



Review

Recent advances in lanthanide luminescence with metal-organic chromophores as sensitizers



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ABSTRACT

This review article focuses on recent advances in sensitized lanthanide luminescence from heteronuclear complexes with metal-organic chromophores as light-harvesting sensitizer through intercomponent energy transfer. Depending on the ligands and the metal ions, p–f, d–f and f–f heteronuclear assemblies exhibit various colored visible or NIR (near infrared) luminescence following energy transfer from metal-organic chromophores. When the emission of metal-organic sensitizer shows complementary color with the sensitized lanthanide luminescence, white light emitting is successfully generated by incomplete energy transfer to the lanthanide center.

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1. Introduction

Since the f–f transitions of lanthanide(III) ions are forbidden with low absorption coefficient, the luminescence from Ln(III) ions is mostly achieved through indirect sensitization process from light-harvesting systems instead of direct excitation into the Ln(III) centers. For lanthanide coordination systems, narrow line-like emission bands from f–f states can be sensitized through efficient energy transfer from light harvesting antenna chromophores

[1–6]. On the one hand, sensitization of lanthanide luminescence is achieved by organic aromatic ligands that are directly bound to the lanthanide centers and absorb strongly in UV–vis spectral region [7–12]. To promote the energy transfer from antenna chromophore to lanthanide(III) ion, the energy levels of the ligands should be higher than the lowest excited state of the lanthanide(III) ion within an appropriate range. As organic ligands absorb high-energy UV light in most cases, the sensitization is always low efficient for near infrared (NIR) emitting lanthanide ions. In order to optimize lanthanide luminescence, a feasible approach is to shift the excitation domain toward the visible region by modifying the electronic properties of peripheral ligands through introducing electron-donating and electron-accepting substituents.

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On the other hand, it is well-known that co-doping other metal ions to inorganic lanthanide matrixes is a commonly utilized approach to sensitize lanthanide luminescence in lanthanide-doped glasses [1–4]. Such a strategy is also used to attain sensitized lanthanide luminescence in inorganic materials containing tungstate or molybdate phosphors, in which UV–vis light is strongly absorbed by tungstates or molybdates so that lanthanide luminescence is sensitized through effective excitation energy transfer in lanthanides polyoxometallates.

Inspired by inorganic lanthanide doping systems with sensitized luminescence, an alternate approach for effective sensitization of lanthanide luminescence in heteronuclear metallorganic complexes has been established by Veggle and coworkers [13], and then developed by others [14–21] at the beginning of this century using metal-organic antenna chromophores as lanthanide sensitizers. Compared with traditional light-harvesting organic antenna, the use of metal-organic chromophores is more appealing for achieving highly efficient lanthanide luminescence, particularly for NIR emitting because this approach affords a series of advantages. (1) Metal-organic moiety often exhibits low-energy absorption bands in the visible spectral region arising from red-shifted ILCT (intraligand charge transfer), MLCT (metal-to-ligand charge transfer) or LLCT (ligand-to-ligand charge transfer) excited states, affording better energy match between metal-organic donors and Ln^{III} acceptors and thus less waste in energy. (2) Metal-organic moiety usually shows relatively high triplet state quantum yields resulting from the rapid intersystem crossing induced by the heavy metal effect. (3) Metal-organic chromophore gives relatively long-lived triplet excited states that facilitate energy transfer to adjacent lanthanide centers. (4) Both the emission quenching of metal-organic chromophores and the luminescence sensitization from lanthanide centers can be readily detected in p–f, d–f or f–f heterometallic complexes.

In contrast with other review articles concerning a specific theme for p–f [21], d–f [14–20] or f–f [10] heteronuclear system, this article focuses on the comprehensive advances since 2009 that are relevant to sensitized lanthanide luminescence in heteronuclear complexes through energy transfer from metal-organic sensitizers.

2. p-Block metal-organic chromophores as sensitizers

Relative to the studies on sensitized lanthanide luminescence in transition metal and lanthanide heteronuclear complexes through d→f energy transfer from d-block metal-organic chromophores, the use of p-block metal-organic moieties as sensitizers for visible or NIR emitting lanthanide ions has been relatively neglected.

Albrecht et al. [22] described the preparation of Al–Ln (Ln = Nd, Yb, Er) heteronuclear complexes (Fig. 1) through K^+ templated self-assembly processes using isobutenylidene-bridged heteroditopic (8-hydroxyquinoline)(2-carbamido-8-hydroxyquinoline)-derived ligand. The Al–Ln array adopts a triple-stranded helical structure with an encapsulated central templating K^+ . Replacement of one lanthanide(III) ion in homodinuclear Ln_2 complexes with a smaller Al^{3+} results in obvious increase in both lifetimes and quantum yields, ascribed to more tightly bound ligand strands and more rigid structures of Al–Ln complexes, thus reducing non-radiative deactivation processes in the coordination spheres compared with the corresponding Ln_2 homodinuclear species.

The reactions of $\text{Al}(\text{Mq})_2(\text{OC}_6\text{H}_4\text{CN}-4)$ ($\text{Mq} = 2$ -methyl-8-hydroxyquinolinolate) with $\text{Ln}(\text{hfac})_3(\text{H}_2\text{O})_2$ ($\text{hfac} = \text{hexafluoroacetylacetonate}$) resulted in the isolation of Al_3Ln_2 heteropentanuclear complexes $[\text{Al}_3(\text{Mq})_4(\text{HMq})(\mu_3\text{-OH})_2(\mu\text{-OH})_3\{\text{Ln}(\text{hfac})_3\}_2]$ (Ln = Nd, Eu, Yb) [23]. The Al_3Ln_2 structures (Fig. 2) are linked by two $\mu_3\text{-OH}$, three $\mu\text{-OH}$ and

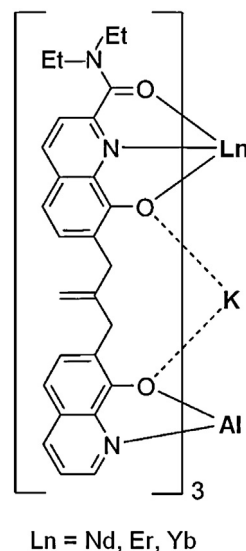


Fig. 1. Al–Ln (Ln = Nd, Yb, Er) heteronuclear complexes with a triple-stranded helical structure.

three μ -phenoxo with one from HMq and two from deprotonated Mq. Upon excitation at 350–420 nm, sensitized lanthanide luminescence is successfully achieved by energy transfer from $\text{Al}(\text{Mq})_2$ light-harvesting chromophores. Interestingly, these Al_3Ln_2 complexes exhibit remarkably fluoride-enhanced lanthanide luminescence by introducing a small amount of $[\text{Bu}_4\text{N}]\text{F}$, ascribed to the formation of strong $\text{F}^- \cdots \text{H}-\text{O}$ hydrogen bonds so as to weaken remarkably the O–H vibrations and thus minimize the nonradiative deactivation processes. Addition of 0.6 equiv. of fluoride to dichloromethane solutions results in 1.1-, 5.5- and 1.3-fold emission enhancement for Al_3Nd_2 , Al_3Eu_2 and Al_3Yb_2 complexes, respectively. Doping 0.6 equiv. $[\text{Bu}_4\text{N}]\text{F}$ in solid states results in a 1.3-fold (Al_3Nd_2), 8.4-fold (Al_3Eu_2), and 2.2-fold (Al_3Yb_2) increase of lanthanide luminescence. Doping 0.6 equiv. $[\text{Bu}_4\text{N}]\text{F}$ in PMMA films gives a 10.4-fold increase for Al_3Eu_2 complex and 2.5-fold increase for Al_3Yb_2 species in emission intensity. Fluoride-induced lanthanide luminescence enhancement follows PMMA film > solid powder > solution for both visible and NIR emitting Al_3Ln_2 species. The Al_3Eu_2 complex exhibits dual emission ascribed to both $\text{Al}(\text{Mq})_2$ and Eu-centered emitters, following incomplete energy transfer from $\text{Al}(\text{Mq})_2$ chromophore to Eu center. Since $\text{Al}(\text{Mq})_2$ displays cyan-light emitting centered at 485 nm which is the complementary color of Eu-based red emission (610 nm), bright white-light emission occurs for Al_3Eu_2 species in both solid state and solution (Fig. 2). Upon excitation at 348 nm, the quantum yield of white-light emission is ca. 6.1%, but increased to 11.6% upon the addition of 0.6 equiv. $[\text{Bu}_4\text{N}]\text{F}$ with the chromaticity coordinates changing from (0.27, 0.36) to (0.34, 0.33).

Two Al–Ln heterodinuclear complexes $[(\text{acacCN})_2\text{Al}(\mu\text{-acacCN})\text{Ln}(\text{CH}_3\text{OH})_3\text{Cl}_3]$ (Ln = Eu, Tb) [24] were reported to exhibit lanthanide-centered luminescence due to the effective energy transfer from the triplet state of $\text{Al}(\text{acacCN})_3$ chromophore to lanthanide center. Since the energy level of the ^3IL (intraligand) state in $\text{Al}(\text{acacCN})_3$ is some higher than that of lanthanide ions, the $\text{Al}(\text{acacCN})_3$ chromophore acts as a favorable sensitizer for Eu or Tb luminescence.

3. d-Block metal-organic chromophores as sensitizers

Since d-block metal-organic moieties usually exhibit intense absorption bands in visible spectral region caused by charge transfer transitions between metal ions and organic ligands, sensitized

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