Polyoxometalate-based Room-Temperature Phosphorescent Materials Induced by Anion-π Interaction

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1. Materials and Physical Measurements

All reagents were used as purchased without further purification. NMR spectrum was recorded with a Bruker Avance III 400 MHz NMR spectrometer. Powder X-ray diffraction (XRD) were collected on Rigaku desktop MiniFlex 600 diffractometer with Cu Kα radiation (λ=1.5418 Å). FT-IR spectra were recorded in the range 4000–400 cm^{-1} on a Bruker Vertex 70 spectrometer with pressed KBr pellets. Carbon, hydrogen and nitrogen elemental analyses were carried out on an Elementar Vario Micro Cube analyzer. Optical diffuse reflectance spectra were measured at room temperature on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer. EPR spectra were recorded on a Bruker BioSpin E500 ESR spectrometer with a 100 KHz magnetic field modulation at room temperature. Photoluminescence spectra at room temperature were recorded on a HORIBA Jobin-Yvon FluoroMax-4 spectrometer. The lifetime of the sample was measured by the time-correlated single-photon counting (TCSPC) upgrade on the FluoroMax-4 spectrometer with a FluoroHub module. Thermal analyses were performed on a TGA/DSC 1 STAR^e system from room temperature to 900°C with a heating rate of 10 K/min under nitrogen.

2. Experimental Section

Synthesis of H_2L: H_2L (H_2L = 3,3'-(1,3,6,8-tetraoxobenzol[lmn][3,8]-phenanthroline-2,7(1H,3H, 6H,8H)diyl)-di-benzoic acid) was synthesized as reported previously. 140mg (1.0 mmol) 3-aminobenzoic acid and 130mg (0.5mmol) 1,4,5,8-naphthalenetetracarboxylic dianhydride were placed in a mortar and pestle. The mixture was solvent drop-grinded with DMF for five minutes at room temperature, then was transferred to an oven and was heated for 14 hours at 150 °C. The resulting yellow powder was characterized by EA and NMR. EA Anal. Calcd (%): C, 66.41; H, 2.79; N, 5.53. Found: C, 66.40; H, 2.78; N, 5.53. ^{1}H

NMR (400 MHz, DMSO-d_6) δ = 13.19 (s, 2H), 8.74 (s, 4H), 8.08 (m, 4H), 7.73 (m, 4H).) (Figure S1).

$[(CH_3)_4N]_4[Eu(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Eu). In a 15 mL glass bottle, $Eu(NO_3)_3\cdot 6H_2O$ (0.029 g, 0.07 mmol), H_2L (0.015 g, 0.03 mmol), and $H_4SiW_{12}O_{40}\cdot xH_2O$ (0.200 g, 0.07 mmol) were dissolved in DMF (4 mL), resulting in a clear solution. Then the tetramethylammonium hydroxide solution (0.08 mol·L^{-1}, 6.0 mL) was added. The mixture was heated in an oven at 353 K for 48h, and then cooled to room temperature at a rate of 2 K·h^{-1}. Yellowish block-shaped crystals of (**1**-Eu) were obtained (yield 58% based on H_2L). Anal. Calcd (%): C, 18.18; H, 2.31; N, 3.17. Found: C, 18.01; H, 2.23; N, 3.11. IR data for **1**-Eu (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w), 1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

$[(CH_3)_4N]_4[Gd(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Gd). The same procedure as that for 1-Eu was followed, except for using $Gd(NO_3)_3\cdot 6H_2O$. Yellowish block-shaped crystals of (1-Gd) were obtained (yield 58% based on H_2L). Anal. Calcd (%): C, 18.16; H, 2.30; N, 3.16. Found: C, 17.92; H, 2.19; N, 3.00. IR data for 1-Gd (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w), 1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

$[(CH_3)_4N]_4[Tb(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Tb). The same procedure as that for 1-Eu was followed, except for using $Tb(NO_3)_3\cdot 6H_2O$. Yellowish block-shaped crystals of (1-Tb) were obtained (yield 58% based on H_2L). Anal. Calcd (%): C, 18.16; H, 2.30; N, 3.16. Found: C, 17.99; H, 2.22; N, 3.07. IR data for 1-Tb (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w), 1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

$[(CH_3)_4N]_4[Dy(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Dy). The same procedure as that for 1-Eu was followed, except for using $DyCl_3\cdot 6H_2O$. Yellowish block-shaped crystals of (1-Dy) were obtained (yield 48% based on H_2L). Anal. Calcd (%): C, 18.14; H, 2.30; N, 3.16. Found: C, 17.99; H, 2.15; N, 3.09. IR data for 1-Dy (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w), 1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

$[(CH_3)_4N]_4[Ho(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Ho). The same procedure as that for 1-Dy was followed, except for using $HoCl_3\cdot 6H_2O$. Yellowish block-shaped crystals of (1-Ho) were obtained (yield 48% based on H_2L). Anal. Calcd (%): C, 18.13; H, 2.30; N, 3.16. Found: C, 18.01; H, 2.23; N, 3.11. IR data for 1-Ho (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w),

1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

$[(CH_3)_4N]_4[Er(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Er). The same procedure as that for 1-Eu was followed, except for using $Er(NO_3)_3\cdot 6H_2O$. Yellowish block-shaped crystals of (1-Er) were obtained (yield 58% based on H_2L). Anal. Calcd (%): C, 18.12; H, 2.30; N, 3.16. Found: C, 17.65; H, 2.15; N, 2.95. IR data for 1-Er (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w), 1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

$[(CH_3)_4N]_4[Tm(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Tm). The same procedure as that for 1-Eu was followed, except for using $Tm(NO_3)_3\cdot 6H_2O$. Yellowish block-shaped crystals of (1-Tm) were obtained (yield 58% based on H_2L). Anal. Calcd (%): C, 18.12; H, 2.30; N, 3.15. Found: C, 18.01; H, 2.23; N, 3.11. IR data for 1-Tm (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w), 1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

$[(CH_3)_4N]_4[Yb(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Yb). The same procedure as that for 1-Dy was followed, except for using $YbCl_3\cdot 6H_2O$. Light-yellow block-shaped crystals of (1-Yb) were obtained (yield 48% based on H_2L). Anal. Calcd (%): C, 18.10; H, 2.29; N, 3.15. Found: C, 18.01; H, 2.23; N, 3.11. IR data for 1-Yb (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w), 1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

$[(CH_3)_4N]_4[Lu(L)_{1.5}(H_2O)_3](SiW_{12}O_{40})\cdot 4H_2O\cdot 3DMF$ (1-Lu). The same procedure as that for 1-Eu was followed, except for using $Lu(NO_3)_3\cdot 6H_2O$. Yellowish block-shaped crystals of (1-Lu) were obtained (yield 58% based on H_2L). Anal. Calcd (%): C, 18.09; H, 2.29; N, 3.15. Found: C, 17.80; H, 2.25; N, 2.92. IR data for 1-Lu (KBr, cm^{-1}): 3489 (br), 1700 (s), 1647 (s), 1539 (s), 1484 (s), 1436 (w), 1406 (s), 1351 (s), 1255 (s), 1201 (w), 1165 (s), 1105 (w), 1014 (w), 972 (s), 918 (s), 882 (s), 798 (s), 773 (s), 533 (w).

3. Crystallographic Data Collection and Refinement

Suitable single crystals of complexes were mounted on loop for the X-ray measurement. Diffraction data were collected on SuperNova (Dual source) diffractometer equipped with the CrysAlis^{pro} X-ray crystallography data systems. The measurements were made by using graphic monochromatic Mo Kα radiation (λ=0.71073 Å) at 100 K under a cold nitrogen stream. All calculations were performed with the SHELXTL-97 program package, and structures were solved by direct methods and refined by full-matrix least-squares against F^2. All non-hydrogen atoms were

refined anisotropically, and hydrogen atoms of the organic ligands and solvent molecules were generated theoretically onto the specific atoms. Crystallographic data has been deposited at the Cambridge Crystallographic Data Center with reference number CCDC 1976081-1976089. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

4. Related Figures of 1-Ln

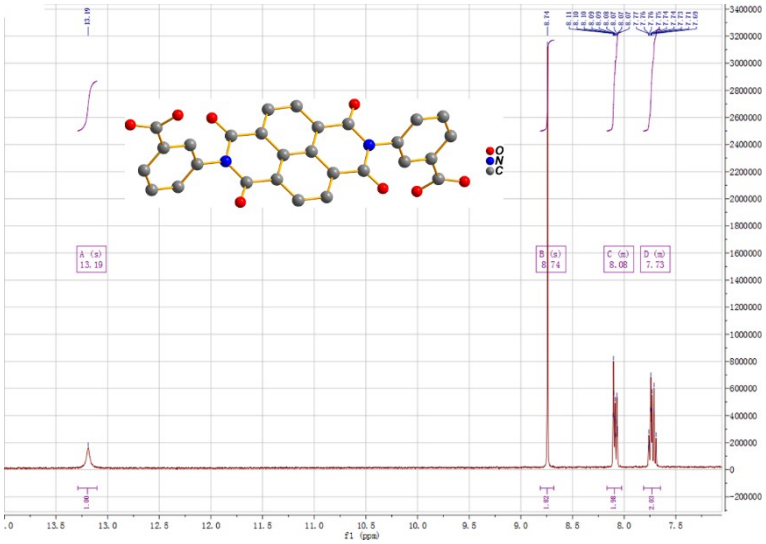

Fig.S1 ^{1}H NMR of the H_2L

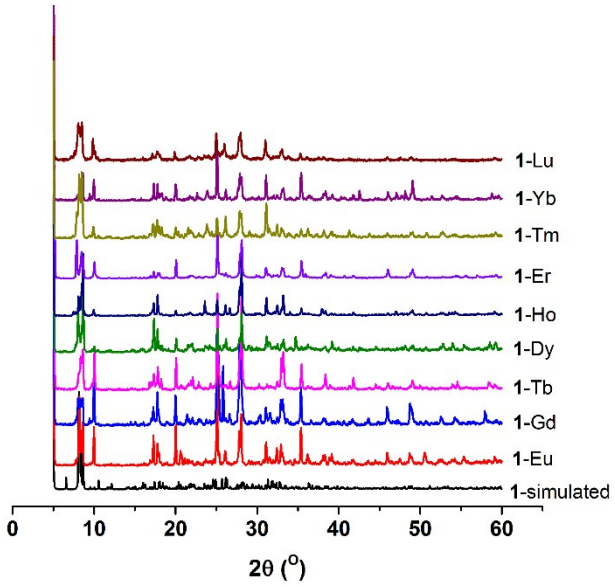

Fig. S2 Comparison of the experimental PXRD patterns of the as-synthesized **1-Ln** with the one simulated from single crystal data.

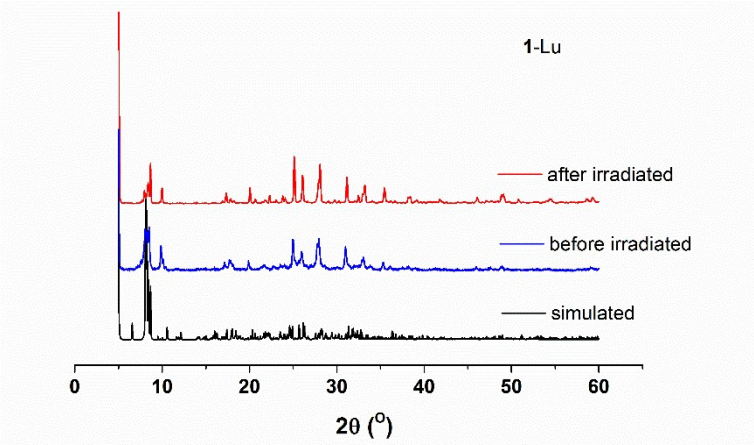

Fig. S3 Comparison of the experimental PXRD patterns of the as-synthesized **1-Lu** before and after being irradiated.

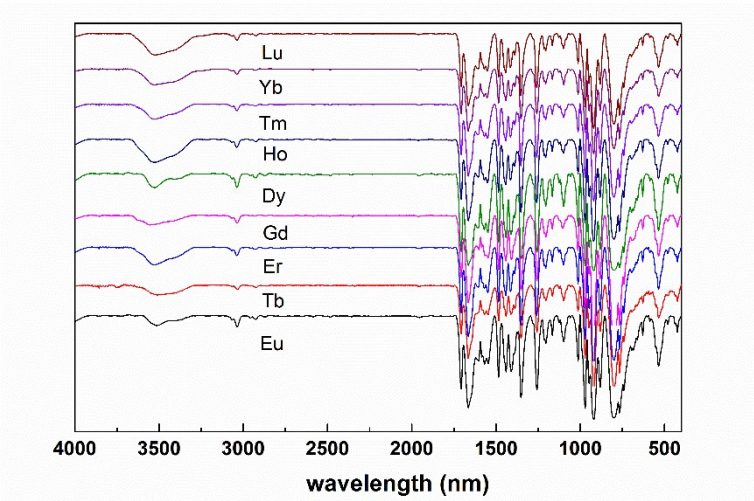

Fig. S4 The IR patterns of the as-synthesized **1-LN**

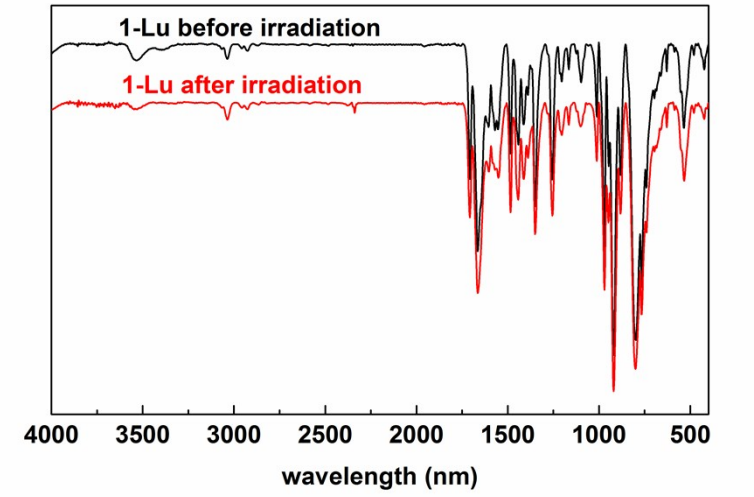

Fig. S5 Comparison of the IR patterns of the as-synthesized **1-Lu** before and after being irradiated.

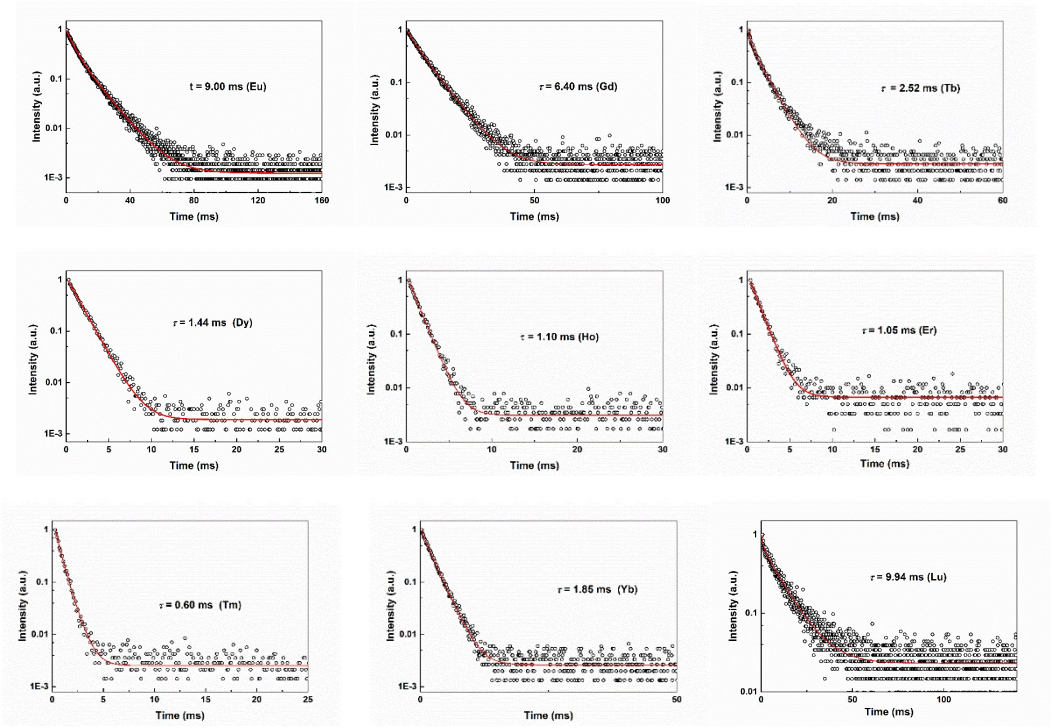

Fig. S6 The lifetime decay curves of **1**-Ln

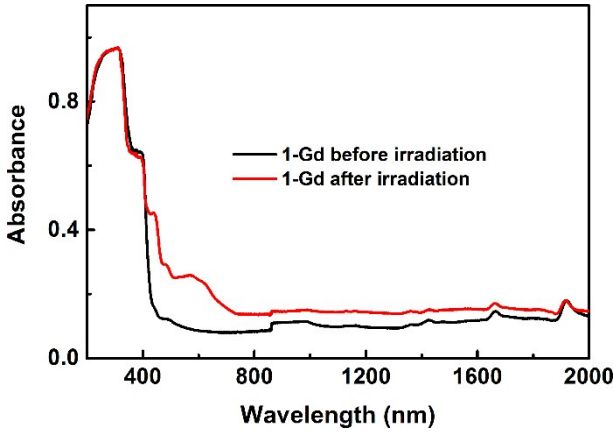

Fig. S7 The in situ UV/Vis spectra show the changes of 1-Gd after irradiation with simulated sunlight.

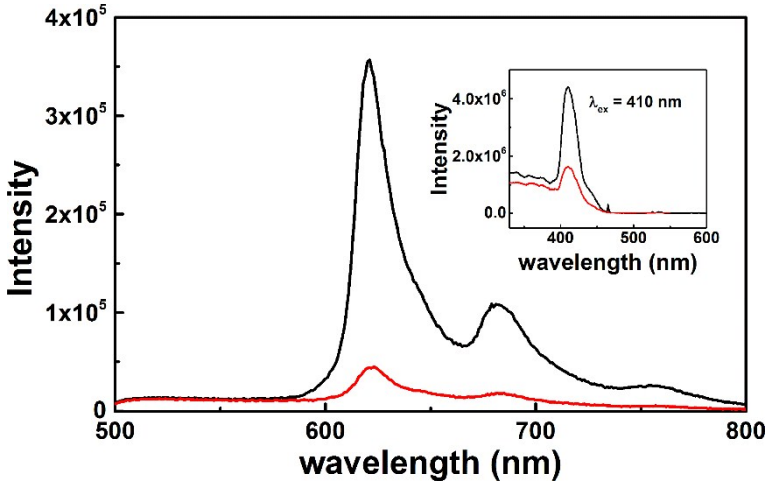

Fig. S8 The emission spectra and the excitation spectra (inset) show the changes of 1-Gd after irradiation with simulated sunlight. (black line: before irradiation; red line: after irradiation)

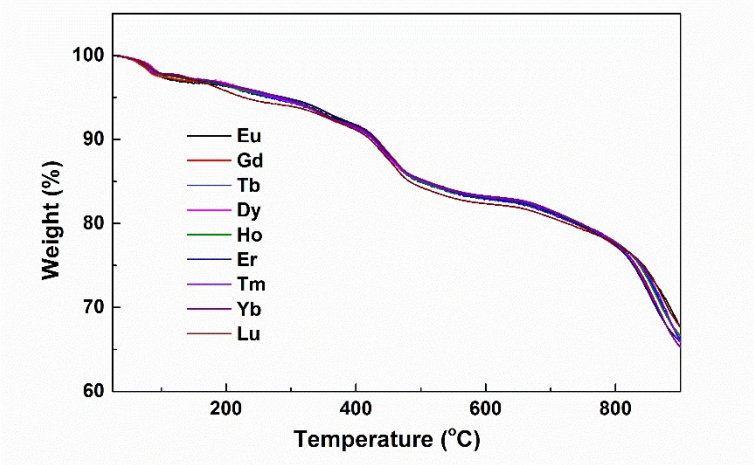

Fig. S9 The TG curves of **1**-Ln

Table.S1 Photophysical parameters of **1**-Ln in the solid state

	Eu	Tb	Er	Gd	Dy	Ho	Tm	Yb	Lu
τ (ms)	9.00	2.52	1.05	6.40	1.44	1.10	0.60	1.85	9.94
Φ (%)	1.4	0.3	0.1	2.0	0.2	0.2	0.6	0.3	1.3