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离子受体对自由卟啉探针荧光识别性能的影响

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摘要:通过对 2 个 *N*,*N*-二吡啶胺基受体修饰的自由卟啉化合物(Porphyrin-2-DPA)光学识别性能的系统研究,可以得知:该卟啉化合物中心刚性共轭的四吡咯环状结构不仅作为灵敏的光学信号基团、更是作为第一离子配位受体,在非共轭的 *N*,*N*-二吡啶胺基受体辅助下,对 Pb^{2+}/Cu^{2+}离子表现出灵敏的多重信号分析识别功能。

关键词:荧光探针;卟啉;*N*,*N*-二吡啶胺基(DPA);阳离子;多重分析物;多重信号

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Receptor Influence on Sensing Performance of Metal-Free Porphyrin Sensor

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Abstract: The optical properties of a metal-free tetra(aryl)porphyrin with two *N*,*N*-di(2-pyridylmethyl)amino groups (Porphyrin-2-DPA) upon respective addition of different metal ion were investigated. Systemic studies show that the rigid π-conjugated tetrapyrrole macrocyclic moiety of Porphyrin-2-DPA is employed not only as the sensitive signaling fluorophore but also as the primary receptor with excellent binding affinity and distinctive selectivity to metal ion, which together with the no-conjugated DPA auxiliary receptor endows Porphyrin-2-DPA the sensitive versatile sensor to Pb^{2+}/Cu^{2+} on the basis of dual-optical signals.

Keywords: fluorescent probe; porphyrin; *N*,*N*-di(2-pyridylmethyl)amino group (DPA); cations; dual-analytes; multi-signals

0 Introduction

Fluorescent molecular sensors, in particular those for detecting the heavy and transition metal (HTM) ions, have attracted increasing attention due to their high sensitivity, rapid responsiveness, and low-detection-limit[1-6]. However, most fluorescent sensors focus just on single-target detection with few dealing with "single sensor for multiple-analytes"[7-12]. Towards future practical applications, it is necessary to develop the single fluorescent sensors with different responses for multiple-analytes since they could shorten the preparation process to multiple sensors and facilitate to detect multiple analytes with high efficiency. For the purpose of realizing the versatile molecular optical detection for multiple-analytes, usually more than one receptors and/or fluorophores have been incorporated into the multiple-detective single fluorescent

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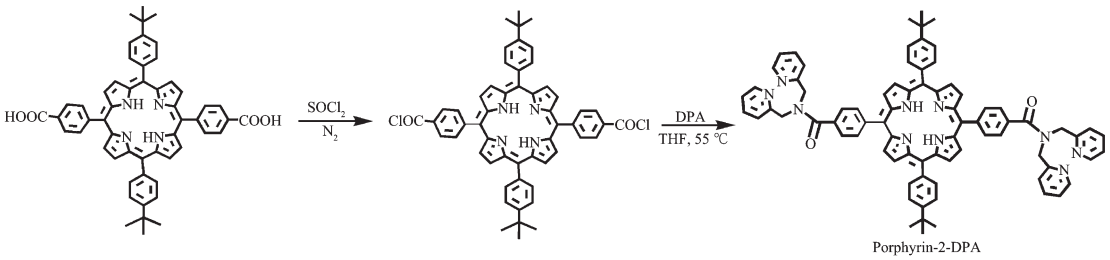
sensors[13-15]. In 2005, a three chromogenic units-containing chemosensor was prepared by Suzuki and co-workers for Fe^{3+}/Pb^{2+}/Al^{3+}/Cu^{2+} on the basis of different coordination mode between metal ion and multi-dentate single receptor[16]. Akkaya synthesized a three-receptor-consisting styryl-Bodipy sensor, which is able to detect Zn^{2+}, Ca^{2+}, and Hg^{2+} [17]. Subsequently, one-receptor and two-fluorophores composed Porphyrin-BODIPY FRET ratiometric sensor for Fe^{2+}/Hg^{2+} was synthesized by our group[18]. Meanwhile, there is less study on single-fluorophore-receptor-constructing chem-osensors for di/tri-analytes associated with the different sensing mechanism[19-20]. Notably, the studies on the multiple-analyte sensors have thus far focused mainly on its multiple-detecting function, and there still exists less investigation over the detecting effect of each receptor for multi-receptor-consisting sensors.

Porphyrin chromophore has been one of the most promising signaling units in constructing fluorescent sensors due to its advantageous photophysical characteristics such as pronounced photostability, high extinction coefficient, and tunable fluorescence emission[21-27]. Moreover, the central tetrapyrrole macrocyclic moiety of porphyrin derivatives are also able to act as excellent functional receptor for various metal ions due to the strong binding ability attributed to four-pyrrole-nitrogen atoms[28]. As a consequence, extensive investigations have been carried out over the porphyrin-based fluorescent sensors for Cu^{2+}, Hg^{2+}, Cu^{2+}/Pb^{2+}, *etc*[29-31]. Our group also prepared a series of *N*,*N*-di(2-pyridylmethyl)amino(DPA)-based porphyrinato zinc complexes to investigate the number effect of DPA receptor on Fe^{3+}-detecting function[32]. Herein, a di-DPA-based metal-free porphyrin, namely 5,15-di(*p*-*N*, *N*-bis (2-pyridylmethyl)amino-phenyl)-10, 20-di (4-tert-butylphenyl)-porphyrin (Porphyrin-2-DPA) was synthesized, as shown in Scheme 1[32]. The tetrapyrrole macrocyclic moiety in Porphyrin-2-DPA as a rigid π-conjugated plane is almost perpendicular to the phenyl plane attached to DPA moiety, indicating the non-electronic coupling nature between porphyrin core and DPA unit. Accordingly, the rigid porphyrin core in Porphyrin-2-DPA is utilized not only as sensitive signaling fluorophore but also as the primary binding receptor with excellent affinity and distinctive selectivity to metal ion, which together with the flexible DPA auxiliary receptor endows Porphyrin-2-DPA the excellent sensing function to Pb^{2+}/Cu^{2+} on the basis of versatile optical-signals.



Scheme 1　Synthesis of Porphyrin-2-DPA

1　Experimental

1.1　Chemicals and measurements

Column chromatography was carried out on silica gel (Merck, Kieselgel 60, 70-230 mesh) with the indicated eluents. The tetrahydrofuran (THF) and methanol used for spectral experiments were purified via the standard methods. Other reagents and solvents were used as received. The reference compounds of 5, 10,15,20-tetra(4-*tert*-butylphenyl)porphyrin (Porphyrin-0-DPA), 5-(*p*-*N*, *N*-bis (2-pyridylmethyl)aminophenyl) 10, 15, 20-tri(4-*tert*-butylphenyl)porphyrin (Porphyrin-1-DPA), 5, 10, 15, 20-tetra(*p*-*N*,*N*-bis(2-pyridylmethyl) aminophenyl)porphyrin (Porphyrin-4-DPA), 5,15-di(*p*-*N*,*N*-bis(2-pyridylmethyl)aminophenyl)10, 20-di(4-*tert*-butylphenyl)porphyrinato zinc complex (Porphyrin-2-DPA-Zn) and 5, 10-di(4-carboxylphenyl)-10, 20-di(4-*tert*-butylphenyl)porphyrin were prepared according to the reported procedures[31-34].

^{1}H NMR spectra was recorded on a Bruker DPX

400 MHz spectrometer in $CDCl_3$ with shifts referenced to $SiMe_4$ (0.00 ppm). Electronic absorption spectra were recorded on a U-4100 spectrophotometer. Steady-state fluorescence spectroscopic studies were performed on an F 4500 (Hitachi). The slit width was 5 nm for emission, and the photon multiplier voltage was 700 V.

1.2 Preparation of Porphyrin-2-DPA

According to the reference[32], the mixture of 5, 10-di(4-carboxylphenyl)-10, 20-di(4-*tert*-butylphenyl) porphyrin (81 mg, 0.1 mmol) and thionyl chloride (15 mL) was refluxed for 2 h under N_2 atmosphere and evaporated by atmospheric distillation. The residue obtained was dissolved in anhydrous THF (10 mL) and then added into the solution of DPA (60 mg, 0.3 mmol), followed by adding two drops of anhydrous triethylamine. After stirring for another 3 h at 55 ℃, the resulting black-green mixture was evaporated under reduced pressure, and the residue was chromatographed on a silica gel column using $CHCl_3$/MeOH (98:2, *V*/*V*) as eluent. Repeated chromatography followed by recrystallization from $CHCl_3$ and MeOH gave Porphyrin-2-DPA, 82 mg in the yield of 70%. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.89 (d, 2H, *J*=8 Hz), 8.78 (d, 4H, *J*=8 Hz), 8.69 (d, 4H, *J*=4 Hz), 8.61 (d, 4H, *J*=8 Hz), 8.23 (d, 4H, *J*=8 Hz), 8.12 (d, 4H, *J*=8 Hz), 7.98 (d, 6H, *J*=8 Hz), 7.77 (d, 8H, *J*=8 Hz), 7.62 (d, 2H, *J*=12 Hz),7.42 (d, 2H, *J*=12 Hz), 5.07 (s, 8H), 1.32 (s, 18H), −2.83 (d, 2H).

2 Results and discussion

2.1 Metal sensing performance

To investigate the sensing function of Porphyrin-2-DPA to metal ions, the photophysical properties of this compound (2 μmol·L^{-1}) upon addition of different metal ion was studied in a mixed in CH_2Cl_2/MeOH (1:1, *V*/*V*). As shown in Fig.1A and 1B, the electronic

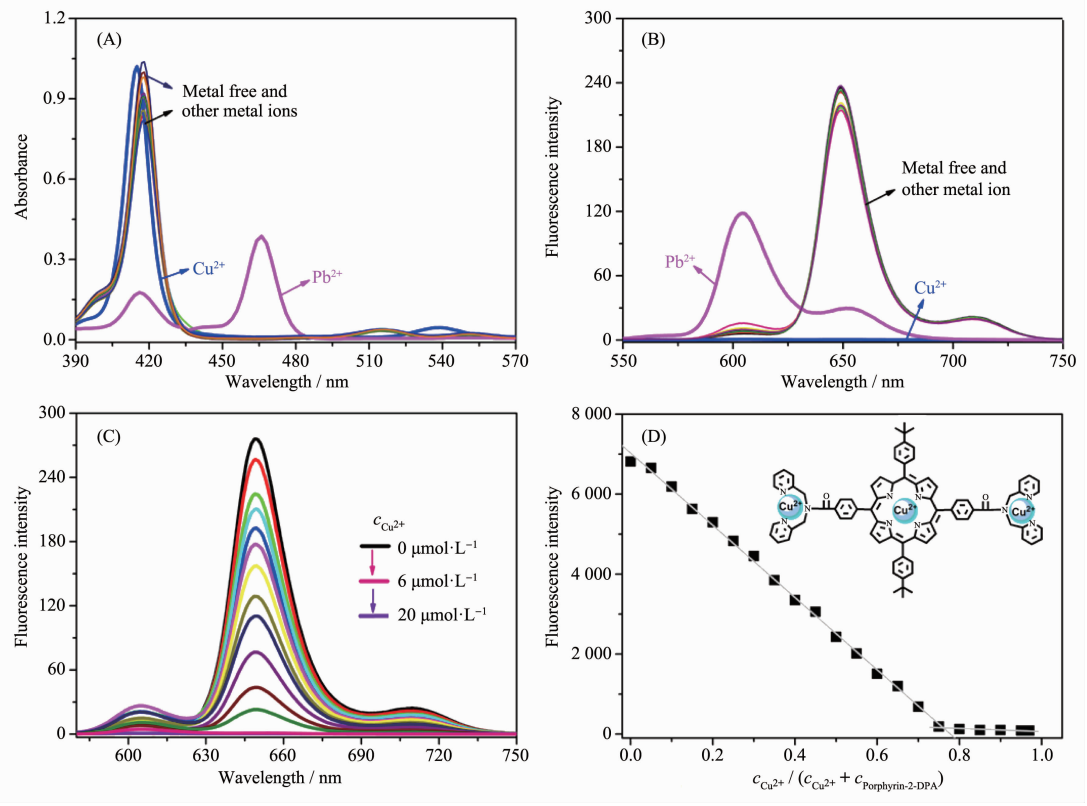


Fig.1 (A) Electronic absorption spectra and (B) fluorescence emission spectra of Porphyrin-2-DPA at the concentration of 2 μmol·L^{-1} in CH_2Cl_2/MeOH (1:1, *V*/*V*) upon addition of different metal ions such as Cu^{2+}, Fe^{2+}, Co^{2+}, Hg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Pb^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Li^+, Na^+, or K^+, respectively; (C) Fluorescence emission spectra of Porphyrin-2-DPA upon addition of increasing amount of Cu^{2+} (0~20 μmol·L^{-1}); (D) Fluorescence Job's plot indicating the 1:3 binding stoichiometry between Porphyrin-2-DPA and Cu^{2+} in Porphyrin-2-DPA-Cu^{2+} system. The inset shows the binding mode between Porphyrin-2-DPA and Cu^{2+}

absorption and fluorescent emission spectra of metal free Porphyrin-2-DPA kept almost unchanged upon addition of different metal ion such as Fe^{2+}, Co^{2+}, Hg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Li^{+}, Na^{+}, or K^{+}, except for Cu^{2+} and Pb^{2+} (20 μmol·L^{-1}). After adding Cu^{2+}, though the maximum absorption of Porphyrin-2-DPA was slightly blue-shifted (from 417 to 415 nm), the Q bands of this compound at 515, 551, and 590 nm disappeared synchronously accompanied by the appearance of a new absorption around 538 nm, leading to the varying ratio of A_{538}/A_{515} from 0.25 to 5.42. Meanwhile a remarkable change also occured in the fluorescence emission of Porphyrin-2-DPA after adding Cu^{2+}: the fluorescence emission of this compound centered at 650 nm was obviously weakened even to be completely quenched. Moreover, the fluore-scence titration experiments for Porphyrin-2-DPA (2 μmol·L^{-1}) with increasing amount of Cu^{2+} (0~20 μmol·L^{-1}) show that the fluorescence decrease mainly occured in the concentration range of Cu^{2+} from 0 to 6 μmol·L^{-1}, suggesting the possible 1:3 binding stoichiometry between Porphyrin-2-DPA and Cu^{2+} in Fig.1C. The fluorescence Job′s plot gave additional support for this point, revealing the possible binding mode between Porphyrin-2-DPA and Cu^{2+} with both DPA moiety and Porphyrin core in Porphyrin-2-DPA as the receptor for Cu^{2+} in Fig.1D. The detection limit for Cu^{2+} ion with Porphyrin-2-DPA was determined to be 1.6×10^{-7} mol·L^{-1} under the present condition, revealing the sensitive dual-optical detecting nature of porphyrin-2-DPA for Cu^{2+}[35-37].

More notably, addition of Pb^{2+} into Porphyrin-2-DPA not only resulted in the quenching of the fluorescent emission of this compound at 650 nm but also induced the remarkable change in its electronic absorption spectrum. As shown in Fig.1, upon addition of Pb^{2+}, the maximum absorption of Porphyrin-2-DPA centered at 417 nm as well as Q bands at 515, 551 and 590 nm was diminished synchronously accompanied the appearance of a new strong absorption band at 467 nm, leading to the multi-ratiometric changes including the intensity radio of A_{467}/A_{417} from 0.01 to 3.38, A_{467}/A_{515} from 0.23 to 42 and A_{467}/A_{551} from 0.42 to 47.5 (A_i is the absorbance at the wavelength i and A_{max} is the maximum intensity). Meanwhile the fluorescent emission of this compound at 650 nm was obviously decreased while the fluorescent emission at 604 nm was increased after adding Pb^{2+}, with a changing ratio of I_{604}/I_{650} from approximate 0.03 to 22. Furthermore, the quantitative fluorescence titration experiments for Porphyrin-2-DPA (at 650 nm) with the increasing amount of Pb^{2+} (0~20 μmol·L^{-1}) showed that the change in fluorescent emission intensity mainly occursed in the concentration range (0~5 μmol·L^{-1}) of Pb^{2+}, and the emission intensity $1/(I_{max}-I)$ increased linearly against the change in $1/(C_{Pb^{2+}})^2$ according to the Benesi-Hildebrand equation, suggesting the possible 1:2 bind-ing stoichiometry between Porphyrin-2-DPA and Pb^{2+}, as shown in Fig.2A. This is confirmed by the absorption titration experiments as well as fluorescent Job′s plot in Fig.2B and 2C, suggesting the most possible binding mode between Porphyrin-2-DPA and Pb^{2+} (Fig.2D).

It is worth noting that upon subsequent addition of Cu^{2+} (20 μmol·L^{-1}), the absorption of Porphyrin-2-DPA-Pb^{2+} system centered at 467 nm got disappeared synchronously accompanied by the appearance of the maximum absorption at 415 nm obviously attributed to the Porphyrin-2-DPA-Cu^{2+} system, indicating the displacement of Pb^{2+} in Porphyrin-2-DPA-Pb^{2+} complex by Cu^{2+}. This is further validated by the disappearance of the fluorescence emission band at 604 nm attributed to Porphyrin-2-DPA-Pb^{2+} complex after addition of Cu^{2+} ion (Fig.3A). In contrast, upon addition of other metal ion such as Fe^{2+}, Co^{2+}, Hg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Li^{+}, Na^{+}, or K^{+}, the electronic absorption and fluorescent emission spectra of Porphyrin-2-DPA-Pb^{2+} system kept almost unchanged, which was also true for the Porphyrin-2-DPA-Cu^{2+} system (Fig.3B), clearly indicating the excellent selectivity of Porphyrin-2-DPA to Cu^{2+} or Pb^{2+} ions among all the tested metal ions. As a consequence, Porphyrin-2-DPA can work as a dual-mode Cu^{2+}-selective sensor via porphyrin fluorescence ON-OFF mechanism as well as dual-signal (the ratio of A_{467}/A_{415} and fluorescence ON-OFF) metal

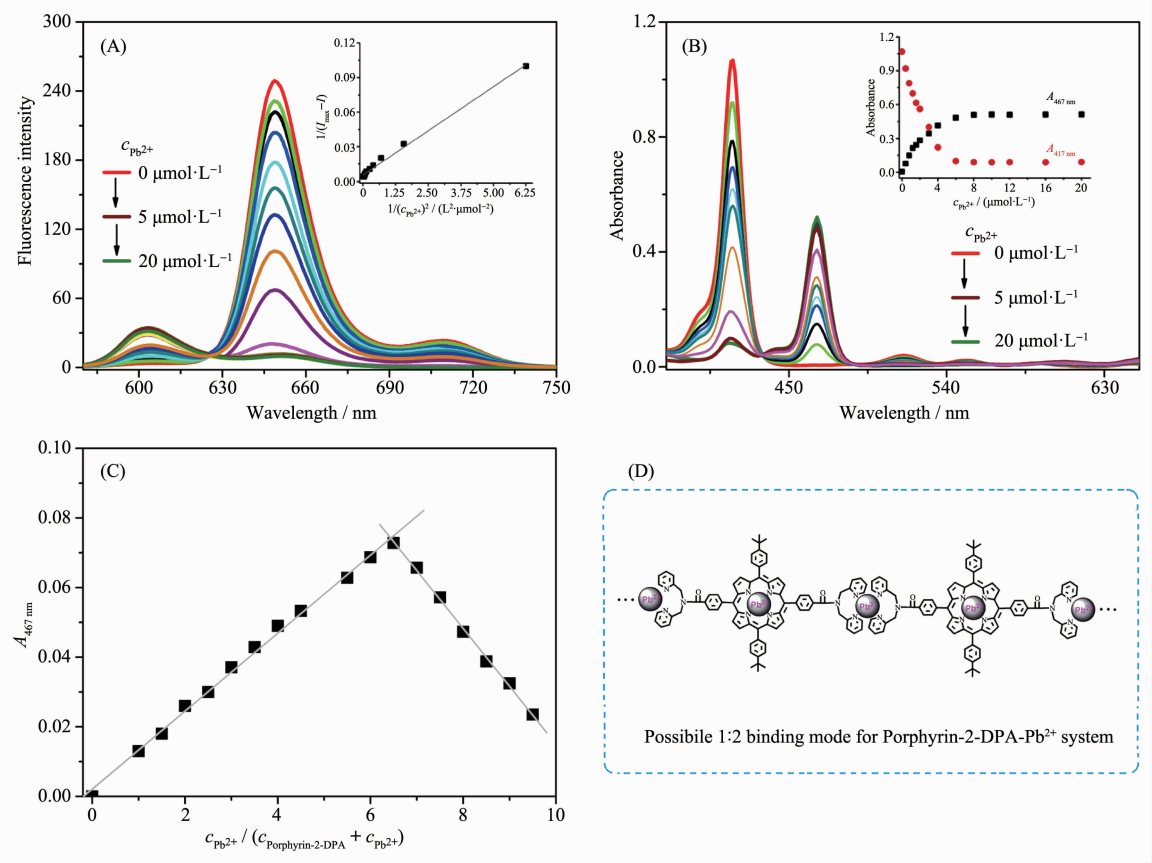


Fig.2 (A) Fluorescence emission and (B) electronic absorption spectra of Porphyrin-2-DPA upon addition of increasing amount of Pb^{2+} (0~20 μmol·L^{-1}); (C) Absorption Job′s plot (at 467 nm) indicating the 1:2 binding stoichiometry between Porphyrin-2-DPA and Pb^{2+} in Porphyrin-2-DPA-Pb^{2+} system; (D) Possible binding mode between Porphyrin-2-DPA and Pb^{2+}

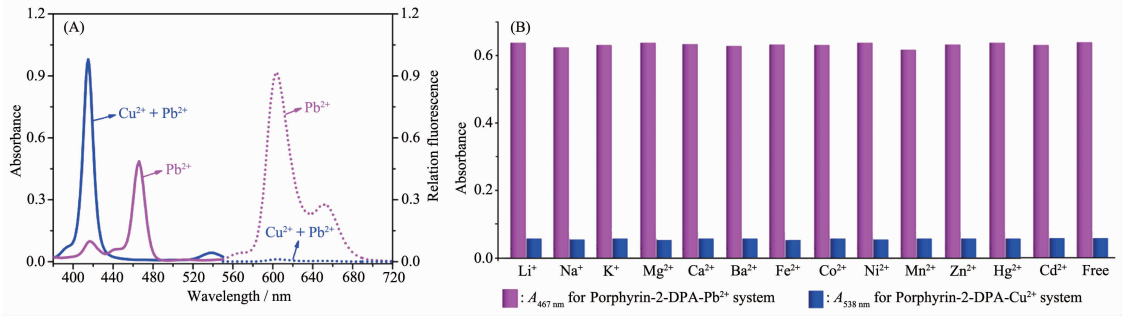


Fig.3 (A) Electronic absorption and fluorescence emission spectra of Porphyrin-2-DPA (2 μmol·L^{-1}) upon sequential addition of Pb^{2+} (20 μmol·L^{-1}) and Cu^{2+} ion (20 μmol·L^{-1}) in CH_2Cl_2/MeOH (1:1, *V*/*V*); (B) Change in the electronic absorption of 467 nm for Porphyrin-2-DPA-Pb^{2+} system and 538 nm for Porphyrin-2-DPA-Cu^{2+} system upon addition of other metal ions such as Fe^{2+}, Co^{2+}, Hg^{2+}, Mn^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ca^{2+}, Ba^{2+}, Mg^{2+}, Li^{+}, Na^{+}, or K^{+}, respectively

displacement from the Porphyrin-2-DPA-Pb^{2+} complex.

2.2 Metal sensing mechanism

To understand the respective sensing role of porphyrin and DPA receptors to Cu^{2+}/Pb^{2+}, the control experiments of the reference porphyrin derivatives including Porphyrin-0-DPA and Porphyrin-*X*-DPA (*X*= 1 and 4) as well as Porphyrin-2-DPA-Zn upon addition of Pb^{2+}/Cu^{2+} have been carried out in a just same manner as for Porphyrin-2-DPA[31-32]. As shown in Fig. 4, upon addition of Pb^{2+}, the electronic absorption and

fluorescence emission spectra of Porphyrin-2-DPA-Zn kept almost unchanged. By contrast, addition of Pb^{2+} into Porphyrin-0-DPA induced the decrease in its maximum absorption at 417 nm synchronously with the appearance of a new strong absorption band at 467 nm. Moreover, the absorption at 417 nm was more weakened while the one at 467 nm obviously increased along with increasing the peripheral DPA number of Porphyrin-X-DPA derivatives from 1 to 2 and 4. Similarly, the fluorescence emission of Porphyrin-DPA derivatives at 650 nm was gradually decreased while the one at 604 nm ncreased along with the increase of the DPA number from 0→1→2→4 upon addition of Pb^{2+}. These results clearly suggest that the rigid Porphyrin core in Porphyrin-DPA derivatives is employed not only as fluorophore signal unit but also as primary binding ligand, which combined with the flexible DPA auxiliary receptor endows Porphyrin-DPA derivatives the excellent detecting potential to Pb^{2+}. This is also true for Cu^{2+} in Fig.4B. However, the optical change degree for Porphyrin-DPA derivatives along with increasing the DPA number from 0 to 4 was slightly less after adding Cu^{2+} than Pb^{2+}, implying that porphyrin core as the firstly binding ligand plays more important role in detecting the former. This may be attributed to the slightly smaller atomic radius together with the distinctive characteristic outermost electronic structure of Cu^{2+}, which can induce the more strong binding affinity of the rigid porphyrin core to Cu^{2+} than Pb^{2+}, thus gives Porphyrin-2-DPA the diverse optical-detecting-signal to Cu^{2+}/Pb^{2+}.

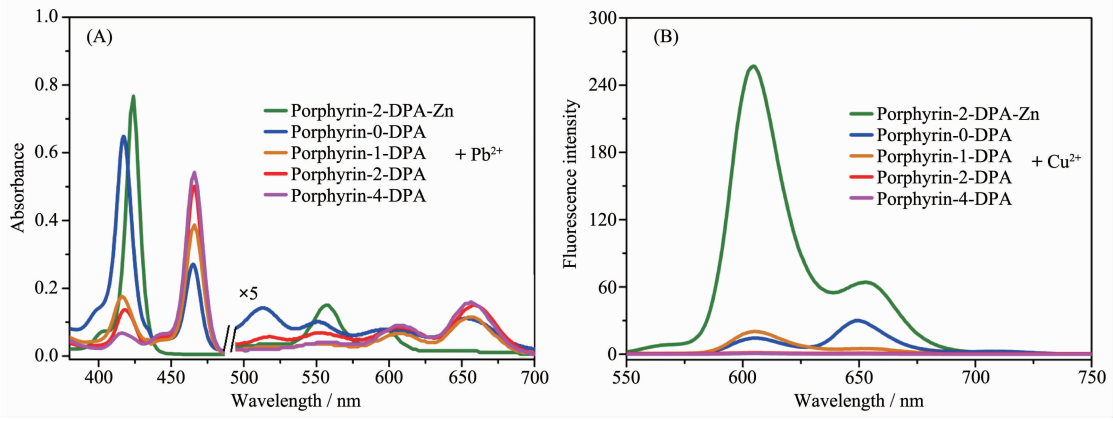


Fig.4　Electronic absorption of Porphyrin-*X*-DPA (*X*=0, 1, 2 or 4) and Porphyrin-2-DPA-Zn upon addition of Pb^{2+}; (B) Fluorescence emission spectra of these porphyrin compounds upon addition of Cu^{2+}

3　Conclusions

Briefly summarizing above, a two-DPA-modified metal free porphyrin compound has been synthesized and characterized. Systemic studies show that the rigid π-conjugated porphyrin core was utilized not only as signaling fluorophore but also as the primary metal ion receptor with the excellent binding affinity and distinctive selectivity, which together with the no-conjugated flexible DPA receptor endows DPA-modified porphyrin compound the excellent sensing function to Pb^{2+}/Cu^{2+} on the basis of versatile optical-signals.

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