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Observation on Symmetry Properties of Sodium Zinc(II)-2,9,16,23-phthalocyanine Tetracarboxylate in Water:NaOH Solution

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Abstract The shift of the Q-band of sodium zinc(II)-2,9,16,23-phthalocyanine tetracarboxylate ($ZnPc(COONa)_4$) to about 800 nm is attributed to the influence of the electron-donating property of the carboxylate groups substituted in the β–position. $ZnPc(COONa)_4$ which was found to have a symmetry of D_{2h} characterized by a splitting of the Q transition. This splitting was interpreted by the formation of dianionic symmetric $ZnPc(COONa)_4$ resulting from the dissociation of the pyrrole protons as well as the possibility of Na^+ dissolution of $ZnPc(COONa)_4$ in the aqueous solution of NaOH.

Keywords Phthalocyanine · Fluorescence · Stokes shift · Absorption · Photodynamic process · HOMO · LUMO

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Introduction

Metallophthalocyanines (MePcs) are based on the delocalized 18 p conjugated electron system. They have been extensively studied because of their special properties such as structural, electronic, and optical ones [1]. Insertion of substituent in the peripheral and nonperipheral positions of MePcs can alter their physical and chemical properties. For example, the insertion can extend the π-electron system, increase or decrease the symmetry, and makes solvation easier [2, 3]. Tetra-substituted phthalocyanines are known to have good solubility attributed to the formation of constitutional isomers. Furthermore, the ionic functional groups such as phosphoric, carboxylic, amino groups, and sulfonic make MePcs water soluble [4, 5]. The dipole moment formed from the unsymmetrical nontransitional metals such as zinc in the centre of the phthalocyanine makes the molecule having radiationless quantum yields especially the intersystem crossing quantum yield and the long triplet lifetime [6, 7].

The aim of the present work was to investigate some symmetry properties of sodium zinc(II)-2,9,16,23-phthalocyanine tetracarboxylate($ZnPc(COONa)_4$) dissolved in water:NaOH solution.

Materials and Methods

Materials

Sodium zinc (II)-2,9,16,23-phthalocyanine tetracarboxylate ($ZnPc(COONa)_4$) was used and kept in the dark at low temperature. The structural formula of $ZnPc(COONa)_4$ is shown in Fig. 1.
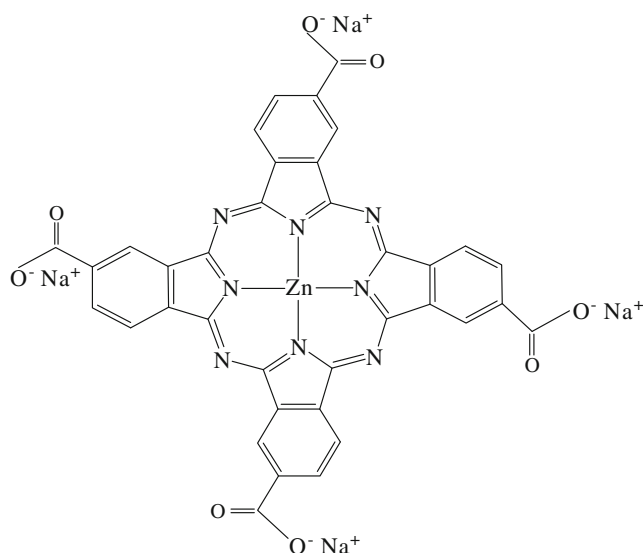
Fig. 1 Structural formula of ZnPc(COONa)$_4$

Electronic structure: Phthalocyanines have an allowed intense $S_0 \rightarrow S_1$ absorption transition of Q band in the red region of the spectrum around 670 nm. In Fig. 1, the molecular structure of the studied ZnPc(COONa)$_4$ is shown. The β and α positions are at, respectively, (2, 3, 9, 10, 16, 17, 23, 24) and (1, 4, 8, 11, 15, 18, 22, 25) [8, 9]. The insertion of substituents in the β and α-positions is acting as electron donors as well as mesomeric and inductive effects affect the p system at the two pyrrole rings resulting in bathochromic shift of the Q band. It was calculated the electron density of substituted MePc for LUMOe$_g(\pi^*)$ and HOMOa$_{1u}(\pi)$ [9]. The electron density of HOMOa$_{1u}(\pi)$ is primarily located at the carbon atoms of the positions of 5, 7, 12, 14, 19, 21, 26 and 28. For carbon atoms of phenyl rings at positions of 1, 4, 8, 11, 15, 18, 22, and 25 a smaller charge density is found. When the molecule is excited in the Q band of the transition from HOMOa$_{1u}(\pi)$ to LUMOe$_g(\pi^*)$ the electron density is strongly altered. In this case, the electron density extends over the p electron system comprising six nitrogen atoms as well as the carbon atoms of the phenyl rings at positions of 2, 3, 16, and 17. The energy gap between HOMOa$_{1u}(\pi)$ and LUMOe$_g(\pi^*)$ becomes smaller due to the substitution resulting in a strong bathochromic shift of the Q band [10].

The B$_1$ and B$_2$ bands belong to the transition of HOMOa$_{2u}(\pi)$ and HOMOb$_{1u}(\pi)$ to LUMOe$_g(\pi^*)$, respectively, while HOMOb$_{1u}(\pi)$ bosses symmetry of LUMOe$_g(\pi^*)$ [8, 11]. The electron density of HOMOa$_{2u}(\pi)$ is localized principally at the eight nitrogen atoms and the electron density of aza-bridge nitrogen atoms is held. For the four pyrrolic nitrogen atoms the electron density is shifted partially to the pyrrolic carbon atoms as well as a smaller portion to the benzene rings. Therefore, the substituents of the benzene rings cannot compensate for stabilizing shifts in the electron density. Hence, the effect of α or β-substituents on the absorption portion of the B band should be small.

Absorption Spectroscopy

Using spectrophotometer Shimadzu UV-1700 at the room temperature, the electronic ground-state absorption spectra were recorded employing quartz cells (10 mm×10 mm path length). The increment step of the measurement was 0.2 nm.

Steady-state Fluorescence Spectroscopy

On JASCO-FP 6500 spectroscopy, the steady-state fluorescence spectra at room temperature were collected using fluorescence quartz cell (10 mm×10 mm path length). The parameters were fixed for each sample enabling a maximum intensity of less than 17,000 count. The excitation wavelength was at 342 nm.

Fluorescence quantum yield of ZnPc(COONa)$_4$ ($\Phi_F^{ZnPc(COONa)_4}$) was determined compared with that of pyropheophorbide methyl ester (PPME) (Φ_F^{PPME}=0.21±0.02 in DMF [12]) as a reference. The sample and standard were adjusted to an optical density of 0.1. The fluorescence quantum yield was obtained using the following formula

$$\Phi_F^{ZnPc(COONa)_4} = \frac{\Phi_F^{PPME} OD^{ZnPc(COONa)_4} n_{ZnPc(COONa)_4}^2 \int I_F^{ZnPc(COONa)_4}(\lambda)d\lambda}{OD^{PPME} n_{PPME}^2 \int I_F^{PPME}(\lambda)d\lambda}$$

(1)

where, OD is the optical density, n is the index of refraction of the solvent, and the integrals represent the calculated area of the corrected fluorescence bands. The fluorescence quantum yield ($\Phi_F^{ZnPc(COONa)_4}$) was found to be 0.1 using Eq. (1).

Results and Discussion

ZnPc(COONa)$_4$ is water-soluble due to the presence of the peripheral carboxylate groups. They also can prohibit the molecules aggregation providing excellent superior photophysical properties [13]. The electronic absorption spectra of ZnPc(COONa)$_4$ investigated in water:NaOH solvent is shown in Fig. 2. As apparent, the general feature of the absorption spectrum looks like those of phthalocyanine derivatives. The absorption of electronic ground-state spectrum of ZnPc(COONa)$_4$ shows bathochromic shift of the Q$_1$ band (transition from HOMOa$_{1u}(\pi)$ into LUMOeg$_x(\pi^*)$) of 691 nm with molar extinction coefficient of $\varepsilon_{691\ nm}$=1.31× $10^4\,M^{-1}\,cm^{-1}$ and Q$_2$ band (transition from HOMOa$_{1u}(\pi)$ into LUMOeg$_y(\pi^*)$) at 641 with ε_{641nm}=1.81×10$^4\,M^{-1}\,cm^{-1}$. The transitions of Q$_1$ and Q$_2$ bands are shown in Fig. 3. The energy difference between the energy positions of the two bands is small and equal to about 0.15 eV. When comparing with other phthalocyanines, ZnPc(COONa)$_4$ demonstrates promising
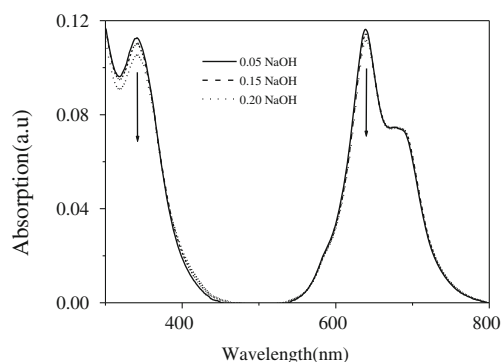
Fig. 2 Electronic absorption of B and Q transitions of ZnPc(COONa)$_4$ in inhomogeneous solution of water-NaOH at room temperature

advantages. It has strong molar absorption coefficients of Q band ($S_0 \rightarrow S_1$) in the red region of the spectrum in aqueous environments. The absorption spectrum in the region of the high energy range is dominated by the B$_2$ band (transitions from HOMOb$_{1u}$ (π) into LUMOeg(π^*)) with maximum at 279 nm ($\varepsilon_{279\ nm} = 2.41 \times 10^4\ M^{-1}\ cm^{-1}$) and by a another one at 341 nm ($\varepsilon_{341\ nm} = 1.58 \times 10^4\ M^{-1}\ cm^{-1}$) due to the B$_1$ band belonging to the transitions from HOMOa$_{2u}$(π) into LUMOeg(π^*).

Incorporation of a central metal in the structure of phthalocyanine (Pc) results in high efficiency of light absorption [14] as noticed from the molar absorption coefficients of Q and B bands (see Fig. 2). It also increases the symmetry of the compound. Therefore, it is observed the existence of only two Q bands ($S_0 \rightarrow S_1$) positioned, respectively, for Q$_1$ at 691 nm and for Q$_2$ at 641 nm. In contrast to porphyrins, the absorption spectra of Pcs have allowed Q transitions in the bathochromic region [6].

Geometry optimization using the Arguslab program [15] on ZnPc(COONa)$_4$ in vacuum at room temperature showed that the planar structure of the molecule remains, whereas the tetra-carboxylate groups point out of the molecule plane (Fig. 4). The out-of-plane of the carboxylate groups should reduce the tendency of the molecules to aggregate. A nitrogen atom of the phthalocyanine ring system sticks out of the molecular plane, probably because of the central metal which is bonded to two nitrogen atoms of the Pc ring system.

Compared to metal-free phthalocyanine, the absorption of ZnPc(COONa)$_4$ demonstrates a bathochromic shift of the Q
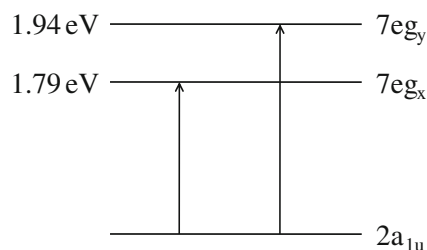
Fig. 3 The molecular optical transitions of ZnPc(COONa)$_4$ in Q band
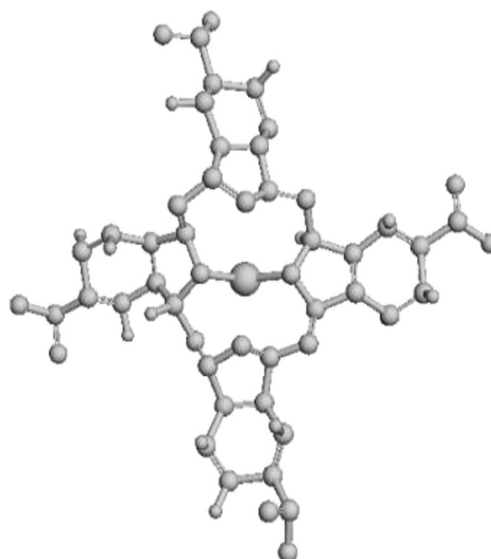
Fig. 4 Geometry optimization of the steric conformation of ZnPc(COONa)$_4$ in vacuum at room temperature showing the out-of-plane geometry of the carboxylate groups

band which possibly is attributed to its π-system which in turn is extended by the electron donating carboxylate bonded at the β-positions. The red shift of the absorption resulting from enlarging the π electron system is well-known phenomenon [16–18]. In addition, as documented, as the planarity of the molecule increases its absorption becomes more bathochromic [17, 18].

The absorption spectra of metal Pcs are often have a single Q band transition due the symmetry of D_{4h} in contrast to those of metal-free Pcs which have a symmetry of D_{2h} and characterized by a splitting of the Q transition. As apparent from Fig. 2, the main broad Q-band of ZnPc(COONa)$_4$ splits into a major pair of vibrational bands. It seems that the degeneracy of Q-band transition becomes D$_{2h}$ symmetry. In this context, it was reported [19] that the spectra of unsubstituted H$_2$Pc with D_{4h} symmetry of the Q band are solvent-dependent and splitted. This splitting was interpreted by the formation of
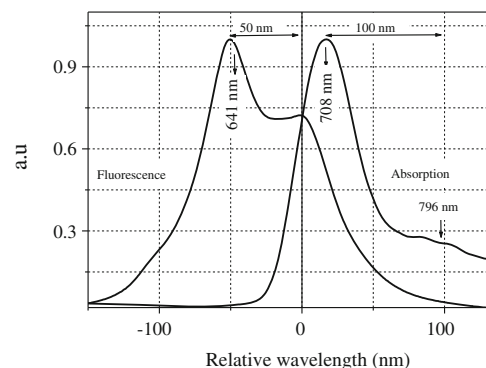
Fig. 5 Comparison of the steady state fluorescence and absorption spectra in the Q-band region of ZnPc(COONa)$_4$ demonstrating the asymmetry

dianionic symmetric Pc resulting from the dissociation of the pyrrole protons. Attributed to the possibility of Na^+ dissolution of $ZnPc(COONa)_4$ in the aqueous solution of NaOH, it is possible to have symmetric Pc(–2) species. Therefore, the absorption spectrum of the Pc is pH-dependent [20]. Furthermore, it should be also taken into consideration that the forbidden vibrational modes become allowed as the symmetry of the nonplanar state decreases resulting in splitting appearance in the spectrum [17].

As mentioned above the carboxylate group at the β-position exhibits an influence on the absorption properties. In general, also dianion formation and/or aggregation [8] could account for this effect. In order to notice the effect of increasing the NaOH concentrations on the absorption feature, the absorption spectra were reordered at different NaOH concentration as depicted in Fig. 2. As seen, the peaks of the energetic positions, the vibrational bands width, the splitting of Q band, and the relative maxima of Q and B bands are almost not affected by adding different concentrations of NaOH. That means that, despite the expected dissolution of the ionic periphery (Na^+O^-) of the molecule by releasing Na^+ (O^- is still covalently bonded to the molecule, see Fig. 1) to the solution as well as the dissolution of the ionic sodium hydroxide(NaOH) in the water to Na^+ and OH^-, they did not attack the molecular structure in a way that they could alter or even damage it. Therefore, it could be concluded that the ionic species of Na^+, OH^-, NaOH, and H_2O do not disturb the π-conjugated system of $ZnPc(COONa)_4$ molecule. Indeed, this should be an advantage for this molecule. Since, if it is injected in the blood for the treatment, it should be expected that the molecule will preserve on its photophysical properties by which can destroy the cancerous tissues by the manner of photodynamic processes [21].

The concentration dependency of $ZnPc(COONa)_4$ absorption was investigated in order to eliminate the responsibility of aggregates for the spectral splitting. No evidence of aggregation was observed in the concentration range from 10^{-8} to 10^{-4} M. As mentioned above, the outer substituents have a strong influence on the absorption especially in the Q-spectral region of the phthalocyanines. In this spectral region, it is observed a broadening reflecting the merger of at least two envelopes of the Q-band. This band broadening can be as a result of an effective coupling between Pc molecules and solvent molecules. Thus, new vibrational modes result in extending and enlarging of the absorption bands to about 800 nm. Similar findings were also observed upon the coordination of ethanol molecules with phthalocyanine [18].

The fluorescence spectrum of $ZnPc(COONa)_4$ is shown in Fig. 5 in comparison with the absorption spectrum in the Q-band region. The figure shows asymmetry between fluorescence and absorption. In this frame, asymmetry between fluorescence and absorption was found for some unsubstituted MePcs [22].

Stokes shift is the difference between the energy positions of fluorescence and absorption peaks (Fig. 5). It is also proportional to the difference values between ground and excited states of the molecular dipole moments [16, 17, 23]. The current molecule has relatively large Stokes shift with a wavenumber of 1,476 cm^{-1}, indicating a more planar of the first excited state compared to that of the ground state [17]. Therefore, it is concluded that the condition for a good coplanarity between the two states is not achieved.

Conclusions

It was investigated a class of far red-absorbing photosensitizers. The shift of the Q-band of $ZnPc(COONa)_4$ to about 800 nm is attributed to the influence of the electron-donating property of the carboxylate groups substituted in the β - position. It was shown that upon bonding of the carboxylate group *via* the carbon on the Pc rings the planar structure of the Pc ring is not changed. But the carboxylate groups point out of the plane of the Pc ring system. This should lead to some aggregation and good solubility. $ZnPc(COONa)_4$ was found to have a symmetry of D_{2h} characterized by a splitting of the Q transition. This splitting was interpreted by formation of dianionic symmetric Pc resulting from the dissociation of the pyrrole protons as well as attributed to the possibility of Na^+ dissolution of $ZnPc(COONa)_4$ in the aqueous solution of NaOH.

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