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

Received 00th January 20xx, Accepted 00th January 20xx Xiao-Yuan Wu^a, Hai-Long Zhang ^{a,b}, Sa-Sa Wang^a, Wei-Ming Wu^a, Lang Lin^c, Xiao-Yu Jiang^c, Can-Zhong Lu^{*a,b}

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A series of host-guest materials containing polyoxomatalate anions and lanthanide-organic layers have been synthesized and structurally characterized. By anion- π interaction between the anions and the π -acidic naphthalenediimide moieties, the materials emit strong red room-temperature phosphorescence and exhibit reversible photochromism.

Room-temperature phosphorescent (RTP) materials with persistent luminescence have attracted enormous attention due to their important applications in biological imaging,^[1] lightemitting devices,^[2] information storage and encryption,^[3] chemical sensing,^[4] etc.. There are two key strategies for yielding efficient RTP materials: promoting intersystem crossing (ISC) and suppressing the non-radiative decay processes.^[5] It has been proofed that introducing heavy-atom or electron donor into an intraligand charge-transfer state could lead to more efficient ISC, and result in fluorescence/RTP dual emission.^[6] Polyoxometalates (POMs), a large family of nanosized inorganic clusters with oxygen-rich surfaces, are promising candidates for architecting efficient fluorescence/RTP materials with photoactive organic molecules because they hold several advantages including strong capacity to undergo multi-electron redox processes, tunable structure and strong electrostatic, Hbonding, charge-transfer interactions with organic molecules.^[7] Dessapt et. al. successfully tuned the emission color of an archetypal Ir(III) complex from green to red through controlling the crystal packing mode with different POMs.^[8] Recently, they reported two new supramolecular fluorescent materials through combining POM anions with an "aggregation-induced emission"-active phospholium.^[9] In these materials, the nucleophilic oxygen-rich POM anions exalt the solid-state luminescence through strengthening the rigidity of the phospholium and preventing the π - π stacking interactions between the luminophores. Moreover, POMs have a widely applications in electrochemistry, optics, magnetism, medicine, and catalysis.^[10] Introducing POMs into the luminescent materials, more multifunctional systems will be developed. So design and syntheses of versatile POMs-based luminescent materials have become attractive and challenging branch.^[11]

Naphthalenediimide (NDI) derivatives have been widely used as light-harvesting chromophore in solar cells and molecular probes, due to their intense absorption in the visible region or high fluorescence quantum yield.^[12] Interacting with suitable electron donor, NDI derivatives not only show tunable color luminescence,^[13] but also exhibit π -localized RTP owing to the intramolecular charge-transfer states bridging the relatively large energy gap between the NDI-localized ${}^{1}\pi$ - π^{*} and ${}^{3}\pi$ - π^{*} states.^[14] Furthermore, due to the long π -conjugation plane and the strong π -acidity, NDI derivatives can easily form charge transfer complexes with anions, such as fluorion, chloridion, and high negative-charge POMs.^[15] More recently, our research group reported a series of photochromic materials based on POMs and pyridine-substituted NDI derivatives, which show the strong anion- π interactions and hydrogen bonding interactions.^[16] Herein, carboxyphenyl-substituted NDIs (3,3'-(1,3,6,8-tetraoxobenzol[lmn][3,8]-phenanthroline-2,7(1H,3H, 6H,8H)diyl)-di-benzoic acid, abbreviated as H₂L^[17]) as organic Odonor ligand was applied to assemble a novel host-guest

materials with Ln and POM ions. By charge transfer between the POMs and NDIs, the materials emit strong red RTP. Meanwhile, the charge-transfer-induced NDI radicals and the variation of the tungsten valence state lead to significant photochromism.

The solvothermal reaction of $H_4SiW_{12}O_{40}$ ·xH₂O, Ln(NO₃)₃·6H₂O/LNCl₃·6H₂O, H₂L and Tetramethylammonium hydroxide in the solvent mixture of N,N-dimethylformamide (DMF) and water at 80 °C for 48h yielded yellowish blockshaped crystals of [(CH₃)₄N]₄[Ln(L)_{1.5}(H₂O)₃](SiW₁₂O₄₀)·4H₂O·3DMF (**1**, Ln= Lu, Yb, Tm, Er, Ho, Dy, Tb, Gd, Eu).

X-ray single-crystal analysis reveals that the nine compounds are isostructural and crystallize in the *P*-1 space group. The compounds consist of $\{LnL_{1.5}(H_2O)_3\}_n$ layers, Keggin-type anions $\{SiW_{12}O_{40}\}^{4-}$, tetramethylammonium $[(CH_3)_4N]^+$ counter cations, as well as several lattice water and DMF molecules. Herein, only

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the crystal structure of 1-Lu is intensively described. The Lu³⁺ cation is coordinated to eight oxygen atoms. Among them, five come from three carboxyl groups of three ligands, and the other three belong to water molecules. Totally deprotonated ligand L adopts two coordinated types. In type-I, each carboxylate group of the ligand bridges one Lu³⁺ cation with the $\mu_1-\eta^1:\eta^1$ coordination mode. In type-II, each carboxylate group is in the $\mu_1 - \eta^1: \eta^0$ coordination mode to link one Lu³⁺ cation. The dihedral angles between the NDI core and two benzoate rings are 61.71°, 70.51° (for type-I) and 77.71° (for type-II), respectively. Remarkably, neighbouring Lu³⁺ cations are connected into a wave-like chain by the ligand in type-I configuration. Such chains are arranged in ABAB-type to form a square-window about 20.4 × 21.0 Å. Furthermore, the ligands in type-II model link the neighbouring chains into two-dimensional layer, and divide the square-window into triangle-grid. Along the *a* axis, such layers arrange in a line to form one-dimensional channels. The POM anions locate in the channels suitably (Fig. 1a). It is noteworthy that each POM anion is surrounded by three NDI tectons in bowl-like. Meanwhile, each NDI tecton is sandwiched by two POM anions (Fig. 1b). The trinuclear subunit {W₃O₁₃} and the NDI rings arrange in face-to-face manner, while the dihedral angles are 1.56°, 2.18° and 6.75°, respectively. The distances between the oxygen atom of the POM anions and the NDI tectons are range from 2.790 Å to 3.638 Å, which exhibit typically anion- π interactions.^[16]. These anion- π interactions offer effective pathways for the charge transfer and play an important role in the progress of photochromism and photoluminescence. Additionally, there are two types of hydrogen bonds between the Ln-L layers and the POM anions. One is the O-H…O (2.818 Å) hydrogen bonds between the coordinated water molecules and the POMs. The other is the C-H…O (3.334 Å) hydrogen bonds between the benzoate rings and the POMs. These hydrogen bonds further stabilize the crystal frameworks.



Fig 1. (a) The framework of 1-Lu viewed along the *a* axis. (b) The anion– π interactions between adjacent POMs and NDI moieties (all the coordinated DMA/water molecules and hydrogen atoms are omitted for clarity).



Fig 2. The in situ UV/Vis spectra (a) and the in situ EPR spectra (b) show the changes of **1**-Lu after irradiation with simulated sunlight light (red line) and kept in dark for 1 day (blue line); the inset shows the photochromic images of **1**-Lu.

All of the compounds exhibit the photochromic transformation from yellowish to light brown while they are irradiated by simulated sunlight light (Xenon Lamp, 300W, PLS-SXE 300/300UV, 320-780nm) for 30 minutes. Then keeping in the dark under ambient conditions, all of the compounds return to yellowish slowly. The UV/Vis spectra were carried out for 1-Lu samples before and after light irradiation to support photoinduced transformation. As shown in Fig. 2a, in the range of 200-400 nm, the spectral shapes and intensities are almost unchanged after irradiation, which can mainly be assigned to the π - π * transitions of NDIs tectons (350 – 400 nm) and the ligand-to-metal charge transfer (LMCT) transitions ($O_{h,c} \rightarrow W$) within the POMs anions (200-350 nm).^[8, 18] It's notabl that the absorbance intensity of the broad band above 400nm is obviously increased after irradiation. The two shoulder peaks at 438nm and 485nm may be attributed to the organic radicals, which formed by the intermolecular charge-transfer between the electron-deficient naphthalenic rings and the electron-rich POM anions.^[16b, 19] In the UV-vis spectra, the weak peak in the range of 400 nm and 500 nm is already present before irradiation, indicating that the material is very sensitive to light. The absorbance between 600-2000 nm can be mainly assigned to the variation of the tungsten valence state by photoinduced charge-transfer transition through the bridging oxygen bonds in POMs. In the POM structure, the lowest unoccupied molecular orbitals (LUMO) is mainly localized on the W atoms, and the highest occupied molecular orbital is mainly localized on the bridging oxygen atoms. The fact of the charge transfer between W^{VI} and W^V through the bridging oxygen bonds in POM is known to be the origin of the typical NIR absorption of POMs.^[20]

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Keeping irradiated sample in dark for one day, the two shoulder peaks show negligible decrease, while the absorbance intensity above 800nm is almost decreased to the original. It is demonstrated that the organic radicals are stable under ambient conditions, while the reduced tungsten are oxidized in air.^[21] The generation of organic radical and W^V species has been confirmed by the signals at g = 2.0039 and g = 1.9249 in the EPR spectra (Fig. 2b), respectively.

The as-synthesized bulk samples of **1**-Ln show a PXRD pattern basically identical to the simulated one from the single-crystal X-ray data but with the weakening of some diffraction peaks, which confirming the phase purity of the samples (Fig. S2 in the ESI†). The crystal structure of **1**-Lu after irradiation is identical to that before irradiation (Fig. S3). The results of FT-IR spectra (Fig. S4, S5) also correspond well with the above conclusion. Therefore, the photochromic phenomenon arises from photoinduced charge transfer process rather than structural transformation or photolysis.



Fig 3. The emission spectra of H_2L and 1-LN (LN = Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) under the excitation at 410 nm at room temperature. The inset shows the excitation spectrum.

The solid photoluminescence properties of 1-Ln have been measured with their crystalline samples under the excitation of unfocused UV light at room temperature in air. In the excitation spectrum, the excitation peak at 410 nm was detected and kept its position after irradiation (Fig. S8). Consequently, the POMs do not participate to the excitation processes because their absorption is localized at higher energies (200-350 nm). As shown in Fig 3, the sample of the organic ligand is almost nonfluorescent, probably due to the large singlet-triplet energy gap that is intrinsic to π - π * transitions. Notably, compared to the with traditional POMs-based hybrid materials photoluminescence reduced or quenched, [22] all of these samples exhibit the identical strong red photoluminescence with two main peaks separately. One of the monomer emission peaks is at 621 nm, and the other is a broad peak at around 680 nm. The highest photoluminescence quantum yield (OLQY) of these solid sample is 2.0% for Gd (Table S1). The interesting and practically important photoluminescence properties of these crystals may be ascribed to the interactions between the NDIs and the POMs. In 1-Ln, POM anions act as the electron donor to modify the NDIs rings. The obvious intermolecular anion- π interactions result in the donor to acceptor charger transfer states which has reduced ΔE_{ST} and enhanced SC processes, consequently leading to RTP. ^[14, 16a] In the nine compounds, the special emission peaks for the lanthanides couldn't be found.

Moreover, to further insight into the photophysical properties and excited-state information on the emissions for these compounds, the lifetime were measured under the strongest emission at 621 nm and the excitation at 410 nm. The corresponding emission decay curves were fitted to a double exponential function $[I = A1 \exp(-t/\tau_1) + A2 \exp(-t/\tau_2)]^{[23]}$ (Fig. S6). The average emission lifetimes (τ_{av}) of the nine compounds are in the range of 0.60 - 9.94 ms (Table S1). These results indicate that the photoluminescence of **1**-Ln is a photoluminescence emission resulting from the excited electronic charge-transfer states of the crystals.^[16a, 19b]



Fig 4. The emission spectra of **1**-Gd at room temperature after irradiation with simulated sunlight (300 W) at 0, 2, 4, 6, 8, 10, 12 min. The inset shows the time-dependent phosphorescence intensity upon irradiation.

Interestingly, while irradiated under the ultraviolet visible light, the phosphorescence intensity decreases with unchanged emission peak positions. As shown in Fig.4, the phosphorescent intensity of the **1**-Gd sample decreases gradually to 12% of the initial intensity after irradiation for 12 minutes. Considering the close distance (2.790-3.638 Å) between the POMs and the NDIs, the quenching of the luminescence should originated from the fluorescence resonant energy transfer (FRET) effect, ^[24] which produced based on the substantial overlap of the emission bands of the luminophore (NDIs) and the significantly increased photogenerated absorption bands of the W^V at 600-800 nm wavelength region. Besides, the variation of the energy levels for the bridging intermolecular charge-transfer states occurs accompanied irradiation, which may lead to lower efficiencies of ISC processes and weaker RTP.

Conclusions

In conclusion, we have utilized a carboxyphenyl-substituted NDI ligand for successfully synthesizing a serials of host-guest materials based on POMs and Ln-organic layers, which exhibits distinct room-temperature phosphorescence as well as

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reversible photochromism upon simulated sunlight light irradiation. The single-crystal structural analysis clearly indicates that the significant intermolecular anion– π interactions between the POMs and NDIs provide efficient charge-transfer pathways between the POMs and the π -acidic NDI, resulting in additional intermolecular charge-transfer states that serve to bridge the large ΔE_{ST} between the lowest local-excited states and thus trigger efficient RTP. Clearly, this new strategy extends the scope of anion- π engineering to develop solid-state emitters. Finally, as POMs can also exhibit intrinsic photoactive, redox or magnetic properties, this work opens the way towards the design of novel multifunctional hybrid systems.

Conflicts of interest

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There are no conflicts to declare.

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A series of polyoxometalate-based host-guest materials emit strong red room-temperature phosphorescence attributed to intermolecular charge-transfer states which was caused by the unorthodox anion- π interactions.