Electronic Supplementary Material (ESI) for ChemComm.

# Lanthanide doped coordination polymers with tunable afterglow based on phosphorescence energy transfer

YongshengYang,[a] Ke-Zhi Wang,*[a] and Dongpeng Yan*[ab]

[a]Beijing Key Laboratory of Energy Conversion and Storage Materials College of Chemistry, Beijing Normal University, Beijing 100875 (P. R. China )E-mail: yandp@bnu.edu.cn; kzwang@bnu.edu.cn

[b]State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, P. R. China.

# EXPERIMENTAL SECTION

**Materials**: Analytically pure $Cd(NO_3)_2·4H_2O$, $Eu(NO_3)_3·6H_2O$, $Tb(NO_3)_3·6H_2O$, m-benzenedicarboxylic acid (m-BDC) and benzimidazole (BIM) were purchased from the Sigma Chemical. Co. Ltd. and used without further purification.

**Characterization**: Single–crystal X–ray diffraction data of all compounds were collected on a Bruker SMART APEX CCD diffractometer[1] equipped with graphite monochromatized Mo $K_\alpha$ radiation ($\lambda$ = 0.71073 Å) at room temperature using the ω–scan technique. Empirical absorption corrections were applied to the intensities using the SADABS program.[2] The structures were solved using the program SHELXS–97[3-4] and refined with the program SHELXL–97.[5]All non–hydrogen atoms were refined anisotropically.

Powder XRD patterns of all compounds were collected on a Rigaku Ultima–IV automated diffraction system with Cu $K_\alpha$ radiation ($\lambda$ = 1.5406 Å). Measurements were made in a $2\theta$ range of 5–50° at room temperature with a step of 0.02° ($2\theta$) and a counting time of 0.2 s/step. The operating power was 40 kV and 50 mA. IR spectra were recorded in the range of 4000–400 $cm^{-1}$ on a Tensor 27 OPUS (Bruker) FT–IR spectrometer. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin–Elmer Diamond SII thermal analyzer from room temperature to 800ºC with a heating rate of 10ºC $min^{-1}$. Room temperature time–resolved photoluminescence (PL) experiments were conducted on an Edinburgh FLS980 fluorescence spectrometer. The inductively coupled plasma (ICP) analysis was performedwith a JY ULTIMA spectrometer.

**Electronic structure calculations of Cd-CP:**

All calculations were performed with the periodic density functional theory (DFT) method using the Dmol3[6-7] module in the Material Studio software package.[8] The initial configuration was fully optimized by the Perdew−Wang (PW91)[9] generalized gradient approximation method with thedouble numerical basis sets plus polarization function (DNP). Thecore electrons for metals were treated by effective core potentials. The self-consistent field converged criterion was within $1.0 \times 10^{-5}$ hartree $atom^{-1}$, and the converging criterion of the structure optimization was $1.0 \times 10^{-3}$ hartree bohr$^{-1}$. The Brillouin zone is sampled by 1 × 1 × 1 k-points, and test calculations reveal that the increase of *k*-points does not affect the results.

**Synthesis of Cd-CP:** A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.5 mmol, 0.160 g), BIM (0.2 mmol, 0.026 g), m-BDC (0.5 mmol, 0.083 g), $CH_3CN$ (2 mL) and water (8 mL) was sealed in a 23 mL Teflon reactor kept under autogenous pressure at 150 ºC for 72 hours and then cooled at a speed of 10 ºC per minute to room temperature. Colorless bulk crystals were filtered off, washed with distilled water and ethanol in turn, and dried in air. Yield: 75% (based on Cd). The as–synthesized crystal is insoluble in water and common organic solvents. IR spectrum (KBr, cm$^{-1}$): 3388 s, 3272 s, 2395 w, 1618 vs, 1555 vs, 1382 vs, 1169 w, 1098 w, 1050 w, 961 w, 849 w, 753 s, 672 m, 543 w, 464 m. Elemental Anal. Calc. (Found %) for Cd-CP: C, 32.59 (32.39); H, 2.04 (1.92); O, 27.16 (27.00).

**Synthesis of Cd-Eu-CP:** A mixture of $Cd(NO_3)_2{\cdot}4H_2O$ (0.5 mmol, 0.160 g), $Eu(NO_3)_3{\cdot}6H_2O$ (0.005mmol, 0.002 g), BIM (0.2 mmol, 0.026 g), m-BDC (0.5 mmol, 0.083 g), $CH_3CN$ (2 mL) and water (8 mL) was sealed in a 23 mL Teflon reactor kept under autogenous pressure at 150 ºC for 72 hours and then cooled at a speed of 10 ºC per minute to room temperature. Colorless bulk crystals were filtered off, washed with distilled water and ethanol in turn, and dried in air. Yield: 70% (based on Cd). The as–synthesized crystal is insoluble in water and common organic solvents. IR spectrum (KBr, cm$^{-1}$): 3384 s, 3279 s, 2389 w, 1623 vs, 1561 vs, 1380 vs, 1172 w, 1098 w, 1055 w, 962 w, 851 w, 758 s, 672 m, 536 w, 468 m. Elemental Anal. Calc. (Found %) for Cd-Eu-CP: C, 32.59 (32.15); H, 2.04 (2.01); O, 27.16 (27.18).

**Synthesis of Cd-Tb-CP:** The synthesis method of Cd-Tb-CP is similar to that for Cd-Eu-CP, expect for the replace of $Eu(NO_3)_3{\cdot}6H_2O$ by $Tb(NO_3)_3{\cdot}6H_2O$. Yield: 75% (based on Cd). The as–synthesized crystal is insoluble in water and common organic solvents. IR spectrum (KBr, cm$^{-1}$): 3378 s, 3279 s, 2995 m, 2389 w, 1629 vs, 1568 vs, 1380 vs, 1178 w, 1111 w, 1067 w, 968 w, 852 w, 764 s, 684 m, 548 w, 456 m. Elemental Anal. Calc. (Found %) for Cd-Tb-CP: C, 32.59 (31.56); H, 2.04 (2.10); O, 27.16 (26.98).

**Synthesis of Cd-Gd-CP:** The synthesis method of Cd-Gd-CP is similar to that for Cd-Eu-CP, expect for the replace of $Eu(NO_3)_3 \cdot 6H_2O$ by $Gd(NO_3)_3 \cdot 6H_2O$. Yield: 75% (based on Cd). The as–synthesized crystal is insoluble in water and common organic solvents. IR spectrum (KBr, $cm^{-1}$): 3384 s, 3275 s, 2389 w, 1629 vs, 1556 vs, 1380 vs, 1172 w, 1024 w, 1104 w, 962 w, 851 w, 746 s, 690 m, 536 w, 450 m. Elemental Anal. Calc. (Found %) for Cd-Gd-CP: C, 32.59 (32.23); H, 2.04 (2.07); O, 27.16 (27.31).

## REFERENCES

(1) SMART and SAINT. *Area Detector Control and Integration Software,* Siemens Analytical X-Ray Systems, Inc., Madison, WI, 1996.

(2) G. M. Sheldrick, *SADABS 2.05*, University of Göttingen, Germany.

(3) G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*1990, **46**, 467–473.

(4) G. M.Sheldrick, *SHELXS-97, Program for Solution of Crystal Structures*, University of Göttingen, Germany 1997.

(5) G. M.Sheldrick,*Sect. A: Found. Crystallogr.* 2008, **64**, 112–122.

(6) B. Delley, *J. Chem. Phys.*, 1990, **92**, 508−517.

(7) B. Delley, *J. Chem. Phys.*, 2000, **113**, 7756−7764.

(8) Dmol3 Module. MS Modeling, version 2.2; Accelrys Inc.: SanDiego, CA, 2003.

(9) J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson,M. R. Pederson, D. J. Singh and C. Fiolhais, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 6671−6687.

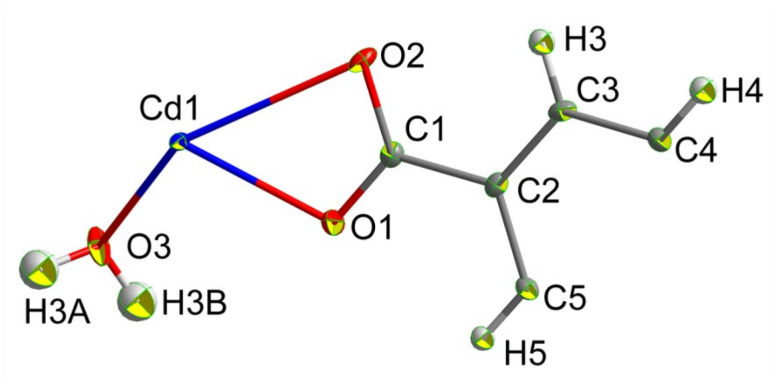

**Figure S1.** The asymmetric unit of Cd-CP.

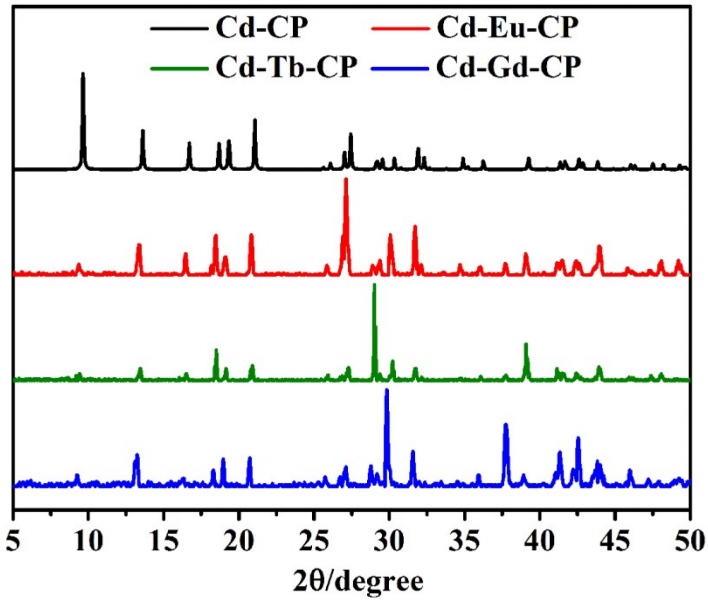

**Figure S2.** The PXRD patterns for Cd-CP and Cd-Eu\Tb\Gd-CPs.

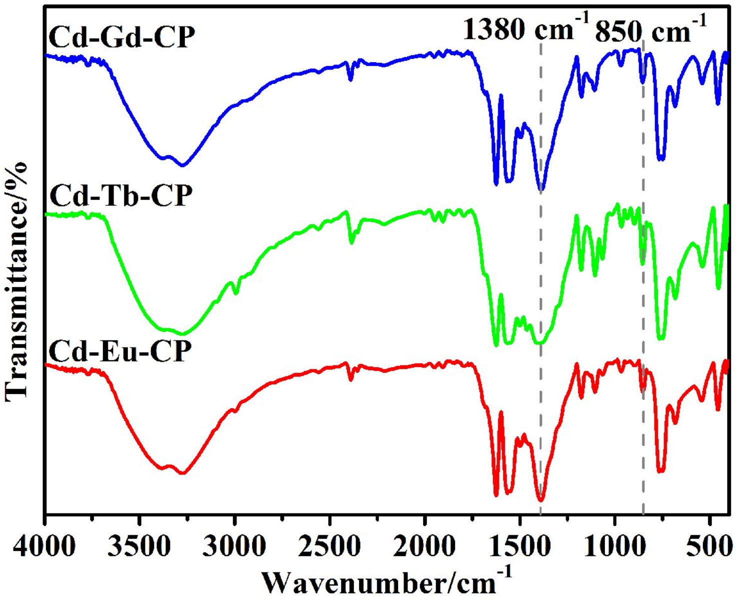

**Figure S3.**The FTIR spectra for Cd-Eu\Tb\Gd-CPs.

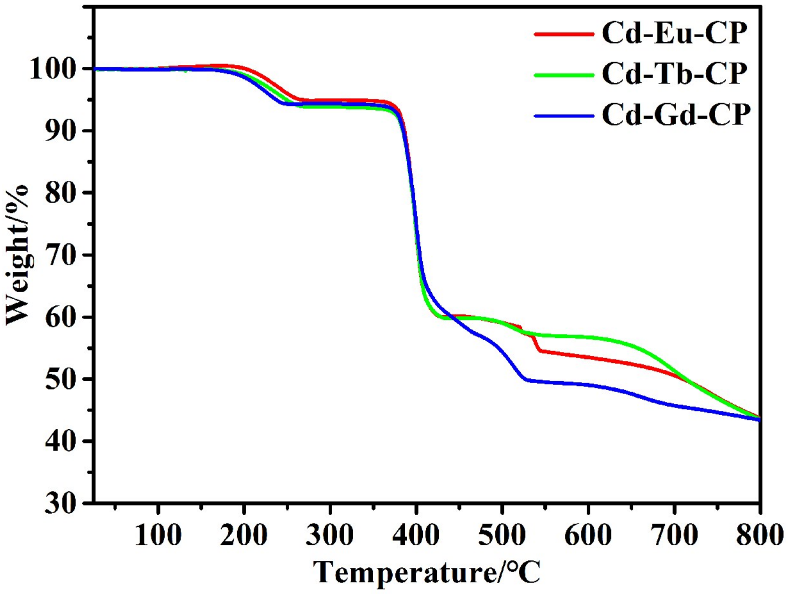

**Figure S4.**The TGA curves for Cd-Eu\Tb\Gd-CPs.

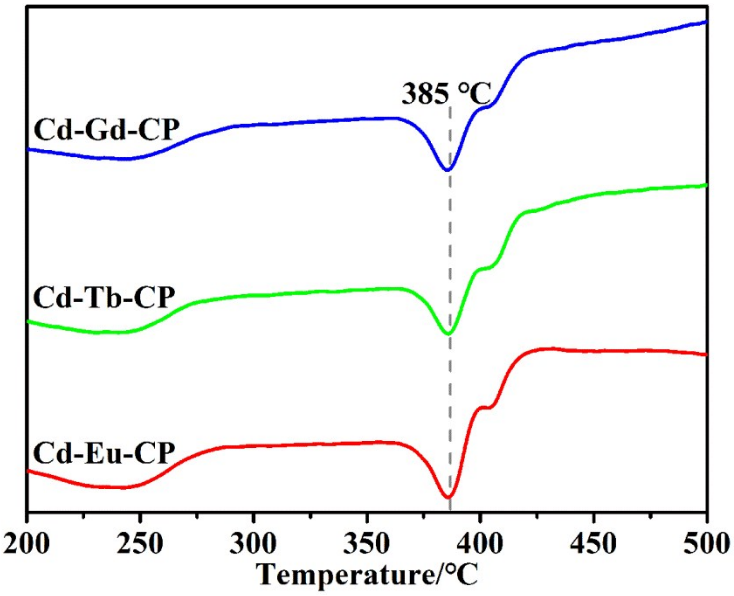

**Figure S5.**The DSC traces for Cd-Eu\Tb\Gd-CPs.

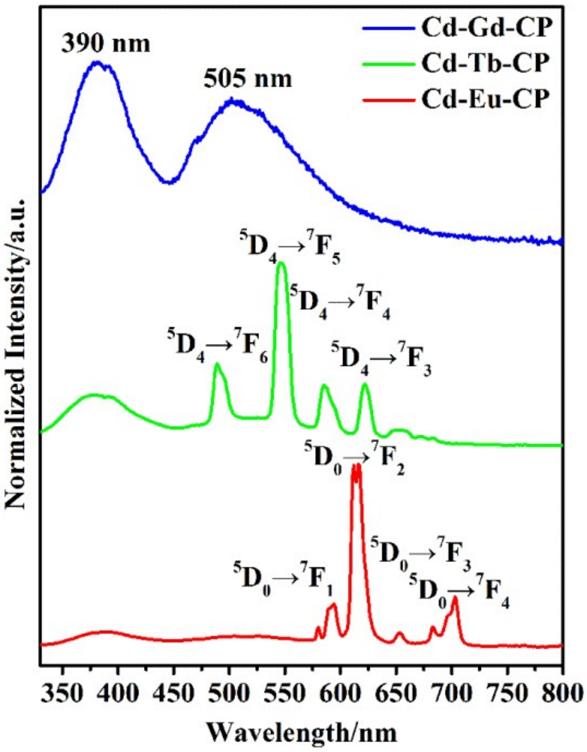

**Figure S6.** Room-temperature solid-state emission spectra of Cd-Eu\Tb\Gd-CPs under excitation wavelength at 310 nm.

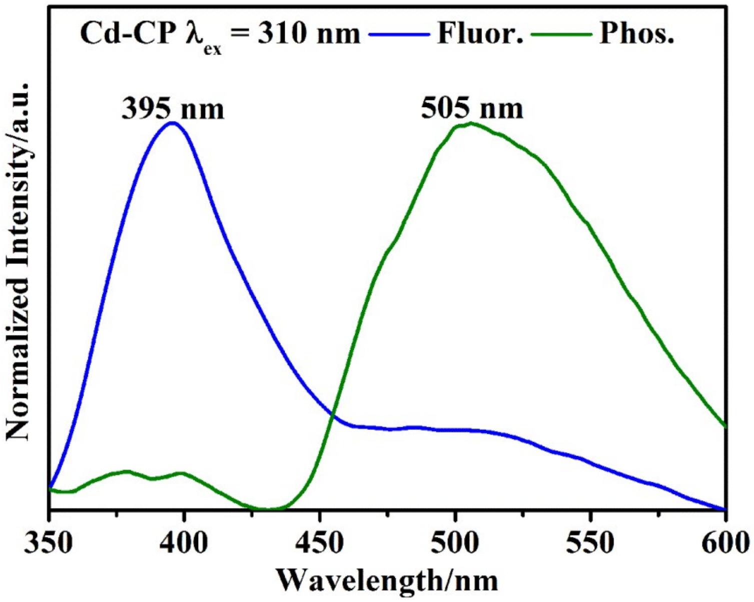

**Figure S7.** Room-temperature solid-state emission spectra of Cd-CP under excitation wavelength at 310 nm.

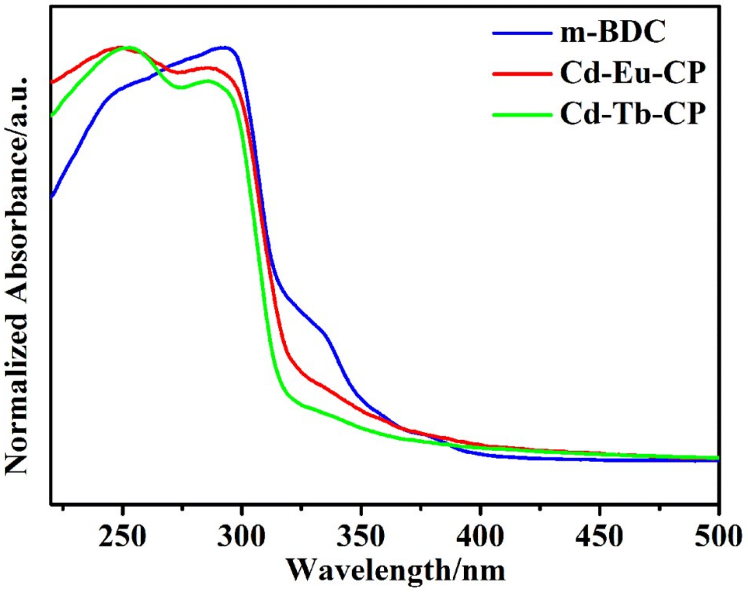

**Figure S8.** Solid-state UV-visible absorption spectra for m-BDC and Cd-Eu/Tb-CPs.

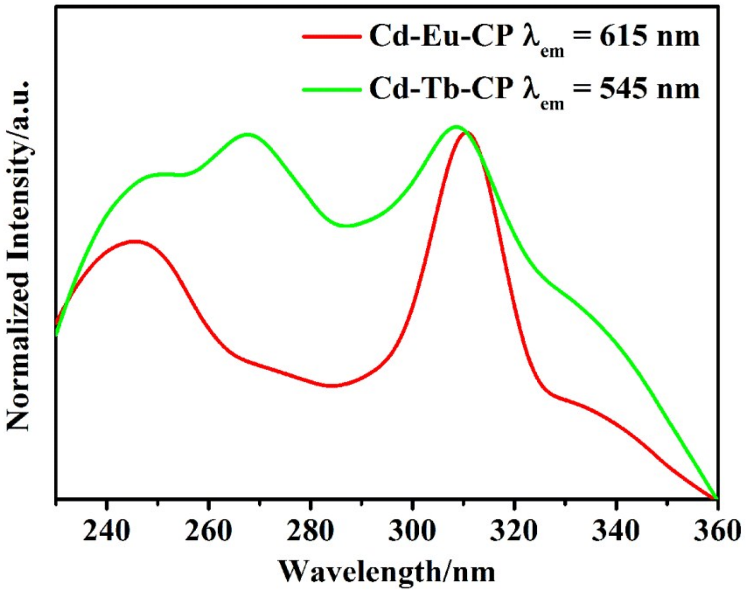

**Figure S9.** The room-temperature solid-state excitation spectra of Cd-Eu/Tb-CPs

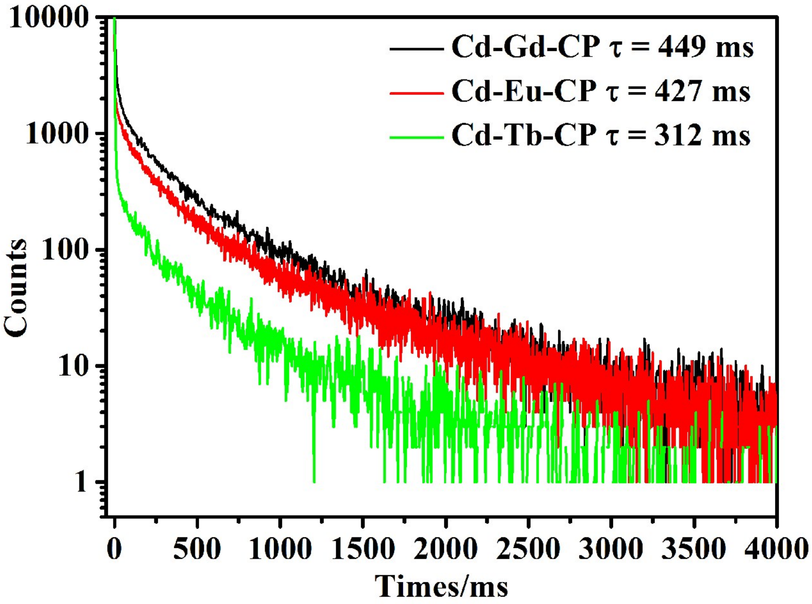

**Figure S10.** Time-resolved emission decay curves at 505 nm for Cd-Eu/Tb/Gd-CPs under ambient conditions.

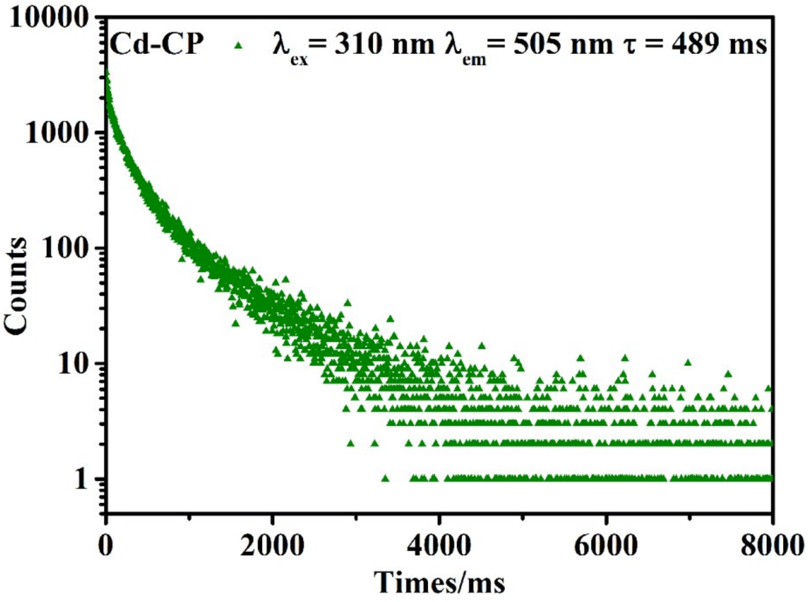

**Figure S11.** Time-resolved emission decay curves at 505 nm for Cd-CPs under ambient conditions.

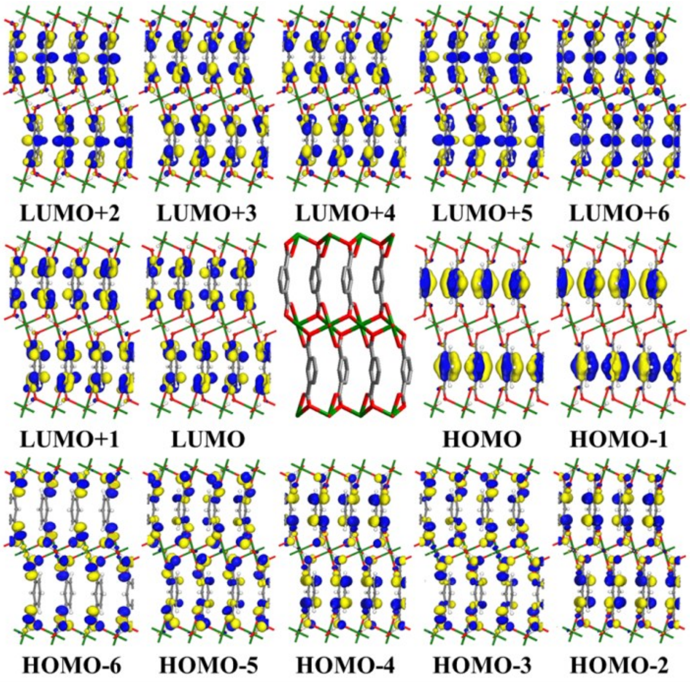

**Figure S12.** Frontier orbitals for Cd-CP. The blue/yellow colors denote ± wave functions.

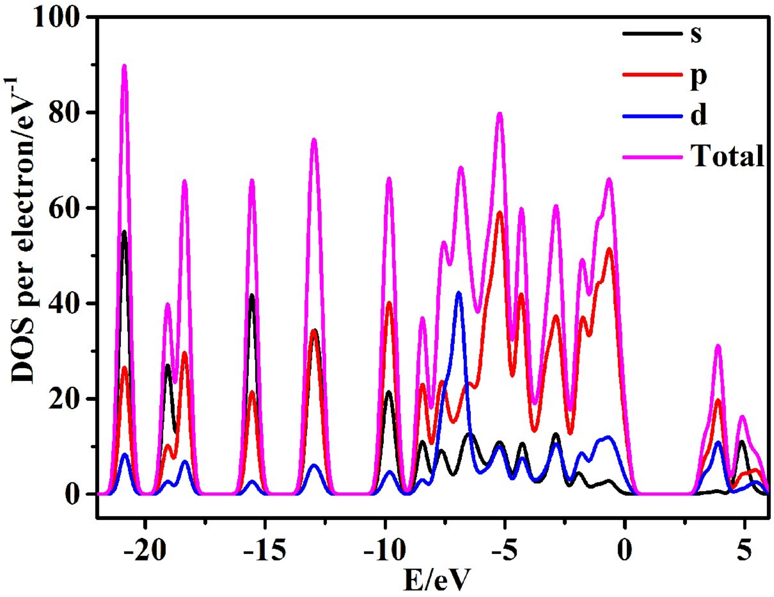

**Figure S13.** Total/partial electronic density of states (TDOS/PDOS) for Cd-CP.

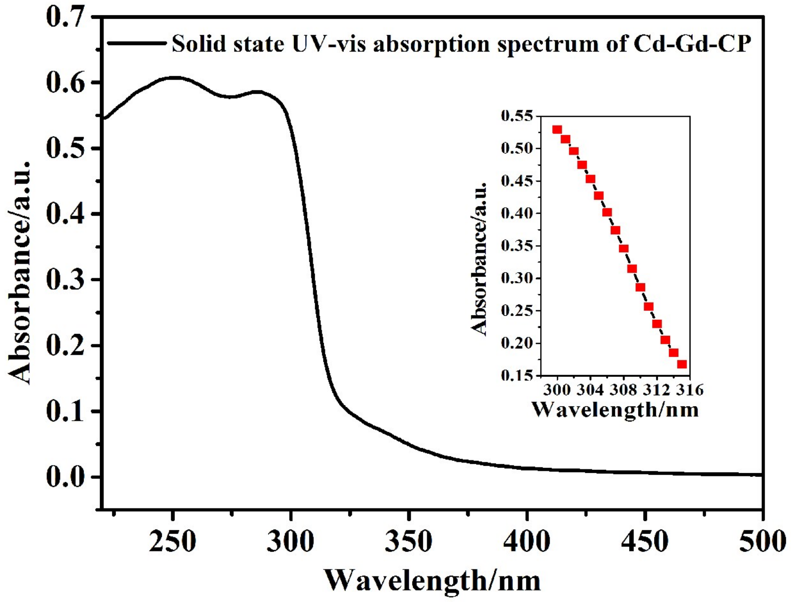

**Figure S14.** Solid state UV-visible absorption spectrum for Cd-Gd-CP.

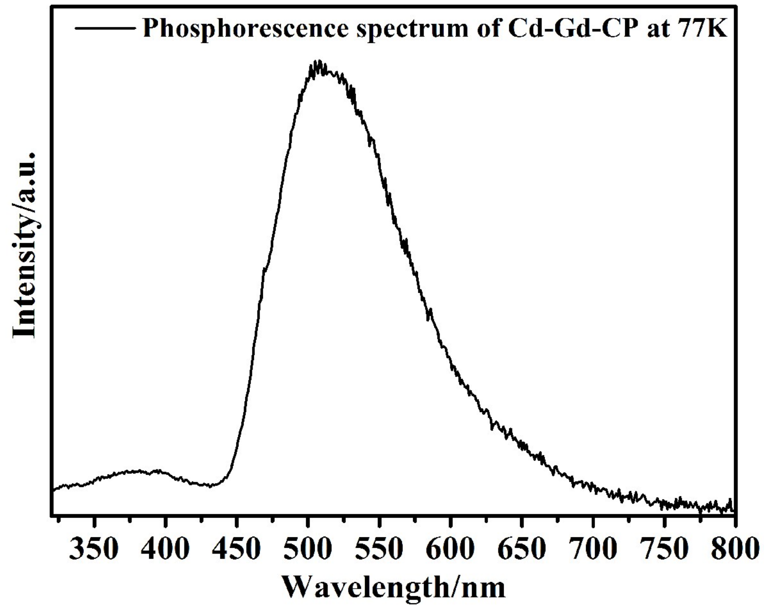

**Figure S15.** Solid-state phosphorescent emission spectra of Cd-Gd-CP at 77 K.

**Table S1**The inductively coupled plasma (ICP) analysis of Cd-Eu/Tb/Gd-CP

| | Cd (μg/mL) | Eu (μg/mL) | Tb (μg/mL) | Gd (μg/mL) | $Cd_{1-x}Ln_x$-CP |
|---|---|---|---|---|---|
| Cd-Eu-CP | 1834 | 3.752 | | | $Cd_{0.998}Ln_{0.002}$-CP |
| Cd-Tb-CP | 2241 | | 3.028 | | $Cd_{0.999}Ln_{0.001}$-CP |
| Cd-Gd-CP | 1714 | | | 7.766 | $Cd_{0.995}Ln_{0.005}$-CP |