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Three Cd(II) Coordination Polymers Constructed From a Series of Multidentate Ligands Derived From Cyclotriphosphazene: Synthesis, Structures and Luminescent properties

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Experimental sections

Materials and General Methods.

All reagents were purchased from commercial sources and were used without further purification. FT-IR spectra were recorded as KBr pellets with an Equinox 55 FT-IR spectrophotometer (4000-400 cm^{-1}). Thermal gravimetric analyses (TGA) were performed under N_2 atmosphere (100 ml/min) with a heating rate of 4°C/min between ambient temperature and 500°C using a Pyris1 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected over the 2θ range 5~60° using a X'Pert PRO automated diffractometer at room temperature, with a step size of 0.02° in 2θ angle. The synthesis routes of H_6L1 and H_6L2 were carried out according the references.[1,2]

Synthesis of hexakis(4-(1H-tetrazol-5-yl)phenoy) cyclotriphosphazene (H_6L3).

Potassium carbonate (6.00 g, 0.043 mol) was added into a solution of anhydrous acetone (50 mL) containing 4-hydroxybenzonitrile (5.00 g, 0.042 mol) and $P_3N_3Cl_6$ (2.44 g, 0.007 mol). The mixture was stirred overnight at 80°C. The solvent was removed by evaporation under reduced pressure, and the obtained solid was re-dissolved in 50 mL dichloromethane. The organic phase was washed with water and then dried over anhydrous Na_2SO_4. The volatiles were removed by evaporation under

reduced pressure, and the product was dried as white powder (5.46 g, 92.4% yield based on $P_3N_3Cl_6$).

To a solution of $P_3N_3(OC_6H_4COOOCH_3)_6$ (5.46 g, 0.0065 mol) in anhydrous DMF (60 mL) was added NaN_3 (3.85 g, 0.058 mol), followed by ammonium chloride (3.13g, 0.058 mol). The resulting mixture was stirred at 100°C for 24 h before cooled to room temperature. Then, 250 mL water was added to the reaction and the mixture was stirred for 10 min. The mixture was extracted with water (50 mL) for 3 times and the combined aqueous phase was acidified with 3 M HCl solution. The suspension was filtered to afford the product as a solid (3.77 g, 83.7%). ^{1}H-NMR spectra of H_6L3 was shown in Figure S5.

Synthesis of $\{[Cd_3(L1)(H_2O)_5]\}_n$.

A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.16 mmol, 36.5 mg) and H_6L1 (0.02 mmol, 19.1 mg) was dissolved in distilled water (6 mL) and acetonitrile (4 mL) in a 25 mL Teflon-lined stainless steel vessel. The mixture was stirred at room temperature for 5 min, and then heated at 155℃ for 72h, which was allowed to cool to room temperature at a rate of 5℃/h. Hexagon-like crystals were obtained in 68% yield (based on Cd). Anal. Calcd for $C_{42}H_{34}Cd_3N_3O_{23}P_3$: H 2.48%, C 36.58%, N 26.69%; found H 2.65%, C 36.84%, N 26.93%. IR (KBr, cm^{-1}): 3413(m), 1601(s), 1536(s), 1507(m), 1414(s), 1295(m), 1234(s), 1181(s), 967(s), 862(m) and 768(s).

Synthesis of $\{[Cd_4(L2)_2(H_2O)_8]\}_n$.

The synthesis process was very similar to 1 except adding H_6L2 (0.03 mmol, 28.7 mg), distilled water (6 mL) and acetonitrile (6 mL) in the reaction system. Square-like crystals was obtained in 72% yield (based on Cd). Anal. Calcd for $C_{84}H_{64}Cd_4N_6O_{44}P_6$: H 2.58%, C 40.41%, N 3.37%; found H 2.65%, C 36.84%, N 26.93%. IR (KBr, cm^{-1}): 3479(m), 1687(s), 1608(m), 1548(s), 1443(s), 1403(s), 1305(m), 1275(m), 1186(s), 1108(m), 968(s), 841(m) and 770(s).

Synthesis of $\{[Cd_2(L3)_2(H_2O)_2]\cdot(H_2O)\}_n$.

A mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.12 mmol, 37 mg) and H_6L3 (0.02 mmol, 22.2 mg) was dissolved in distilled water (10 mL) and methanol (0.5 mL) , then the synthesis process was very similar to 1. Rod-like crystals was obtained in 55% yield (based on Cd). Anal. Calcd for $C_{84}H_{64}Cd_2N_{54}O_{14}P_6$: H 2.62%, C 40.94%, N 30.69%; found H 2.65%, C 40.84%, N 30.72%. IR (KBr, cm^{-1}): 3418(m), 1611(m), 1498(m), 1450(s), 1273(m), 1211(s), 1182(s), 962(s), 889(s), 848(s) and 767(s).

X-Ray Structural Determination

X-ray diffraction data of **1-3** were collected on Bruker diffractometer MD2 of BL17B beamline of National Center for Protein Sciences Shanghai (NCPSS) at Shanghai Synchrotron Radiation Facility for **1**, XtaLAB Mini (JP) for **2** and SuperNova diffractometer for **3** based diffractometer. The structures of complexes were solved by direct methods, and the non-hydrogen atoms were located from the trial structure and then refined anisotropically with SHELXTL using a full-matrix least squares procedure based on F^2 values. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. CCDC-1565708(**1**), 1565709(**2**) and 1565710(**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

References:

1 S. Liu, X. Wu, A. Q. Zhang, J. J. Qiu and C. M. Liu, *Langmuir.*, 2011, **27**, 3982

2 B. Li, X. Dai, X. Meng, T. Zhang, C. Liu and K. Yu, *Dalton Trans.*, 2013,**42**, 2588.

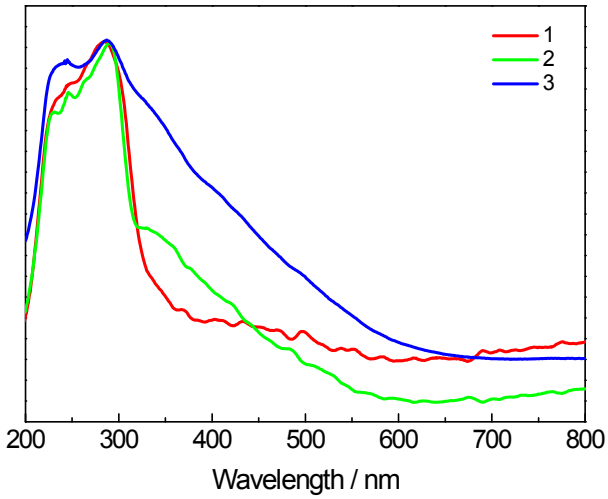

Figure S1. UV-vis absorption spectra for three Cd-CPs in the solid state.

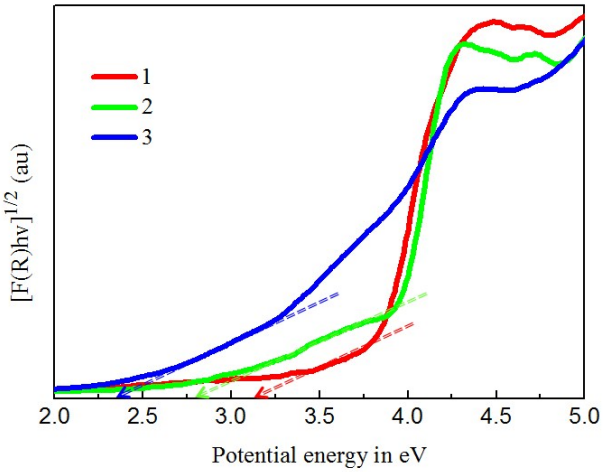

Figure S2. The diffuse reflectance spectra of three CPs **1** and **2** in Kubelka–Munk functions

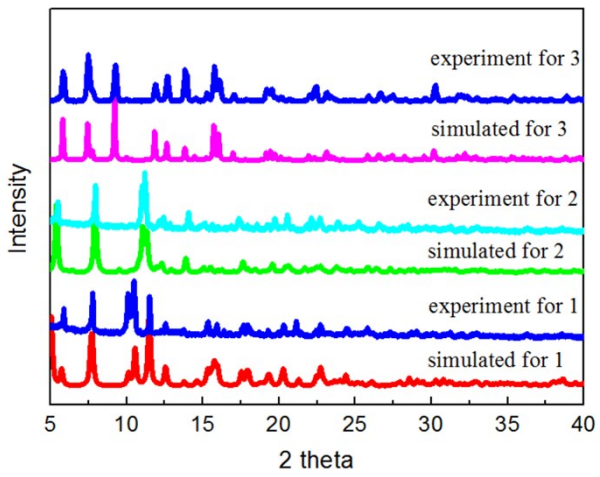

Figure S3. XRD spectra of **1-3**

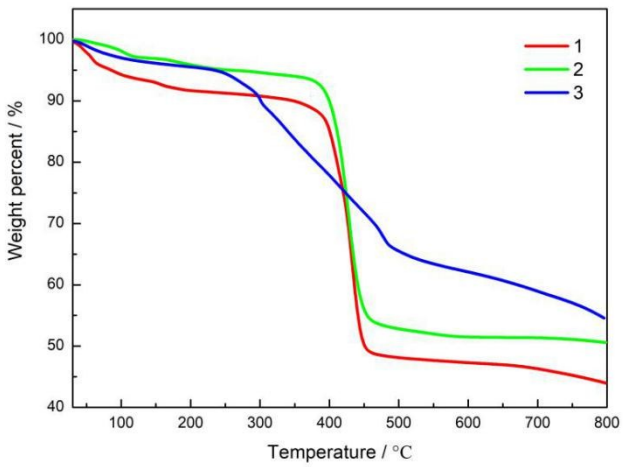

Figure S4. TGA curves of **1-3**

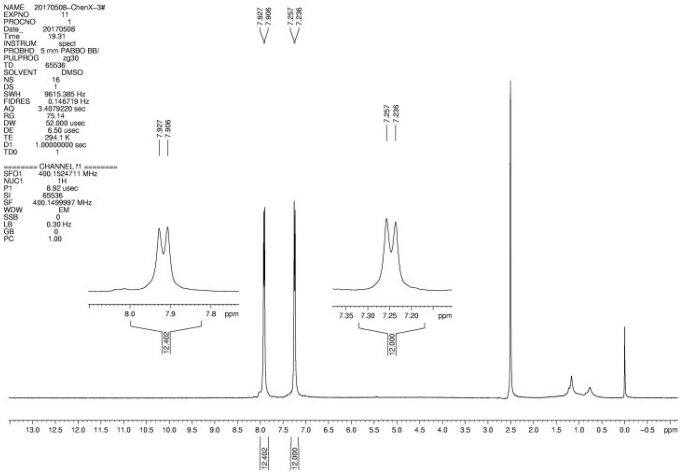

Figure S5. ^{1}H-NMR spectra of H_6L3