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RESEARCH ARTICLE

Selective detection of phosphaphenanthrene-containing luminophors with aggregation-induced emission enhancement to transition metal ions

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Transition metal ions (Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Hg^{2+}, Ag^{+}, Fe^{3+}) in water are used to quench emission of 2-(6-oxido-6H-dibenz < c,e > < 1,2 > oxaphosphorin-6-yl)-1,4-phenylene-bis(p-pentyloxylbenzoate)s (MD5) with aggregation-induced emission enhancement (AIEE) in water-acetonitrile (AN) mixture (80:20 by volume). Among all metal ions, Fe^{3+} exhibits the highest quenching efficiency on AIEE of MD5 even when the concentration of Fe^{3+} is lower than 1×10^{-6} mol/L. The quenching efficiency of Hg^{2+} is lower than that of Fe^{3+} at the same concentration, though MD5 is used to detect Hg^{2+} efficiently, too. To other metal ions, low quenching efficiency has few relations with a wider concentration range. The UV absorbance spectra show only red shift of absorbance wavelength in the presence of Hg^{2+} and Fe^{3+}, which indicates a salt-induced J-aggregation. SEM photos reveal larger aggregation and morphological change of nanoparticles of MD5 in water containing Hg^{2+} and Fe^{3+}, which reduce the surface area of MD5 emission for further aggregation. The selective quenching effect of transition metal ions to emission of MD5 has a potential application in chemical sensors of some metal ions.

Keywords AIEE, phosphaphenanthrene, transition metal ions, quenching effect

1 Introduction

The development of selective and sensitive imaging tools capable of monitoring heavy- and transition-metal ions Fe^{3+} and Hg^{2+} has attracted considerable attention because Fe^{3+} plays a pivotal role in many biochemical processes in a cellular level, and Hg^{2+} is one of the most hazardous components in the environment [1–6]. Many fluorescent probes for the detection of Fe^{3+} and Hg^{2+} have been proposed so far [7–13].

A number of compounds exhibiting aggregation-induced emission (AIE), aggregation-induced emission enhancement (AIEE) or crystallization-induced emission enhancement (CIEE) have been developed in recent years [14–33]. Because they exhibit stronger emission in the solid state than in solution, these compounds show great potentials for such applications as highly selective and stable fluorescence sensors for proteins [25–27], DNA [28], organic vapors [29,30], explosives [31,32], metal ions [33], and so on.

In our previous study, as one type of AIEE compound family, 2-(6-oxido-6H-dibenz < c,e > < 1,2 > oxaphosphorin-6-yl)-1,4-phenylene-bis(p-pentyloxylbenzoate)s (**MD5**) can be observed with AIEE and CIEE effects [34] due to the progressively fortified restriction of its intramolecular rotation in the different physical phases. The morphological structure of the thin solid film of **MD5** between amorphous and crystalline phases can be changed by vapor-fuming process as well as fuming–heating and heating–cooling cycles, leading to emission switching between bright and dark states [34]. The phosphaphenanthrene-containing compound is obviously different from others reported, which has negative P = O bond and refers capable of easy interaction with positive molecules or ions. If positive ions are introduced during forming the aggregation of **MD5**, the aggregation packing structure and organizational morphology of **MD5** would be obviously changed and lead to “bad” emission of **MD5** aggregates to some extent. In this paper, we will report that some transition metal ions, such as Fe^{3+} and Hg^{2+}, have rapid and sensitive quenching effect on **MD5** AIEE, which means that it has a factual application like chemosensor of some transition metal ions.

2 Experimental

2.1 Materials

2-(6-oxido-6H-dibenz < c,e > < 1,2 > oxaphosphorin-6-yl)-

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1,4-phenylene-bis(p-pentyloxylbenzoate)s (**MD5**) was prepared in our laboratory. Acetonitrile (AN) (of pesticide residue grade) was purchased from American Honeywell B&J. $Pb(NO_3)_2$, $Zn(NO_3)_2$, $Cd(NO_3)_2$, $Co(NO_3)_2$, $Mn(NO_3)_2$, $CuSO_4$, $Ni(NO_3)_2$, $Hg(NO_3)_2$, $AgNO_3$, and $FeCl_3$, $Ce(NO_3)_3$ were all analytical reagent and purchased from Beijing Chemical Reagent Co. Ltd.

2.2 Instrumentation

UV spectra were recorded on a HITACHI Spectrophotometer U-2800. Photoluminescence (PL) spectra were recorded on a Perkin-Elmer VARIAN 55 spectrofluorometer. SEM images were taken on a HITACHI S-4800 Scanning Electron Microscope with EDS.

2.3 Preparation of MD5 nanoaggregates in mixture containing metal ions

The solution of **MD5** in AN with concentration of 1×10^{-4} mol/L was first prepared. Aliquots of the solution were transferred into 10-mL volumetric flasks, into which appropriate volumes of AN and water were added dropwise under vigorous stirring to furnish 1×10^{-5} mol/L solutions with different water contents (0–90 vol%) in the absence or presence of metal ions with appropriate concentration. UV and PL spectra were immediately performed once the solutions were prepared.

2.4 Results and discussion

Figure 1 shows the fluorescence spectrum of **MD5** in the absence or presence of three metal ions (Fe^{3+}, Hg^{2+} and Cu^{2+}) in water-AN mixture (80∶20 by volume). **MD5** shows strong emission in absence of metal ions because of its AIEE property. After addition of metal ions, the PL intensity of **MD5** at 359 nm decreased, which contributed to the quenching effect of the transition metal ions on AIEE of **MD5**. Outstanding differences in emission intensity were observed with samples mixed with Fe^{3+} and Hg^{2+} whose relative quenching efficiency reached 56% and 28%, as shown in Figs. 1 and 2. Cu^{2+} shows low quenching efficiency (about 10%) which may be deemed having no quenching ability.

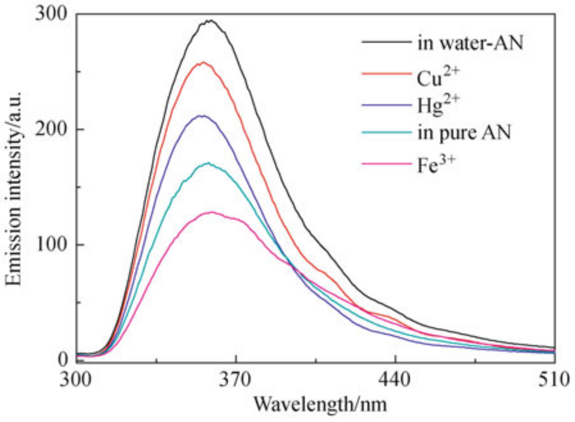

Figure 1 PL spectra of **MD5** in water-AN mixture (80∶20 by volume) solution in the presence of different transition metal ions in water. Excitation wavelength: 275 nm. Concentration of metal ions was 1×10^{-4} mol/L.

The fluorescence spectra of **MD5** in the aggregation state were also measured in the presence of other metal ions including Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+}, Ni^{2+} and Ag^{+} under identical conditions. As shown in Fig. 2, quenching efficiency of the eight metal ions on **MD5** aggregates at 359 nm was rather small (less than 10%) after addition of 10.0 equiv of the respective metal ions. It is obvious that the emission of **MD5** has different responses to all the 10 transition metal ions, with the highest response ability to Fe^{3+} and next to Hg^{2+}. Other competitive metal ions such as Pb^{2+}, Mn^{2+}, Ni^{2+}, Co^{2+} etc., however, induce a rather low interference effect on this fluorescence assay for Fe^{3+} and Hg^{2+}.

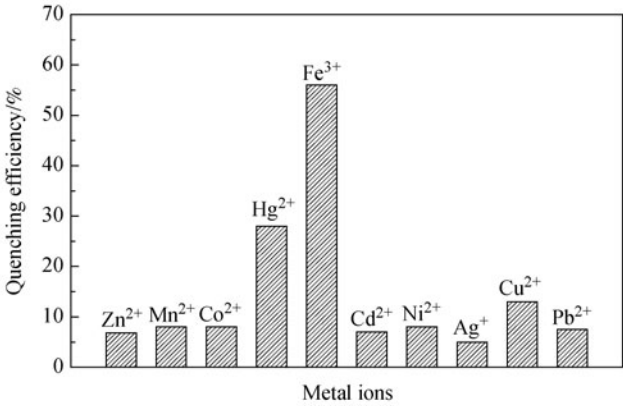

Figure 2 Relative quenching efficiency of ten transitional metal ions on emission of **MD5** aggregated in water-AN mixture (80∶20 by volume) solution.

The PL intensities of **MD5** were measured in water-AN mixture (80∶20 by volume) solution containing different concentrations of metal ions from 1×10^{-3} mol/L to 1×10^{-6} mol/L, respectively, as shown in Figs. 3 and 4. The experimental results indicate that the detection sensitivity distinctly increases with the increase of the concentration of metal ions. Among all metal ions used in our work, Fe^{3+}, however, exhibits the highest quenching efficiency even when the concentration of Fe^{3+} was lower than 1×10^{-6} mol/L. The quenching efficiency of Hg^{2+} is lower than that of Fe^{3+} at the same concentration. For Cu^{2+}, the low quenching efficiency has little relation with its concentration ranged from 1×10^{-3} mol/L to 1×10^{-6} mol/L. Thus, the emission of **MD5** aggregation is thought to have selective responses to Hg^{2+} and Fe^{3+} and thereby has a potential application such as transition metal ion chemosensors.

To find the reason of different quenching effects of metal ions on **MD5** AIEE, UV spectra of **MD5** aggregation in water-AN mixture (80:20 by volume) in the presence of these metal ions were detected. Figure 5 shows that UV spectra of **MD5** aggregation state in the presence of Fe^{3+} and Hg^{2+} ions exhibit an obvious difference from those of other ions, which show the outstanding red shift from 268 nm for other metal ions to 276 nm for Fe^{3+} or 281 nm for Hg^{2+}. The absorption wavelength red shift and PL emission quench of **MD5** in the presence of Fe^{3+} and Hg^{2+} reveal only that the packing style of **MD5** is a salt-induced J-aggregate state [34]. The polar $P=O$ structure in **MD5** molecule strongly interacts with Hg^{2+} or Fe^{3+} and their hydrolysate because part of Hg^{2+} or Fe^{3+} hydrolyzes to form $Hg(OH)^+$ or FeO(OH) in neutral solution, respectively [35–37]. Compared with pure Hg^{2+} and Fe^{3+} ion, their hydrolysate is a kind of sorbents which tend to adhere to the particle of **MD5** at initial stages. It is the main reason of higher aggregation degree of **MD5** in water containing Hg^{2+} or Fe^{3+}. Except for Fe^{3+} and Hg^{2+}, all other metal ions have UV absorbance curves that show the similar absorption feature of **MD5**, which corresponds to their weak quenching efficiency on emission of **MD5**.

The morphology of **MD5** aggregated in water containing different transition metal ions was further detected by SEM in Fig. 6. The results reveal that the average diameter of nanoparticles with irregular shape in the absence of metal ions is about 30 nm. With the addition of metal ions, the average diameters of nanoparticles are increased to 100 nm (Cu^{2+}), 150 nm (Fe^{3+}) and 300 nm (Hg^{2+}) respectively, which are 3–

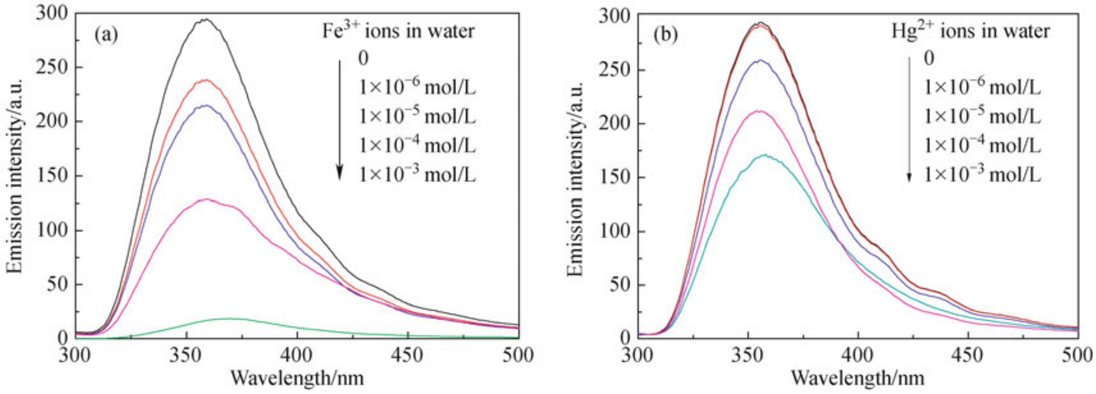

Figure 3 PL spectra of **MD5** in the presence of (a) Fe^{3+} and (b) Hg^{2+} in water-AN mixture (80:20 by volume) (the concentrations of metal ions (mol/L): 0, 1×10^{-6}, 1×10^{-5}, 1×10^{-4}, 1×10^{-3}). Excitation wavelength: 275 nm.

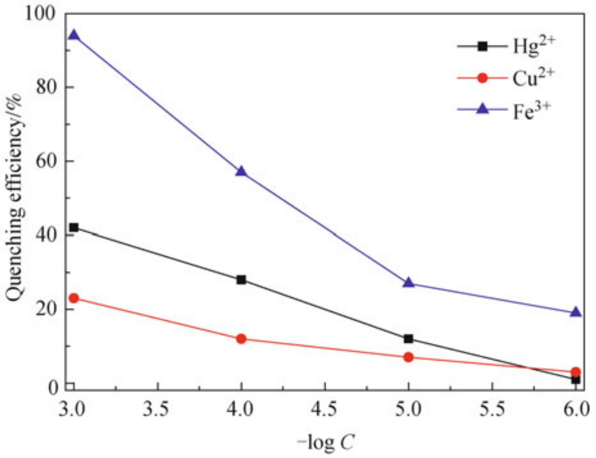

Figure 4 Relation between quenching efficiency of Fe^{3+}, Hg^{2+}, Cu^{2+} on **MD5** emission and concentration of metal ions in water-AN mixture (80:20 by volume).

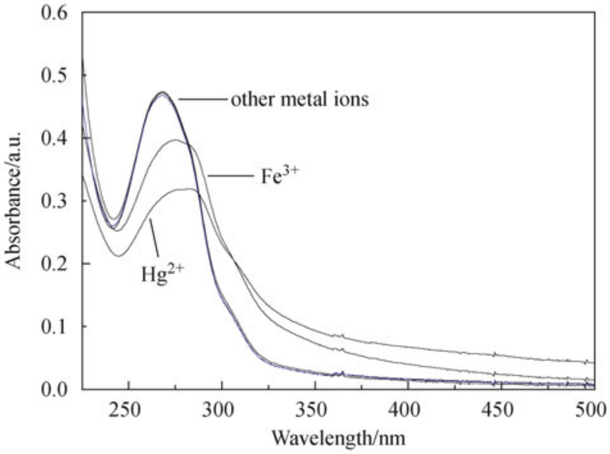

Figure 5 UV absorbance curves of **MD5** in water-AN mixture (80:20 by volume) in the presence of transition metal ions. Transition metal ions concentration: 1×10^{-4} mol/L.

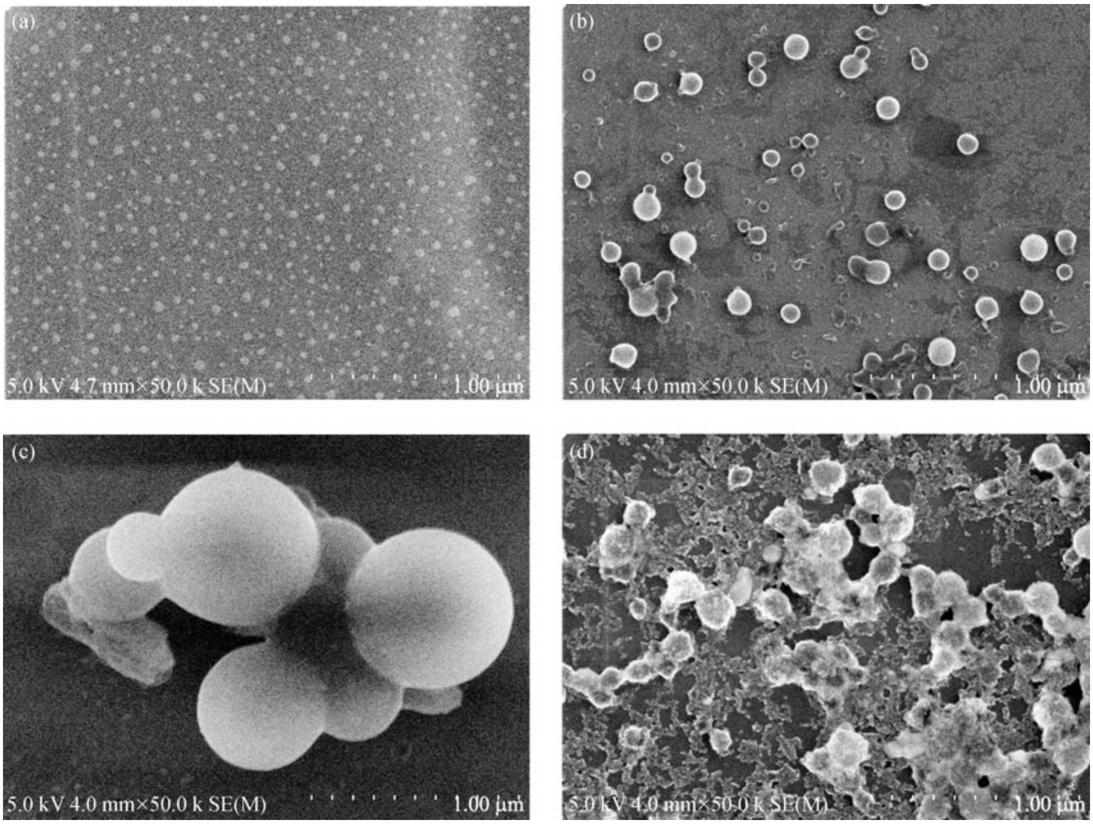

Figure 6 SEM photos of **MD5** aggregates in water-AN mixture (80:20 by volume) in the presence of 1×10^{-4} mol/L metal ions. The sequence of metal ions are (a) no, (b) Cu^{2+}, (c) Hg^{2+} and (d) Fe^{3+}.

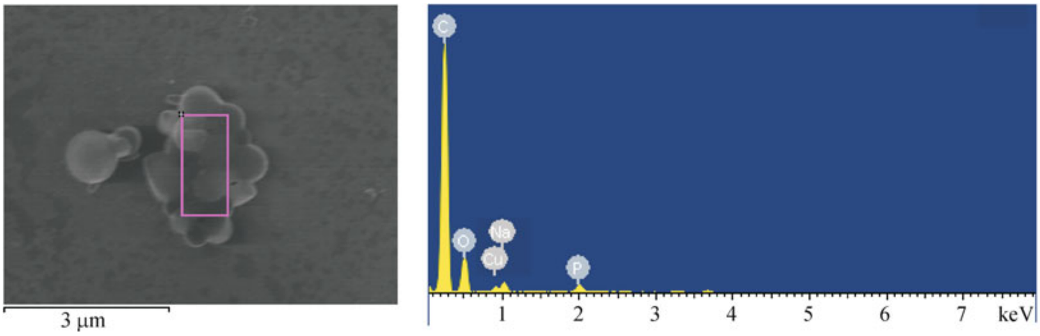

Figure 7 The surface element analysis of **MD5** aggregated particles in the presence of Hg^{2+} by EDS.

10 folds bigger than those with the absence of metal ions. The increase of diameter directly affects the aggregation degree. Therefore, it can be concluded that the increasing volume of **MD5** nanoparticles reduces their emission area and weakens the emission [38]. The change of **MD5** aggregation reveals that the molecule stacking style in metal ion solution is absolutely different. Moreover, it should be emphasized that the nanoparticles from Hg^{2+} solution have the biggest size in a shape of regular sphere. It is a direct evidence of change of aggregation morphology between aggregation in pure water and in water containing transition metal ions. It has relation to the high quenching efficiency of some ions (Fe^{3+} and Hg^{2+}).

We also detected the elementary disperse of **MD5** aggregates by EDS to explain aggregation of **MD5** in water containing Hg^{2+}. Figure 7 shows that the elements of C, O, P, Cu, Na are detected (Cu and Na elements are from copper net). The Hg element can not, however, be found at the surface of nanoparticles. It means that the nanoparticles are made up of **MD5**, and the Hg^{2+} did not combine with **MD5** evenly in particles. So, we deduce that the Hg^{2+} as a center first forms a complex with **MD5** before the process of nanoparticle forming. More detailed mechanism analysis is currently underway in our laboratory.

3 Conclusion

In summary, transition metal ions (Pb^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Mn^{2+},Cu^{2+}, Ni^{2+}, Hg^{2+}, Ag^{+}, Fe^{3+}) in water are used to quench emission of 2-(6-oxido-6H-dibenz < c,e > < 1,2 > oxaphosphorin-6-yl)-1,4-phenylene-bis(p-pentyloxylbenzoate)s (**MD5**) with AIEE in water-AN mixture (80:20 by volume). Among all metal ions, Fe^{3+} exhibits the highest quenching efficiency even when the concentration of Fe^{3+} is lower than 1×10^{-6} mol/L. The quenching efficiency of Hg^{2+} ion to AIEE of **MD5** is lower than that of Fe^{3+} at the same concentration, though **MD5** is used to detect Hg^{2+} efficiently, too. To other ions, the low quenching efficiency has, however, little relation with wider concentration range. The UV absorbance spectra show only red shift of absorbance wavelength in the presence of Hg^{2+} and Fe^{3+}, which indicates salt-induced J-aggregation. Therefore, the quenching results from the fact that energy of exiting state of **MD5** is transferred into thermal energy of metal ions. At the same time, SEM photos reveal larger aggregation and morphological change of nanoparticles of **MD5** in water containing Hg^{2+} and Fe^{3+}. The larger aggregation reduces the surface area of **MD5** emission for further aggregation. However, other transition ions also have slightly quenching effect on emission of **MD5** aggregate state. The selective quenching emission of **MD5** to transition metal ions has a potential application in chemical sensors of some metal ions.

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