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Photostability and Emission Characteristics of In(III)octaethylporphyrin– and In(III)tetraphenylporphyrin–chloride

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The absorption, emission and excitation spectra of indium(III) tetraphenylporphyrinchloride (In(III)-TPPCl) and indium(III)octaethylporphyrinchloride (In(III)OEPCl) methanolic solutions have been studied and compared with their metal-free bases. The study reveals a strong interaction between indium ion and the porphyrin π-systems.

The photolability of the above-mentioned compounds has been studied in deoxygenated methalonic solutions using sunlight and/or UV-light in excitation. A fragmentation mechanism is proposed to account for the consumption of the porphyrin systems.

Introduction

There is interest in the application of porphyrin compounds as photosensitisers, and in In(III)porphyrin complexes as surface complexes on low bandgap In-containing semiconductor electrodes in photoelectrochemical systems. The preparation of some In–porphyrin complexes has been reported earlier [1–3].

Most of the spectroscopic data available on In(III)-tetraphenyl porphyrin chloride (In(III)TPPCl) and In(III)octaethylporphyrin chloride (In(III)OEPCl) are mainly for preparative characterization [1–4]. In this paper we report the room temperature absorption, emission and excitation spectra of In(III)-TPPCl and In(III)OEPCl as contrasted to their metal-free bases. We also describe photostability and fluorescence ageing.

Experimental

The materials used in this study were prepared and purified according to literature procedures [1–5].

The absorption spectra were recorded on a Unicam SP8000 spectrophotometer. Both fluorescence and excitation spectra were recorded on a Shimadzu spectrofluorophotometer RF510. Sample irradiation was performed using the excitation light of the spectrofluorophotometer and light intensities were measured using ferrioxalate actinometry [6]. The solvent used in this study was a spectroscopic grade methanol and the solutions were deoxygenated prior to irradiation by flushing with N_2 gas for 15 minutes.

Results

(i) Metal-free Porphyrins

The absorption spectra of metal-free octaethylporphyrin (H_2OEP) and tetraphenylporphyrin (H_2-TPP) are in agreement with previously published spectroscopic data [4, 7, 8]. Upon irradiation with UV-light of wavelength $\lambda = 254$ nm, considerable consumption of the materials occurs. Figure 1 shows the effect of irradiation of 1.26×10^{-6} *M* methanolic

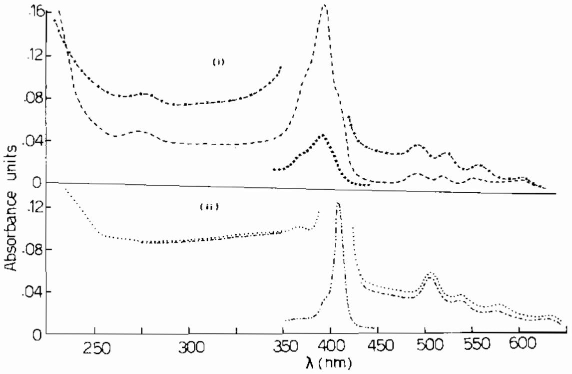

Fig. 1. Absorption spectra of metal-free porphyrins: (i) Absorption of 1.26×10^{-6} *M* H_2OEP methanolic solution; before (–X–) and after (- - -) irradiation with UV-light ($\lambda = 254$ nm) for 65 mins. (ii) Absorption of 1.5×10^{-6} *M* H_2TPP methanolic solution before (· · ·) and after (– · –) irradiation with UV-light ($\lambda = 254$ nm) for 50 mins. Both (XXX) and (– ·· –) represent the initial absorption of soret bands scaled to one fifth intensity.

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solution of (H_2OEP) using light of wavelength $\lambda = 254$ nm. The same behaviour is displayed to a lesser extent by (H_2TPP). The absorption spectra of both (H_2OEP) and (H_2TPP) compare with their excitation spectra shown in Fig. 2, indicating the purity of the samples.

We have also studied the changes in emission spectra as a result of irradiation ageing. Figure 3 shows the changes in emission spectra of 1.5×10^{-6} *M* methanolic H_2TPP solution as a result of irradiation either with UV-light ($\lambda = 254$ nm) or sunlight. The irradiation in each case results in the decrease of the red emission intensity at *ca.* $\lambda = 620$ nm with a concomitent increase in the blue emission region around $\lambda = 460$ nm. Figure 4 shows the emission spectrum of a fresh 1.26×10^{-6} *M* methanolic solution of (H_2OEP) together with the spectral changes accompanying various irradiation treatments.

Both sunlight and UV-light ($\lambda = 254$ or 366 nm) cause a decrease in the intensity of the red emission at *ca.* $\lambda = 620$ and 575 nm. A complete consumption of the red-emitting porphyrin is achieved upon irradiation with UV-light ($\lambda = 254$ nm) for *ca.* 10 hrs. (intensity = *ca.* 5.8×10^{-10} Ein/min). This is accompanied by the appearance of a fairly intense emission at *ca.* $\lambda = 440$ nm. Figure 4 also shows the excitation spectra of the photolysis product(s) that appears on irradiating (H_2OEP) methanolic solutions using UV-light ($\lambda = 254$ nm). The excitation spectra were taken by following the emission band at 440 nm and has excitation peaks in the range 300–400 nm. This blue-emitting species is, in turn, photolabile and a considerable decrease in the excitation intensity is observed

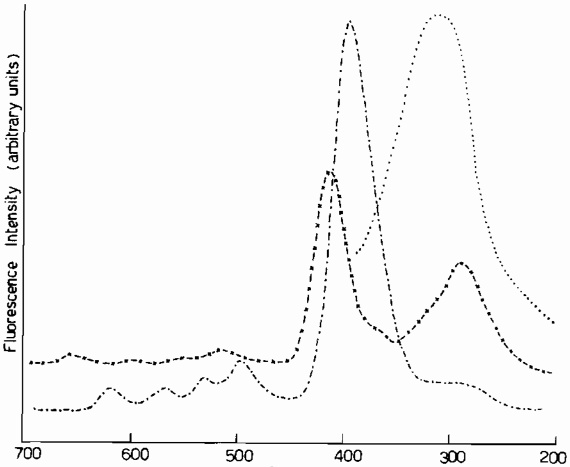

Fig. 2. Excitation spectra of (— · —) 1.26×10^{-6} *M* of H_2OEP fresh methanolic solutions by following the emission band at $\lambda = 620$ nm, (–X–) 1.5×10^{-6} *M* of H_2TPP fresh methanolic solution by following the emission band at 650 nm, and (· · ·) H_2TPP methanolic solution irradiated for 4 hrs using UV-light ($\lambda = 254$ nm) by following the developing emission at $\lambda = 410$ nm.

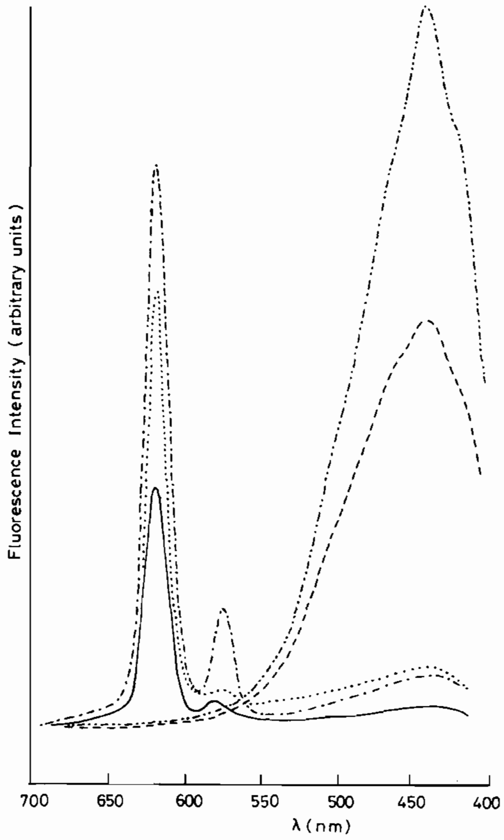

Fig. 3. Emission from H_2TPP methanolic solutions ($\lambda_{ex} = 390$ nm): (— · —) fresh 1.26×10^{-6} *M*, (· · ·) after irradiation in sunlight for 3 days in a Pyrex vessel, (— ·· —) after irradiation for 10 hrs using 254 nm light, (- - -) after irradiation of the photolysed sample (— ·· —) for 30 mins. using 365 nm light, and (——) after irradiation of fresh H_2OEP methanolic solution using 365 nm light.

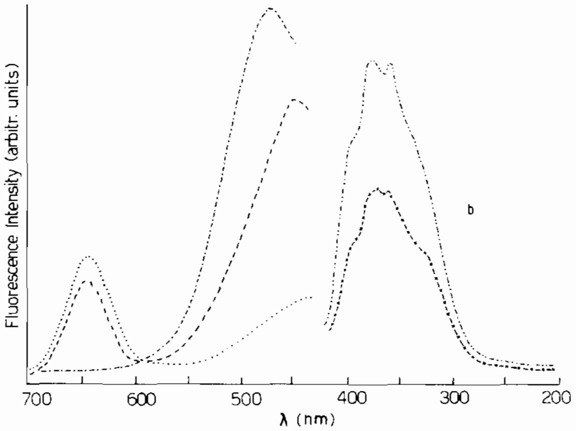

Fig. 4. (a) Emission spectra of 1.5×10^{-6} *M* H_2OEP methanolic solutions: (· · ·) fresh, (— · —) after irradiation for 4 hrs using 254 nm light (scale X one/fifth), (- - -) after irradiation in sunlight for 3 days in a Pyrex vessel. (b) (— ·· —) excitation spectrum of photolysis product(s) obtained by irradiating H_2-OEP as (a) for 10 hrs, and (–X–) after irradiating it for 30 mins. using 365 nm light.

on irradiation with UV-light (λ = 366 nm), as shown in Fig. 4.

(ii) In(III) Porphyrin Chlorides

Figure 5 shows the absorption spectra of In(III)-OEPCl and In(III)TPPCl. The spectral patterns are different from the corresponding metal-free porphyrins, especially in the Q-band spectral regions. In In(III)TPPCl, the four Q-bands that appear in the absorption spectra of metal-free (H_2TPP) are replaced by two relatively strong bands at λ = 580 nm (the α-band) and λ = 550 nm (the β-band) together with two less intense bands at λ = 520 nm and λ = 490 nm. The very intense soret band appears at λ = 415 nm (the B-band) and there are weaker bands at λ = 400, 315, 250 and 225 nm. The excitation spectrum of In(III)TPPCl methanolic solution, taken by following the emission band at 600 nm, gives nearly the same band positions in both Q- and B-band regions as shown in Fig. 6. In(III)OEPCl methanolic solutions display nearly the same general characteristic absorption spectra as In(III)TPPCl, with some blue shift in the absorption maxima as shown in Fig. 5. The Q-bands in In(III)OEPCl absorption spectrum appear at λ = 575 nm (α-band), λ = 540 nm (the β-band) together with two weaker bands at λ = 500 and λ = 460 nm. The B-band is obtained at λ = 405 nm, and added to the blue of this band there are weaker bands at λ = 380, 260 and 225 nm.

Both the absorption spectra of In(III)TPPCl and In(III)OEPCl are in agreement with the general characteristic spectra mentioned earlier for metalloporphyrins [4, 7, 8].

We have studied the room temperature emission from In(III)OEPCl and In(III)TPPCl, and observed very strong reddish emissions in methanolic solutions. This is in agreement with the general characteristic of closed shell metal porphyrins having full d-shells that generally show only fluorescence at room temperature in fluid media [9]. Figure 7 shows the emission spectra of In(III)TPPCl methanolic solution. The emission consists of an intense peak at λ = 600 nm and another less intense one at λ = 650 nm (λ_{ex} = 365 nm). Upon irradiation with UV-light (λ = 254 nm) this reddish emission completely disappears, with the appearance of a strong emission in the blue region at λ = 450 nm. Figure 7 shows also the emission from In(III)OEPCl methanolic solution. The emission is blue-shifted compared with In(III)TPPCl, and a strong emission peak at λ = 575 nm is observed together with a less intense one at λ = 625 nm (λ_{ex} = 365 nm). Upon irradiation with UV-light (λ = 254 nm) the long wavelength emission decreases in intensity with the appearance of a blue emission at λ = 450 nm, as shown in Fig. 7.

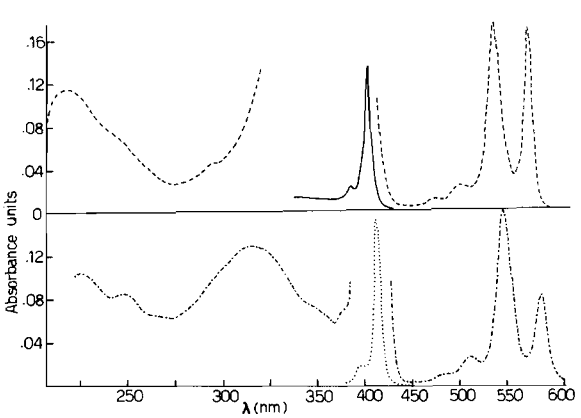

Fig. 5. Absorption spectra of In(III)porphyrin chlorides: (– · –): absorption of 4.7 × 10^{-5} *M*, (· · ·) 3.9 × 10^{-6} *M* In(III)TPPCl methanolic solutions, (- - -) 1.3 × 10^{-6} *M* and (——) 4.5 × 10^{-5} *M* In(III)OEPCl methanolic solutions.

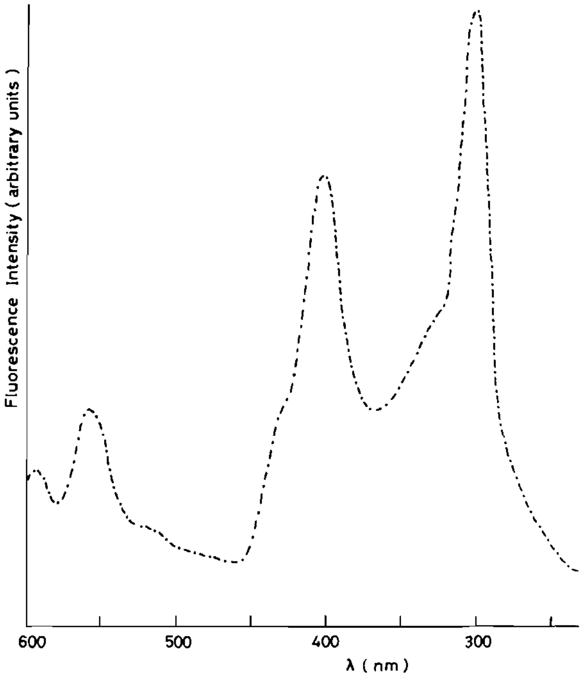

Fig. 6. Excitation spectrum of 3.9 × 10^{-6} *M* In(III)TPPCl methanolic solution taken by following the emission band at 600 nm.

Discussion

The photoreactivity of porphyrins has been studied earlier in various media containing various oxidizing or reducing agents [10–13]. The role of oxygen in photo-oxidation of porphyrins has also been investigated by Gurinovich *et al.* [12], who suggested that irreversible addition of oxygen occurs with destruction of conjugated bond systems in a series of porphyrins and their zinc derivatives.

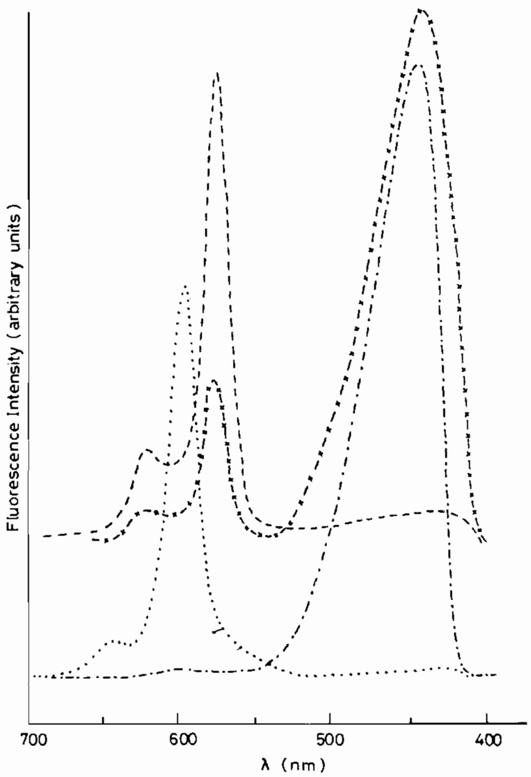

Fig. 7. Emission spectra of In(III) porphyrin chlorides (λ_{ex} = 365 nm); (· · ·) fresh 3.9 × 10^{-6} *M* In(III)TPPCl methanolic solution, (– · –) after irradiation for 90 mins. using 254 nm light, (- - -) fresh 1.3 × 10^{-6} *M* In(III)OEPCl methanolic solution and (–×–) after irradiation for 30 mins. using 254 nm light.

Hopf and Whitten [10] described three possible processes to deactivate excited states of porphyrins and their metal complexes. These processes are:

(1) unimolecular reactions (*i.e.* isomerization or fragmentation processes);

(2) bimolecular reactions (including complex formation, electron transfer and addition reactions), and

(3) energy transfer processes.

Since the irradiation of H_2TPP, H_2OEP, In(III)-TPPCl and In(III)OEPCl is performed in deoxygenated metal-free methanolic solutions, we rule out a significant contribution of processes (2) and (3).

Alternatively, since the UV-light of wavelength $\lambda = 254$ nm has a photon energy of the same order of magnitude as a chemical bond, we propose a fragmentation mechanism to account for the consumption of these porphyrins. The photon energy may break the methine bridges resulting in pyrrole derivatives that absorb and emit at short wavelengths. This, however, needs further investigation using various kinetic, isolation and identification techniques.

In metalloporphyrins, both the energy (E_Q) and the oscillator strength (f_Q) of the lowest energy absorption band depend upon the central metal ion [14] and have been suggested as a measure of the degree of interaction between the metal ion and the porphyrin π-system [15]. The energy is raised at increased interaction accompanied by a reduction in the oscillator strength [16]. We calculated E_Q for both In(III)TPPCl and In(III)OEPCl as $E_Q = 17.2 \times 10^3$ and 17.3×10^3 cm^{-1} respectively. These high values indicate a strong interaction according to the energy scale reported earlier [16]. This strong interaction is verified by the remarkably low values of the oscillator strengths f_Q for In(III)TPPCl and In(III)-OEPCl that are calculated as $f_Q = 0.04$ and 0.05 respectively. This strong metal-porphyrin interaction is in fact a disadvantage of In(III)TPPCl and In(III)-OEPCl as solar energy harvesting dyes [16]. The photolability of these compounds might influence their application as solar energy harvesting dyes.

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