

Figure S9. Thermogravimetric curve of **3**.

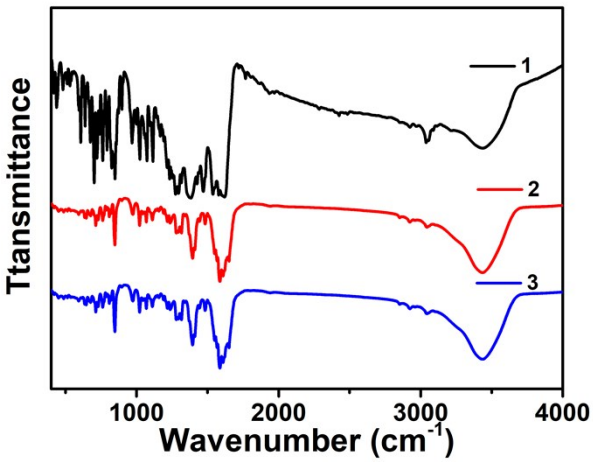

Figure S10. FT-IR spectra of **1**-**3**.

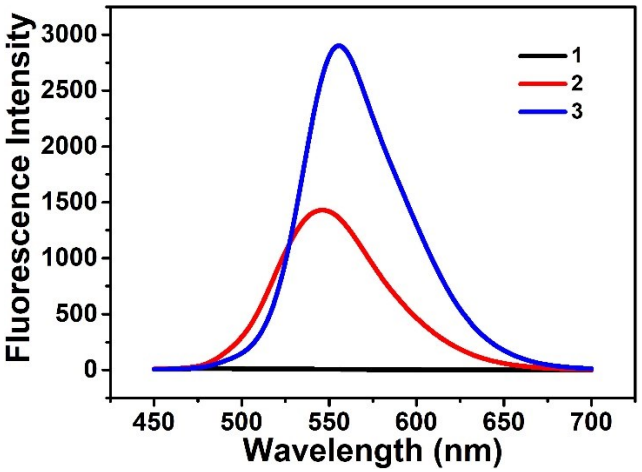

Figure S11. Fluorescence spectra of **1**-**3**.

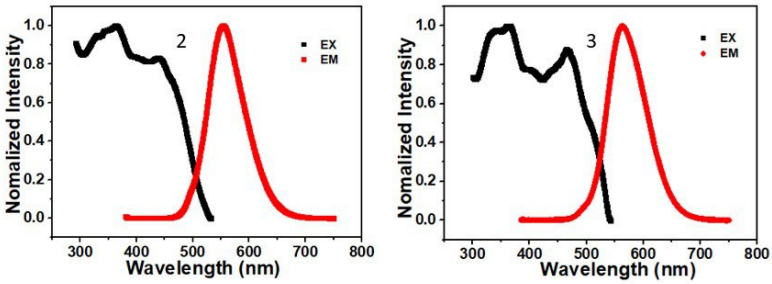

Figure S12. Excitation and emission spectra of **2** and **3**.

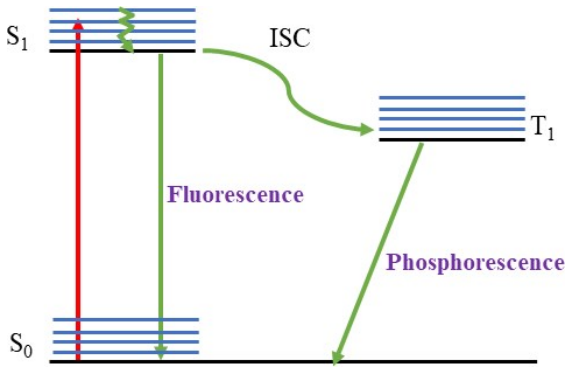

Figure S13. Schematic representation of fluorescence, phosphorescence and intersystem crossing (ISC).

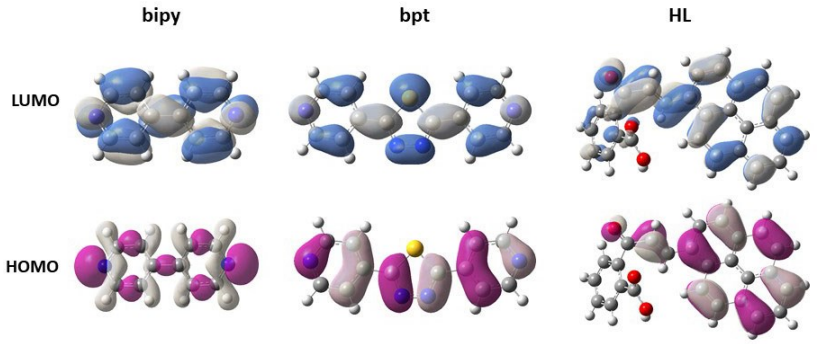

Figure S14. HOMO (down) and LUMO (top) profiles for bipy, bpt, and HL.

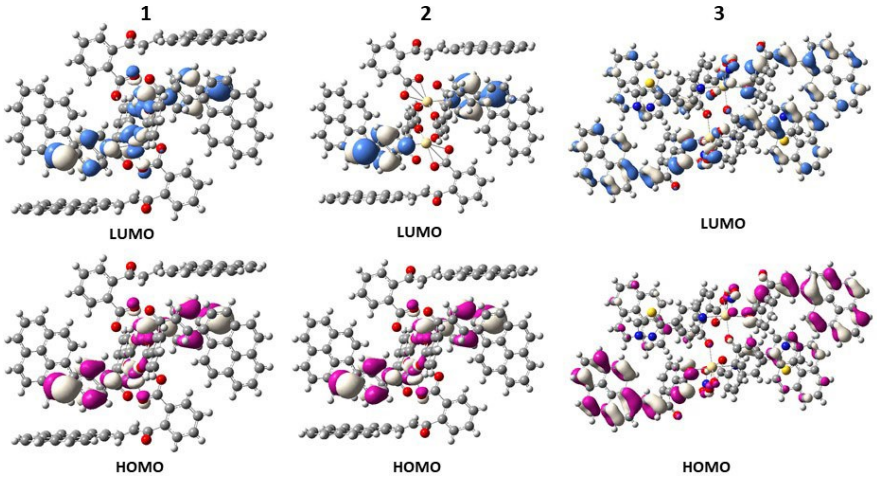

Figure S15. HOMO (down) and LUMO (top) profiles for CPs **1**-**3**.

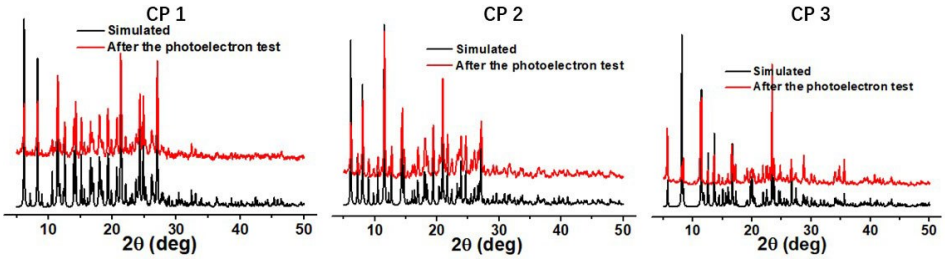

Figure S16. PXRD patterns of CPs **1**-**3**; the simulated and after the photoelectron performance test.

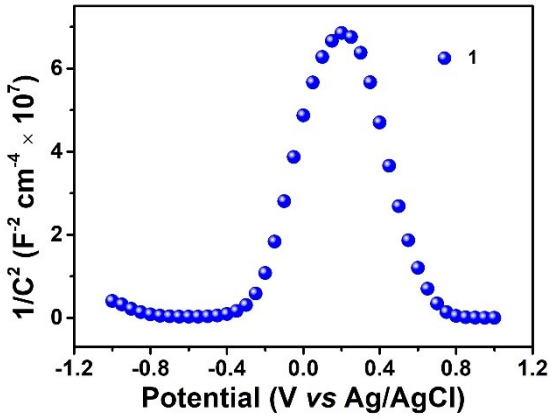

Figure S17. Mott–Schottky plots of **1** at an AC frequency of 1 kHz.

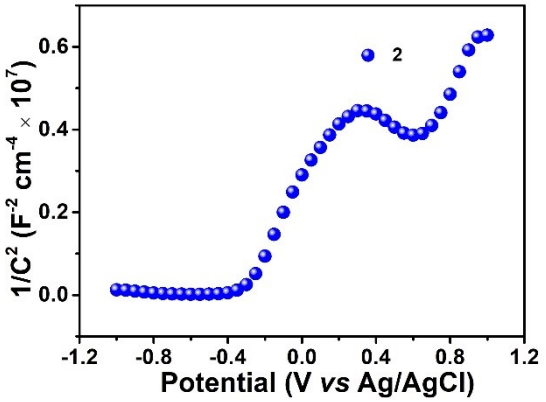

Figure S18. Mott–Schottky plots of **2** at an AC frequency of 1 kHz.

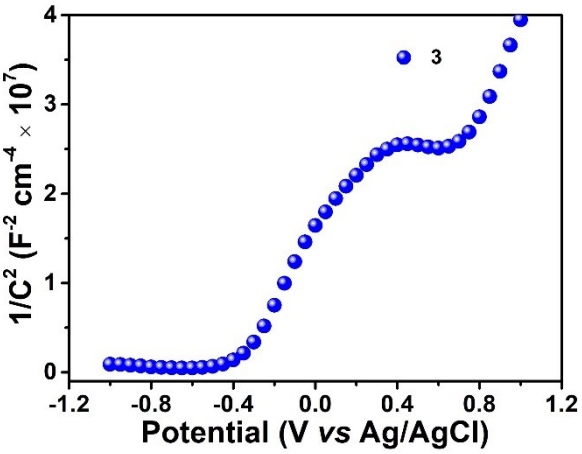

Figure S19. Mott–Schottky plots of **3** at an AC frequency of 1 kHz.

Table S1. Crystallographic data and structure refinement details for CP **1, 2** and **3**.

Compound	**1**	**2**	**3**
formula	$C_{57}H_{34}CoNO_6$	$C_{57}H_{34}CdNO_6$	$C_{64}H_{38}N_6O_{12}Cd_2S$
F_w	887.78	941.26	1339.88
T/K	293	293	293
I (Mo–Ka)/Å	0.71073	0.71073	0.71073
Crystsyst	*triclinic*	*triclinic*	*triclinic*
Space group	*P*-1	*P*-1	*P*-1
a/Å	11.1479(11)	11.4181(7)	7.5667(4)
b/Å	12.9707(13)	12.7554(8)	11.4452(7)
c/Å	15.2733(15)	15.1421(9)	16.3468(9)
α (deg)	102.828(3)	101.695(2)	72.161(2)
β (deg)	102.909(3)	100.518(2)	83.560(2)
γ (deg)	97.198(3)	97.560(2)	87.273(2)
V ($Å^3$)	2063.1(4)	2090.5(2)	1338.97(13)
Z	2	2	1
D_{calcd}(g cm^{-3})	1.429	1.495	1.662
F(000)	916.0	958.0	672.0
μ (mm^{-1})	0.475	0.581	0.908
GOF	1.109	1.013	1.035
R_1 ($I > 2\sigma(I)$)	0.0731	0.0520	0.0297
wR_2 ($I > 2\sigma(I)$)	0.1293	0.1333	0.0643

$$R = [\sum || F_0| - |F_c|| / \sum |F_0|], \; R_W = \sum_W [|F_0^2 - Fc^2|^2 / \sum_W (|F_w|^2)^2]^{1/2}$$

Table S2. Selected bond lengths (Å) and bond angles (deg) for **1**-**3** crystal structure description.

1			
Co(1)-O(1)	1.999(2)	Co(1)-O(3)	1.944(3)
Co(1)-O(4)	2.322(3)	Co(1)-O(6) #1	1.957(3)
Co(1)-N(1)	2.053(3)	O(1)-C(10)	1.276(4)
O(2)-C(22)	1.226(4)	O(3)-C(2)	1.232(4)
O(4)-C(10)	1.245(4)	O(5)-C(6)	1.213(4)
O(6)-C(2)	1.247(4)	N(1)-C(23)	1.326(4)
N(1)-C(35)	1.342(4)		
O(1)-Co(1)-O(4)	60.28(9)	O(1)-Co(1)-N(1)	103.59(11)
O(1)-Co(1)-C(10)	30.57(10)	O(3)-Co(1)-O(1)	111.81(11)
O(3)-Co(1)-O(4)	95.31(12)	O(3)-Co(1)-O(6) #1	134.50(12)
O(3)-Co(1)-N(1)	86.57(7)	O(4)-Co(1)-C(10)	29.71(9)
O(6)#1-Co(1)-O(1)	108.53(12)	O(6)#1-Co(1)-O(4)	92.39(13)
O(6)#1-Co(1)-N(1)	94.91(13)	O(6)#1-Co(1)-C(10)	102.24(13)
N(1)-Co(1)-O(4)	163.77(10)	N(1)-Co(1)-C(10)	134.12(12)
C(10)-O(1)-Co(1)	96.6(2)	C(2)-O(3)-Co(1)	144.1(2)
C(2)-O(6)-Co(1)#1	134.9(2)	C(23)-N(1)-Co(1)	122.7(3)
C(23)-N(1)-C(35)#1	116.4(3)	C(35)-N(1)-Co(1)	120.8(2)
Symmetry codes:	#1 -x,-y+2,-z		

2			
Cd(1)-O(1)	2.334(3)	Cd(1)-O(2)	2.242(2)
Cd(1)-O(6)#1	2.238(6)	Cd(1)-N(1)	2.254(3)
Cd(1)-C(1)	2.618(4)	Cd(1)-O(5)	2.183(4)
O(1)-C(1)	1.243(4)	O(2)-C(2)	1.246(4)
O(3)-C(8)	1.218(4)	O(4)-C(34)	1.206(6)
O(6)-C(27)	1.253(6)	N(1)-C(53)	1.333(5)
N()-C(57)	1.329(5)		
O(1) -Cd(1)-C(1)	28.34(10)	O(2)-Cd(1)-O(1)	56.72(9)
O(2)-Cd(1)-N(1)	103.17(10)	O(2)-Cd(1)-C(1)	28.39(9)
O(6) #1-Cd(1)-O(1)	94.57(18)	O(6)#1-Cd(1)-O(2)	95.96(17)
O(6)#1-Cd(1)-N(1)	91.92(18)	O(6)#1-Cd(1)-C(1)	96.66(17)
N(1)-Cd(1)-O(1)	159.39(11)	N(1)-Cd(1)-O(1)	159.39(11)
N(1) -Cd(1)-C(1)	131.34(12)	O(5)-Cd(1)-O(1)	97.80(15)
O(5)-Cd(1)-O(2)	129.15(16)	O(5)-Cd(1)-O(6) #1	132.1(2)
O(5)-Cd(1)-C(1)	115.2716)	C(1)-O(1)-Cd(1)	88.6(2)
C(1)-O(1)-Cd(1)	92.8(2)	C(1)-O(1)-Cd(1)#1	113.8(5)
C(53)-N(1)-Cd(1)	113.8(5)	C(53)-N(1)-Cd(1)	122.3(3)
C(57)-N(1)-C(53)	116.3(3)	O(1)-C(1)-Cd(1)	63.0(2)
O(1)-C(1)-O(2)	121.8(3)		
Symmetry codes:	#1 -x,-y+1,-z+1		

3			
Cd(1)-O(1) #1	2.3241(16)	Cd(1)-O(2)#2	2.3820(15)
Cd(1)-O(2)#1	2.4590(17)	Cd(1)-O(3)	2.3125(15)
Cd(1)-O(4)	2.3984(19)	Cd(1)-O(5)	2.366(2)
Cd(1)-N(1)	2.3555(19)	Cd(1)-C(26)#1	2.735(2)
O(1)-C(26)	1.245(3)	O(2)-C(26)	1.282(3)
O(3)-C(19)	1.231(3)	O(4)-N(2)	1.261(3)
O(5)-N(2)	1.261(3)	O(6)-N(2)	1.219(3)
N(1)-C(27)	1.321(3)		
O(1)#1-Cd(1)-O(2)#2	102.69(5)	O(1)#1-Cd(1)-O(2)#1	54.77(5)
O(1)#1-Cd(1)-O(4)	134.81(7)	O(1)#1-Cd(1)-Cl(2)	90.48(6)
O(1)#1-Cd(1)-N(1)	83.25(7)	O(1)#1-Cd(1)-C(26)#1	26.97(6)
O(2)#2-Cd(1)-O(2)#1	76.49(6)	O(2)#2-Cd(1)-O(4)	83.90(6)
O(2)#2-Cd(1)-C(26)#1	91.49(6)	O(2)#1-Cd(1)-C(26)#1	27.93(5)
O(3)-Cd(1)-O(1)#1	87.37(6)	O(3)-Cd(1)-O(2)#2	95.67(5)
O(3)-Cd(1)-O(2)#1	137.04(5)	O(3)-Cd(1)-O(4)	137.04(7)
O(3)-Cd(1)-O(5)	83.90(7)	O(3)-Cd(1)-N(1)	87.60(6)
O(3)-Cd(1)-C(26)#1	113.04(6)	O(4)-Cd(1)-O(2)#1	84.80(6)
O(4)-Cd(1)-C(26)#1	137.51(6)	O(5)-Cd(1)-O(2)#2	91.09(7)
O(5)-Cd(1)-O(2)#1	137.51(6)	O(5)-Cd(1)-O(4)	53.23(8)
O(5)-Cd(1)-C(26)#1	162.50(7)		
Symmetry codes:	#1 -x+1,-y,-z	#2 x+1/2,-y+1/2,z-1/2	

Table S3. The phosphorescence exponential lifetime (τ_i), preexponential factor (A_i) of **2** and **3** at room temperature.

CPs	Phosphorescence			
	$\tau_1(\mu s)$	$A_1(\%)$	$\tau_2(\mu s)$	$A_2(\%)$
2	2.63	24.95	10.69	75.05
3	2.79	26.17	10.00	73.83