Association Complexes between Cationic Metallophthalocyanines and Anionic Metalloporphyrins I: Spectrometric Studies of Electronic Interactions†

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The formation and spectroscopic properties of several metalloporphyrin−metallophthalocyanine complexes have been investigated. The complexes consist of negatively charged tetrasulfonatophenyl or tetracarboxyphenyl porphyrins in ion pairs with positively charged crown ether substituted metallophthalocyanines. The positive charge was delivered to the modified phthalocyanine molecules by inserting potassium ions into the crown ether cavities. The complexes were formed by mixing the constituent tetrapyrrole compounds in DMSO or ethanol. UV−vis spectrophotometric studies of the ground-state complexes showed loss of the metallophthalocyanine spectrum and the appearance of new spectral bands at longer wavelengths, indicating strong electronic coupling between the components. Analysis of the porphyrin−phthalocyanine complex by the method of continuous variations revealed formation of dimeric and trimeric species. Cyclic voltammetric and spectroelectrochemistry experiments indicated a degree of partial charge transfer character for the ground-state complexes. The free-base/free-base complex showed emission only from the charge transfer state, regardless of the excitation wavelength. The lifetime of the charge transfer state was 3.65 ns. Ultrafast transient absorption studies of the free-base/free-base complex showed that the charge transfer state was fully formed in less than 5 ps after excitation at either 400 or 720 nm. The observed transients were independent of the excitation wavelength and showed little decay on the 500 ps time scale, consistent with the observed fluorescence lifetime.

Introduction

The nature and properties of the "special pair" in the photosynthetic reaction center has stimulated intense investigation of model systems that might mimic its photoproperties. The quasi co-facial geometry of the special pair has led to investigations of a number of co-facial assemblies of metallotetrapyrrole (MTP) compounds. In such systems, the molecules have been linked through oligomeric chains[1,2] or spacers,[3] joined by chelating a common metal ion,[4−6] or self-assembled via axial ligands[7] forming in some cases co-facial multistacks.[8] Another way of building a co-facial complex between two MTPs has been to use ion pair interactions between oppositely charged components.[9−16] In such cases, the electrostatic attractions between the charged substituents and the hydrophobic interaction of the aromatic macrocycles cooperate in holding the individual species in close proximity such that extensive orbital overlap can occur. Formation of complexes between oppositely charged porphyrins has been reported.[10,17,18] In contrast to the natural photosynthetic systems where the absorbed light wavelength extends from UV to near-IR,[19] the porphyrin systems display absorptions restricted by the transitions of the Soret band in the UV around 400 nm and low-intensity Q-bands in the 500−650 nm region.[20] Complexes between metalloporphyrins (MP) and metallophthalocyanines (MPc) are particularly intriguing since MPcs are easier to reduce and oxidize than porphyrin macrocycles,[21,22] and the absorption bands of the two families occur in different spectral regions. Formation of complexes consisting of negatively charged tetrasulfonated tetraphenylporphyrins and either tetrakis (3-methylpyridyloxy)phthalocyanine or tetrakis (*N*-methylpyridino)-porphyrazines has been reported.[23,24] Interpretation of the spectral properties of the ground states of such complexes relies on molecular exciton theory and/or electron donor−acceptor complex theory.

The molecular exciton model was defined by Kasha [23] as the resonance interaction between the excited states of weakly coupled supramolecular systems. In this model, the intermolecular interaction in an aggregate is expressed by a sum of multipoles (dipole−dipole, quadrupole-quadrupole, octapole-octapole, dipole−quadrupole, etc.). Since electronically excited states usually possess electric-dipole character, it is reasonable to use only the dipole−dipole term in the exciton model as an approximation. If a pair of degenerate dipolar states on one chromophore interacts with a similar pair on the other chromophore, the nature of exciton coupling and the energy of the resulting states will depend on the dimer geometry.[24]

If the formed complex involves an electron acceptor and an electron donor with electronic interactions between the components, a new absorption band, which is characteristic of neither the donor nor the acceptor, is commonly observed.[25] This charge-transfer band is attributed to a donor−acceptor complex formed by the partial or complete transfer of an electron from donor to acceptor.[26] Mulliken developed the theory of donor−acceptor interaction and charge-transfer spectra.[27]

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The wave functions of the ground and excited states of the donor−acceptor complex can be written as

$$\psi_N(D,A) = a\psi_0(DA) + b\psi_1(D^+A^-)$$

$$\psi_E(D,A) = a^*\psi_0(DA) + b^*\psi_1(D^+A^-)$$

where ψ_0 is the no-bond wave function of the donor−acceptor structure and ψ_1 is the dative-bond wave function for the D^+A^- structure, in which an electron is transferred from the donor to the acceptor. In case of weak interactions in the donor−acceptor complex, $a^* \approx a \approx 1$ and $b^* \approx b \approx 0$.

There has been a continuing interest in this laboratory in characterizing the excited-state dynamics of molecular associations created via electrostatic interactions,[5,6,28−33] and here we extend this to co-facial porphyrin−phthalocyanine complexes. In these studies, positively charged entities were generated from MPc molecules carrying a crown-ether cavity on each of the four benzo-residues and doping the crown with potassium ions. This allowed us to selectively introduce a Coulombic interaction in addition to the hydrophobic interactions between the molecules in polar solvents. This paper is concerned largely with spectrometric, spectro-electrometric, and steady-state fluorescence properties of complexes formed between such K^+-doped phthalocyanines and anionic porphyrins; the succeeding paper is largely concerned with the excited-state dynamics of such complexes.

Experimental Section

Materials. The solvents dimethyl sulfoxide (SPECTRANAL, >99.7%, Aldrich), ethanol (95%, McCormick Distilling Co.), methanol (99%, Fisher), acetonitrile (99%, Aldrich), ethylene glycol (99%, Fisher), dimethylformamide (99%, Aldrich), dichloromethane (99%, Aldrich), and chloroform (99% Fisher) were used as received. Gases (Ar, O_2) were obtained from Liquid Carbonic. Benzo-18-crown-6 (Alfa Aesar), Ni(II) tetrakis(4-sulfophenyl)−porphine, Cu(II) tetrakis(4-sulfophenyl)−porphine, *meso*-(4-carboxylphenyl)−porphine, Ni(II) (4-carboxylphenyl)−porphine, Cu(II) (4-carboxylphenyl)−porphine, Zn(II) (4-carboxylphenyl)−porphine, and Co(II) (4-carboxylphenyl)−porphine were obtained in the highest available purity grade and were used without further purification.

Metal-substituted 18-crown-6 tetra-substituted phthalocyanines (metals were Co, Cu, Zn, 2H) were synthesized by Nikolaitchik.[5,6] Nickel 18-crown-6 tetra-substituted phthalocyanine was synthesized by refluxing benzo-18-crown-6 dinitrile [34] and nickel acetate in ethylene glycol for 6 h. Purification of benzo-18-crown-6 dinitrile was finished by column chromatography on neutral alumina. Monitoring of the useful fraction was accomplished by irradiating the column with a UV lamp at 368 nm. The desired product had blue luminescence and could be easily distinguished from the other components. The nickel 18-crown-6 tetra-substituted phthalocyanine synthesis procedure was similar to the one described by Kobayashi and Lever.[35] Ni 18-crown-6 tetra-substituted phthalocyanine: ^{1}H NMR ($CDCl_3$) δ 8.02 (8 H, m), 4.7−3.6 (80 H, m). Purification of the nickel substituted 18-crown-6 tetra-substituted phthalocyanine was accomplished by chromatography on basic alumina with a chloroform-ethanol mixture. The ratio of the components in the mixture was gradually varied from 1% ethanol to 8% ethanol or until the desired separation was achieved.

Iron powder (Aldrich), iodine (Aldrich), bromine (Aldrich), magnesium sulfate (Aldrich), copper cyanide (Aldrich), and sodium hydroxide (Fisher) were used without further purification.

Platinum gauze, 100 mesh (Aldrich) was used as a working electrode in the spectroelectrochemical studies.

Column chromatography medium neutral alumina (Scientific Adsorbents Incorporated) and basic alumina (Scientific Adsorbents Incorporated) were used as received. The columns were wet packed following standard procedures.

Preparation of the Free-Base Complex for Transient Absorption Studies. An ethanol solution of H2TPPC (50 μM), H2crPc (100 μM), and KCl (10 mM) was prepared. Under these conditions, the Job procedure leads to the conclusion that trimeric complexes (ratio of porphyrin to phthalocyanine was 1:2) were the preponderant species present.

Procedures. *UV−Vis Spectrometric Studies.* All spectroscopic measurements were performed at ambient temperature using a 0.1 or 1 cm path length quartz cuvettes. The ground-state absorption spectra were recorded on either a double beam scanning spectrometer (GBC) with a resolution of 1.5 nm or a home-built spectrometer employing an Ocean Optics CHEM2000 2048-element linear CCD-array fiber optic spectrometer (350−900 nm) with an LS-1 tungsten halogen light source (Ocean Optics Inc.) optimized for the VIS−NIR (360 nm-2 mm). In each measurement, the sample was referenced to a background measured using a matched cuvette containing pure solvent. The recorded spectra were imported into ASCII format and stored on a disk. All spectrophotometric titrations were conducted in a 1 cm quartz cuvette. For all titration series, the concentration of titrate was 10 μM, and the concentration of titrant was 1 mM.

Spectroelectrochemistry. Electrochemical oxidations and reductions (controlled-potential coulometry) were carried out by using a BAS 100W electrochemical system. A standard three-electrode system was used. Potassium acetate or potassium chloride was used as a supporting electrolyte. A homemade spectroelectrochemical cell was used in the experiments. The cell consisted of a 1 mm rectangular screw top spectrophotometric cuvette that was screwed into the bottom of a Teflon beaker. Platinum gauze, 100 mesh, woven from 0.07 mm diameter wire was used as a transparent working electrode. The electrode was placed in a 1 mm spectrophotometric cell and connected to the potentiostat output by a platinum wire. The potential applied to the electrode produces reduced or oxidized species that diffuse away from the wire electrode to saturate the 1 mm layer of the solution inside the spectrophotometric cell. The absorption spectra of the sample are taken until the potential induced spectral evolution is complete. It usually takes 1 or 2 min for the equilibrium to establish. This time may vary with the solvent. The spectroelectrochemical cell filled with pure solvent was used as a reference.

Time-Correlated Single Photon Counting. Luminescence lifetimes were obtained with a single photon counting spectrofluorimeter from Edinburgh Analytical Instruments (FL/FS 900). The temperature in the fluorimeter was maintained at 25 °C (±1 °C for all measurements with a Neslab RTE−111 circulating bath). The excitation was accomplished with a nanosecond flashlamp operating under an atmosphere of H_2 gas (0.50−0.55 bar, 0.7 nm fwhm, 40 kHz repetition rate). The flashlamp was optically coupled to a monochromator (2 nm), and the emission was gathered at 90° and passed through a second monochromator (2 nm). The luminescence was measured with a Peltier-cooled (−30 °C), R955 red-sensitive photomultiplier tube (PMT). The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using software provided by Edinburgh Instruments and MicroCal Origin software package.

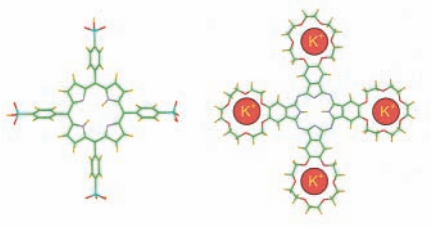

Figure 1. Models of free-base tetrakis(4-sulfonatophenyl)−porphine (left panel) and free-base 18-crown-6 tetrasubstituted phthalocyanine (right panel).

Transient Absorption Spectroscopy. The laser system and apparatus for the ultrafast transient absorption spectroscopy experiments has been described elsewhere.[5] Recent modifications have incorporated an optical chopper to modulate the excitation beam in order to switch the sample between excited and ground states at a frequency of 15 Hz. The continuum was coupled into a 400 μm fiberoptic cable after the sample cell and thereafter input into the CCD spectrograph (Ocean Optics, SD2000 or Control Development) for time-resolved spectral information (380−780 nm). The CCD spectrograph was externally triggered by the chopper in order to distinguish between the continuum spectra corresponding to the ground or excited states of the sample. Typically, 500 excitation pulses were averaged to obtain the transient spectrum at a particular delay time. The CCD spectrograph, the delay line, and the shutters were driven by a computer-controlled system. In-house LabView (National Instruments) software routines allowed automatic spectral acquisition over a series of delay line settings. Kinetic traces at appropriate wavelengths were assembled from the accumulated spectral data. The instrument rise time of the ultrafast spectrometer was ca. 250 fs. The sample solutions were prepared to have an absorbance of 1.2−1.4 at the excitation wavelength in the 2 mm flow cell. The absorption spectra of the solutions were measured before and after the experiment to check for possible sample decomposition.

Results

Absorption Spectrometric Studies. The structures of the metalloporphyrins (MP) and metallophthalocyanines (McrPc) employed in this work are shown in Figure 1. Mixtures of the oppositely charged compounds were studied by UV-vis spectrometry. Figure 2 represents the spectral evolution of a DMSO solution of Ni(II) 18-crown-6 tetra-substituted phthalocyanine (NicrPc) (10 μM) upon incremental addition of a 1 mM Ni(II) Tetrakis(4-sulfonatophenyl)−porphine (NiTPPS) in DMSO. Prior to the addition of the porphyrin, a solution of 1 mM potassium acetate or potassium chloride was made. In the absence of K^+ ions, the spectral behavior seen in Figure 2 was not observed, and the absorption spectrum of the mixture was simply the sum of the component monomer spectra. In another experimental series, the sequence was reversed, viz., the phthalocyanine was titrated into the porphyrin. The typical spectral changes in this series are shown in Figure 3. The results of identical titrations for NicrPc with CuTPPS, CucrPc with CuTPPS, and CucrPc with NiTPPS in DMSO solutions were very similar to those obtained for the titrations of NicrPc with NiTPPS (Figures 2 and 3), and the details are not shown. In all cases, the major effects were small blue shifts of the porphyrin Soret band, complete loss of the McrPc Q-band and the appearance of a new band in the red spectral region.

In contrast to the metal-centered systems described above, titration of the free-base tetrakis(4-sulfonatophenyl)−porphine (H2TPPS) and the K^+-doped free-base, Co(II) or Zn(II) 18-crown-6 substituted phthalocyanines, showed different behavior, whether in DMSO, ethanol, methanol, or water solutions. Although the spectral changes observed for these free-base porphyrin systems were similar to those described above for the metal-centered systems, the isosbestic points were considerably smeared, and the absorption spectra continued to evolve even after several minutes following vigorous mixing of the components in the system. However, the replacement of H2TPPS with the free-base *meso*-tetrakis(4-carboxylphenyl)−porphine (H2TCPP) resulted in the formation of stable porphyrin−phthalocyanine spectra in both ethanol and methanol. The results of a spectrophotometric titration of H2TCPP with H2TPPS are shown in Figure 4. The results for the titration of CocrPc with H2TPPC in ethanol were very similar to those shown in Figure 4; addition of CocrPc to H2TCPP produced a 4 nm red shift of the porphyrin Soret band, and addition of H2 porphyrin to CocrPc resulted in loss of the phthalocyanine Q-band and the appearance of a new red band.

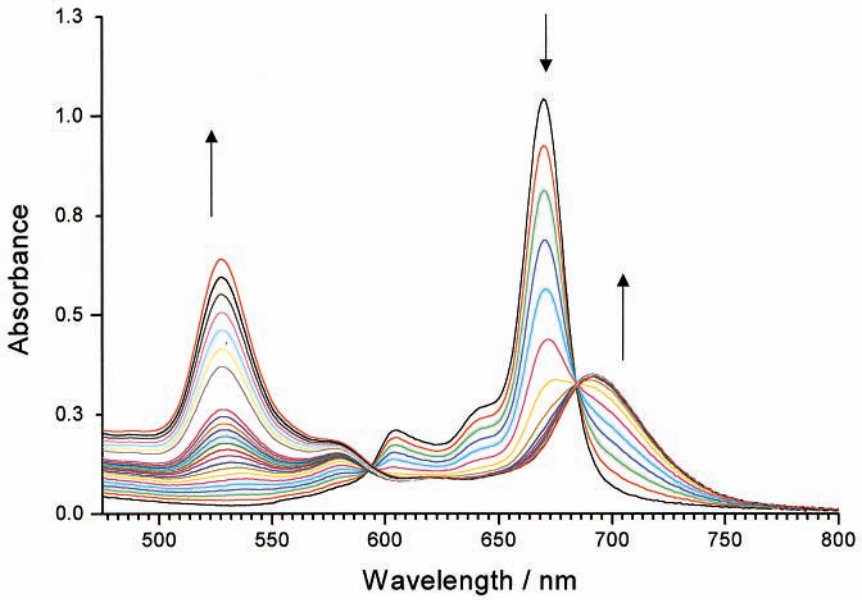

Figure 2. Evolution of the absorption spectrum of NicrPc upon addition of NiTPPS in DMSO.

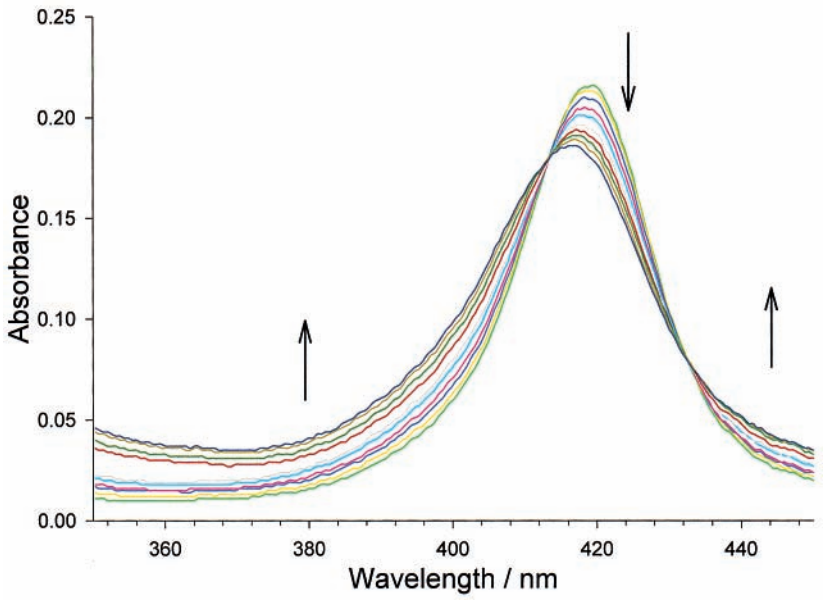

Figure 3. Evolution of the absorption spectrum of NiTPPS upon addition of NicrPc in DMSO.

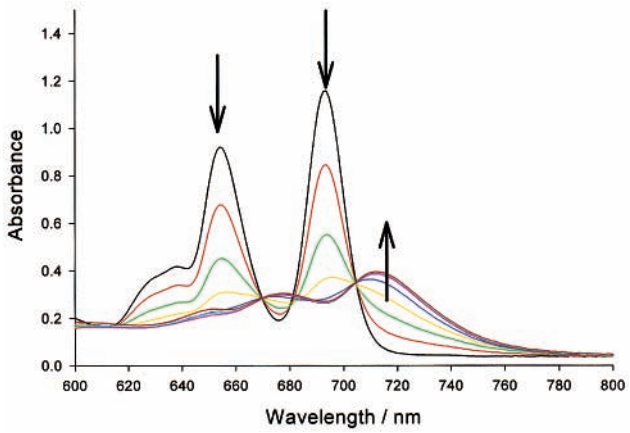

Figure 4. Evolution of the absorption spectrum of H2crPc upon addition of H2TPPC in ethanol.

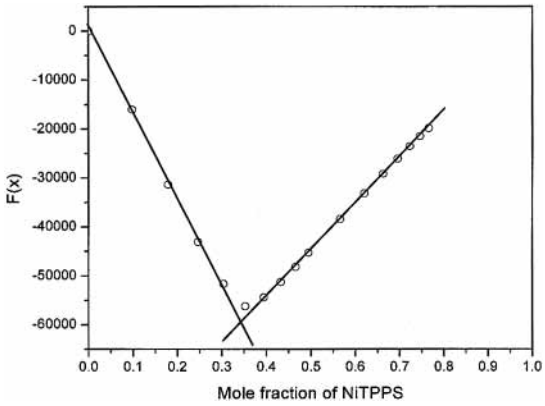

Figure 5. Job's plot for the NiTPPS−NicrPc complex in DMSO measured at 670 nm.

Job Plots. The most commonly used method to determine the stoichiometry of molecular complexes is that due to Job.[36] This method, also called the method of continuous variation, is a straightforward and effective approach to the determination of the complex stoichiometry. It relies on the fact that the absorbance of a mixture of chromophores that do not interact is equal to the sum of absorbances of the chromophores separately. Departure from additivity can be interpreted as the formation of a complex. The amplitude of the departure is recorded versus the composition of the mixture, and the stoichiometry of the complex can be determined by the composition of the mixture at which the deviation from additivity is greatest. The titration data such as those presented in Figures 2 through 4 were used to construct Job plots. The expression employed was

$$F(x) = d(x) - (\epsilon_{pc} - \epsilon_p)x - \epsilon_p$$

where x is the mole fraction of phthalocyanine, ϵ_{pc} and ϵ_p are the extinction coefficients of the phthalocyanine and the porphyrin respectively, and $d(x)$ is the optical density of the mixture at a selected wavelength divided by the sum of concentrations of the chromophores. The parameter $F(x)$ represents the deviation from additivity of the absorbance of a mixture of x M solution of the phthalocyanine and $(1 - x)$ M solution of the porphyrin in molar absorbance units. Job diagrams were obtained by plotting $F(x)$ as x was continuously varied. Figure 5 shows the Job plot for the NicrPc−NiTPPS experiment (spectrometric data from Figure 2). The wavelengths used for the plots corresponded to either the maximum of the phthalocyanine Q-band or the maximum of the porphyrin B-band in order to provide the best signal-to-noise ratio. The Job plots for the systems NicrPc−NiTPPS, NicrPc−CuTPPS, CucrPc−CuTPPS, CucrPc−NiTPPS, and H2crPc−H2TPPC in DMSO all showed phthalocyanine-to-porphyrin ratios of 2:1, when the titrations were conducted starting with pure phthalocyanine. Titration of H2TPPC with CocrPc in ethanol resulted in a Job plot with 1:1 stoichiometry (See Figure 6).

Spectroelectrochemistry. Spectroelectrochemical investigation of NicrPc under oxidizing conditions in acetonitrile generated the spectrum shown in Figure 7 (black curve). Under these conditions, the phthalocyanine Q-band disappears, and a new absorption band at around 720 nm is formed. Very similar results were obtained for H2crPc in acetonitrile, which showed a new absorption band at around 735 nm, corresponding to the oxidized form (Figure 8). Acetonitrile was used as a solvent in these experiments because the phthalocyanine radical cation formation could not be observed in DMSO solutions, presumably due rapid reaction with residual impurities. The absorption

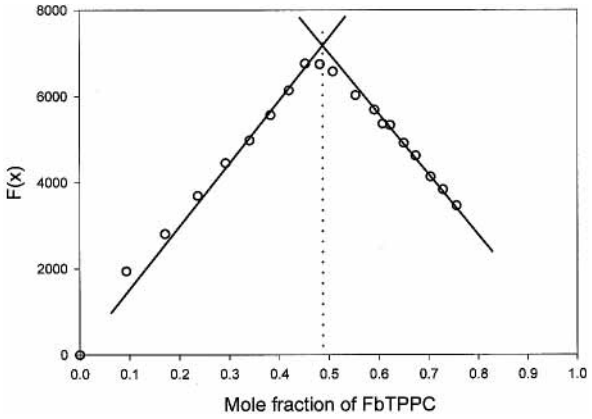

Figure 6. Job's plot for the CocrPc−H2TPPC complex in ethanol measured at 418 nm.

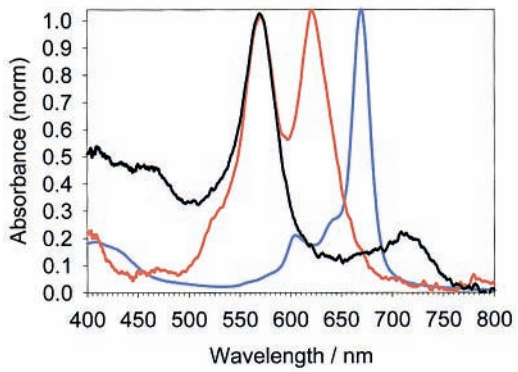

Figure 7. Ground-state absorption spectra (normalized) of neutral (blue), reduced Pc(3-) (red), and oxidized Pc(1-) (black) NicrPc in acetonitrile.

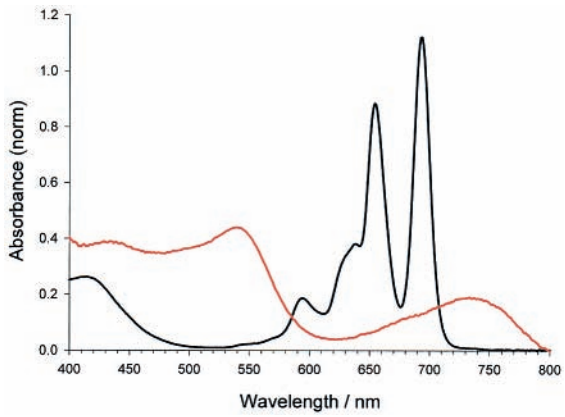

Figure 8. Ground-state absorption spectra of the oxidized (red) and neutral (black) H2crPc in acetonitrile.

spectrum of NiTPPS under reducing conditions (the radical anion) is shown in Figure 9.

Luminescence Studies. Those mixtures containing metallotetrapyrroles with transition metal centers showed no indication of luminescence when excited. The mixture of H2TPPC and H2crPc was the only binary system to show luminescence. The evolution of the emission spectrum of H2TPPC upon addition of H2crPc was studied. The excitation wavelength of 408 nm was chosen for this experiment, as it is the isosbestic point observed in the spectrophotometric titration of the H2TPPC with H2crPc. Thus, the number of absorbed photons was kept constant throughout the titration. A steady-state luminescence experiment showed that the emission spectrum of H2TPPC diminishes in intensity as H2crPc was added incrementally to the system (Figure 10). As the fluorescence of the porphyrin decreased, a new emission band corresponding to the H2crPc−H2TPPC complex appeared near 765 nm, which increased in amplitude as the porphyrin fluorescence diminished. Eventually, the porphyrin fluorescence was totally depleted. An isoemissive point was observed at 740 nm, indicating that a single fluorescent product was formed throughout the titration.

Direct excitation of the mixture of free-base tetrapyrroles into the absorption band at 715 nm resulted in the emission spectrum ($\lambda_{max} = 765$ nm) shown in Figure 11, where the absorption band is also shown.

To examine this fluorescence in more detail time-correlated, single photon counting experiments were performed. The mixture was excited at 410 nm, and the resulting emission decayed in a single exponential manner (Figure 12). The excitation of the complex directly into the charge-transfer band at 715 nm yielded very similar results to those obtained with the 410 nm excitation, the mean luminescence lifetime from both excitation wavelengths (measured at 765 nm) was 3.65 ns.

Femtosecond Transient Absorption Studies Of Free-Base Complex. An ethanol solution of the H2/H2 complex was prepared as described in the Experimental Section. This solution was excited at 400 nm, and an absorbance-wavelength−time dynamic surface was assembled from spectrographic data files recorded at a series of settings of the delay stage, which provided the time axis. Figure 13 presents a spectrum taken at a delay line setting corresponding to 5 ps post zero. This spectrum showed ca. 10% decay over a window of 600 ps, consistent with a lifetime in the nanosecond range.

Discussion

Complexing of Porphyrins and Phthalocyanines. The cavities of the crown ether residues at the periphery of the Pc π systems are capable of acting as ligands for cations of the alkali and alkaline earth metals.[37,38] The degree of penetration into the crown cavity has been shown to depend on the size of the cation. For the 18-crown-6 moieties used here, K^+ ions penetrate deeply into the cavity. This imparts a tetracationic nature to the Pc, thereby providing the potential for the K^+-doped McrPc to participate in electrostatically bound association complexes. This is the basic principle behind the experiments reported here. Figures 2 and 3 show that complexation occurs for the Ni−Ni system; when the K^+ ions were not present, complexation, as indicated by the spectral patterns, did not occur. Thus, the incremental addition of the porphyrin eventually caused the complete suppression of the marker Q-band of the Pc (670 nm), whereas the Soret and Q-bands of the porphyrin suffered only minor shifts (the Soret band of the complex was blue-shifted by ca. 3 nm from that of NiTPPS). In addition, a new spectral band grew in at 690 nm. There are sharp isosbestic points between the Pc spectrum and the new band and between the Pc spectrum and the porphyrin-like spectrum. Figure 3 shows the results of the titration carried out in the reverse sense. This shows a 3 nm blue shift in the spectral maximum as the porphyrin (415 nm) is converted into the complex (412 nm and that an isosbestic point appears at 432 nm between the porphyrin and the complex. The significant inference from these spectra is that a complex is formed as mixing occurs and when fully formed it has absorption bands at 412, 531, 575, and 690 nm. Perhaps the most remarkable ramification is that the complex possesses the full spectral signature of its constituent porphyrin, but the signature of its phthalocyanine constituent has been strongly affected.

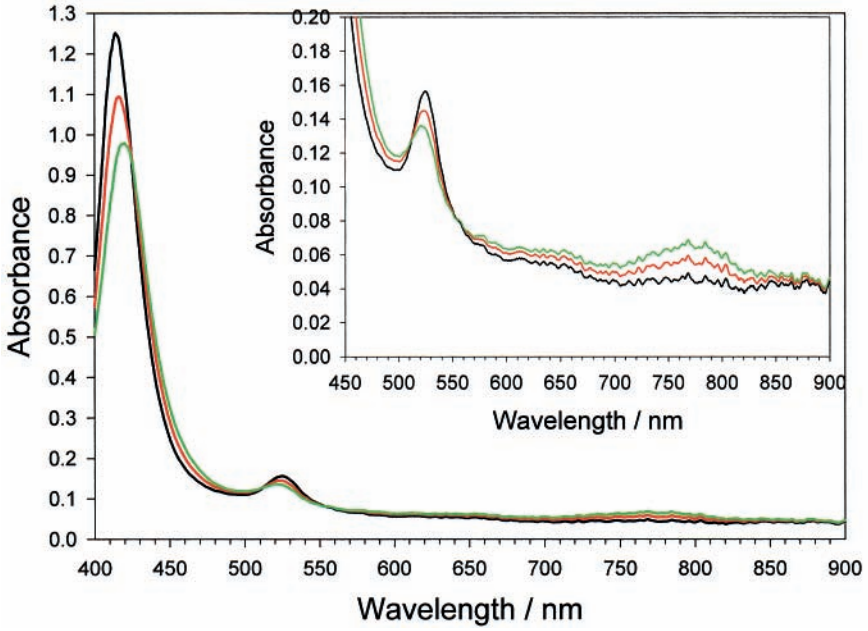

Figure 9. Behavior of the Soret band of NiTPPS in acetonitrile under reducing conditions, the black line represents neutral porphyrin. The inset shows the detail of the 500−800 nm region.

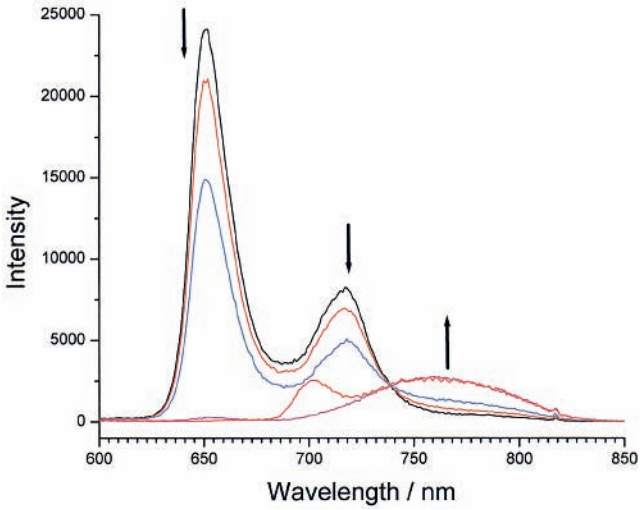

Figure 10. Evolution of the emission spectrum of H2TPPC upon addition of H2crPc, excitation at 408 nm. The black line represents the spectrum of pure porphyrin.

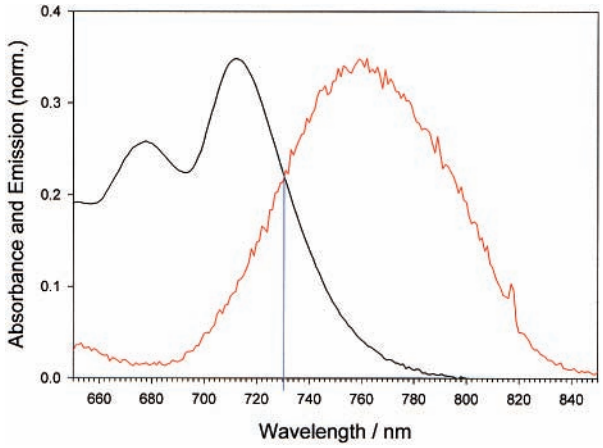

Figure 11. Normalized emission (red) and absorption spectra (black) of the H2TPPC−H2crPc. The excitation wavelength for emission was 408 nm.

When the titration data were converted and plotted in the manner of Job (Figure 5 for the Ni−Ni case), the positive and negative regions converged at a molar ratio of 2:1, in favor of the phthalocyanine. Even though this molar composition was unexpected, the data are clear, and the same behavior was observed for all the pairs when the porphyrins were tetrasulfonated phenyl derivatives and the solvent was DMSO. Scrutiny of Figure 5 shows no evidence of departure from linearity that would indicate the intermediacy of a 1:1 complex, and the conclusion must be that in these systems, the 1:1 complex has an extremely low equilibrium constant. Only in the case of CocrPc−H2TCPP in ethanol was a 1:1 complex observed (Figure 6).

In an effort to understand the origin of the new red band in the complexes (Figure 2), spectroelectrochemical experiments were carried out to examine the spectral properties of electrochemically reduced and oxidized monomeric phthalocyanine molecules. The spectra are shown in Figures 7 and 8. In both NicrPc and H2crPc, the spectra show that the radical cation of the Pc has a distinct maximum between 700 and 750 nm due, presumably to a $\pi-\pi^*$ transition in the Pc radical cation. The fact that the most red bands in both the complexes and the Pc radical cations are in the same spectral region (near 700 nm) implies that the complexes have significant charge transfer (CT) character in the ground state, with a significant contribution from Pc^+. This is supported by the lack of any similarity between the absorption spectra of the complexes and that of the radical anions of the Pc constituents.

If indeed the complexes have CT character in the ground state, one might expect them to have in addition a spectral band reminiscent of the $\pi-\pi^*$ transition in a porphyrin radical anion. Spectroelectrochemical observations on NiTPPS showed that the radical anion spectrum (Figure 9) has a broad absorption band with a maximum near 770 nm, reduced intensity and blue shift (5 nm) at the 525 nm Q-band, and reduced intensity and red shift (6 nm) at the 412 nm Soret maximum. This information, coupled to the observation that the Pc^+ radical also has spectral intensity near 570 nm, is not inconsistent with the above rationalization of the nature of the red band in the complexes.

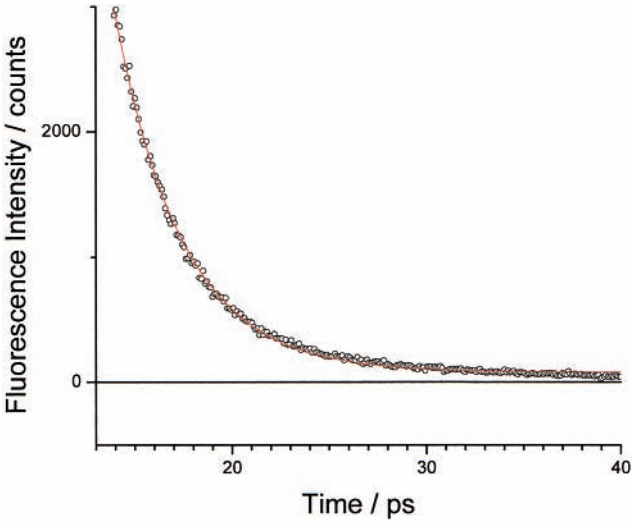

Figure 12. Decay of 765 nm luminescence of H2crPc−H2TPPC complex after 410 nm excitation.

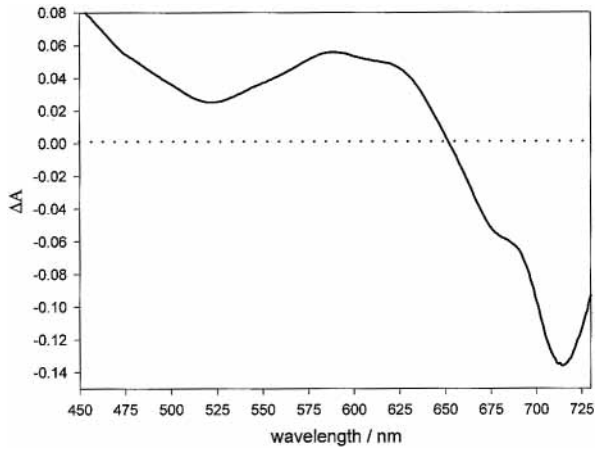

Figure 13. Transient absorption spectrum of the free-base/free-base complex recorded at 5 ps probe delay.

That the Soret band maximum of the reduced porphyrin is slightly red shifted with respect to the Soret band of the neutral species is in agreement with the results obtained for H2TPPC−H2crPc and H2TPPC−CocrPc complexes where red shifts at the Soret maxima were observed. However, the blue shift of the porphyrin B-band observed during the spectrophotometric titration for NicrPc−NiTPPS, NicrPc−CuTPPS, CucrPc−CuTPPS and CucrPc−NiTPPS systems seems to be at odds with the above argument. It appears that there is another factor contributing to the spectral changes. It could be noticed from the ground-state absorption spectra that there is some degeneracy for $S_0 \rightarrow S_2$ transitions of porphyrins and phthalocyanines, meaning that there should be exciton coupling in the complexes. Exciton theory [23] predicts that the monomeric tetrapyrrole orbitals interact in the dimer, generating a pair of orbitals that are separated in energy by an amount that depends on the distance between the macrocycles. In face-to-face homodimers, theory predicts that optical transitions between the ground state and the lower exciton state are symmetry-forbidden. The transition dipole for the $S_0 \rightarrow S_2$ transition for the phthalocyanine is smaller than that for the $S_0 \rightarrow S_2$ transition for the porphyrin. Therefore, the transition to the lower-lying excited state will not be forbidden but will occur with lower probability than the transition to the higher-lying excited state of the complex. This can be observed as the spectral broadening and the blue shift of the porphyrin Soret band. Consequently, two types of interactions between the porphyrin and the phthalocyanine determine the position of the Soret band of the complex. Since the charge transfer interactions and the exciton coupling tend to generate the opposite spectral shifts, the experimentally observed red and blue shifts in the spectra must be the resultant of exciton coupling and charge-transfer interactions.

The spectrophotometric data reported here indicate that strong complexes are formed between the ground states of porphyrins and phthalocyanines in polar solvents. The driving force for complex formation is electrostatic attraction between the oppositely charged groups. Once the complexes are formed, the mutual proximity of the orbitals allows charge-transfer interactions to occur, as evidenced by the appearance of a new band at wavelengths to the red side of the low-lying Pc Q-band. Although these electron donor−acceptor interactions and the hydrophobic interactions between the tetrapyrrole π-systems might be thought to be sufficient in themselves to generate the observed spectra, this is clearly not the case because mixing of the porphyrins and the phthalocyanines in the absence of potassium ions did not generate the identifying spectral features. Subsequent addition of potassium ions to the system rapidly produced the spectral changes identified with complex formation.

The results obtained here indicate that the direction of the electron transfer in the ground state is from phthalocyanine to porphyrin. This is an interesting observation when one considers that this transfer is against the potential gradient generated by the electrical charges on the molecular contributors to the complex. The field direction would be expected to impede electron transfer from the cationic Pc. These observations are in line with those of Tran-Thi et al.[14] who reported ground state absorption spectra for electrostatic complexes between positively charged porphyrins and negatively charged phthalocyanines. Taken together, these results indicate that the driving force for the complex formation is sufficient to offset any opposing effects of the static electric field.

Turning now to the luminescence measurements of the H2−H2 complex (Figures 10 and 11) it is clear that the addition of the Pc to the porphyrin solution causes emission changes that track the changes in the absorption spectrum. Eventually by adding sufficient Pc the emission of the porphyrin was suppressed and the sole emitting species is the excited state of the complex at 765 nm. This experiment was carried out with 408 nm excitation, close to the peak of the porphyrin-like absorption of the complex. No higher energy emissions arising from the complex were found. Therefore, the excitation of the H2crPc−H2TPPC complex into its higher lying porphyrin-like excited state results in the emission from the CT excited state. The crossing point between the normalized absorption and emission spectra of the H2crPc−H2TPPC complex (Figure 11) can be used to estimate the energy of the 0,0 transition. Taking the wavelength of the transition as 730 nm leads to an energy of 1.70 eV. As seen in Figure 12, the fluorescence lifetime of the CT state was measured as 3.65 ns. Moreover, the facts that the transient absorption spectrum of the H2:H2 complex when excited at 400 nm developed very rapidly (within 5 ps) to that shown in Figure 13 and that no spectral changes other than decay were observed over 600 ps allow the conclusion that the 5 ps spectrum is that of the CT state.

Thus, the only emissive state of the free-base complex is the CT state with the energy of 1.70 eV, and it is formed within a few picoseconds. However, as will be seen in the succeeding paper,[39] there are early picosecond dynamic events in the H2:

H2 complex, as well as all the transition metal centered ones, that can be resolved.

Conclusions

The properties and formation of self-assemblies between oppositely charged tetrapyrroles were studied. Free-base and metal-centered 18-crown-6 modified phthalocyanines were positively charged by filling the crown-ether cavities with potassium ions. Metallo−tetrasulfonatophenyl porphyrins, tetracarboxyphenyl porphyrin, and its metal derivatives were used as negatively charged components in preparation of the complexes. It was shown that stable complexes can be formed in DMSO and ethanol. The ratio of porphyrin to phthalocyanine in the complexes was determined to be 2:1 and 1:1 for different complexes. Ground-state absorption spectra of the assemblies significantly differ form those of monomeric compounds. This indicates strong electronic interactions between the components in a complex. The spectroelectrochemical data obtained for the monomeric compounds suggest that the ground state of the complexes possesses a charge-transfer character. The energy of the charge transfer state of the H2crPc−H2TPPS complex has been estimated to be 1.70 eV. Its lifetime was measured to be 3.65 ns

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