# ANNELIDES
## XII: PHOTOCHEMICAL ASSOCIATION PROPERTIES OF PHTHALOCYANINE-BASED DISCOGENS[†]

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## Summary

A metal-free phthalocyanine octasubstituted by paraffinic chains shows a strongly increased tendency to aggregate compared with unsubstituted phthalocyanine. The aggregation leads in concentrated solutions to a red-shifted fluorescence, whereas at low concentrations the monomer emission predominates. In a heavy-atom-free solvent like benzene an E-type delayed fluorescence is observed. The fluorescence is partially quenched by octa-substituted copper phthalocyanine. Solid crystals can clearly be differentiated from thermotropic liquid crystals by means of emission spectroscopy.

## 1. Introduction

Octasubstituted phthalocyanine derivatives have been shown to form new thermotropic mesophases of the discotic type [2, 3] (Fig. 1). The phthalocyanine (Pc) subunits, which are planar and rigid, stack into columns, whereas the flexible paraffinic chains form a quasi-liquid medium surrounding these columns. The luminescence properties of such liquid crystal dyes are unknown. Studies in solution have been carried out on numerous unsubstituted phthalocyanines [4 - 18]. Only one study has been devoted to the luminescence properties of unsubstituted Pcs in the solid state [19]. In this paper the emission spectra of 2, 3, 9, 10, 16, 17, 23, 24-octa(1-dodecyloxymethyl)-29$H$,31$H$-phthalocyanine (($C_{12}$)$_8$PcH$_2$) (Fig. 1) have been studied in solution as a function of concentration and temperature and in the solid state at various temperatures, and have been compared with the spectra of metal-free unsubstituted phthalocyanine (PcH$_2$). The
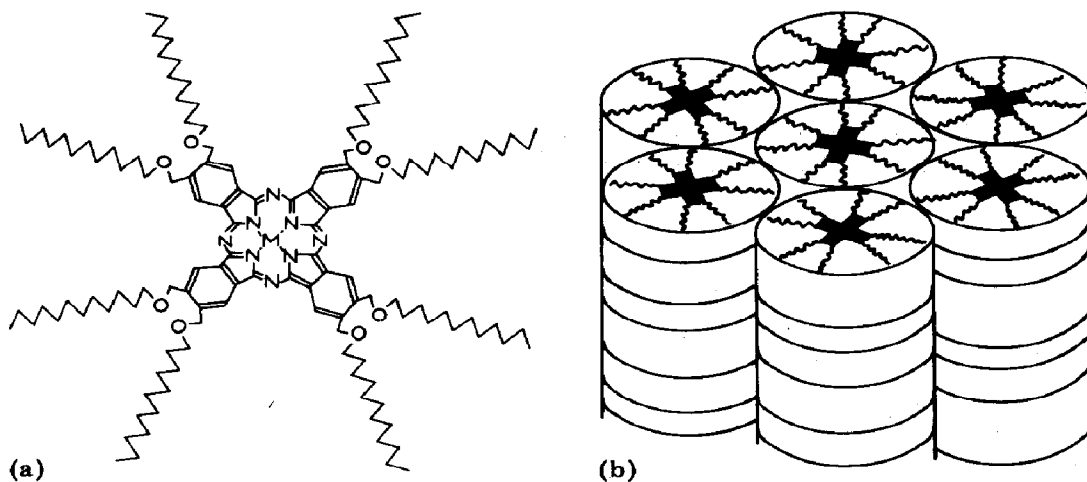
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[†] For Part XI see ref. 1.

Fig. 1. (a) Octasubstituted metal-free phthalocyanine $(C_{12})_8PcH_2$ used in the present studies ($M \equiv H_2$); (b) schematic representation of the structure of the discotic liquid crystals obtained with $(C_{12})_8PcH_2$ [2].

effect of dimerization or the formation of aggregates on the absorption and emission characteristics of octasubstituted Pc is discussed.

## 2. Experimental details

The syntheses of $(C_{12})_8PcH_2$ and its copper homologue $(C_{12})_8PcCu$ have been described previously [2]. $PcH_2$ is commercially available from Eastman Kodak; it is purified by sublimation under vacuum (7 Torr) in a stream of nitrogen. Spectroscopic grade 1-chloronaphthalene (Prolabo) and benzene (Merck Uvasol) were used without further purification.

The absorption spectra were recorded using a Shimadzu UV-240 spectrophotometer. The spectrofluorometer was a thermostatted Fica 55 model, yielding spectra which were corrected up to 800 nm. The excitation wavelength $\lambda_{exc}$ was chosen so as to operate at a suitable optical density. The pattern of the emission spectra did not depend on the excitation wavelength. Bubbling argon through the solutions for 1 h did not change the emission characteristics with respect to the air-saturated solutions. Solid state emission at $90°$ was observed by irradiating the front surface of the polycrystalline compound, which was ground and pressed between two quartz slides, at an incident angle of $60°$.

## 3. Results and discussion

The absorbance values of unsubstituted $PcH_2$ in chloronaphthalene are measurable in the concentration range from $6.3 \times 10^{-5}$ M (saturated solution) to $6.3 \times 10^{-6}$ M (limit of absorption detection). The Beer–Lambert

law is approximately obeyed over this concentration domain. The classical absorption patterns described in the literature are observed [9]. In contrast, the corresponding fluorescence spectra are concentration dependent in the range $6.3 \times 10^{-5}$ - $6.3 \times 10^{-11}$ M (Fig. 2). At the highest concentration the main band ($\lambda_1 = 707$ nm) is accompanied by two other peaks ($\lambda_2 = 739$ nm and $\lambda_3 = 787$ nm). The intensities of the latter two peaks decrease on dilution and become constant relative to the $\lambda_1$ band at a concentration of $6.3 \times 10^{-6}$ M. On heating the solutions from 293 K to 353 K the luminescence intensities decrease slightly and reversibly, as is generally observed for most radiating molecules where the excited states may thermally deactivate in a collisional–vibrational way. The fluorescence excitation spectra follow the corresponding absorption curves for the three bands.

Octasubstituted $(C_{12})_8PcH_2$ is far more soluble in organic solvents. Thus the spectroscopic properties can be determined over a wider concentration range in chloronaphthalene. As before, the absorption spectra are not conspicuously altered by dilution. In contrast the emission characteristics are strongly dependent on concentration (Fig. 3). At $5 \times 10^{-4}$ M only two luminescence bands are observed ($\lambda_2 = 755$ nm and $\lambda_3 = 796$ nm). On dilution, a new band gradually appears at 711 nm. For the more dilute concentrations the pattern obtained for $(C_{12})_8PcH_2$ is very similar to that observed for the unsubstituted compound, except for a small red shift $\Delta\tilde{\nu}$ of about
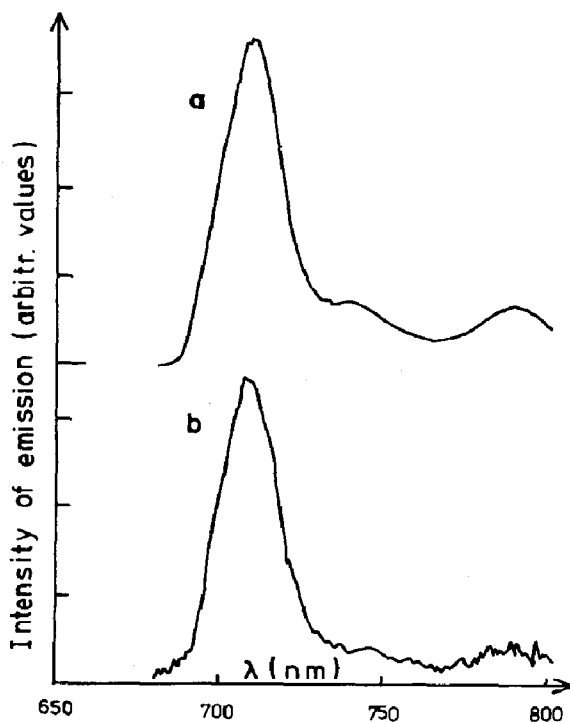


Fig. 2. Luminescence spectra of unsubstituted metal-free phthalocyanine in 1-chloronaphthalene at room temperature ($\lambda_{exc(a,b)} = 665$ nm): curve a, $3.2 \times 10^{-5}$ M; curve b, $6.3 \times 10^{-10}$ M.
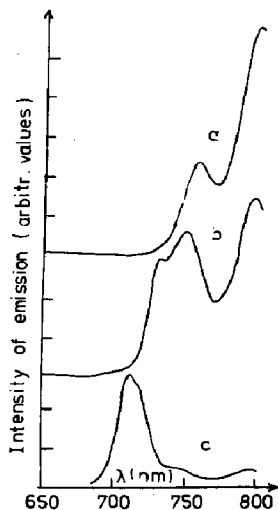
Fig. 3. Luminescence spectra of $(C_{12})_8PcH_2$ in 1-chloronaphthalene at room temperature ($\lambda_{exc(a)}$ = 540 nm; $\lambda_{exc(b)}$ = 560 nm; $\lambda_{exc(c)}$ = 680 nm): curve a, $5 \times 10^{-4}$ M; curve b, $10^{-4}$ M; curve c, $10^{-6}$ M.
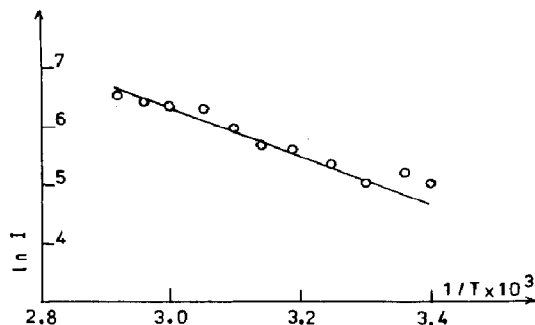
Fig. 4. E-type delayed fluorescence of $2 \times 10^{-4}$ M $(C_{12})_8PcH_2$ in benzene: plot of the logarithm of the intensity of fluorescence (total emission) vs. the reciprocal absolute temperature ($\lambda_{exc}$ = 540 nm).

80 cm$^{-1}$ for the $\lambda_1$ band and 140 cm$^{-1}$ for the $\lambda_3$ band. As before, luminescence intensities slightly decrease on heating to 353 K.

Very similar results have been obtained for $(C_{12})_8PcH_2$ dissolved in benzene with a slight hypsochromic solvent effect ($\lambda_1$ = 706 nm, $\lambda_2$ = 740 nm and $\lambda_3$ = 788 nm). However, in this case a temperature rise leads to a marked increase in the overall luminescence intensities although the shape of the spectrum is unchanged. By plotting the logarithm of the luminescence intensity versus the reciprocal of absolute temperature a straight line is obtained with a slope of $4.15 \times 10^3$ K between 303 and 343 K (Fig. 4). The excitation spectra of luminescence in both solvents and at all temperatures correspond to the absorption spectrum of $(C_{12})_8PcH_2$ at all emission wavelengths. The $\lambda_1$ band near 710 nm can be assigned to the first singlet emission of the isolated phthalocyanine species as previously described in the literature for PcH$_2$ [9, 10, 12, 17].

Some workers [9, 10, 12, 13, 17, 19] have also reported two additional weak bands at the red side of the spectrum separated by 700 - 750 cm$^{-1}$ which correspond to the $\lambda_2$ and $\lambda_3$ bands. They attributed them to vibrational contributions related to the strong IR absorption band observed at 750 cm$^{-1}$ [20]. The concentration effect observed in this work is not compatible with such an interpretation. It is more likely that the luminescence behaviour is influenced by an association process. The two long-wavelength peaks at $\lambda_2$ and $\lambda_3$ are probably due to an aggregated form. Monomer−

dimer equilibria have been observed for tetrasulphophthalocyanine derivatives in water [21 - 35]. The tetraoctadecylsulphonoamidophthalocyanine complex also forms aggregates in non-polar solvents [36, 37] as well as in solid solutions of PcCu [37, 38]. However, only absorption spectra have been used to characterize the aggregation process in previous studies; it has been shown in the present work that these spectra are far less sensitive to concentration effects than are emission spectra. In some cases aggregation cannot be detected by examination of the absorption spectra [13]. Moreover, the fluorescence excitation spectrum of the aggregated form is always very similar to that of the corresponding monomer [12, 13]. The aggregated species is generally considered to consist mainly of the dimer, but the existence of higher degrees of association cannot be excluded [13, 15, 27, 31, 32]. The aggregation number has rarely been related to the luminescence wavelengths of the Pcs [13]. Red shifts relative to the monomer emission which increase from dimer to higher polymer forms have been reported for porphyrin parent compounds [39 - 41].

These literature data support the assignment of the $\lambda_2$ and $\lambda_3$ emission to a reversible association between the Pc subunits which is strongly favoured by long-chain octasubstitution. Some workers have suggested that aggregated dye molecules cannot luminesce because of the increase in radiationless transitions [33, 34, 42]. The results of the present study do not support this hypothesis. The aggregation number has not been determined in the present investigation. However, the invariance of $\lambda_2$ and $\lambda_3$ with varying concentrations suggests that only one species, probably the dimer, is present.

The unusual temperature behaviour of the benzene solutions can be explained by assuming a reversed thermal intersystem crossing from the populated non-radiating triplet state to the radiating singlet level (E-type delayed fluorescence). Such a mechanism has already been suggested for chromium(III) complexes [43], porphyrins [44, 45] and PcH$_2$ [11]. The absence of this phenomenon in chloronaphthalene may be due to an external heavy atom effect; the chlorine atom favours singlet → triplet intersystem crossing. The triplet level is then deactivated in a radiationless way [12, 13, 45]. The linearity of the plot of Fig. 4 demonstrates the existence of a Boltzmann-type activation barrier between the radiating singlet level and a hypothetical triplet level [45]. The energy difference $\Delta E$ between the two levels, calculated from the slope of the curve, is 0.36 eV which agrees well with the energy difference of 0.37 eV between the lowest-lying emitting level (788 nm) and the triplet level (1032 nm) of PcH$_2$ in chloronaphthalene determined by flash photolysis [15].

Absorption spectroscopy and electron spin resonance studies have shown that PcCu [37] and $(C_{12})_8$PcCu [46] polymers can be separated into the monomeric form when excess PcH$_2$ or $(C_{12})_8$PcH$_2$ respectively is added to the solid metal Pc matrices. Conversely, it would be interesting to perform an emission spectroscopy study of the influence of $(C_{12})_8$PcCu on the aggregation of $(C_{12})_8$PcH$_2$ in solution. Figure 5 shows that the addition of
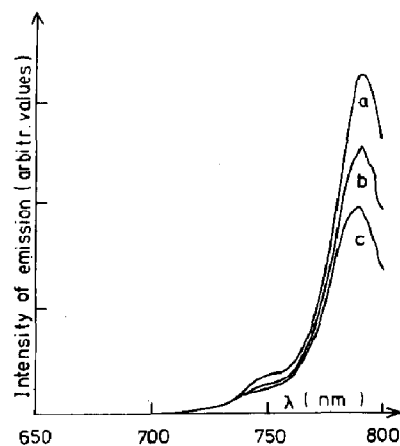
Fig. 5. Luminescence spectra of a solution of $2 \times 10^{-4}$ M $(C_{12})_8PcH_2$ in benzene at room temperature in the presence of $(C_{12})_8PcCu$ $(\lambda_{exc} = 540$ nm): curve a, pure $(C_{12})_8PcH_2$; curve b, $(C_{12})_8PcCu + 10$ wt.% $(C_{12})_8PcH_2$ after 1 h; curve c, $(C_{12})_8PcCu + 10$ wt.% $(C_{12})_8PcH_2$ after 24 h.

10 wt.% $(C_{12})_8PcCu$ to a solution of aggregated $(C_{12})_8PcH_2$ in benzene ($c = 2 \times 10^{-4}$ M) produces a significant decrease in the emitted intensity $I$ with respect to the original value $I_0$ ($I/I_0$ has values of 0.82 and 0.64 after standing for 1 h and 24 h respectively), but no monomer fluorescence appears at 706 nm. This means that the copper complex disperses slowly through the radiating aggregated species and quenches it but does not separate it into monomers. It also confirms that the excited species is in the singlet state $\cdot PcH_2$ which, since it has a lower triplet energy (120 kJ mol$^{-1}$) than that of PcCu (150 kJ mol$^{-1}$), cannot be quenched by the latter species [15]. The excited singlet state of PcCu lies between the two split singlet levels of $PcH_2$ [11], so that partial fluorescence quenching of $PcH_2$ by PcCu is possible. This situation probably exists in the octasubstituted derivatives, as indicated by the absorption spectra.

It has been shown elsewhere [3, 46] by differential scanning calorimetry, optical microscopy and X-ray diffraction examination that $(C_{12})_8PcH_2$ undergoes a transition from a solid crystalline state to a liquid crystal state near 353 K. This transition can also be detected by measuring the intensity of emission of the solid powder at 800 nm (limit of the spectrometer) and temperatures between 293 and 368 K (Fig. 6). Actually the solid emits at 800 nm at room temperature, but the fluorescence intensity drops rapidly near 353 K to a much lower value in the liquid crystal domain. This behaviour, which is entirely reversible on cooling, may correspond to either an actual decrease of the fluorescence through an increase in the radiationless deactivation of the more mobile species or a red shift of the emission maximum which is related in some way to the new mesomorphic phase organization. Yoshino et al. [19] did not detect any fluorescence at 800 nm for $PcH_2$ in the same temperature range under the same conditions.
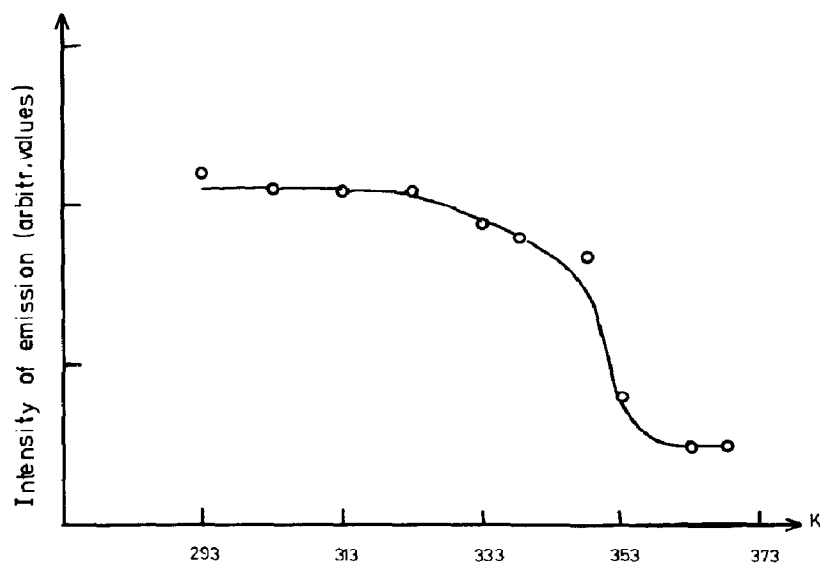
Fig. 6. Intensity of emission at 800 nm of polycrystalline $(C_{12})_8PcH_2$ powder between two quartz slides subjected to front surface irradiation at $\lambda_{exc} = 665$ nm as a function of temperature.

## 4. Conclusion

Emission spectroscopy has been shown to be a very sensitive and useful tool for the observation of the association of Pcs in solution as well as in the solid state. A reversible aggregation, strongly favoured by the long-chain octasubstitution of the Pc rings, is clearly revealed by this method. The solid state structure previously observed by other methods seems to be confirmed; however, the number of aggregations in solution cannot be determined unambiguously but corresponds to at least a dimer. Various solvents are being investigated in the hope of obtaining well-defined aggregates of higher molecular weights. Such "polymers" studied in connection with fluorescence quenchers such as PcCu would be suitable models for studying the energy transfer within compounds like the stacks which participate in chlorophyll synthesis. The corresponding water-soluble octasubstituted Pcs [46] can thus be considered as potential photosensitizers in solar energy conversion.

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