

PAPER



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Unraveling the highly selective nature of silver-based metal–organic complexes for the detection of metal ions: the synergistic effect of dicarboxylic acid linkers†

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Photoluminescent metal–organic complexes (PLMOCs) have become attractive materials for highly selective metal ion detection because of their unique physical and chemical properties. However, the fundamental understanding of the characteristics of PLMOCs and metal ion sensing is still lacking. We report the synthesis of a series of Ag(bpy)(DA) PLMOCs (DA = dicarboxylic acids) and unravel key factors of the Ag-based PLMOCs regarding sensitivity in metal ion detection. The DA linkers with strong electron-donating groups (–NH₂ and –OH) resulted in a red-shift in the PL emission of the Ag-based PLMOCs. Ag(bpy)(DA), displaying emission peaks in the UV region, showed higher sensitivity for Fe³⁺ compared to Ag-based PLMOCs with the emission peaks located in the vis region. Moreover, Ag(bpy)(DA) comprised of DA linkers with an amine group could exhibit sensitive detection toward Pb²⁺.

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1 Introduction

Photoluminescent metal–organic complexes (PLMOCs) comprised of metal ions or metal clusters and organic linkers have been widely used in many applications because of their extraordinary emission, inherent modularity and diverse structures.^{1–6} Among them, silver-based PLMOCs (Ag-PLMOCs) are one of the most interesting light emitters since they have unique photophysical properties and are highly stable in applied environments, making them a promising candidate for photocatalysis,^{7,8} sensing applications,^{9,10} light-emitting diodes (LEDs),¹¹ and energy applications.¹²

Recently, Ag(bpy)(L) (bpy = 4,4'-bipyridine and L is a second ligand), a new class of Ag-PLMOCs, have been extensively studied because of their intriguing structures and interesting photophysical and chemical characteristics, which can be manipulated by introducing a second organic ligand into the

Ag-bpy skeleton.^{13–18} Oliver *et al.* reported the incorporation of 1,2-ethanedithiolonic acid (EDSA) into Ag-bpy cationic chains to form the stable Ag(bpy)(EDSA) structure and enhance the Lewis acidity.¹⁵ Besides, the substitution of different dicarboxylic acids in Ag-PLMOCs exhibited excellent photocatalytic activity due to intense photoluminescence.^{14,19} The PL emission of Ag-PLMOCs was also applied to detect and recognize the chemical and molecular properties of metal ions.¹⁰ Furthermore, Ag(bpy)(L) can be easily prepared by mixing silver salt (AgNO₃) and organic ligands in an aqueous environment under ambient conditions.

Metal ion sensing based on quenching or enhancement of the photoluminescence intensity of PLMOCs has been paid significant attention since this methodology is highly efficient.^{20,21} The iron (Fe³⁺) and lead ions (Pb²⁺) are the most attractive and extensively studied metals.^{22–27} Iron ions are an indispensable element in humans and other living organisms. They are also important for many biological systems and biochemical processes, including oxygen storage and transport, enzymatic reactions, and electron transfer.^{27,28} On the other hand, lead ions are toxic to human health and the environment.^{29,30} A variety of PLMOCs have been used as sensors for the detection of these metal ions, with high sensitivity and selectivity.^{10,22,23,31–33} Previous studies suggested that the PL intensity of PLMOCs was quenched upon the addition of Fe³⁺ or Pb²⁺ ions, resulting from the collapsed crystal structure,³⁴ photo-energy transfer *via* the interaction between metal ions and organic linkers,^{35,36} competitive absorption of photo-energy,³⁷ or cation exchange.^{26,38} However, the

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