

Supramolecular assemblies of pyridyl porphyrin and diazadithia phthalocyanine

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In this paper we report for the first time on a mixed complex between the cationic porphyrin 5, 10, 15, 20-tetra-*N*-methyl-pyridinium-*p*-il porphyrin (TMPyP) and a new metal phthalocyanine with four 16-membered diazadithia macrocycles (denoted here as Pc16), in order to obtain an active complex with an intense absorption on the lower energy side of the visible spectrum and with a higher sensitivity in photodynamic therapy of cancer. The dimerization constant for Pc16 and also the ratio between the oscillator strengths for monomeric and dimeric forms of this compound, were evaluated. The ratio between these oscillator strengths was 2.01 showing a certain dimerization process. The Job mathematical method allowed the establishment of the stoichiometry and the formation constants for the heteroaggregates between the porphyrin and the phthalocyanine (a diad between one phthalocyanine molecule and one porphyrin molecule and a triad between two phthalocyanine molecules and only one porphyrin molecule). The coulombic attraction resulting from the π - π interaction of the two highly conjugated macrocycles and from the interaction between the substituents, favors a face-to-face geometry.

Key words: porphyrin, phthalocyanine, heteroaggregation, coordination chemistry.

During the last decade, the coordination chemistry has offered many examples of supramolecular assemblies, and a special pair with two chromophores formed by pairing cationic and anionic water soluble compounds.¹⁻³

The porphyrins and phthalocyanines represent two classes of chemically very versatile compounds. Depending on the nature of the central metal and/or the peripheral substituents, a wide range of photophysical and photochemical properties can be obtained.⁴⁻¹⁰

The heteroaggregates of porphyrins and phthalocyanines grafted with ionic substituents of opposite charges have been subjected to extensive investigations in the last two decades, because such assemblies can provide promising properties in the search for new molecular materials for electronics or photodynamic therapy.^{8,11-16}

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The phthalocyanines containing 16-membered diazadithia macrocycles, show typical electronic spectra with two strong absorption regions, one in the visible region at 682 nm (Q band), and the other in the UV region at 332 nm (B band).

In the literature, only a few cases of phthalocyanines bearing sulphur donors are presented.^{17–20} The 16-membered symmetrical tetrabenzo-diazadithia macrocycle metallic phthalocyanine (M being copper and nickel) derivative which carry sulfo groups, having diaza- and dithia-donor groups has been reported in the literature as a new polynuclear compound highly coordinated by metal ions inside the macrocyclic substituents.²⁰

The electronic spectra of porphyrins differ drastically from those of the phthalocyanines. The porphyrins display an intense Soret band and four Q bands in the 500–700 nm spectral region.²⁰ Also, TMPyP has a low aggregation capacity or does not aggregate in the concentration range of 10^{-5} – 10^{-7} M.^{9–12}

In this paper we report, for the first time the heteroaggregation between a cationic porphyrin – 5,10,15,20 tetra-*N*-methyl-pyridinium-*p*-il porphyrin (TMPyP) – and the phthalocyanine 16-membered symmetrical tetrabenzo diazadithia complexed with Cu and Ni (denoted here as Pc 16) which has negative charges on its molecule. In this study, the Job method was used in order to establish the stoichiometry and formation constant of such a heterocomplex. The dimerization of Pc 16 in DMSO (including the equilibrium constant determination) and the axial coordination of DMSO at nickel (the central metallic ion from the phthalocyanine macrocycle) are also discussed in this paper.

EXPERIMENTAL

Materials

The cationic porphyrin 5,10,15,20 tetra-*N*-methyl-pyridinium-*p*-il porphyrin (TMPyP) (Fluka) was used without any purification.

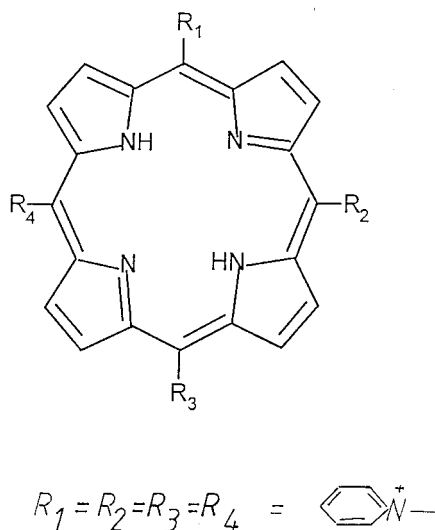


Fig. 1. The structure of TMPyP.

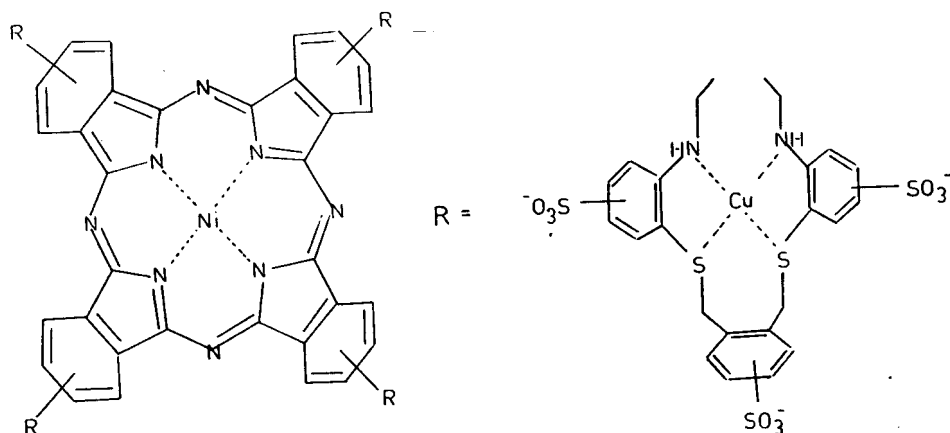


Fig. 2. The structure of Pc16.

The phthalocyanine 16c was prepared and purified as reported elsewhere.²¹ The structure of the studied compounds are shown in Figs. 1 and 2. All the experiments were performed in DMSO.

Apparatus

The absorption spectra were recorded using a SPECORD M 400 Carl Zeiss Jena Spectrophotometer with a double beam and microprocessor and also with a PYE-UNICAM spectrophotometer.

RESULTS AND DISCUSSION

The existence of heterodimers and heterotrimers between the porphyrin and the phthalocyanine has been demonstrated by titration using spectrophotometric methods, such as absorption spectroscopy.²¹

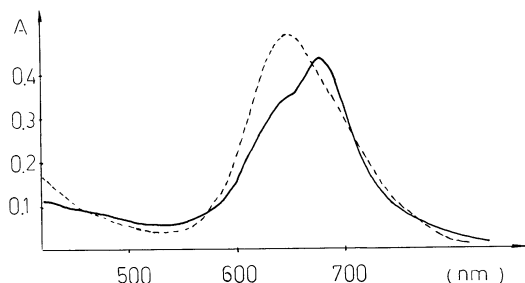


Fig. 3. The changes in the absorption spectra of Pc16 in DMSO at different concentrations: 1) 2.61×10^{-5} M; 2) 1.1×10^{-75} M; 3) 0.57×10^{-5} M; 4) 0.37×10^{-6} M; 5) 1×10^{-6} M

The studied phthalocyanine shows a dimerization process both in DMSO. This is reflected spectrophotometrically by the blue shift of the absorption peak from 682 nm to shorter wavelengths (with 34 nm), as well as by hypochromism of this band, Fig. 3. The absorption bands of the monomer and the dimer are quite well separated, and the extinction coefficient of the monomer at 682 nm can be estimated from the dilute dye solutions where the Lambert-Beer law is followed ($\epsilon_m^{682} = 3.56 \times 10^4$

$\text{mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$; $\epsilon_d^{648}=2.30 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$. From these values the equilibrium constant K was estimated.

$$K = [\text{dimer}]/[\text{monomer}]^2$$

At dimerization (in the concentration range of $1 \times 10^{-6} - 2.62 \times 10^{-5} \text{ M}$), the absorption at 682 nm of the monomer decreases in intensity whereas the intensity of the absorption of the dimer at 648 nm, increases. The fractions of monomer and dimer and the equilibrium constant K values for this phthalocyanine are summarized in Table I. The high value of K ($6.336 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$) suggests the feasibility of achieving dye aggregation even in dilute solutions of the dye. If aggregation dominates at high dye concentrations, one would expect a square dependence on the monomer concentrations. Indeed the plot of $\log [\text{dimer}]$ versus $\log [\text{monomer}]$ was linear with a slope of 2. The plot is illustrated in Fig. 4.

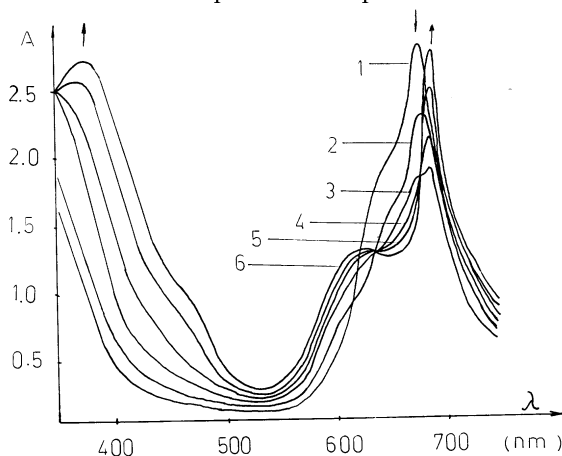


Fig. 4. Plot of $\log [\text{dimer}]$ versus $\log [\text{monomer}]$ for solutions of Pc16 in DMSO.

TABLE I. Fractions of monomer and dimer and equilibrium constant K for Pc16 in DMSO

Pc16 mM	A_D 648 nm	A_M 682 nm	[M] mM	[D] mM	$K \times 10^{-6}$ $\text{mol}^{-1} \text{ dm}^3$
1	0.483	0.665	0.187	0.21	5.99
0.357	0.673	0.758	0.213	0.292	6.408
0.575	0.816	0.829	0.233	0.354	6.503
11.1	0.918	0.893	0.251	0.399	6.333
26.12	1.108	0.971	0.273	0.481	6.45

Average media = $6.336 \times 10^6 \text{ mol}^{-1} \text{ dm}^3$

For such dimers, the exciton model requires the oscillator strength of the dimers to be twice as large as that of the monomer. In the Pc16 case, this ratio (deduced from the integrated absorptivities of the 648 nm band) calculated by a TURBO-PASCAL program is 2.01.

The spectral evolution of a solution of Pc16 in DMSO upon addition of TMPyP is shown in Fig. 5. The interactions between both reagents cause the destabilization of the HOMO of the porphyrin. In fact, the E_B-E_Q parameter of the porphyrin (where E_B is the energy difference of the Soret band for TMPyP before and after the interaction with Pc16) and E_Q is the energy difference for the Q-band of the same porphyrin before and after interaction with the phthalocyanine^{1,32} decreased from 4545 cm^{-1} to 4373 cm^{-1} on aggregation with phthalocyanine. Similar calculations were reported by Shelnutt.^{26,27} Due to its negative charges, the phthalocyanine is able to neutralize the positive charges of the porphyrin. The Job method has been used to determine the stoichiometry of the mixed complexes.²⁸⁻³¹ It relies on the fact that the absorption of a mixture of chromophores, which do not interact with each other, is the sum of the absorptions due to each chromophore separately. Departure from the value of $F(x)$ parameter (additivity of the absorption of a mixture of $x\text{ mol/l}$ of Pc16 and $(1-x)\text{ mol/l}$ of TMPyP, in molar absorption units) as the composition of the solution is continuously varied can be interpreted as evidence of complex formation.

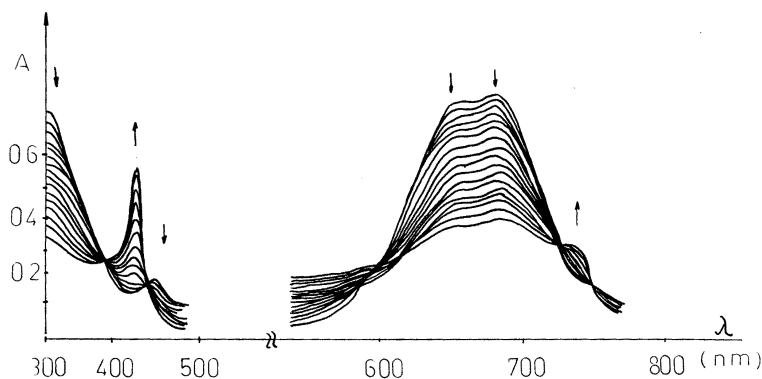


Fig. 5. The spectral evolution of a solution of Pc16 $2.1 \times 10^{-4}\text{ M}$ in DMSO upon titration with a solution of TMPyP $0.207 \times 10^{-3}\text{ M}$.

Job diagram is obtained by plotting $F(x)$ as x (the mole fraction of phthalocyanine) is continuously varied. In practice, the absorptions measured at a given wavelength for mixtures with various ratios of porphyrin and phthalocyanine have been used to calculate the expression:

$$F(x) = d(x) - (\epsilon_{\text{Pc}} - \epsilon_{\text{P}})x - \epsilon_{\text{P}}$$

where: $x = [\text{Pc}] / ([\text{P}] + [\text{Pc}])$, is the mole fraction of phthalocyanine Pc and ϵ_{Pc} are the molar absorptivities of the phthalocyanine and of the porphyrin, respectively, and $d(x)$ is the actual optical density of the solution divided by the total concentration of chromophores.

In our case the Job diagram shows three slopes:

– for $x < 0.5$, $F(x)$ varies linearly with x ;

- for $x > 0.5$, the evolution has two distinct linear stages with an intersection at 0.87, Fig. 6.

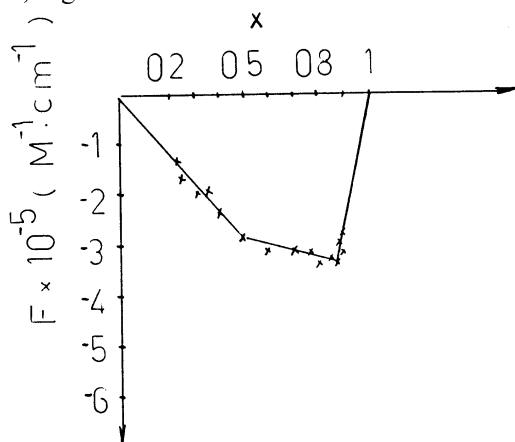


Fig. 6. The Job diagram for the TMPyP/Pc16 system.

The association constants for the phthalocyanine/porphyrin system were determined by the method described in one of the previous paper.²³ The formation equilibrium constants for these complexes can be calculated from this diagram:

$$K_d = [\text{PPc}]/[\text{P}][\text{Pc}] = 0.137 \times 10^5 \text{ mol}^{-1} \text{ dm}^3$$

$$K_T = [\text{PPc}^2]/[\text{P}][\text{PC}]^2 = 8.145 \times 10^{10} \text{ mol}^{-2} \text{ dm}^6$$

DMSO is a strongly coordinating solvent with a high donor number.²² It has both a "hard" site (the oxygen atom) and a "soft" one (the sulphur atom) and it is

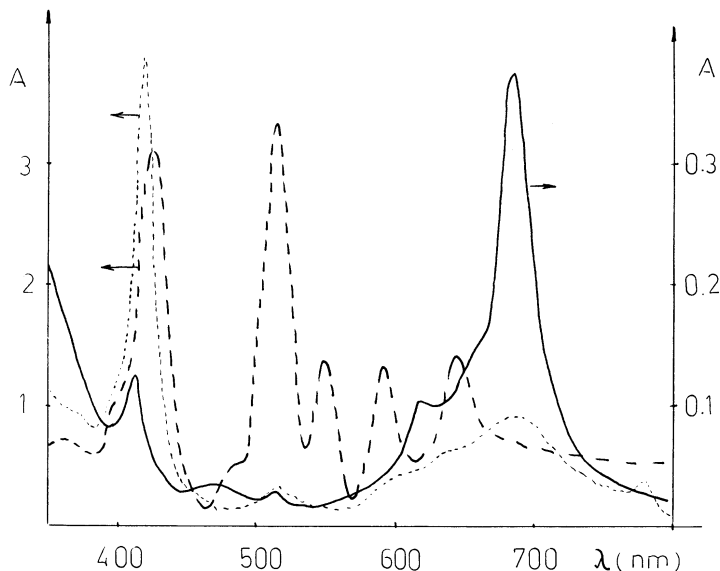


Fig. 7. The absorption spectra of TMPyP/Pc16 system in the diad (...) and triad (—) configurations; (---) TMPyP.

able to coordinate most transition metal ions and also the central metal from porphyrins or phthalocyanines macrocycles.^{24,32,33}

When TMPyP is dissolved in DMSO (in the complete absence of the dimerization processes³⁷⁻⁴⁰), each porphyrin molecule is located between two DMSO molecules through hydrogen bonds between the NH groups inside the macrocycle and the oxygen atom from DMSO. These hydrogen bonds can be detected by the red shift of the Soret band (3–5 nm) and the blue shifts of the Q bands of the porphyrin (2–4 nm) in DMSO with respect to the same porphyrin in other solvents.²⁴ When the phthalocyanine comes in contact with porphyrin, the hydrogen bonds porphyrin–DMSO are broken and the porphyrin again becomes planar and it is able to form heterodimers and heterotrimers with one phthalocyanine in the first case (1:1 stoichiometry) and two phthalocyanines separated by a porphyrin in the second case (1:2 stoichiometry). In this case, both the coulombic attraction between the charged substituents and the π – π interaction between the aromatic macrocycles act to hold the individual components together.^{21,23,25}

The Q band of the phthalocyanine at 684 nm will become less intense and broader until it also disappears, Fig. 7. The wavelength shift (51 nm) of the Q (0,0) band of the porphyrin (from 517 nm) of a face-to-face configuration relative to that

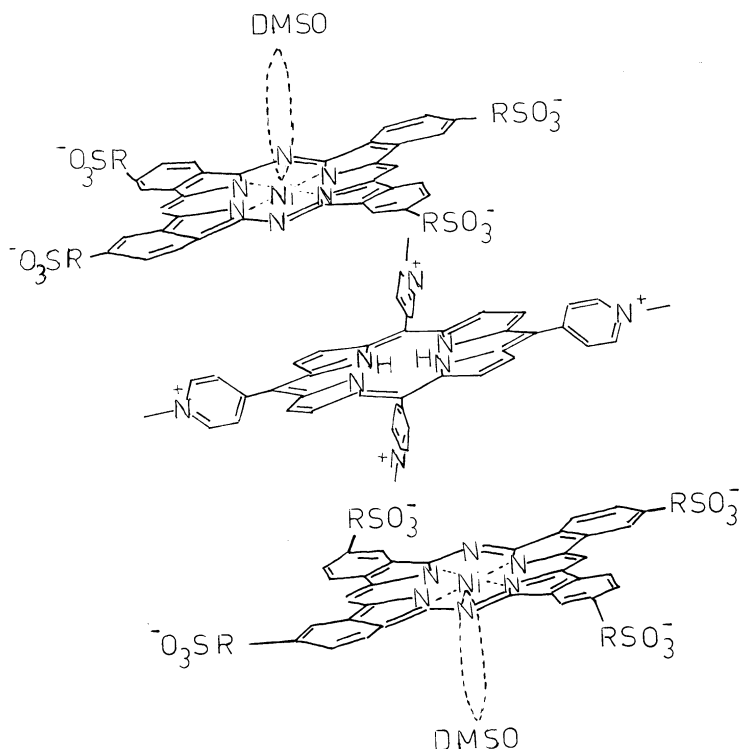


Fig. 8. The proposal spatial configuration of Pc16/TMPyP heterocomplex in DMSO.

of the corresponding monomeric porphyrin is strongly affected by the distance between the two components. A heteroaggregate with shorter distances between the components exhibits a larger shift of the Q (0,0) band of the porphyrin (from 517 nm).³⁶ Also, in the case of the face-to-face dimer, a red shift of the Soret band was observed and explained in terms of charge-transfer interaction between the two-rings.⁴¹ The heteroaggregation will occur only between N⁺ substituents from the porphyrin and the sulfonated ones in the 4,4',4'',4''' positions of the phthalocyanine ring.³⁵ The existence of axial binding of solvent molecules (DMSO) on the central metal will hinder the attachment of new chromophores to a pre-existing heterodimer or heterotrimer. It is well known that the porphyrin molecules are about 30 Å in diameter and the distance between the positive charge sites of the acceptor molecules varies from 5 to 7 Å.²⁸⁻³¹ Since the studied compound have large macromolecular conjugated ring systems, as well as two sterically hindered groups, the actual centre-to-centre distance should be much larger than 7 Å. This aspects will be reported subsequently. The proposed structure for such hetero-aggregated structure is shown in Fig. 8.

CONCLUSIONS

This study concerning the heteroaggregation of opposite charged porphyrins and phthalocyanines gave evidence of well-defined heterodimer and heterotrimer. All these aggregated forms were established for the first time for such a porphyrin-phthalocyanine pair.

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ИЗВОД

СУПРАМОЛЕКУЛСКА СПАЈАЊА ПИРИДИЛ ПОРФИРИНА И ДИАЗАДИТИА ФТАЛОЦИЈАНИНА

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У овом раду први пут је констатовано стварање мешовитих комплекса између катјонског порфирина 5,10,15,20-тетра-*N*-метил-пиридинијум-*p*-ил порфирина (ТМРyP) и новог метал фталоцијанина са четири 16-то члана диазадитиа макроцикла (означеним у овом раду као Pc16) у циљу добијања активног комплекса који показује интензивну апсорпцију у делу видљивог спектра ниже енергије и већу осетљивост при фотодинамичкој терапији канцера. Утврђени су константа димеризације за Pc16 и однос између осцилаторних веза за мономерни и димерни облик овог једињења. Однос ових осцилаторних веза је 2,01 и указује на сигуран процес димеризације. Job-ов математички модел омогућава утврђивање стехиометрије и константи стварања хетероагрегата између порфирина и фталоцијанина (дијада између једног молекула фталоцијанина и једног молекула порфирина и тријада између два молекула фталоцијанина и само једног молекула порфирина). Кулонске интеракције као последица π-π интеракција два високо

конјугована макроциклична молекула као и интеракције између супституената фаворизује геометрију лицем-у-лице.

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