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The photophysical properties of metal complexes of fluorescein–porphyrin dyads

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Abstract

Zn, Cu and Ni complexes of fluorescein–porphyrin dyads were synthesized and characterized by ESI-MS and their photophysical properties were studied. Each of the complexes possessed Q band degeneration in their absorption spectra. The Zn complex displayed a blue shifted fluorescence emission and shorter fluorescence lifetime compared with the parent fluorescein–porphyrin dyads, whilst the Cu and Ni complexes were not fluorescent. These findings imply that different electron transfer processes are occurring in the complexes.

Keywords: Metal complex; Porphyrin dyads; Absorption spectrum; Fluorescence spectrum; Fluorescence decay

1. Introduction

Porphyrins are tetrapyrrolic macrocycles and have special structure with big π-orbital on the carbon–nitrogen framework. Because of the large conjugational effect of the tetrapyrrolic macrocycle, porphyrins have special photophysical properties and have been used in many fields [1]. Metal porphyrin research is at the centre of research in porphyrin chemistry because the metal ions within porphyrin complexes change the electronic structure of porphyrins and give them many characteristics.

It is well known that chlorophyll, haem and cytochrome, each of which plays a key role in life, are tetrapyrrole compounds that contain Mg^{2+}, Fe^{3+} ions, etc [2]. In recent years, dyads and triads containing porphyrins as electron acceptor or donor, have proven to be of interest as photosynthetic model compounds [3]; metal porphyrins have also been widely used in photocatalysis, light-energy conversion and various medical applications [4–6].

Fluorescein exhibits strong absorption and fluorescence in the UV–vis region; fluorescence is a convenient way of revealing electron transfer in photosynthesis model compounds. Fluorescein is a good candidate to form dyads with porphyrin in order to research the photoelectron properties. In the near past we had synthesized a series of fluorescein–porphyrin dyads and had discussed their photoproperties [7,8]. In this study, we have synthesized a series of metal complex of fluorescein–porphyrin dyads and discussed the properties of these compounds.

2. Experimental

UV–vis spectra were measured on Varian Cary 500 and steady-state fluorescence spectra were obtained on Cary Eclipse Fluorescence Phosphospectrometer, respectively. The Fluorescence decay curves were obtained using EdinBurgh FL920 Spectrofluorimeter. ESI-MS were obtained from Micromass GCT Spectrometer. Reactions were monitored by Thin-layer Chromatography (TLC) on silica gel plates exposed to ether:petroether (3:1).

Fluorescein–porphyrin dyads were prepared using the procedure described in Ref. [6]. Zn, Cu and Ni complexes of

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fluorescein–porphyrin dyads were synthesized as shown in Scheme 1 using the following procedure [9,10].

2.1. Preparation of Zn fluorescein–porphyrin dyad complex (*1*)

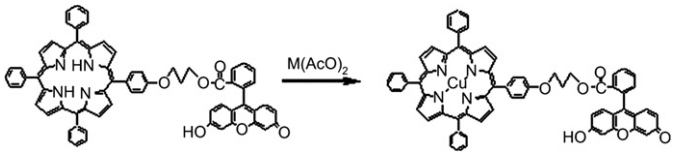
Predried CH_2Cl_2 (45 ml) and 5 ml of CH_3OH were placed in a 100 ml round bottom flask equipped with a magnetic stirrer. Fluorescein–porphyrin dyad (20 mg) and 1.5 times equiv. zinc acetate were added and stirring was carried out for 3 h. TLC was used to follow the extent of the reaction. At the end of reaction, the mixture was poured into ethyl acetate and washed with 5% aq. $NaHCO_3$ solution and water. The organic layer was dried with anhydrous Na_2SO_4 and was then separated on a column of silica gel (200∼300 mesh) using ethyl:petroleum ether (2:1) as eluent. From the main band on the column, a brown solid was obtained (19.1 mg). Yield: 90%. ESI-MS ($[M+H]^+$): calcd. for $C_{67}H_{45}N_4O_6Zn$ 1065.5, found 1065.1.

2.2. Preparation of Cu fluorescein–porphyrin dyad complex (*2*)

The preparation of Cu fluorescein–porphyrin dyad complex was very similar to that of the Zn fluorescein–porphyrin dyad complex, described above, except that zinc acetate was replaced with cupric acetate. Also, 24.3 mg of fluorescein–porphyrin dyad and 1.5 times equiv. cupric acetate were added to the mixture of CH_2Cl_2 and CH_3OH. A brown product (24.0 mg) was obtained. Yield: 94%. ESI-MS ($[M+H]^+$): calcd. for $C_{67}H_{45}N_4O_6Cu$ 1063.5 found 1064.2.

2.3. Preparation of Ni fluorescein–porphyrin dyad complex (*3*)

DMF (30 ml) was placed in a 100 ml flask under N_2 and 20 mg fluorescein–porphyrin dyad and 1.5 times equiv. $Ni(CH3COO)_2$ was added. The mixture was heated to 120 °C under N_2 with stirring. TLC was used to monitor the course of the reaction. After 3 h, the DMF was removed under reduced pressure distillation and the residual solid was extracted with water and ethyl acetate. The organic layer was dried with anhydrous Na_2SO_4 and the desired product was separated using a column of silica gel (200∼300 mesh) employing ethyl acetate:petroleum ether (2:1) as eluent. We got 16.9 mg product. Yield: 80%. ESI-MS ($[M+H]^+$): calcd. for $C_{67}H_{45}N_4O_6Ni$ 1058.8, found 1059.2.



Scheme 1. The synthesis of metal fluorescein–porphyrin dyad complexes.

Table 1
The absorption data of fluorescein–porphyrin dyads and their metal complexes

Compounds	Soret band (nm)	Q band (nm)
Fluorescein–porphyrin dyads	418.1	513.1, 551.0, 591.2, 645.2
1	422.3	537.8, 595.2
2	414.7	538.6
3	414.7	526.9

3. Results and discussion

3.1. The steady-state absorption spectra

The absorption spectra of fluorescein–porphyrin dyads and their metal complexes were measured in CH_2Cl_2 (Table 1 and Fig. 1).

It is evident that the Q bands of the porphyrin dyads degenerated after being incorporated with metal ions; the Soret band also had changed, respectively. When the Zn ion was inserted into the porphyrin core, the Soret band red shifted 4 nm compared with the fluorescein–porphyrin dyad, and the Q bands degenerated from 4 peaks to 2 peaks. In contrast, in the case of the Ni^{2+} and Cu^{2+} ion complexes, the Soret band blue shifted 4 nm, and the Q band degenerated from 4 peaks to 1 peak. Zn^{2+} has d^0 and d^{10} electron distribution [11]; after incorporation into porphyrin, there was no obvious electron interaction between the porphyrin ring and the Zn^{2+} ion. However, when Zn^{2+} was incorporated into the porphyrin, its symmetry was enhanced, resulting in the degeneration of the Q bands and the red shift of the Soret band. Both Cu^{2+} and Ni^{2+} are transition metal ions and it can be proposed that electronic interaction occurred between the LUMO e_g of the porphyrin and the spin orbit of the metal ions. Hence, the porphyrin Q bands degenerated into one peak, corresponding to the S_0–S_1 transition.

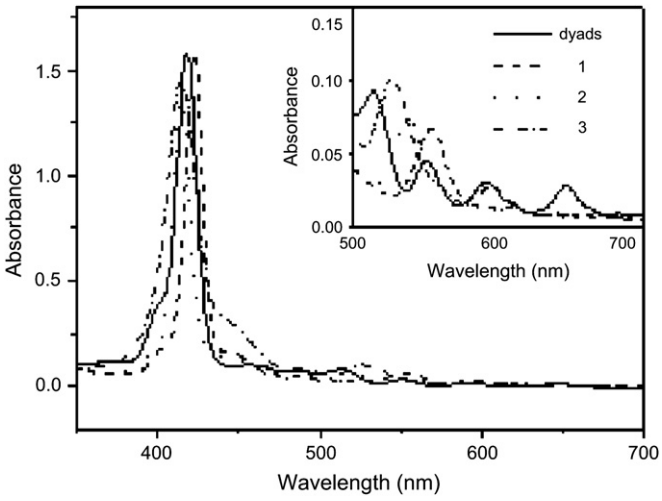


Fig. 1. Absorption spectra of fluorescein–porphyrin dyads and their metal complexes **1**, **2**, and **3**. The inset is the enlarged view of the Q band absorption.

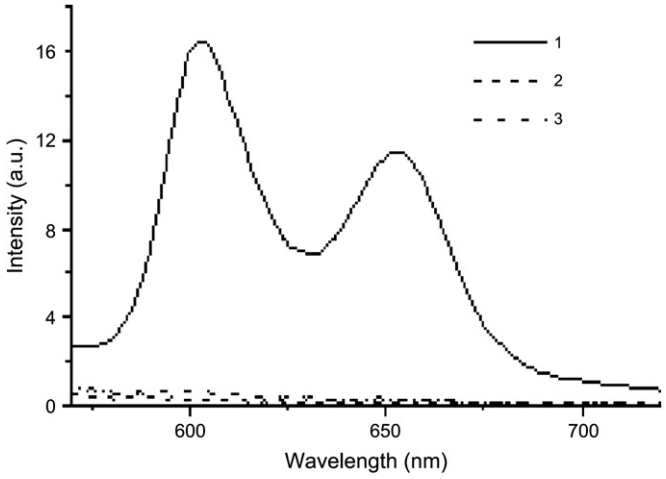


Fig. 2. Fluorescence spectra of the three metal dyad complexes **1**, **2**, and **3** recorded in CH_2Cl_2.

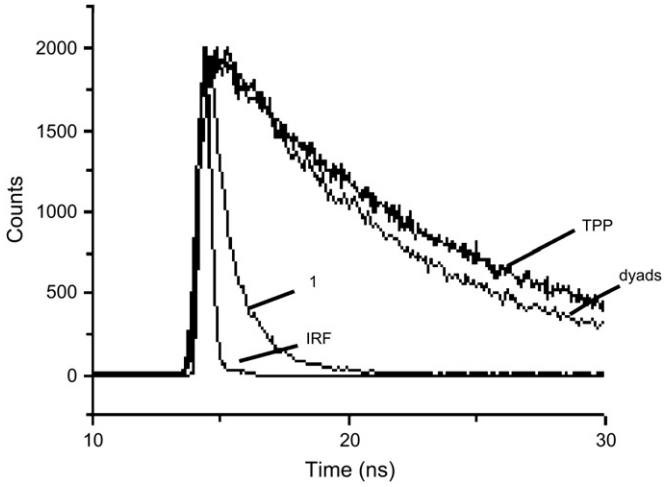


Fig. 3. Fluorescence decay curve of H_2TPP, fluorescein–porphyrin dyad and **1** recorded in CH_2Cl_2.

3.2. Fluoresence spectra

The fluorescence spectra of the three metal fluorescein–porphyrins are shown in Fig. 2 from which it is apparent that only the Zn^{2+} complex had a fluorescence emission. There was no obvious emission band in the fluorescence spectra of the Ni^{2+} and Cu^{2+} complexes. Also, the maximal emission position of the Zn^{2+} complex was at 603 nm and 652 nm, blue shifted from 652 nm and 717 nm compared to the fluorescein–porphyrin dyad. The incorporation of metal ions influenced the emission of the porphyrin; in the case of the Zn^{2+} complex, the emission band blue shifted about 50 nm. The symmetry of the porphyrin enhanced after incorporation of the Zn^{2+}, and the LUMO e_g energy increased resulting in the observed blue shift of the emission band. In contrast, Zn^{2+} had little electronic interaction with the porphyrin as the excited state energy of the Zn complex cannot be released by the energy transfer from the porphyrin to the metal; hence, the energy was released by fluorescence emission. For the Ni^{2+} and Cu^{2+} complexes, after excitation with light, the excited energy can transfer to the metal ions because of electronic interaction without fluorescence emission.

The fluorescence decay curve of the porphyrin component was measured (Fig. 3). The Zn^{2+} complex had much shorter fluorescence lifetime (0.539 ns) compared with the free prophyrin dyad (7.6 ns) and H_2TPP (9.8 ns) because the electronic structure of the excited porphyrin was affected by the Zn^{2+} ions and the electron density of e_g increased, resulting in the observed shorter fluorescence lifetime of the Zn^{2+} complex.

4. Conclusions

Each of the three complexes exhibited degeneration in their absorption spectra. The emission spectra of the Zn^{2+} complex underwent a blue shift and possessed a shorter fluorescence lifetime because of little electronic interaction between the metal ions and the porphyrin moiety. The Cu^{2+} and Ni^{2+} complexes each had strong electronic interactions and did not have emission spectra.

Acknowledgements

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