PAPER

Organic–inorganic hybrid rare earth complexes based on polymolybdates with intrinsic photosensitive properties†

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A series of organic–inorganic hybrid rare earth complexes {[RE$_2$(PO)$_2$(H$_2$O)$_{10}$][H$_2$Mo$_{36}$O$_{112}$(OH$_2$)$_{12}$-(PO)$_4$]}·5PO·2(CH$_3$CN)·nH$_2$O [n = 23–42, RE(III) = Nd(III), **1**; Sm(III), **2**; Eu(III), **3**; Gd(III), **4**; Dy(III), **5**; Er(III), **6**; Tm(III), **7**; Yb(III), **8**; Lu(III), **9**; Y(III), **10**; PO = piperidin-2-one] have been synthesized and fully characterized by single-crystal X-ray diffraction, powder X-ray diffraction, elemental analysis, IR spectra, thermogravimetric analysis and UV-vis spectra. Structural analysis reveals that compounds **1–10** are isostructural and crystallize in the monoclinic *P*2(1)/*n* space group. Each compound contains a centrosymmetric anionic cluster [Mo$_{36}$O$_{112}$(OH$_2$)$_{12}$(PO)$_4$]$^{8-}$, which could be described as the derivative of [Mo$_{36}$O$_{112}$(OH$_2$)$_{16}$]$^{8-}$ with four water molecules substituted by organic PO molecules. Each {Mo$_{18}$} subunit connects with one RE(III) ion *via* its two terminal O atoms from two independent {MoO$_6$} octahedra. The eight coordinated RE(III) ion with a distorted tetragonal antiprism coordination geometry is also surrounded by another six oxygen atoms, five of them from five water molecules and the final one from one PO molecule. Compounds **1–10** show considerable photosensitive behavior under visible light excitation. In addition, compound **3** exhibits three emission bands at 580, 595 and 617 nm in the solid state, which could be assigned to $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu(III) ions, respectively.

Introduction

Photochromic materials that are able to modify their coloration under light have received much attention due to their wide variety of applications such as in ophthalmic lenses, printing, cosmetics, optical power-limiting switches, optical information, *etc.*[1–10] Among the promising systems in this field are hybrid organic–inorganic materials based on polyoxomolybdates (POMs) and organic cations (mainly organoammonium cations).[3–7,11] To date, the photochromism mechanism of such materials has been investigated in detail. Namely, the physical process involved implies the photoreduction of Mo(VI) cations into Mo(V) ones within the POM's block, with a conco-

mitant displacement of a labile hydrogen atom from the N$^+$–H bond of the organic component to the mineral one.[2–4,12]

Nevertheless, it must be underlined that the photogenerated hue of such hybrid materials depends on the chemical composition and topology of the POMs, whatever the nature of the associated organoammonium cations. As a result, a large amount of POMs, such as {Mo$_3$}, {Mo$_6$}, {Mo$_7$}, {Mo$_8$} clusters,[2,3,12] as well as some phosphomolybdates[4–7] have been selected as the inorganic components of photochromic hybrids. Although such hybrid materials offer a wide range of UV-induced coloration with remarkable color contrast, very few of them are sensitive to visible light.[3,9] Indeed, visible-light photochromism will be useful in the design of compact storage devices as well as in solar energy conversion applications.[9] Noticeably, it has been demonstrated that the increase of corner-shared connection between the {MoO$_6$} octahedra while increasing the size of POMs should favor the electronic delocalization *via* intervalence transfers.[6] Concomitantly, the optical band gap will generally red-shift as a consequence of the decrease of the electronic excitation energy.[10] The ring-like isopolymolybdate {Mo$_{36}$} cluster, containing at least eighteen corner-shared {MoO$_6$} octahedra around the outside of the ring,[13] should be a type of potential visible light sensitive mineral backbone of photochromic hybrid POMs, while this feature is mostly ignored in the literature.[13–18] Recently, it has been highlighted that a more convenient way

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for obtaining photochromic POM materials would be to co-valently link a hydrogen donor organic group on the inorganic core.[7] Such a strategy may allow optimization of the proton-transfer reaction, which governs the photochromic kinetics of the POM fragment.[7] Fortunately, the {Mo$_{36}$} cluster is well suited for such a purpose as it exhibits a significantly high coordination ability towards various organic molecules.[13–15]

Meanwhile, considering the special electronic, magnetic and optical properties of RE(III) ions,[17] we present here the synthesis of a series of RE-{Mo$_{36}$} clusters using piperidin-2-one (PO) as the hydrogen donor organic group. As we know, *N*-methyl-2-pyrrolidone, one of the lactam homologue of PO, is an excellent ligand to the RE(III) ion[19] or protonated to act as an organic cation.[20] In this work, the PO molecule is also linked to the {Mo$_{36}$} backbone *via* its amide oxygen atom during the self-assembly processes. As predicted, such hybrid POMs show significant photosensitive behavior under visible light irradiation. Furthermore, to the best of our knowledge, these compounds represent the first amide oxygen atom grafted case and the highest substitutes of a giant organic functioned {Mo$_{36}$} isopolyanion.[14,15]

Results and discussion

Structure description

Compounds **1–10** were synthesized in aqueous solution by one-pot reaction of the corresponding RE salt, PO and Na$_2$MoO$_4$ (see ESI S-1.2†). As revealed by the single-crystal XRD, compounds **1–10** are isostructural and crystallize in the monoclinic *P*2(1)/*n* space group (Table S1†). Considering that the Gd(III) ion is in the center position of lanthanides, the structure of **4** will be discussed in detail as an example. As shown in Fig. 1a, **4** contains a centrosymmetric anionic cluster [Mo$_{36}$O$_{112}$(OH$_2$)$_{12}$(PO)$_4$]$^{8-}$, which could be described as the derivative of [Mo$_{36}$O$_{112}$(OH$_2$)$_{16}$]$^{8-}$ (ref. 13,16,21,22) with four organic PO molecules grafting water molecules. In the asymmetric unit of **4**, there exists one {Gd–Mo$_{18}$–(PO)$_2$} fragment (Fig. 1b), one free PO molecule, one protonation [POH]$^+$ cation and several water molecules of crystallization. The {Mo$_{18}$–

(PO)$_2$} subunit is constructed from the combination of sixteen {MoO$_6$} pseudo-octahedra [two of them grafted by two PO molecules, see Mo3 and Mo13, bond lengths of Mo3–O12 and Mo13–O52 are 2.357(6) and 2.348(6) Å, respectively] and two distorted {MoO$_7$} pentagonal bipyramids (Mo8 and Mo16). There are eight Mo–O bond lengths more than 2.35 Å [Mo1–O4 2.458(6), Mo15–O4 2.423(6), Mo7–O32 2.512(6), Mo9–O32 2.450(6), Mo4–O16 2.386(6), Mo5–O23 2.366(6), Mo11–O43 2.367(8), Mo12–O49 2.424(7) Å], confirming that the corresponding terminal O (O16, O23, O43, O49) and bridged O atoms (O4 and O32) should be from water ligands (Fig. S1†).[14,15] This is further confirmed by the Bond Valence Sum (BVS) calculations (Table S2†). Two centrosymmetric {Mo$_{18}$–(PO)$_2$} moieties are connected *via* sharing the edges (O44, O50 and O44′, O50′) of two MoO$_6$ octahedra (Mo18′ and Mo18). Furthermore, each {Mo$_{18}$–(PO)$_2$} subunit coordinates to one Gd(III) ion *via* its two terminal O atoms (O51 and O53) from two independent {MoO$_6$} octahedra (Mo12 and Mo13). It should be noted that the {MoO$_6$} octahedra of Mo13 is not only coordinated to the Gd(III) metal ion, but also covalently grafted by one PO molecule. The eight coordinated Gd(III) ion with a distorted tetragonal antiprism coordination geometry (Fig. 1c) is also surrounded by another six oxygen atoms, five of them from five water molecules and the final one from one PO molecule. Bond lengths of compounds **1–10** are with a slight difference, which is probably due to lanthanide contraction.[17] The Mo4, Mo5 and Mo12 atoms in each compound are disordered, and the occupancy values are listed in Table S3.† Compounds **1–10** are further characterized by elemental analysis, IR, UV-vis spectra, powder X-ray diffraction, thermogravimetric and electrochemistry analyses, and the results (See ESI S-3†) are in accordance with the single-crystal XRD analysis.

Photochemistry of compounds 1–10

Hybrid organic–inorganic materials based on POMs and organoammonium cations represent a certain class of potentially photochromic materials.[2] When irradiated with visible light ($\lambda > 420$ nm, generated by a 300 W xenon lamp equipped with a UVCUT420 transmission filter), compounds **1–10** show significant photosensitive responses with high coloration contrasts, their color gradually changes from yellow to dark blue with irradiation times. The photoinduced color does not evolve after approximately 20 min, as illustrated in Fig. 2 and S8.† In the dark, only a slight color change could be observed.

Obviously, the different RE(III) ions of compounds **1–10** are almost not responsible for photosensitive behavior. This is in accordance with the reported results that a hybrid material with a given inorganic block displays a well-defined hue in its photoinduced state.[2] In order to understand the photosensitive mechanism, compound **4** has been selected as an example. The solid-state photosensitive property of compound **4** has been investigated under ambient conditions by diffuse reflectance spectroscopy (Fig. 2). Yellow microcrystalline powder of compound **4** in the ground state exhibits an optical gap of 668 nm (1.83 eV, Fig. S9†), which is much less than that of some reported hybrid organic–inorganic materials based on
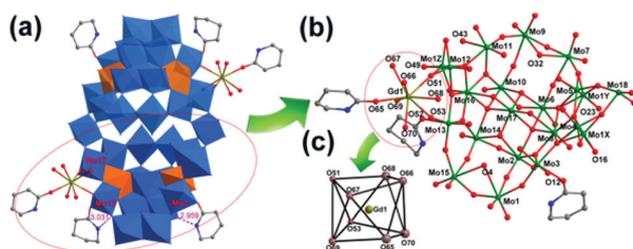

Fig. 1 (a) The polyhedral view of compound **4**, the intramolecular hydrogen bonds between nitrogen atoms of the grafted PO molecules and Mo–O–Mo oxygen atoms are represented as dotted lines; (b) ball and stick view of the {Gd–Mo$_{18}$–(PO)$_2$} fragment; (c) coordination environment of the Gd(III) ion. The color codes are as follows: Mo, green spheres; O, red spheres; C, gray spheres; N, blue spheres; {MoO$_6$} octahedra, blue; {MoO$_7$} pentagonal bipyramids, orange.

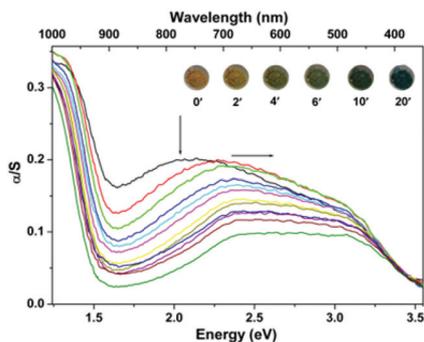**Fig. 2** Kubelka–Munk transformed reflectivity of compound **4** measured in the 350–1000 nm range after 0, 1, 2, 3, 4, 5, 6, 8, 10, 12, 16, 20 and 40 min of visible light (λ > 420 nm) irradiation. Inset: the color of compound **4** at different irradiation times.

Fig. 4 UV-vis spectra (400–1000 nm) of compound **4** in pH = 1 H_2SO_4 (concentration: 100 μM) in the ground state (a) and with UV irradiation (b). Inset: UV-vis spectra (200–400 nm) of compound **4** in pH = 1 H_2SO_4 (concentration: 1 μM) in the ground state (c) and with UV irradiation (d); color variations of compound **4** in pH = 1 H_2SO_4 (concentration: 1 μM) in the ground state (e) and with UV irradiation (f).

polyoxomolybdates (usually 3.20–3.70 eV),[1,6,7] clearly establishing the low energy triggering the photochromic reaction.[5] However, the absorption threshold for **4** is progressively blue-shifted with irradiation time, accompanied with notable hypochromicity at the maximum absorption wavelength, which may explain the photosensitive phenomenon.[2] Concomitantly, a red shift of the optical gap (1.50 eV, 815 nm) is also observed.[1,6,7] In fact, compound **4** maintains its backbone structure during the irradiation process, which is confirmed by similar PXRD (Fig. 3) and IR spectra (Fig. S10†) before and after irradiation.

As obtained from the BVS calculations, the oxidation state values of Mo atoms are in the range of 5.806–6.386 (Table S2†). According to the Yamase's model,[12] it is proposed that the coloration is due to the photoreduction of Mo^{6+} ($4d^0$) to Mo^{5+} ($4d^1$). It is notable that the organic composition plays the major role in the optical properties of this family of complexes, since the reference compound $K_8[Mo_{36}O_{112}(H_2O)_{18}]\cdot 36H_2O^{22}$ (the structure was confirmed by the IR spectrum, see Fig. S3†) was not photosensitive at all under the same conditions even after irradiation for 40 min (Fig. S11†). Importantly, there are classic hydrogen bonds between the grafted PO molecules and Mo–O–Mo oxygen atoms (shown in Fig. 1a, atom distances of N1···O3 and N2···O56 being 2.959 and 3.031 Å, respectively), while there are no obvious counteractions between the crystal PO molecules

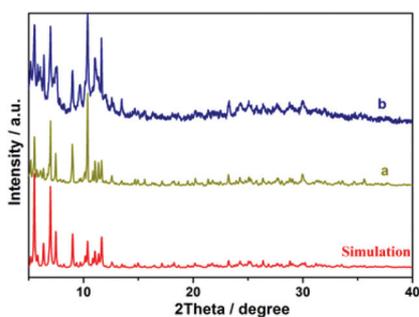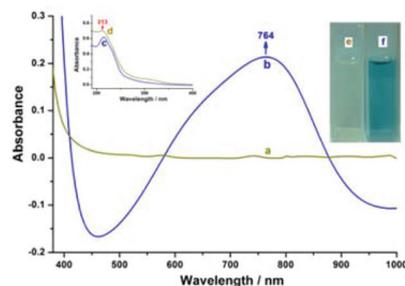and {Mo$_{36}$} clusters. Therefore, it is supposed that the POM's backbone may transfer its protons to the covalently grafted PO molecules under excitation, thus the N^+–H···O hydrogen bonds at the organic–inorganic interface are formed, which then lead to the photosensitive phenomenon.[3,10,12] In any case, this demonstrates that the organic–inorganic hybrid {Mo$_{36}$} clusters may be a class of perfect photosensitive materials under visible light irradiation, although the color change is irreversible.

As reported previously, organoammonium cations with POMs are photosensitive both in the solid state and in solution.[12] However, different from the photosensitive behavior in the solid state, the slight yellow color of compound **4** in pH = 1 H_2SO_4 solution is unchangeable under sunlight even after five hours. Interestingly, it turns deep blue (Fig. 4) under UV irradiation by a xenon lamp (λ = 365 nm, 300 W, 10 min). The UV absorption band at 732 nm of the irradiated solution confirms the existence of the typical aqueous molybdenum blue species.[23] In addition, the above mentioned two UV spectra in the range of 200–400 nm (λ$_{max}$ = 213 nm, attributing to the pπ–dπ charge-transfer transition of the $O_t\rightarrow Mo$ bond[15]) are quite similar to each other, establishing that the {Mo$_{36}$} backbone is stable enough in solution under UV irradiation. Obviously, the photosensitive behaviors of compound **4** in such two states are of great difference. This may be explained by two aspects: (i) the absorption band of the $O_t\rightarrow Mo$ transition in the solution is red-shifted in the solid state, implying the higher electron excited energy in the solution; (ii) the POM's backbone is surrounded by a large amount of water molecules in solution, and thus more difficult to transfer its protons to the grafted PO molecules under excitation than in the solid state, which decreases the formation rate of N^+–H···O hydrogen bonds at the organic–inorganic interface.

Solid state fluorescence spectroscopy

It is well known that the luminescence of lanthanide(III) ions have low molar absorptivity and the f–f transitions are usually generated via the "antenna effect", because the f–f transition is spin- and parity-forbidden.[24] In addition, Nd(III), Er(III), and Yb(III) are well-known for their near-infrared luminescence.[26]

Fig. 3 PXRD spectra of compound **4** in the solid state, before (a) and after (b) visible light irradiation.
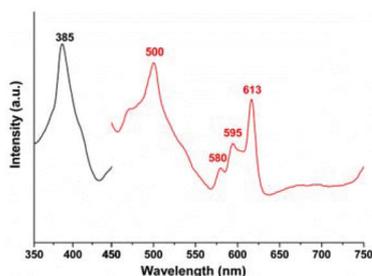
Fig. 5 Excitation (black) and emission (red) spectra of compound **3** in the solid state.

However, considering the excellent luminescence behaviors of the Eu(III) ion, only the f–f transition in the visible area of compound **3** is discussed in this work. Different from the other compounds (emission bands at 500 and 604 nm, Fig. S12†), when excited at 385 nm, compound **3** exhibits three emission bands at 580, 595 and 617 nm in the solid state (except 500 nm), which could be assigned to $^5D_0 \rightarrow ^7F_0$, $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions of the Eu(III) ion,[24,25] respectively. It is obvious that the intensity of the red emission corresponding to the $^5D_0 \rightarrow ^7F_2$ transition is stronger than the other two emissions, implying that the PO ligand may be suitable for the sensitization of the red luminescence for the Eu(III) ion. Generally, the emission bands at 500 and 604 nm (absent in compound **3**) in all ten compounds could be contributed to the inorganic components, since the reported compound $K_8[Mo_{36}O_{112}(H_2O)_{18}] \cdot 36H_2O$ has similar ones. However, once dissolved in pH = 1 H_2SO_4 solution, only one emission band at 470 nm could be observed for all compounds (Fig. S13,† λ_{ex} = 410 nm). Obviously, the solvate effect of water may quench the Eu(III) ion characteristic emission of compound **3** (Fig. 5).[25]

Conclusions

In summary, we have synthesized a new class of organic–inorganic hybrid rare earth complexes based on the {Mo$_{36}$} cluster. These compounds represent the first amide oxygen atom grafted case and the highest substitutes in the framework of a giant organic functioned {Mo$_{36}$} isopolyanion. All compounds in the solid state show considerable coloration under visible light irradiation (λ > 420 nm), while the photosensitive behavior in aqueous solution should be induced by UV irradiation (λ = 365 nm). This demonstrates that the organic–inorganic hybrid {Mo$_{36}$} clusters are a class of perfect photosensitive materials. In addition, compound **3** exhibits the characteristic emission of the Eu(III) ion in the solid state.

Acknowledgements

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