Spectroscopic studies of supramolecule formation through cation-induced aggregation of phthalocyanine with four crown ether voids

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Abstract

The alkali cation complexation of phthalocyanine substituted with four crown ether rings (H_2CRPc) was studied by UV–visible absorption and fluorescence spectroscopy. Cation-induced aggregation of the crowned phthalocyanine occurred in solution. When the diameters of the cations (K^+, Rb^+) slightly exceeded that of the crown ether ring, they acted cooperatively leading to the formation of a cofacial dimer. Smaller cations (Li^+, Na^+), which could be encapsulated into the cavity of the crown ether voids, were unable to cause complete conversion to a cofacial dimer. Large Cs^+ ions induced sandwich-like aggregation in solution more rapidly. The monomer–dimer equilibrium formation constants for K^+- and Rb^+-induced aggregation were calculated to be of the order of $10^9 \, l^2 \, M^{-2}$.

Keywords: Supramolecular formation; Agrregation; Phthalocyanine; Crown ether

1. Introduction

Phthalocyanines substituted by crown ether rings, which show a high tendency towards aggregation by solvents and cations, have been described independently by Kobayashi and Nishiyama [1], Koray et al. [2] and Hendriks et al. [3]. They can be used for the colorimetric determination of alkali cations [1] and as selective extracting reagents [2]. They are expected to form ion channels, and transport ions and electrons by arranging the pendant crown ether rings in stacks [3]. They also exhibit increased electrical conductivity compared with unsubstituted phthalocyanines [4]. The design of ionoelectronics networks based on the non-linear complexation of ions by crowned phthalocyanines has been demonstrated recently [5]. We are interested in the synthesis of phthalocyanines with different pendant groups capable of performing light-induced functions. Thus covalently linked porphyrin–phthalocyanine dimers [6] and phthalocyanines substituted with acceptor functionalities [7,8] have been synthesized to determine the molecular mechanism involved in energy transfer and photoinduced electron transfer and charge separation respectively. In this paper, we report the cation complexation behaviour of phthalocyanine with four 15-crown-5 ether voids (H_2CRPc) as multiple host sites, and study the intramolecular quenching of phthalocyanine excited states by insertion of alkali cations of different sizes.

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2. Experimental details

2.1. Materials

The crowned phthalocyanine (H_2CRPc, $C_{64}H_{72}N_8O_{20}H_2$) (Fig. 1) was synthesized in our laboratory. The FD mass spectrum showed an m/e value of 1274 (M^+). The details of synthesis will be described elsewhere. All solvents and reagents were of analytical grade and used as received.
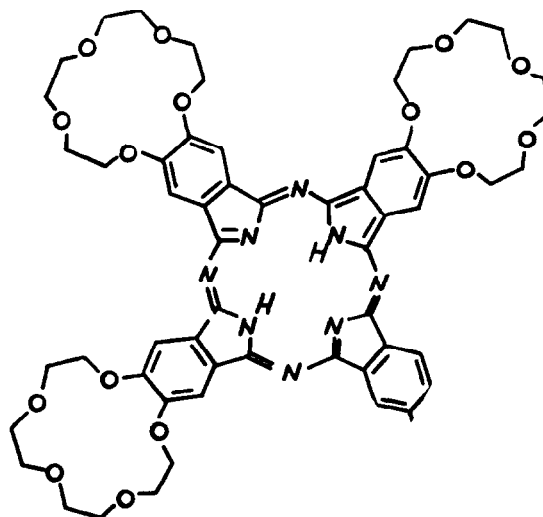

Fig. 1. Structure of the crowned pht'

2.2. Instruments and methods

FD mass spectra were obtained on a Hitachi 80 mass spectrometer. The UV–visible absorption spectra were measured on a Hitachi 557 spectrometer. The fluorescence spectra were recorded using a Perkin–Elmer LS-5 fluorometer with an excitation wavelength of 350 nm and excitation and emission slits of 5 nm. A change in the absorption spectrum of H$_2$CRPc was recorded by the addition of alkali salts in CHCl$_3$–CH$_3$OH (5 : 3, v/v) to 3 ml of a CHCl$_3$ solution of H$_2$CRPc (1 × 10^{-5} M) in a 10 mm cell. The concentrations of the alkali salts were 3.0 × 10^{-3} M (LiCl), 3.0 × 10^{-3} M (NaCl), 2.1 × 10^{-3} M (KCl), 2.3 × 10^{-3} M (RbCl) and 1.5 × 10^{-3} M (CsCl), and they were added with a microsyringe (60 μl in all). The fluorescence quantum yield was determined using zinc phthalocyanine ($\Phi = 0.30$) [9] as standard.

3. Results and discussion

3.1. Absorption spectroscopy: cation-induced dimerization

The UV–visible absorption of H$_2$CRPc exhibits a typical free base phthalocyanine spectrum consisting of two closely spaced Q bands at 662 and 700 nm with two associated vibrational overtones at 600 and 645 nm and an intense, broad Soret absorption around 300 nm. In addition, a weaker absorption in the 400–500 nm region is observed, which may involve the ether oxygen lone pairs and has not been detected in mononuclear phthalocyanine.

The addition of Li$^+$, Na$^+$, K$^+$, Rb$^+$ and Cs$^+$ salts alters the spectrum of H$_2$CRPc appreciably, but not in the same fashion. Thus the successive addition of K$^+$, Rb$^+$ and Cs$^+$ causes a decrease in the Q band intensities at 662 and 700 nm (the so-called monomer peak) and an increase in the peak intensity around 642 nm (the so-called dimer peak). At the same time, the intensity of the Soret band around 344 nm is reduced, and with continuing addition of K$^+$, Rb$^+$ and Cs$^+$, a new peak at 332 nm appears. The 420 nm absorption decreases with some broadening in the Q band region. Finally, a single, broad, symmetrical dimer absorption, blue shifted by 20–60 nm relative to both of the Q bands, is obtained (Fig. 2).

The addition of Li$^+$ and Na$^+$ causes a marked reduction of the Q band (662 nm, 700 nm) intensities, but the change in dimer absorption at 642 nm is not significant (Fig. 3). In addition, the intensities of the Soret band and the 420 nm absorption gradually decrease in all cases.

The intensity changes in the monomer (700 nm) and dimer (642 nm) absorptions were plotted against the molar ratio [M$^+$]/[H$_2$CRPc]. In the case of K$^+$ and Rb$^+$, with diameters of 2.66 and 2.96 Å respectively which slightly exceed that of the crown ether ring (1.70–2.20 Å), the cation-induced dimerization proceeds in three stages. The first, second and third stages occur approximately at [K$^+$]/[H$_2$CRPc] values of 0–0.5, 0.5–2.0 and over 2.0 (inset of
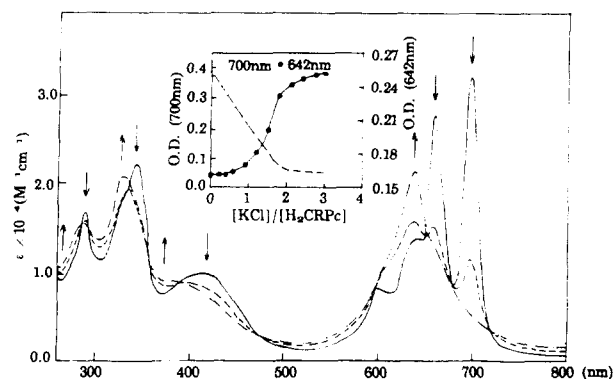

Fig. 2. Change in absorption spectrum of H$_2$CRPc in CHCl$_3$ (1 × 10^{-5} M) on addition of KCl (2.1 × 10^{-3} M) in CHCl$_3$–CH$_3$OH (5 : 3, v/v). Inset shows the dependence of the monomer (700 nm) and dimer (642 nm) absorbance of H$_2$CRPc on [K$^+$]/[H$_2$CRPc].
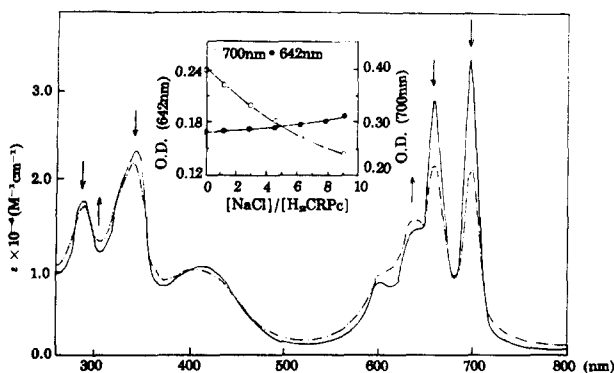

Fig. 3. Change in absorption spectrum of H$_2$CRPc in CHCl$_3$ (1 × 10^{-5} M) on addition of NaCl (3.0 × 10^{-3} M) in CHCl$_3$–CH$_3$OH (5 : 3, v/v). Inset shows the dependence of the monomer (700 nm) and dimer (642 nm) absorbance of H$_2$CRPc on [Na$^+$]/[H$_2$CRPc].

Fig. 4. Proposed structure of cation-induced non-cofacial dimer of H$_2$CRPc.

Fig. 2). Although not shown, a similar behaviour is observed at [Rb$^+$]/[H$_2$CRPc] values of 0–0.5, 0.5–1.5 and over 1.5. It is believed that the four crown ether voids in H$_2$CRPc are available for cation insertion. They act cooperatively. When cations whose diameters slightly exceed that of the crown ether ring are added to H$_2$CRPc solution, the monomer absorbance decreases until [M$^+$]/[H$_2$CRPc] = 0.5. This corresponds to one M$^+$ ion being held by two adjacent H$_2$CRPc units with the two crowned phthalocyanine units tilted away from each other as indicated in Fig. 4. With

increasing M^+ ion concentration, in the region $0.5 \leqslant [K^+]/[H_2CRPc] \leqslant 2.0$ and $0.5 \leqslant [Rb^+]/[H_2CRPc] \leqslant 1.5$, the two phthalocyanine rings encapsulate second and third cations. The encapsulation continues until two H_2CRPc units share four M^+ ions, i.e. $[M^+]/[H_2CRPc] = 2.0$, leading to the formation of a cofacial dimer with the plane of the two phthalocyanine rings parallel; a supramolecular phthalocyanine is attained.

Assuming a monomer–dimer equilibrium for K^+- and Rb^+-induced spectroscopic changes in the region in which the molar ratio $[M^+]/[H_2CRPc]$ varies in the range 0–0.5 (Fig. 2)

$$n M^+ + 2\ \text{Monomer} \overset{K}{\longleftrightarrow} \text{Dimer-}M_n^+ \qquad (1)$$

the specific monomer and dimer concentrations were calculated with a computer program based on the approximation method of Pearce and West [10] using the change in intensity of absorption at 700 and 642 nm as a function of $[M^+]/[H_2CRPc]$ (Fig. 2). The pure monomer spectrum was assumed to be present in the absence of M^+. The monomer–dimer equilibrium formation constants were derived from Eq. (2)

$$K = \frac{[\text{Dimer} \cdot M^+]}{[\text{Monomer}]^2 \cdot [M^+]} \qquad (2)$$

to be $K_K^+ = (2.9 \pm 1.0) \times 10^9\ l^2\ mol^{-2}$ and $K_{Rb}^+ = (5.0 \pm 1.0) \times 10^9\ l^2\ mol^{-2}$ respectively.

In contrast, the smaller Li^+ (1.20 Å) and Na^+ (1.90 Å) ions reside within the cavity (1.70–2.20 Å) of the crown ether rings in H_2CRPc. Thus higher concentrations of the cations are needed to promote the spectroscopic change. However, Li^+ and Na^+ are unable to cause complete conversion to the cofacial dimer, and they do not produce an appreciable change in dimer absorbance (Fig. 3). The size of Cs^+ (3.38 Å) is so large that much lower concentrations of the cation are required to effect dimerization. The intensity of dimer absorption increases linearly with $[Cs^+]/[H_2CRPc]$ (inset of Fig. 5).
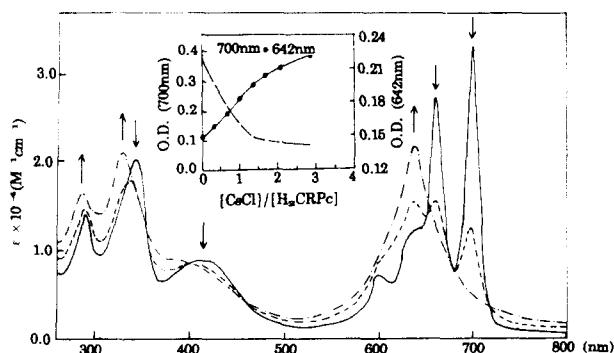

Fig. 6. Change in fluorescence spectrum of H_2CRPc in $CHCl_3$ $(1 \times 10^{-5}$ M) on addition of K^+ $(\lambda_{ex} = 350$ nm).
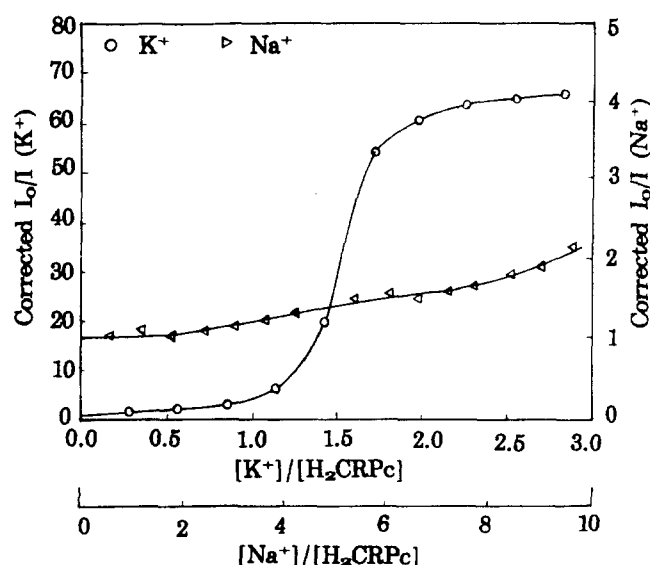
Fig. 7. Stern–Volmer plot of the fluorescence of H_2CRPc quenched by K^+ and Na^+ ions.

3.2. Fluorescence spectroscopy

H_2CRPc exhibits very strong emission at 707.5 nm (S_1) (quantum yield $\Phi_f = 0.6$) and weak emission in the region 400–500 nm (S_2), which has not been detected in mononuclear phthalocyanine and may involve the crown ether oxygen lone pairs.

The addition of K^+ to H_2CRPc in $CHCl_3$, as an example, leads to strong quenching of the 710 nm emission with less marked quenching of the 450 nm fluorescence (Fig. 6). A Stern–Volmer plot of the quenching of the S_1 emission at 710 nm is consistent with stepwise insertion of the K^+ ion (Fig. 7).

In the region in which the molar ratio $[K^+]/[H_2CRPc]$ varies from 0–0.5, the quenching is small. However, with a further increase in K^+ ion concentration, quenching is greatly enhanced until a molar ratio of unity is reached. The fluorescence intensity then changes slowly and becomes almost constant when the molar ratio $[K^+]/[H_2CRPc]$ reaches greater

Fig. 5. Change in absorption spectrum of H_2CRPc in $CHCl_3$ $(1 \times 10^{-5}$ M) on addition of CsCl $(1.5 \times 10^{-3}$ M) in $CHCl_3$–CH_3OH $(5 : 3, v/v)$. Inset shows the dependence of the monomer (700 nm) and dimer (642 nm) absorbance of H_2CRPc on $[Cs^+]/[H_2CRPc]$.
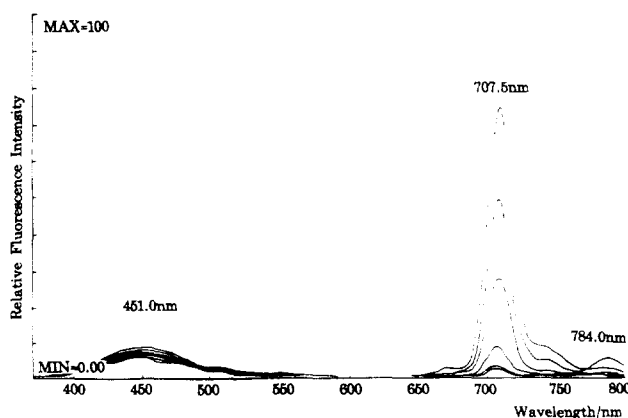
than 1.5, indicating that a face-to-face cofacial dimer conformation is attained. The addition of smaller ions, such as Na^+, to H_2CRPc in $CHCl_3$ also leads to quenching, but to a lesser degree for both S_1 and S_2 emissions (Fig. 7). A much higher concentration of Na^+ ions is required and it is clearly much less efficient. This may be explained by the fact that Na^+ is unable to effect the formation of a cofacial dimer.

4. Conclusions

Alkali ion complexation of crowned phthalocyanine is cation dependent. K^+ and Rb^+ ions, whose diameters slightly exceed that of the crown ether ring, are encapsulated between two crowned units and act cooperatively to promote cofacial dimer formation. Smaller Li^+ and Na^+ ions, which reside within the cavity of the crown ether voids, are unable to effect sandwich-like aggregation. Large Cs^+ ions induce dimerization more rapidly leading to the formation of a cofacial dimer.

Acknowledgement

References

[1] N. Kobayashi and Y. Nishiyama, J. Chem. Soc., Chem. Commun., (1986) 1462.

[2] A.R. Koray, V. Ahsen and O. Bekaroglu, J. Chem. Soc., Chem. Commun., (1986) 932.

[3] R. Hendriks, O.E. Sieleken, W. Dreath and R.J.M. Nolte, J. Chem. Soc., Chem. Commun., (1986) 1464.

[4] O.E. Sielcken, J. Schram, R.J.M. Nolte, J. Schoonman and W. Dreuth, J. Chem. Soc., Chem. Commun., (1988) 108.

[5] T. Toupance, V. Ahsen and J. Simon, J. Am. Chem. Soc., 116 (1994) 5352.

[6] H.J. Tian, Q.F. Zhou, S.Y. Shen and H.J. Xu, J. Photochem. Photobiol. A: Chem., 72 (1993) 163.

[7] S.Y. Shen, L. Li, Q.F. Zhou and H.J. Xu, Chinese Chem. Lett., 1 (1990) 201.

[8] H. Xu, T. Shen, Q. Zhou, S. Shen, J. Liu, L. Li, S. Zhou, X. Zhang, Q. Yu, Z. Bi and X. Xiao, J. Photochem. Photobiol. A: Chem., 65 (1992) 267.

[9] P.G. Selybold and M. Gouterman, J. Mol. Spectrosc., 31 (1969) 1.

[10] S. Pearce and W. West, J. Phys. Chem., 69 (1965) 1894.