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Crown Ether Substituted Monomeric and Cofacial Dimeric Metallophthalocyanines. 1. Photophysical Studies of the Free Base, Zinc(II), and Copper(II) Variants

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Metallophthalocyanines have been prepared with 18-crown-6 residues at the four peripheral benzo sites (McrPc). Metal centers employed have been H_2 (free base), Zn(II), and Cu(II). In ethanol solution containing potassium acetate, such species incorporate K^+ cations into the crowns, one K^+ per crown, and are monomeric in nature. When cesium acetate is present, Cs^+ cations complex with a pair of crown residues, resulting in cofacial dimer species (McrPcD) in which one Cs^+ ion links two ethers in a kind of sandwich arrangement. This dimerization results in spectral shifts to the blue. Photophysical examinations of these monomeric and dimeric entities have been carried out. For H_2crPc and Zn^{II}crPc the excited-state dynamics are those of the π-macrocycle, and dimer formation caused no major changes except for increasing the rate constants of the excited-state deactivation. Such increases are anticipated owing to the proximity of the lower exciton state and the ground state. For Cu^{II}crPc where now a d^9 metal is present within the π-system, a deactivation event with a 22 ns lifetime was attributed to the decay of the ^4T state of the complex. The corresponding state of the cofacial dimer had a lifetime of 5.7 ns. Ultrafast experiments with ca. 500 fs resolution provided evidence of earlier processes in the Cu(II) system. Thus, in the monomer, a 2.9 ps lifetime event preceded the quartet-state decay. This may be attributable either to the decay of the ^2T precursor to the ^4T state or to the population of a CT state situated between ^2T and $^2S_0$ in energy. Similar early-time behavior was noted for the Cu(II) dimer. Triplet-state properties are reported for the monomeric and dimeric free base and Zn(II) Pcs. Notably, the bimolecular rate constants for O_2 quenching were lower for the dimers compared to the monomers. This can be understood if the dimerization yields a triplet state with an energy lower than that of singlet oxygen, $O_2(^1\Delta_g)$.

Introduction

Metallophthalocyanines (MPcs) are highly stable macrocyclic π-systems that display interesting properties that make them potential candidates for applications in optoelectronics, photoconducting materials, and tumor photodynamic therapy.[2] Such applications are generally related to their efficient light absorption characteristics in the visible and near-infrared regions of the optical spectrum. The properties of phthalocyanines, their derivatives, and assemblies thereof have been characterized using a variety of optical spectrometric techniques including CD, MCD, and fluorescence spectroscopy,[2,3] and in recent years a number of reports concerning the excited-state dynamics of MPcs have appeared in the literature.[4−9] Similar to metalloporphyrins, the central metal has a significant effect on the nature and the lifetime of the excited states of metallophthalocyanines. Thus, excited-state characterization is important in determining possible applications of these compounds.

An interesting property of MPcs is their ability to participate in stacked assemblies with other MPcs or with metalloporphyrins. Investigations of such assemblies[10] have shown that their chemical and optical properties depend largely on the nature of the central metal ion. As with metalloporphyrins, MPcs and their assemblies, where M is a transition metal, frequently display an excited-state relaxation pathway associated with the interactions of the macrocyclic π-system with the d-orbitals of the central metal.[11,12] Such interactions frequently cause the electronic excited states to be short-lived.

In the case of the porphyrins, several strategies have been employed to achieve cofacial dimer formation. One such strategy has been to prepare μ-oxo dimers, an example of which is represented by the work of Gouterman et al.,[13] who employed $(OEPSc)_2O$ and $(TPPSc)_2O$ to study exciton behavior in such systems. A second method that has been employed to bring the π-systems of porphyrins into proximity has been through the synthesis of covalently linked units. These have been extensively studied for their ability to demonstrate oxygen-activating properties.[14,15] Dimers have been prepared containing a pair of porphyrin rings that sandwich between them an octacoordinate metal center (lanthanide or actinide, for example). In a study of sandwich complexes of OEP and TPP with U(IV), Bilsel et al.[16] showed that ground-state repopulation and intersystem crossing occurred in less than 1 ps. The same group earlier had found similar deactivation rates in Ce(IV)-centered porphyrin sandwich dimers.[17] In a similar vein, Tran-Thi et al. characterized the spectroscopic properties and triplet state yield in a Th^{IV}TPP trimer.[18]

Dimeric assemblies of porphyrins with phthalocyanines have been actively studied, and the optical and spectroscopic properties of many of these heterodimers have been reviewed by Tran-Thi.[10] As with the porphyrin homodimers, dimeric (and layer) complexes have been prepared by covalent linking, by sandwich formation, or by self-assembly of ionic systems. In such species excited-state lifetimes are short; and in some cases, ligand-to-ligand charge transfer has been shown to be an effective

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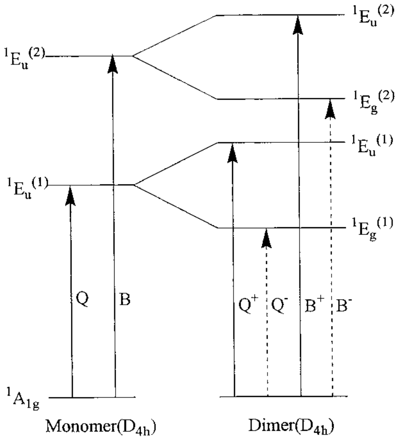

Figure 1. Energy diagram for a monomeric metallophthalocyanine and the corresponding cofacial dimer.

deactivation pathway. Finally, for phthalocyanine homodimers, a Lu(III) bis(phthalocyanine) was shown to undergo rapid excited-state deactivation via a low-lying doublet state having charge-transfer character.[19]

Dimeric assemblies of phthalocyanines, where the participating pair of molecules is arranged in a cofacial manner, can be considered as model systems for cofacially stacked Pc polymers, such as (phthalocyanato)polysiloxanes. These polymers display a variety of interesting properties and have been successfully employed in the fabrication of planar photodiodes and sensors.[20] A significant amount of theoretical work has been conducted in attempts to characterize the electronic structure of cofacial dimers.[13,21] Exciton theory[21] predicts that the monomeric Pc 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 (Figure 1). In face-to-face dimers, theory predicts that optical transitions between the ground state and the lower exciton state are symmetry-forbidden. Under such conditions, the Q-band maximum of the monomeric unit is absent and is replaced by a band that appears at shorter wavelengths (some 30−40 nm to the blue), corresponding to the transition labeled Q^+ in Figure 1. The complete lack of fluorescence in such systems indicates that the upper exciton state rapidly converts to the lower one, which undergoes subsequent nonradiative relaxation, including intersystem crossing.[22] Enhanced intersystem crossing was reported for bis(phthalocyanato)disiloxane dimers,[22] indicating a relatively low internal conversion contribution to the relaxation dynamics of Pc dimers.

An elegant method for preparing cofacial dimers of MPc-based systems is to prepare variants with crown ether residues at the peripheral benzo sites and to use appropriately sized alkali metal cations to "cement" the pair together.[23−26] Phthalocyanines with 18-crown-6 substitution (McrPc) were first synthesized and characterized by Sielcken et al.,[23] while the 15-crown-5 variants were reported by Kobayashi and Lever.[25] In $CHCl_3$ solution such compounds exist in a monomeric form, but upon addition of alkali metal cations such as K^+, the formation of cofacial dimers was noted. The distance between the Pc subunits in these dimers was estimated to be 4.1 Å, which is larger than that in the bis(phthalocyanato)disiloxane dimers (3.3 Å).[27] Steady-state spectrometric techniques such as UV−vis, fluorescence, and CD have been employed for the characterization of crown ether substituted cofacial MPc dimers.[3,23−26] In the present work the synthesis, characterization, and photophysical behavior of monomeric and dimeric phthalocyanines that have been prepared with 18-crown-6 substitution at the four peripheral benzo residues are presented. Central metals substituents were Co(II), Ni(II), Cu(II), Zn(II), and H_2 (free base). In this report photophysical characterizations of the monomer and dimer systems of the Cu(II), Zn(II), and H_2 (free base) are presented. The Co(II) and Ni(II) variants are presented in the adjoining report. Transient absorption spectroscopy with time resolution at the nanosecond and femtosecond levels has been employed to evaluate the dynamics of the repopulation of the ground states and the effect of the central metal thereon.

Experimental Section

Materials. Ethanol and methanol (spectrophotometric grade, Aldrich) were refluxed with CaH_2, distilled, and stored over molecular sieves (3 Å, Aldrich). Potassium acetate (99.98%), cesium acetate (99.9%), benzo-15-crown-5 and benzo-18-crown-6 were purchased from Aldrich. All other reagents were of commercial origin and were used without further purification.

Synthesis of Crown Ether Substituted Phthalocyanines. Metal-substituted 18-crown-6 tetrasubstituted phthalocyanines (M = Co(II), Cu(II), Ni(II)) were synthesized by refluxing benzo-18-crown-6 dinitrile and the appropriate metal acetate in ethylene glycol for 6 h; the procedure used was similar to that described by Kobayashi and Lever.[25] Purification was accomplished by repeated washing of the resulting solid with hot ethanol followed by chromatography on basic alumina with $CHCl_3$−EtOH (15:1 by volume). Free-base 18-crown-6 tetrasubstituted phthalocyanine was synthesized by refluxing benzo-18-crown-6 dinitrile in (*N*,*N*-dimethylamino)ethanol under NH_3 for 20 h, using the procedure described by Sielcken et al.[23] The solvents used followed the prescriptions of the original authors.[23,25] Zn(II)-substituted 18-crown-6 phthalocyanine was synthesized by refluxing free-base 18-crown-6 tetrasubstituted phthalocyanine and anhydrous zinc acetate (Aldrich, 99%) in 1,2-dichloroethane/ethanol (3:1) under argon for 2 days in the dark. This was followed by repeated washing with water and then chromatography on basic alumina with $CHCl_3$−EtOH (15:1 by volume). The optical absorption spectra of the 18-crown-6 tetrasubstituted phthalocyanines were identical to those reported previously.[23]

15-Crown-5 tetrasubstituted phthalocyanines were synthesized from benzo-15-crown-5 dinitrile using a procedure described by Kobayashi and Lever.[25] The UV−vis spectra of the synthesized phthalocyanines were identical to those reported previously.[25]

Steady-State Absorbance and Fluorescence Measurements. Steady-state UV−vis spectra were collected with a GBC 918 spectrophotometer. Fluorescence spectra were obtained using a Spex Fluorolog 2 spectrofluorometer. For the S_1 fluorescence quantum yield measurements, $Zn^{II}Pc$ in 1-propanol was used as a reference (632 nm excitation, $\phi_f = 0.45$).[28] For the S_2 emission quantum yield measurements, a solution of anthracene in EtOH was used as a reference ($\phi_f = 0.23$, 25 °C).[29]

Singlet O_2 emission spectra from the phthalocyanine solutions were obtained using a Bruker ISF 55 FTNIR spectrometer modified to operate in the emission mode. A liquid N_2-cooled Ge detector/amplifier combination (Applied detector Corp., model 403HS) was used to monitor the near-IR signals. Sample excitation was accomplished using a 50 mW beam at 632.8 nm from a continuous wave (cw) HeNe laser (Spectra-Physics model 127). The final spectrum was obtained by averaging 128 individual scans.

Flash Photolysis Experiments. Nanosecond flash photolysis studies were performed using a kinetic absorption spectrometer system described previously.[30] In some cases the third (355 nm) or second (532 nm) harmonic of a Q-switched Nd:YAG laser (Continuum Surelite I) was used for excitation. The excitation pulse width was ca. 7 ns. In other cases excitation at 605 nm was accomplished using an OPOTEK MagicPrism optical parametric oscillator pumped by the third harmonic of the Nd:YAG laser. Typical excitation energies were a few millijoules per pulse. The computer-controlled kinetic spectrophotometer used for monitoring the transient spectra and time profiles has been described previously.[30] For O_2-free experiments the sample solutions were purged with argon saturated with EtOH vapor. Otherwise, air-saturated solutions were used.

Picosecond flash photolysis experiments were performed with 355 nm excitation pulses (30 ps) generated by an active-passive mode-locked Nd:YAG laser (Continuum YAG571C). Detection of the transient absorbance was accomplished using a dual-diode-array spectrographic detector system (Princeton Instruments ST120), previously described.[31] Solutions were flowed through a cell of optical path 1 cm to eliminate the effects of sample decomposition.

The laser system for the ultrafast transient absorption spectrometry experiments included a Ti:sapphire seed laser (Spectra-Physics Tsunami model 3941-MIS) pumped with a diode-pumped 5 W cw Nd:YAG laser (Spectra-Physics Millennia). The Tsunami output (ca. 10 nJ, 70 fs) was steered into a Ti:sapphire regenerative amplifier (Positive Light Spitfire) which was pumped with a frequency-doubled (527 nm), Q-switched Nd:YLF laser (Positive Light Merlin). The output of the amplifier was typically 1 mJ/pulse (fwhm = 100 fs) at a repetition rate of 1 kHz. To obtain useful excitation wavelengths, the output of the amplifier was coupled into a second or third harmonic generator (CSK Super Tripler), or into an optical parametric amplifier (Spectra-Physics OPA 800). When excitation at 400 nm was employed, 70% of the amplifier output was used to generate the second harmonic, while 30% was used for white light generation. In some cases this latter was accomplished by focusing (100 mm focal length lens) the fundamental (typically 800 nm) into an ethylene glycol flow-through cell (1 cm); in other cases a 3 mm thick sapphire plate (Crystal Systems, Inc., HEMLUX grade) was used for continuum generation. The OPA was used to generate excitation pulses at 650 nm (the second harmonic of the 1300 nm OPA signal beam). Under these conditions the residual fundamental light (0.2 mJ/pulse) was used for continuum generation. Figure 2 shows the layout of the ultrafast spectrometer.

Prior to generating the probe continuum, the amplified fundamental (typically 800 nm) was passed to a delay line (Newport MM4000) that provided an experimental time window of 1.6 ns with a step resolution of 6.6 fs. The energy of the probe pulses was $<5\ \mu J/cm^2$ at the sample. The pump beam was typically arranged to be 50 μJ/pulse with a spot size of about 2 mm diameter at the sample. The angle between the pump and probe beam was 5−7°. The sample flow-through cell had an optical path of 2 mm and was connected to a solution reservoir and flow system. The continuum was split into two 50% beams to produce test and reference paths in the spectrometer. Both beams were coupled into 100 μm fiberoptic cables after the sample cell and thereafter input into the two channels of a double CCD spectrograph (Ocean Optics, SD2000) for time-resolved spectral information (420−750 nm). Typically, 4000 excitation pulses were averaged to obtain the transient spectrum at a particular delay time. Shutters were used to block the pump beam for balancing the spectrograph channels and to minimize the exposure. For single wavelength kinetic measurements, two amplified Si diodes (EG&G HUV-1100) in combination with interference filters (10 nm half-bandwidth) were used. A polarizer was placed after the white-light continuum generator to improve the noise. 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. 500 fs. The phthalocyanine solutions were prepared to have an absorbance of 1.2−1.4 at the excitation wavelength in the 2 mm flow cell. The absorbance spectra of the solutions were measured before and after the experiment to check for possible sample decomposition.

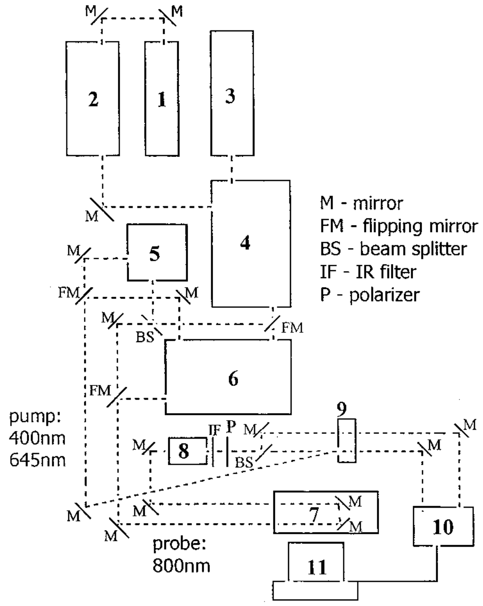

Figure 2. Ultrafast spectrometer schematic: 1, Millennia Nd:YAG laser; 2, Tsunami Ti-sapphire laser; 3, Merlin Nd:YLF laser; 4, Spitfire Regenerative Amplifier; 5, CSK Super Tripler; 6, OPA-800; 7, delay line; 8, white light continuum generator; 9, sample cell; 10, CCD spectrograph; 11, personal computer.

Determination of the Extinction Coefficients for Triplet−Triplet Absorptions. The kinetic scheme for the triplet sensitization process is shown in Scheme 1:

SCHEME 1

$$^3D \xrightarrow{k_0} D$$

$$^3D + A \xrightarrow{k_q} A^3 + D$$

$$^3A \xrightarrow{k_d} A$$

where A is an acceptor and D is a triplet donor. When $[^3D]_0 \ll [A]_0$, a first-order treatment can be applied.[32] The following relationships can be derived from the above scheme:

$$d[^3D]/dt = (k_0 + k_d[A])[^3D] = k[^3D]$$

$$[^3D] = [^3D]_0 \exp(-kt)$$

$$\begin{aligned} d[^3A]/dt &= k_q[A][^3D] - k_d[^3A] \\ &= k_q[A][^3D]_0 \exp(-kt) - k_d[^3A] \end{aligned}$$

and since

$$d[^3A]/dt = 0 \quad \text{for} \quad [^3A] = [^3A]_{max} \quad \text{and} \quad t = t_{max}$$

it follows that the maximum concentration of the triplet acceptor is given by

$$[^3A]_{max} = (k_q[A]/k_d)[^3D]_0 \exp(-kt_{max})$$

whence the extinction coefficient of A becomes

$$\epsilon_{T-T}(A) = \Delta A_{max}/[^3A]_{max}$$

where $[^3D]_0$ is the initial concentration of the donor triplet state and ΔA_{max} is the difference absorbance at the selected wavelength. This latter was calculated using a known value for the triplet−triplet extinction coefficient of the donor (Zn octaethylporphine, ZnOEP) in EtOH (ϵ = 99 000 M^{-1} cm^{-1} at 440 nm)[33] and an initial value of ΔA at 440 nm for ZnOEP in EtOH in the absence of the Pc quencher. The same kinetic trace was used to calculate the value of k_0 by fitting the time profile with a first-order decay ($k_0 = 9.37 \times 10^3$ s^{-1}; 107 μs triplet lifetime). The values for t_{max} and ΔA_{max} were obtained from the kinetic trace of the acceptor triplet state at 525 nm. At this wavelength, the Pc compounds have very low extinction coefficients, and it is an isosbestic point in the donor triplet difference absorption spectrum. A typical fitted time profile is presented in Figure 3. The value of ϵ_{T-T} was calculated for five different Pc concentrations and an average value was computed.

Measurement of Triplet Quantum Yields. Tetraphenylporphinato−Zn(II) (ZnTPP) in EtOH (ϵ_{T-T} (470 nm) = 71 000 M^{-1} cm^{-1}, ϕ_t = 0.90)[34] was used as a reference solution to determine the Pc triplet quantum yields. The excitation wavelength was set at 605 nm to accomplish initial population of the first excited singlet state. The absorbances of the reference and unknown solutions at 605 nm were adjusted to be equal. The amplitudes of the initial transient absorbance signal at 525 nm for the Pc solutions and at 470 nm for the ZnTPP solution were measured, thereby allowing the calculation of the Pc triplet quantum yields (average of five samples) when combined with the extinction coefficient data (see above).

Results

Metallophthalocyanines tetrasubstituted with 18-crown-6 moieties (McrPc) were synthesized using a procedure similar to that reported for the 15-crown-6 moieties (Kobayashi and Lever).[25] The structures of the McrPcs synthesized and employed in this work are represented in Figure 4. These compounds are soluble in $CHCl_3$ (up to mM range) where they were shown by UV−vis spectroscopy to be present in monomeric form. In polar solvents such as anhydrous EtOH, McrPc showed poor solubility (<10^{-6} M) and the resulting absorption spectra indicated cofacial dimerization. The free-base Pc dimer was somewhat more soluble in polar solvents than the metalated analogues. Marked increases in solubility were induced by the presence of water in the ethanol, or by the presence of the acetate salts of K^+, Rb^+, or Cs^+. With K^+ ions in the solution, the UV−vis spectrum indicated that McrPc were monomeric in nature (Figure 4), while cofacial dimers were formed in the presence of Rb^+ or Cs^+, as indicated by characteristic blue shifts in the UV−vis absorption spectra (Figure 4).

The blue shift in the ZncrPcD cofacial dimer spectrum corresponded to 1960 cm^{-1} exciton splitting, which is calculated as twice the energy difference between the monomer and the dimer Q-band peaks.

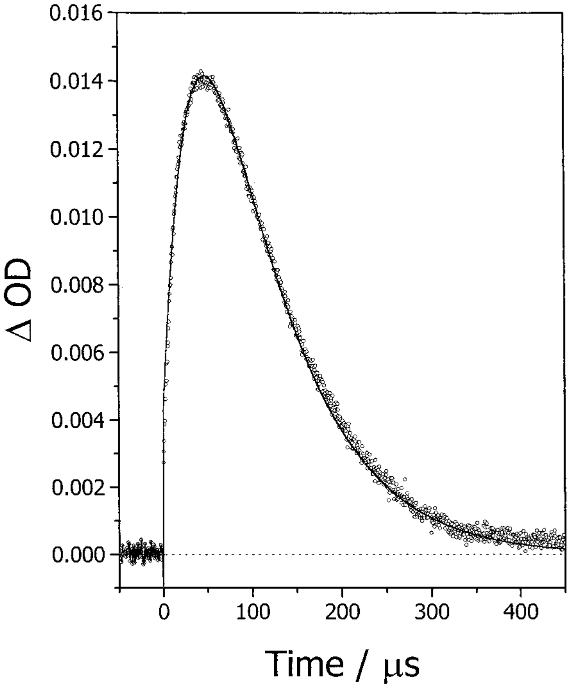

Figure 3. Formation and decay of transient absorption at 525 nm in a solution of ZnOEP and ZncrPc in EtOH with 1 mM KOAc. Excitation was at 532 nm. The solid line represents a least-squares fit to a double-exponential function.

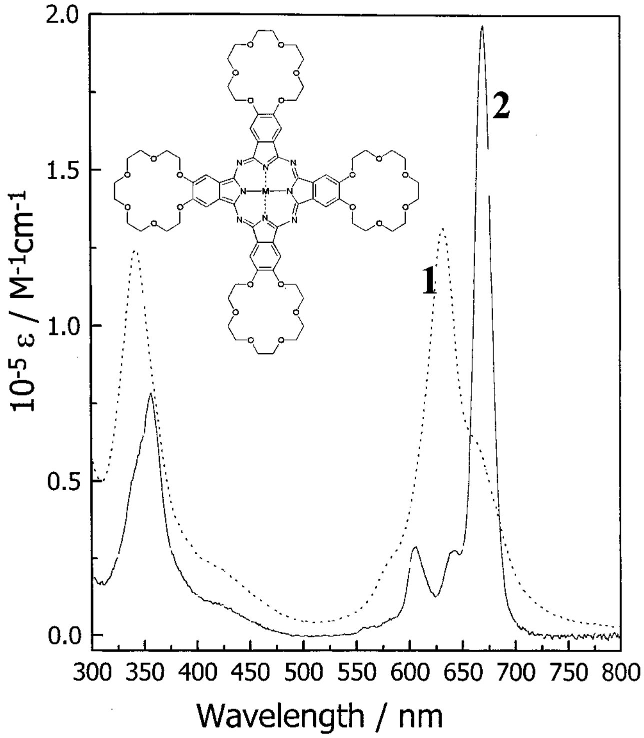

Figure 4. Optical absorption spectra: 1, ZncrPc in EtOH with 1 mM CsOAc; 2, ZncrPc in EtOH with 1 mM KOAc. Upper left: schematic structure of McrPcs employed here; M = H_2, Zn(II), Cu(II), Co(II), and Ni(II).

Steady-State Fluorescence Investigation. The steady-state fluorescence spectra of the Pc monomers (McrPc) and dimers in EtOH yielded results similar to those reported by Kobayashi and Lever for 15-crown-5 substituted Pcs in $CHCl_3$.[25] Fluorescence from the S_1 state was observed in the case of ZncrPc and H_2crPc, the quantum yield of fluorescence being 0.49 and 0.66, respectively. A weak emission originating from the S_2 excited

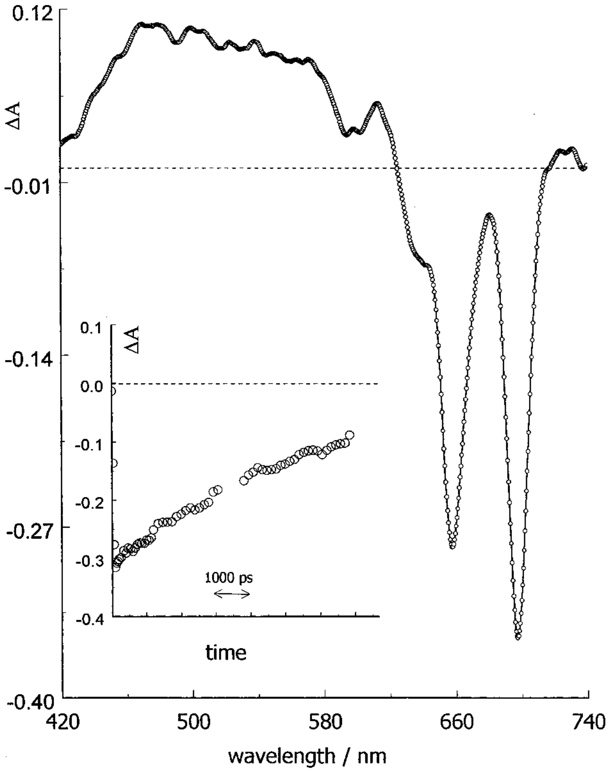

Figure 5. Transient absorption spectrum of H_2crPc in EtOH with 1 mM KOAc recorded 900 ps after the laser pulse. Inset: Ground-state bleaching recovery with excitation at 355 nm and observation at 692 nm.

TABLE 1: Kinetic Parameters for McrPc

phthalocyanine[a]	wavelength/nm	lifetime/ps
H_2crPc	692	6080 ± 100
ZncrPc	670	1180 ± 50
CucrPc	660	22000 ± 100
H_2crPcD	642	113 ± 5
ZncrPcD	637	169 ± 8
CucrPcD	630	5700 ± 100

[a] In ethanolic solution; monomers in the presence of 1 mM KOAc, dimers in the presence of 1 mM CsOAc.

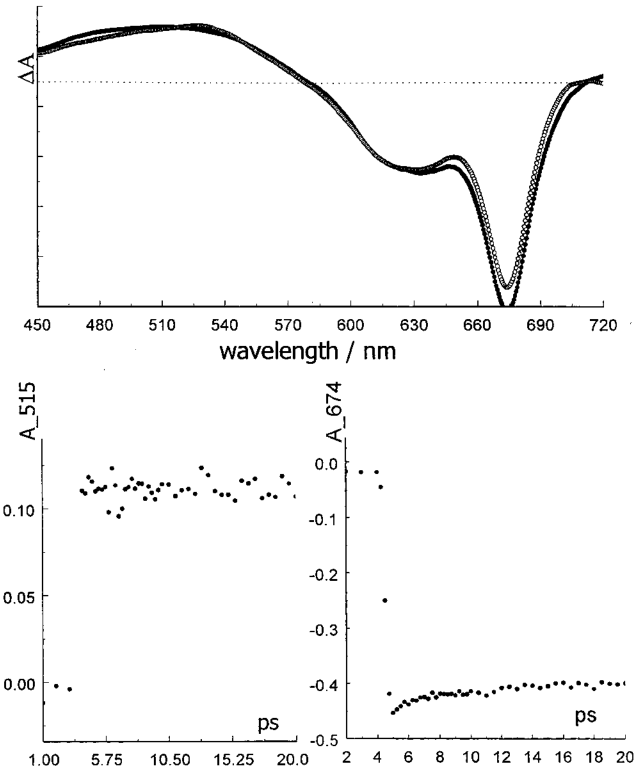

Figure 6. Ultrafast results recorded for CucrPc in ethanol solution containing 1 mM KOAc (monomeric Pcs). Upper panel: spectra recorded at 500 fs (●) and 5 ps later (○). Lower panels: time profiles at 515 nm (left) and at 674 nm (right). Excitation was at 400 nm.

state was detected when monomers and dimers of ZncrPc and H_2crPc were excited into the B-band. Such S_2 fluorescence in Pcs has been reported earlier.[25]

Ultrafast Transient Absorbance Studies. *(a) Monomeric Compounds.* A solution of H_2crPc in EtOH (9×10^{-6} M) containing 1 mM KOAc was subjected to 30 ps, 355 nm excitation pulses, and the transient absorption (TA) spectra were recorded at a series of times after the pulse. The most prominent features of the TA spectra (Figure 5) were negative absorption bands in the 600−700 nm region arising from ground-state removal. Formation of the bleaching signal at 692 nm was complete within the laser pulse width (30 ps). The kinetic profile at 692 nm, corresponding to the recovery of ground-state bleaching, was best fit by the combination of an exponential recovery ($\tau = 6.08 \pm 0.1$ ns) to a nonzero baseline. Similar TA spectra were recorded for ZncrPc in EtOH (3×10^{-5} M) containing 1 mM KOAc; again, the most intense signal corresponded to ground-state bleaching in the Q-band region. The recovery of the ground-state recovery kinetics was described with a single exponential ($\tau = 1.18 \pm 0.05$ ns) plus a constant function. In addition to the negative absorption due to ground-state bleaching, both free-base and Zn(II) compounds showed long-lived positive absorptions in the 500−600 nm spectral region.

Ethanol solutions of CucrPc (7×10^{-6} M) containing 1 mM KOAc were excited at 355 nm. With the experimental time resolution obtainable with a 30 ps pulse, an immediate ground-state bleaching at 670 nm and a positive absorption at 520 nm were observed. At both wavelengths the kinetic profiles decayed to the zero level, according to a single-exponential process having a lifetime of 22 ± 1 ns. Kinetic data for the monomeric phthalocyanines are collected in Table 1. In an effort to examine whether there were any more rapid excited-state dynamics, the CucrPc system was examined with the ultrafast apparatus with excitation at 400 nm. The spectrum presented in Figure 6 (upper panel) was found to be completely formed within the rise time of the instrument (500 fs), as can be seen from the two lower panels in Figure 6, which show the time evolutions of the bleaching (674 nm) and the positive absorption (515 nm). The latter has no decay over the 20 ps time window, but using longer time windows (see above), the lifetime of 22 ns was recorded. At 674 nm the bleaching showed a small decline (ground-state repopulation) over the first 5 ps or so.

(b) Cofacial Dimers. A study of the excited-state dynamics of the cofacial Pc dimers, McrPcD, where M = H_2, Zn(II), and Cu(II), was carried out in EtOH solution containing 1 mM CsOAc. A negative absorption centered at 640 nm and a positive signal at 575 nm were the main features of the transient spectrum of H_2crPcD (5×10^{-5} M) when excited at 400 nm with the ca. 100 fs pulse. These were formed within the instrument response (500 fs). Figure 7 shows the TA spectrum at 21 ps postpulse and the kinetic profiles at 575 and 640 nm. The TA spectra showed an isosbestic point at 600 nm. The kinetic traces were fitted with a single exponential ($\tau = 113 \pm 5$ ps) plus a constant function.

A solution of ZncrPcD in EtOH (4.5×10^{-5} M) with 1 mM CsOAc added showed similar behavior to the free-base com-

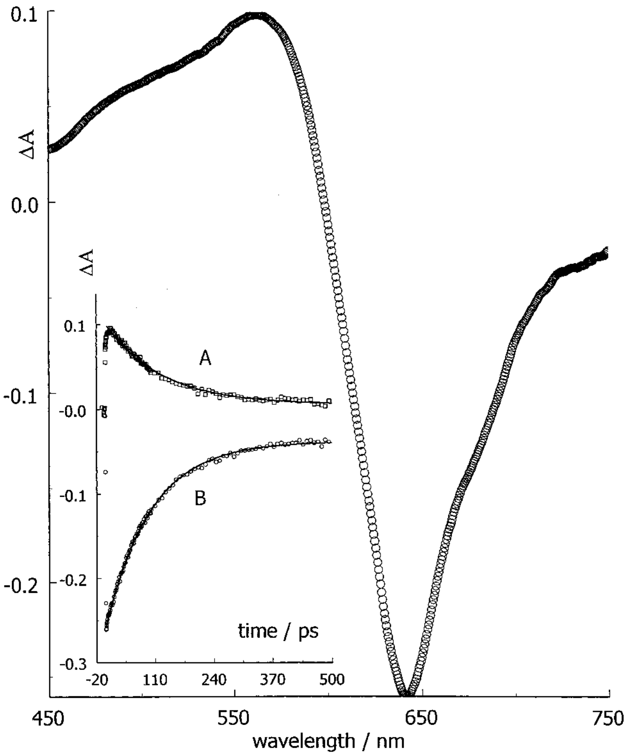

Figure 7. Transient absorbance spectrum of H_2crPcD in EtOH with 1 mM CsOAc taken 21 ps after the pulse. Inset: transient absorbance kinetic profiles: 1, 575 nm; 2, 640 nm, excitation was at 400 nm. The solid lines represent least-squares fits to single-exponential plus a constant.

pound with a negative absorption centered at 637 nm, a positive absorption at 565 nm, and an isosbestic point at 607 nm. The signals were formed within the instrumental response (400 fs). The kinetic profiles at 637 and 565 nm decayed exponentially with a lifetime of 169 ± 8 ps.

The Cu(II)-centered dimer (8 × 10^{-6} M) in ethanol with 1 mM CsOAc present showed a transient absorbance maximum (520 nm), a negative absorbance (630 nm), and an isosbestic point at 580 nm upon excitation at 355 nm with a 30 ps pulse. As for the CucrPc monomer at a resolution of 30 ps, the transient absorbances in the dimer were completely formed by the end of the excitation pulse. A least-squares single-exponential fit of the kinetic profiles at 520 and at 630 nm yielded a common value of 5.7 ± 0.1 ns for the lifetime of the transient species. Kinetic data for the dimers are collected in Table 1. To ascertain whether more rapid changes could be observed with improved time resolution, the CucrPcD system was examined with the ultrafast instrument. The upper panel in Figure 8 shows two spectra in the range 400−720 nm; one was recorded after 500 fs, and the second, some 50 ps later. The temporal changes over the first 100 ps at two wavelengths are shown in the lower panels of Figure 8. Clearly, there are small but significant changes in signal amplitude occurring over ca. 20 ps at both 539 and at 631 nm, and it appears that a fast component of ground-state repopulation is accompanied by increased absorption at 539 nm.

(c) Microsecond Transient Absorption Studies. The Zn(II) and free-base crown-ether-substituted phthalocyanines and the corresponding cofacial dimers in deaerated EtOH solutions were subjected to laser photolysis using 7 ns pulses at 355 nm. Transient spectra on the microsecond time scale were recorded (Figure 9). In all four cases transient absorptions in the 430−580 nm region decaying with lifetimes in the 120−180 μs range were detected. The lifetimes of the transients are recorded in Table 2. The same transient spectra were obtained for the above Pc systems using ZnOEP as triplet sensitizer. The photosensitizer was excited at 532 nm where the absorbance by the Pc was negligible. Molecular oxygen quenched all the transients with bimolecular quenching rate constants near 10^9 M^{-1} s^{-1} (see Table 2).

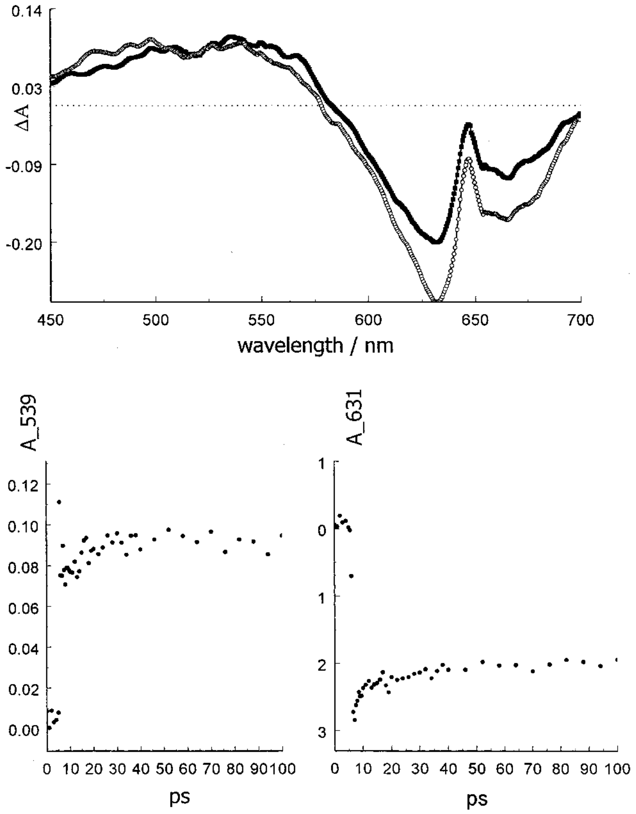

Figure 8. Ultrafast results recorded for CucrPcD in ethanol solution containing 1 mM CsOAc (dimeric Pcs). Upper panel: spectra recorded at 500 fs (○) and 5 ps later (●). Lower panels: time profiles at 539 nm (left) and at 631 nm (right). Excitation was at 645 nm. The upward-going peak centered at 645 nm is excitation light scattered into the spectrographs and inadequately compensated for.

TABLE 2: Triplet-State Parameters

compound[a]	$\tau_t/\mu s$	$10^{-9}k_q(O_2)$, $M^{-1}\,s^{-1}$	$10^{-4}\epsilon_{T-T}$ at 525 nm $M^{-1}\,cm^{-1}$	ϕ_t
ZncrPc	175	1.88	52 300	0.25 ± 0.02
ZncrPcD	129	1.17	62 000	0.10 ± 0.02
H_2crPc	179	1.52	43 800	0.08 ± 0.02
H_2crPcD	120	0.63	61 300	0.01

[a] 1 mM KOAc, EtOH for McrPc; 1 mM CsOAc, EtOH for McrPcD.

Steady-state NIR emission experiments were conducted for ZncrPc and ZncrPcD in O_2-saturated CD_3OD using 632.8 nm light as an excitation source (50 mW HeNe). In both cases singlet O_2 emission at 1269 nm was observed, indicating that the quenching process occurred via a triplet−triplet energy transfer mechanism. The quantum yields for the production of singlet O_2 were not measured due to instability of the samples under the conditions of the experiment.

The triplet sensitization and the oxygen quenching results lead to the conclusion that the transient absorbances in the 430−580 nm region may be assigned to the triplet states of the Pc monomers and dimers. To ascertain whether the Cs^+ cations that were present in the dimers were causing triplet formation in the dimeric Pcs by a heavy atom effect, the experiments described above were carried out for the cofacial dimer formed

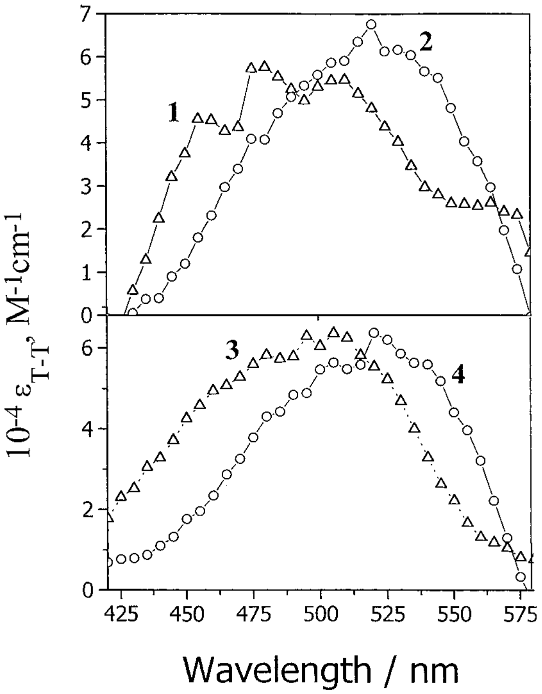

Figure 9. Triplet−triplet absorption spectra: 1, H_2crPc in EtOH with 1 mM KOAc; 2, H_2crPcD in EtOH with 1 mM CsOAc; 3, ZncrPc in EtOH with 1 mM KOAc; 4, ZncrPcD in EtOH with 1 mM CsOAc.

by Zn^{II}Pc tetrasubstituted with 15-crown-5 groups (Zncr(15)-PcD). This compound undergoes cofacial dimerization in the presence of K^+ cations.[25] The ground-state absorption spectrum of this dimer in EtOH was identical to that of ZncrPcD, where the crown ether is 18-crown-6. Laser flash excitation of Zncr(15)PcD in Ar-purged EtOH with 1 mM KOAc yielded a value of 119 μs for the triplet lifetime, which was close to that observed for ZncrPcD.

Triplet−triplet extinction coefficients for the monomers and the dimers were determined using the energy-transfer technique, as detailed in the Experimental Section, and employing ZnOEP as photosensitizer. The growth and decay of the Pc triplet states were monitored at 525 nm, where the triplet of ZnOEP has no absorbance. A typical transient absorbance kinetic profile observed at 525 nm for ZnOEP/ZncrPc, Ar-purged EtOH, 1 mM KOAc solution is presented in Figure 3.

These data and the procedures described in the Experimental Section enabled the extinction coefficients at 525 nm for the triplet−triplet absorptions of ZncrPc, ZncrPcD, H_2crPc, and H_2crPcD to be determined. These data coupled to the absorption spectral information allowed the absolute triplet−triplet spectra to be evaluated (Figure 9). The extinction coefficient data enabled the calculation of the triplet quantum yields for the four compounds (Table 2). The triplet quantum yield was measured for Zncr(15)PcD in EtOH containing 1 mM KOAc as 0.11 ± 0.2, indicating an absence of the metal cation size effect on the triplet quantum yield.

Discussion

Characterization of McrPc and McrPcD in Solution. Observation of monomeric McrPc in EtOH containing 1 mM KOAc solution and cofacial dimers McrPcD in EtOH with 1 mM CsOAc present can be understood as follows. The complexation of K^+ ions with 18-crown-6 results in an encapsulation of the cation into the cavity of the crown.[35] It has been reported[23] that 4:4 crown:cation complexes were formed upon addition of K^+ cations to tetrasubstituted 18-crown-6 Pc in $CHCl_3$ saturated with H_2O. Presumably, cofacial dimerization in polar solvents of such K^+-bearing species is prevented by the electrostatic repulsion between the charges accumulated within the crowns. Cations such as Rb^+ and Cs^+ can associate with 18-crown-6 rings; these larger ions are unable to fit down into the cavity but sit atop the crown. Thus, a second crown ether molecule (alkali metal-free) can join the association, thereby creating a 1:2 alkali metal cation:crown ether structure. For McrPc this causes formation of cofacial dimers with 4:8 alkali metal cation: crown ether ratio.[24]

The results of steady-state fluorescence experiments with monomeric and cofacial dimeric McrPc support the earlier observations for 15-crown-5 tetrasubstituted Pc and the corresponding dimers.[25] Monomeric Pcs, such as ZncrPc and H_2crPc, displayed fluorescence emission similar to that reported for uncrowned family members. Upon cofacial dimerization, this fluorescence was completely absent. This lack of fluorescence can be understood by reference to the energy level diagram in Figure 1. Electronic interaction between the cofacial π-systems in the dimer leads to the indicated exciton splitting. The A_{1g} to E_u transition in the dimer is allowed and is the cause of the blue-shifted ground-state spectrum (Figure 4). The E_u upper exciton state rapidly collapses into the E_g state, which is 1960 cm^{-1} lower, from which a radiative transition to the ground state is forbidden, hence the lack of fluorescence.

Ultrafast Transient Absorption Studies. *(a) Monomeric Phthalocyanines.* The excited-state dynamics of McrPc monomers (where M = H_2 and Zn(II)) represents the least complicated case among the Pc systems presented in this study. These molecules have singlet ground states, and the light absorption event causes population of the first (S_1) or the second (S_2) singlet excited state, depending on the excitation wavelength. For the S_2 initial excitation, the $S_2 \rightarrow S_1$ transition is a fast process that has been estimated to be complete within 10 ps for tetrasulfonated H_2 and Zn^{II}Pc in DMSO.[4] In such compounds central metal effects caused by the presence of unfilled d-orbitals are absent and the electronic excitation is confined to the π-system. The major spectral feature present in these compounds after laser pulse excitation was a negative transient absorption (Figure 5). Such a feature could arise from either bleaching of the ground state or stimulated emission from the sample. Because the spectral shape of the negative absorption was similar to the inverse of the ground-state absorption spectrum, depopulation of the ground states by the laser pulse was assigned to the appearance of this feature. For the compounds described, the ground-state bleaching recovery time profiles were used to monitor the dynamic behavior of the upper states. These time profiles were best fit by an exponential decrease to a nonzero (constant) baseline. Ground-state repopulation postexcitation can arise from the $S_1 \rightarrow S_0$ transition (fluorescence and internal conversion) and the $T_1 \rightarrow S_0$ transition (phosphorescence and internal conversion). The latter occurs on a microsecond time scale in deaerated solution, and the constant term in the decay profile can be attributed to the presence of the T_1 state, which will have negligible decay on the observation time scale (nanoseconds). The initial contributions to the recovery were exponential with lifetimes of 6.08 ± 0.1 ns (H_2crPc) and 1.18 ± 0.05 ns (ZncrPc). Fluorescence lifetimes previously measured for H_2Pc (6 ns)[36] and ZnPc (1.2−3.5 ns in various environments)[37] are close to the ground-state repopulation lifetimes recorded here. These early processes are concluded to be a result of the $S_1 \rightarrow S_0$ transitions in the free-base and Zn^{II}Pc derivatives, thereby providing a measure of the singlet-state lifetime, τ_m. The positive absorption signals in the 500−600 nm region showed little evidence of time dependence. This spectral region is where the T_1 to T_n (see below) and S_1 to S_n transitions in Pcs normally occur. The presence of absorption in this region, and the lack of any clear time dependence, are an indication that the initially formed S_1 states are being converted into long-lived T_1 states and that the absorption spectra of the species are not distinguishable.

In the case of CucrPc, at 30 ps resolution the transient absorbance decay (520 nm) and the recovery of the ground state (660 nm) were single exponential ($\tau = 22 \pm 1$ ns), which is consistent with a report by Kirk et al. in which the excited-state lifetime of tetrasulfonated CuPc was estimated to be longer than 10 ns.[6] By analogy with Cu(II)-centered porphyrins, the ground state of CucrPc is expected to have doublet multiplicity (^{2}S) owing to the d^9 electronic configuration of Cu(II). The $d_{x^2-y^2}$ electron of Cu(II) interacts with the macrocyclic π-system; as a consequence, the first excited state is also a doublet and the triplet state is split into triplet−doublet (^{2}T) and quartet (^{4}T) components, with the quartet state being lower by a few hundred wavenumbers.[38] It has been reported that the intersystem crossing process is greatly enhanced in Cu(II) porphyrins, the $^2S \rightarrow {}^2T/{}^4T$ transition being too fast to be resolved with 300 fs time resolution.[39] Thus, the single-exponential decay (22 ± 1 ns lifetime) of the 660 nm-centered negative absorption is concluded to be due to the repopulation of the ^{2}S ground state from the ^{4}T state. This being so, then the positive absorption at 520 nm can be assigned to the absorption of the ^{4}T state. Interestingly, Figure 6 shows that at early times the time profile at 515 nm shows no temporal changes, whereas that at 674 nm shows a small component of ground-state repopulation occurring in the first 5 ps. The lifetime of this early component was 2.9 ps. In Figure 6 (top panel) are presented two spectra, one recorded immediately after the completion of the rise of the signal and one recorded 7 ps later, after the early component at 674 nm had decayed. Careful scrutiny of the 450−550 nm region indicates that this early decay is accompanied by a slight spectral shift to the red, but the absorption differences were so small that it was impossible to extract any dynamic information. Thus, while some ground-state repopulation occurs very rapidly, corresponding changes in the wavelength range assigned to the quartet state are barely discernible. On the assumption that some dynamic spectral change, albeit minute, occurs around 500 nm partnered with the small but significant repopulation at 674 nm, it is possible to infer that the rapid ground-state repopulation process arises from the spin-allowed conversion

$$^2T \rightarrow {}^2S_0$$

in competition with the process

$$^2T \rightarrow {}^4T$$

with the ^{2}T state being formed within the instrument rise time. On this scheme the barely discernible spectral shift (Figure 6, upper panel) would be due to the $^2T \rightarrow {}^4T$ conversion. It becomes necessary to conclude that the rate constant for this conversion in CucrPc is not as rapid as has been suggested for Cu-centered porphyrins.[39]

On the other hand, the conclusion that the two spectra in Figure 6 (upper) are significantly different may be an over-interpretation, in which case the time profile at 515 nm (Figure 6, lower left panel) is a true representation of the lack of any spectral difference in the region around 500 nm. If so, an alternative scheme can be envisaged wherein the ^{2}T decay process is complete within the rise time of the ultrafast setup. During this decay the ^{2}T state undergoes branching: part leading to ^{4}T and part leading to another state that rapidly decays (2.9 ps lifetime) to the ground $^2S_0$ state. A leading candidate for this unknown intermediate could be a CT state that lies between ^{2}T and $^2S_0$ in energy. In this regard it is noted that Kim et al.[40] have invoked the intervention of a π−d LMCT state in the deactivation of the excited states of Cu(II) porphyrins. In this alternative scheme, the CT and ^{4}T states would be formed from ^{2}S within the experimental rise time and the CT to $^2S_0$ conversion would have a lifetime of 2.9 ps. This latter process would not have a requirement of intersystem crossing, which supports the short lifetime of 2.9 ps as compared with the 22 ns recorded for the intersystem crossing process ^{4}T to $^2S_0$. The current data do not allow a decision to be made as to which of the alternatives is the actual sequence, nor do they allow the evaluation of the fractional conversion of ^{2}S into the putative CT state.

(b) Cofacial Dimers. With CsOAc present in the solution to induce cofacial dimer formation, McrPcD (M = H_2, Zn(II), and Cu(II)) showed excited-state dynamics that displayed similarity in form but differed in lifetime from those of the corresponding monomeric species (Table 1). Thus, for H_2crPcD (Figure 5), ZncrPcD, and CucrPcD, the excited-state lifetimes as determined from the bleaching recovery were measured to be 113 ps, 169 ps, and 5.7 ns for H_2, Zn(II), and Cu(II), respectively—significantly shorter than for the monomers (6.0, 1.18, and 22 ns, respectively). For the Zn and free-base compounds, the bleaching recovery was exponential with a nonzero baseline. In addition, both compounds showed an immediately formed positive absorption near 550 nm (Figure 6), which decayed exponentially to a nonzero baseline. The decaying contribution had the same lifetime as the early component of the ground-state recovery, allowing it to be assigned to the $S_1 \rightarrow S_0$ absorption. The nondecaying contribution is therefore assigned to the $T_1 \rightarrow T_n$ absorption.

In the case of the Cu(II) dimer, at 30 ps resolution the bleach signal at 630 nm and the positive absorption at 520 nm both decay to the prepulse zero baseline in a single-exponential process having a lifetime of 5.7 ± 1 ns. That an isosbestic point at 580 nm intervenes informs that a single transformation, presumably the ^{4}T to ground-state decay process, is responsible.[41] As in the case of the Cu(II) monomer, examination of the early part of the dynamics (Figure 8) provides another level of detail. The upper panel shows the immediately formed absorption spectrum and one recorded some 50 ps later. Scrutiny shows that there is a small but distinct spectral shift to the red over 50 ps. The two lower panels show the time profiles at the two major spectral features. It is clear that small but significant changes occur in both wavelength regions in the first 40 ps or so. Subsequently, the signals remain constant on a 100 ps time scale, eventually decaying away with the lifetime of 5.7 ns, as indicated above. If, as with the Cu(II) monomer, the 540 nm absorption is indeed due to a ^{4}T state, then it seems that additional ^{4}T species are generated postpulse, and these are connected to a rapid ground-state repopulation event. The most straightforward rationale for these observations is that the extra ^{4}T formation is due to the intersystem crossing from ^{2}T, which happens concurrently with some internal conversion of ^{2}T into the ground state, viz., one of the alternative processes invoked to explain the Cu(II) monomer data. If this is the case, then the later time (50 ps) spectrum in Figure 8 is that of the ^{4}T state and the immediate spectrum contains components of the ^{4}T and the ^{2}T states. From the data in Figure 8, it is possible to estimate a lifetime of 8.1 ps for the decay of ^{2}T. Further elaboration of the deactivation dynamics of the primary excited states of the CucrPc dimers and monomers will have to await the development of improved time resolution. Additional comments on the effects of dimer formation will be presented below.

(c) Triplet States. Nanosecond laser excitation of the monomers and dimers of the free-base and Zn(II) compounds revealed the presence of long-lived (many microseconds) absorbances in the 500 nm spectral region that exhibited all the properties of Pc triplet states (see above). Absolute triplet−triplet absorption spectra of the Zn and H_2 dimers were calculated from the extinction coefficient data. These are presented in Figure 9, and the photophysical parameters of the states are collected in Table 2. The formation of significant yields of triplet states for H_2crPc and ZncrPc monomers in ethanol is not unexpected; the literature contains many examples of efficient intersystem crossing for monomeric Pc compounds substituted with various side groups.[42] The values of the triplet lifetimes obtained here (175 μs for ZncrPc and 179 μs for H_2crPc) are similar to the value of 180 μs (in THF) reported for [octa(alkoxy)phthalocyanato]silicon dihydroxide by Ferencz et al.[22] in support of the concept that the central metal in a closed-shell electronic configuration (Zn or Si in this case) has only a minor influence on the triplet-state lifetime. The triplet quantum yields of monomeric Pc presented in this report are also typical for Pc compounds.[42]

The fluorescence quantum yields (ϕ_f), the triplet quantum yields (ϕ_t), and the singlet-state lifetime (τ_m) data reported above together with the familiar relationships

$$k_f = \phi_f \tau_m, \qquad k_t = \phi_t \tau_m, \qquad \text{and} \qquad k_g = (1 - \phi_f - \phi_t)\,\tau_m$$

allow the evaluation of the radiative rate constant (k_f), the intersystem crossing rate constant (k_t), and the internal conversion to the ground-state rate constant (k_g). Values of k_f are 1.1 × 10^8 s^{-1} (H_2crPc) and 4.1 × 10^8 s^{-1} (ZncrPc), k_t values are 1.3 × 10^7 s^{-1} (H_2crPc) and 2.1 × 10^8 s^{-1} (ZncrPc), and k_g values are 4.1 × 10^7 s^{-1} (H_2crPc) and 2.1 × 10^8 s^{-1} (ZncrPc).

Cofacial dimerization of H_2crPc and ZncrPc by inclusion of Cs^+ ions into the solution results in the complete loss of fluorescence, a decrease of the triplet quantum yields (0.01 for H_2crPcD and 0.1 for ZncrPcD), and a shortening of the triplet lifetime. The absence of fluorescence emission in the cofacial dimers is consistent with the rapid population of the lowest singlet exciton state from the initially generated upper exciton state. Simple exciton theory requires that this lower exciton state in cofacial dimers be a “dark” state since the radiative transition from it to the ground state is optically forbidden. The transient absorption measurements detailed above for these two dimer systems showed that ground-state recovery occurred on a subnanosecond time scale: $\tau = 0.11$ ns for H_2crPcD and $\tau = 0.17$ ns for ZncrPcD. Assigning these values as τ_m for the respective compounds and coupling this with the above quoted ϕ_t values and the complete lack of fluorescence allows k_t values of 9 × 10^7 and 5.9 × 10^8 s^{-1} to be computed for the H_2 and Zn(II) dimers, respectively. The same experimental data allow computation of the k_g values of 9 × 10^9 and 6 × 10^9 s^{-1} for the H_2- and Zn(II)-centered dimers, respectively. Comparison of these values with those for the monomer shows that the major effect of dimerization is to dramatically increase internal conversion rates (by a factor of 30−200) and to cause a small enhancement of the rates of intersystem crossing (by a factor of 3−7). This enhancement in internal conversion may be attributable to the fact that the exciton splitting places the lower exciton state closer to the ground state; in addition, an increased contribution of internal conversion in the singlet manifold owing to flexible structures of the cofacial dimers might be anticipated. The increased intersystem crossing rate constant may also be a manifestation of the energy gap law inasmuch as the lower exciton state will be closer in energy to the corresponding triplet state. The situation concerning the dynamics of the Cu(II) systems has been discussed above.

The quenching of the ZncrPcD and H_2crPcD triplet states by molecular O_2 together with the observation of singlet oxygen formation indicates energy transfer from the Pc to O_2. The rate constants for O_2 quenching (Table 1) were lower for the dimers as compared to the monomers, particularly so for the free-base dimer. Earlier reports from this laboratory have indicated that such a lowering arises when the energy of the triplet donor is lower than that of singlet oxygen.[43] The triplet-state energy of bis[octa(alkoxy)phthalocyanato]disiloxane has been estimated at 8451 cm^{-1} (1183 nm).[22] Moreover, recent work in this laboratory demonstrates that μ-oxo Pc dimers with central metals Si, Ge, and Sn have triplet energies that are below that of singlet oxygen, whereas the monomer triplets lie above singlet oxygen.[44] Such evidence allows the conclusion that cofacial dimerization produces a lower-lying triplet state than exists in the monomeric version, probably via exciton-type splitting, as observed in the singlet manifold.

An absence of significant effect of the alkali metal cation size on the triplet lifetime and the triplet quantum yield was demonstrated in the experiments on Zncr(15)PcD dimer. This dimer is formed in the presence of K^+ cations, which do not affect intersystem crossing. However, the values for the triplet lifetime and the triplet quantum yield obtained are comparable with those for ZncrPcD, formed in the presence of Cs^+ cations.

Conclusions

The photophysical properties of tetrasubstituted 18-crown-6 Pc and the corresponding cofacial dimers vary dramatically depending on the nature of the central metal atom. Thus, the conjugated macrocyclic ring dominates the excited-state dynamics of H_2crPc and ZncrPc. Cofacial dimerization produces no major changes in excited-state behavior except for increasing the rate of the deactivation processes. An excited-state lifetime of 22 ns observed for CucrPc was attributed to that of the ^{4}T state of this compound where the d^9 Cu(II) influences the electronic nature of the excited states. Again, cofacial dimerization of this Pc compound enhances internal conversion in the ^{4}T manifold, resulting in an increase of the nonradiative decay rate constant. For the Cu species, observations at improved time resolution showed indications of intersystem crossing from ^{2}T to ^{4}T occurring over a few picoseconds.

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