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Association Complexes between Cationic Metallophthalocyanines and Anionic Metalloporphyrins II: Ultrafast Studies of Excited State Dynamics[†]

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Femtosecond transient absorption studies were conducted for self-assemblies between oppositely charged metal-substituted 18-crown-6 tetrasubstituted phthalocyanines (McrPc) and metal-substituted *meso*-(4-sulfophenyl)-porphine (MTPPS) or *meso*-(4-carboxylphenyl)-porphine (MTPPC). Excitation could be carried out at 400 nm (Ti−Sapphire second harmonic), which populates the porphyrin-localized S_2 state or directly into the CT band (690), and was achieved by changing the pump pulse wavelength with an optical parametric amplifier. Each complex showed the transient features and kinetics that were independent of the excitation wavelength. After 400 nm excitation, all complexes displayed rapid conversion to the low-lying charge-transfer state. Studies of the CuP/CuPc complex showed no significant decay of the transients on the subnanosecond time scale. However, investigations of the complexes containing different transition metals showed that deactivation of the complex excited state occurs through metal-centered (d,d) states. For the mixed metal/free-base complexes, the excited-state relaxation occurred through the metallotetrapyrrole component regardless of whether it was porphyrin or phthalocyanine. In these compounds, the charge transfer state deactivated to form the metal-centered (d,d) state within 2 ps, with lifetimes that varied somewhat with the metal center. This latter state repopulated the ground state with a lifetime of ca. 13 ps (NiP/NiPc), 200 ps (NiP/CuPc), 8 ps (CuP/NiPc), and 7 ps (FbP/CoPc). These metal-to-ground state rates were similar to those measured for the monomeric metallotetrapyrroles.

Introduction

The preceding report in this series[1] describes the preparation and characterization of complexes of anionic metalloporphyrins with cationic metallophthalocyanines in which the cationic residues are crown ethers doped with potassium ions. All complexes investigated showed a charge transfer band near 700 nm in the ground-state absorption spectrum. The formation and properties of ion-pair complexes of oppositely charged porphyrins has been reported,[2−4] as have complexes consisting of negatively charged tetrasulfonated tetraphenylporphyrins and either cationic metallophthalocyanines or cationic metalloporphyrazines.[5] In many cases, the complexes were of the 2:1 phthalocyanine:porphyrin type, as found in this investigation. The literature examples of complexes were composed of charged compounds in which the anionic and cationic residues were sulfonates and quaternary nitrogen entities, respectively, that were covalently attached to the macrocycles. In the complexes investigated here, the cationic centers were potassium ions that were doped into the cavities of crown ether residues at the periphery of the phthalocyanines. The motivation for the research described in the current report was to examine the effect of the observed charge-transfer interaction on the excited-state dynamics.

Experimental Section

Preparation of the Complexes. The complexes were prepared by mixing solutions of porphyrin and phthalocyanine in a ratio corresponding to the desired stoichiometry of the complex as described in the preceding paper in this series.[1] The phthalocyanine solutions contained 100 times molar excess of potassium chloride or potassium acetate to ensure the saturation of the crown-ether moieties with positively charged potassium ions. The composition of the prepared systems was verified using the UV−vis spectroscopy.

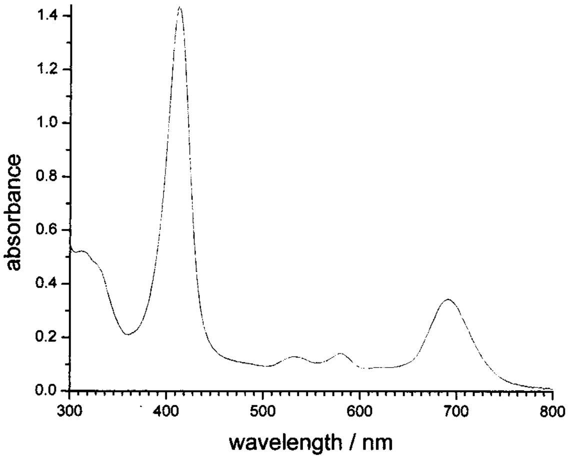

Figure 1. Absorption spectrum of a mixture of NicrPc (10 μM) and NiTPPS (20 μM) in DMSO solution.

Transient Absorption Spectroscopy. The laser system and apparatus for the ultrafast transient absorption spectroscopy experiments is described in the preceding paper in this series.[1]

Results

The excited-state dynamics of NicrPc-NiTPPS, NicrPc-CuTPPS, CucrPc-NiTPPS, and CocrPc-FbTPPC were investigated using excitation at either 400 or 690−710 nm. Figure 1

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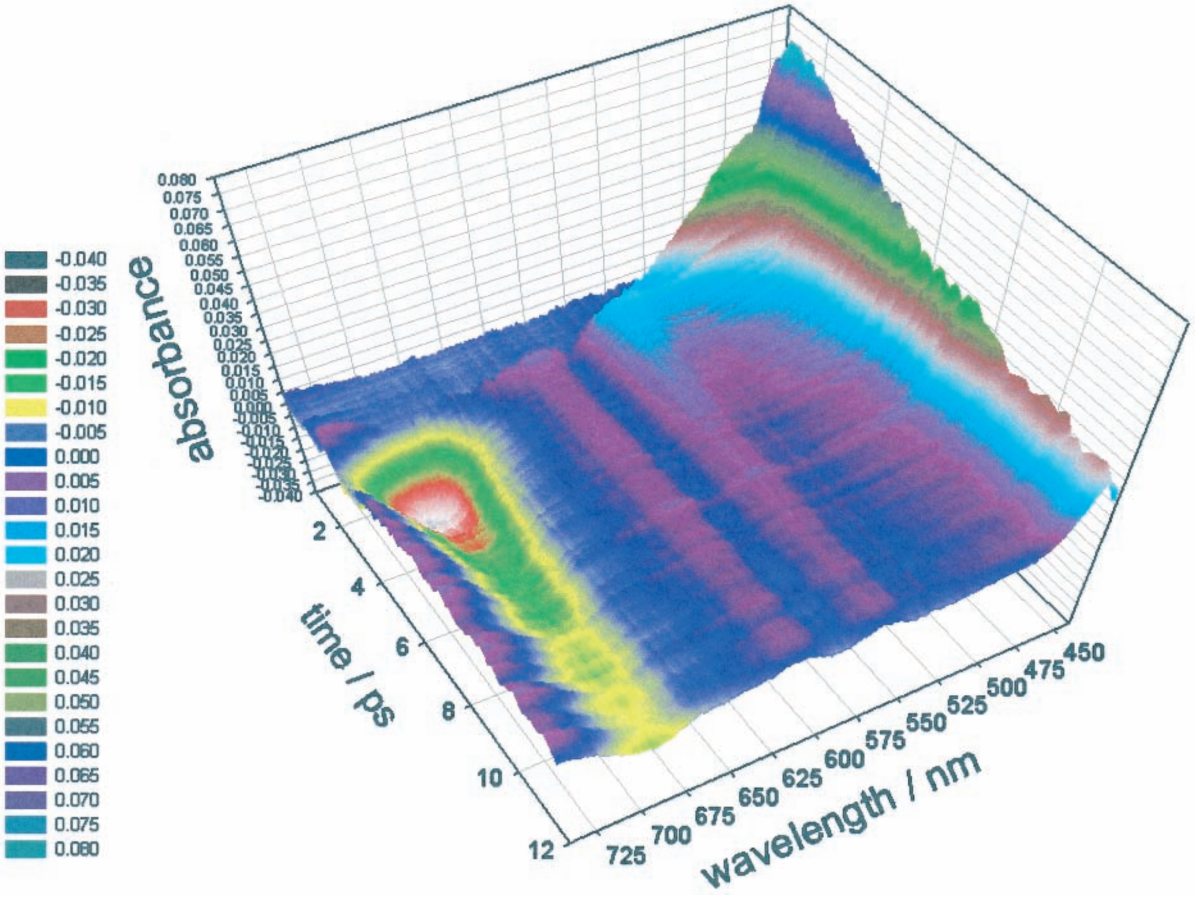

Figure 2. Perspective view of the dynamic surface (absorbance−wavelength−time) generated from transient spectral slices recorded at a sequence of times before and after (to 12 ps) excitation of the solution of Figure 1 by a 100 fs pulse at 400 nm. The spectral feature in the region near 700 nm is negative absorbance caused by bleaching at the CT band.

shows the absorption spectrum of the solution resulting from incrementally adding NiTPPS solution to a solution of NicrPc until the absorption at 690 nm had just reached the plateau value. As presented in the preceding paper in this issue, the resulting solution has absorption characteristics very similar to those of the Soret and Q-bands of NiTPPS and a clearly developed CT band near 700 nm. Light at 690 nm directly pumped the low-lying charge transfer state of the complexes, whereas excitation at 400 nm generated an upper porphyrin-like (π,π^*) state.

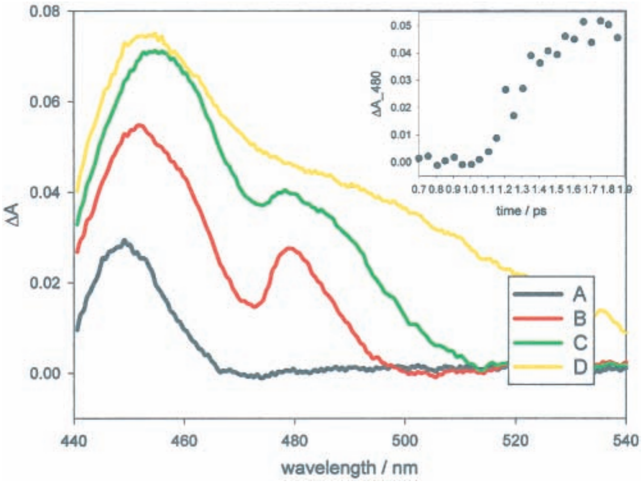

Figure 3. Cuts from the surface shown in Figure 2 at delay line settings corresponding to nominal times of 0.85 (A), 1.20 (B), 1.35 (C), and 1.85 ps (D). The inset shows the early part of the 480 nm time profile.

NicrPc−NiTPPS Complex. A DMSO solution of NiTPPS (50 μM), NicrPc (100 μM) and KCl (10 mM) was prepared. Under these conditions, the Job procedure showed that complexes composed of porphyrin and phthalocyanine in the ratio 1:2 were the preponderant species present.[1] 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. This dynamic surface is shown in perspective view in Figure 2, from which four spectral slices are presented in Figure 3 (labeled A−D). The inset to Figure 3 shows the early part of the temporal profile at 480 nm. Very evident in Figure 3 is the passage of chirp through the spectrometer. At delay line settings corresponding to times less than ca. 2 ps, group velocity dispersion (chirp) in the spectrometer causes the blue end of the spectral range to appear earlier than the red end. Hence, the origin of the time axis is different at different wavelengths. The four spectra shown in Figure 3 show increased red features as the time proceeds from 0.85 ps (A) to 1.85 ps (D). These effects and the resulting assignments are discussed in more detail later. Figures 4 and 5 show series of absorption spectra at times that succeed those displayed in Figure 3, and the insets show time profiles at selected wavelengths. Table 1 summarizes the kinetic parameters obtained results at all selected wavelengths.

In an equivalent experiment to that described above, the complex was excited at 690 nm, corresponding to the direct transition to the CT state. A series of spectra at a succession of delay times is presented in Figure 6, and kinetic parameters extracted at selected wavelengths are collected in Table 1.

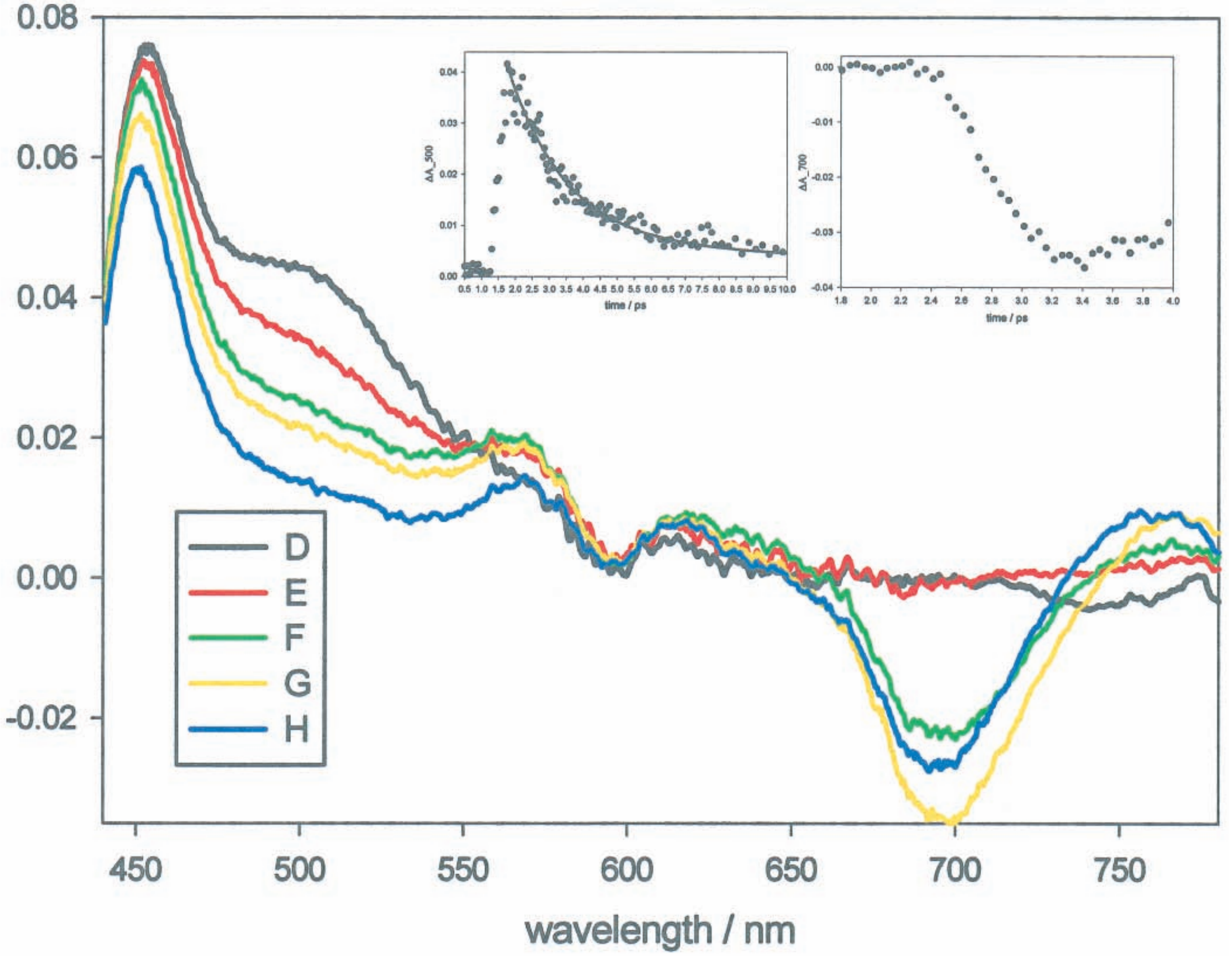

Figure 4. More cuts from the NicrPc−NiTPPS dynamic surface of Figure 2. The nominal times are 1.85 (D), 2.36 (E), 2.86 (F), 3.36 (G), and 4.36 ps (H). The insets show time profiles recorded at 500 (left panel) and 700 nm (right panel).

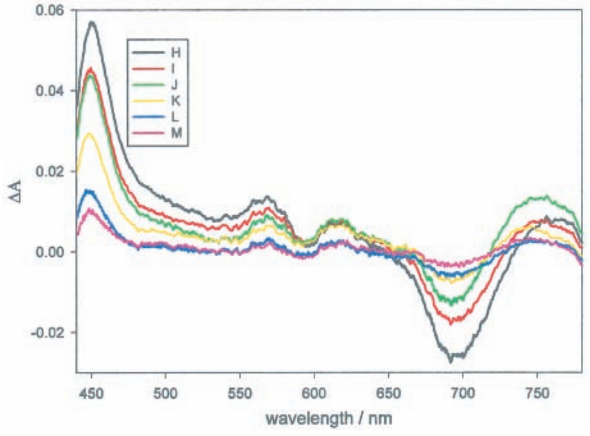

Figure 5. More spectra extracted from the NicrPc−NiTPPS dynamic surface of Figure 2 at nominal times of 4.4 (H), 5.6 (I), 7.6 (J), 11.3 (K), 19.3 (L), and 27.3 ps (M).

NicrPc−CuTPPS Complex. A DMSO solution of CuTPPS (50 μM), NicrPc (100 μM), and KCl (10 mM) was prepared. As for the Ni−Ni complexes above, the Job procedure showed that trimers containing porphyrin and phthalocyanine in the ratio 1:2 were the preponderant species present. Excitation of the complex at 400 nm in the ultrafast pump−probe spectrometer produced data that were composed into a dynamic surface. Spectral slices were extracted, and three of these are shown in Figure 7. Figure 7 (inset) shows the time profile at 450 nm with a biexponential fit superimposed on the data points. Kinetic data at selected wavelengths for this complex are presented in Table 1.

CucrPc−NiTPPS Complex. A DMSO solution of NiTPPS (50 μM), CucrPc (100 μM), and KCl (10 mM) was prepared. The Job procedure showed that trimers of porphyrin to phthalocyanine in the ratio 1:2 were the preponderant species present. Excitation at 400 nm generated dynamic spectra very similar to those shown in Figure 7. The time profile of the 480 nm transient with the superimposed biexponential fit is shown in Figure 8, and the kinetic data for the CucrPc- NiTPPS complex are summarized in Table 1.

CocrPc−FbTPPS Complex. An ethanol solution of CocrPc (100 μM), FbTPPS (100 μM), and KCl (10 mM) was prepared. Under these conditions, the Job procedure lead to the conclusion that 1:1 dimers were the preponderant species present. In the this complex, only the metallophthalocyanine contains a central metal ion with lower-lying metal-centered states capable of participating in fast deactivation of the π-system excited states.[6] Pump−probe spectrometric examination of the CocrPc-FbTPPC complex following excitation at 400 nm generated a dynamic surface from which the spectra displayed in Figure 9 were extracted. The inset to Figure 9 shows the time profile and the

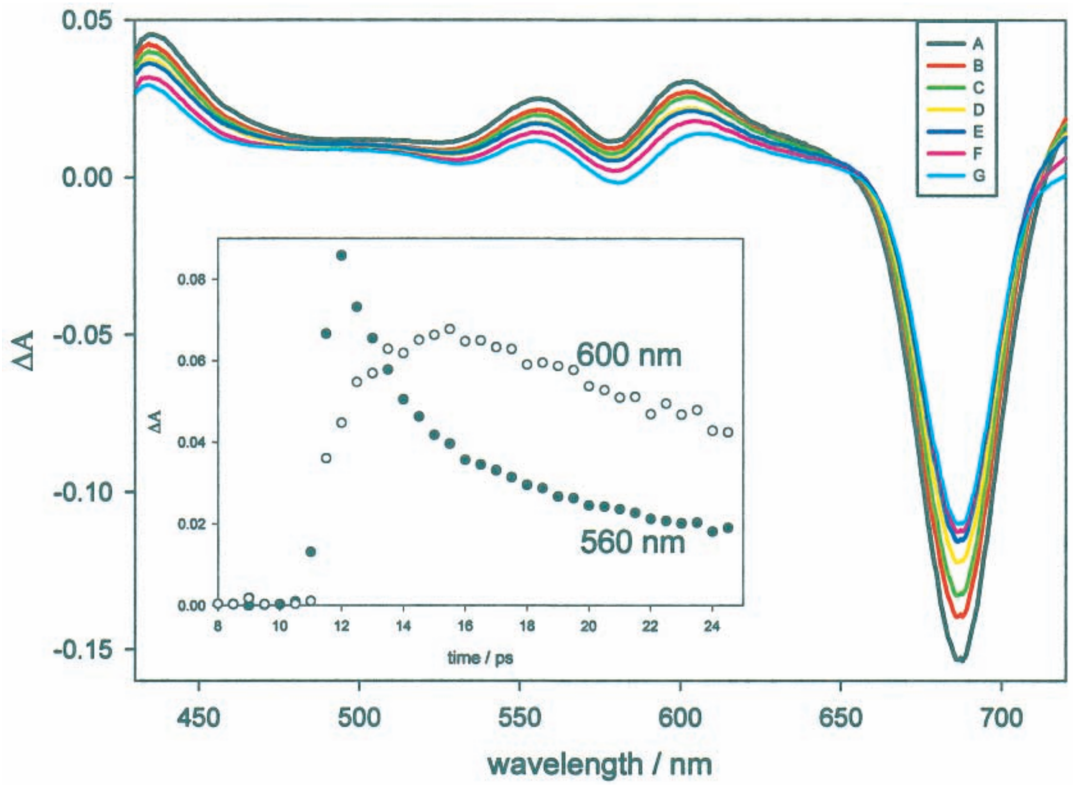

Figure 6. Series of cuts from the NicrPc−NiTPPS dynamic surface obtained with excitation at 690 nm. The time range A−G covers elapsed times of 5−26 ps. The inset shows time profiles at 560 and 600 nm.

TABLE 1

	400 nm excitation		690 nm excitation	
λ/nm	τ (%)/ps	τ (%)/ps	τ (%)/ps	τ (%)/ps
		NicrPc−NiTPPS		
440	–	–	2.3 (43)	11.3 (57)
460	2.3 (46)	11.2 (54)	1.9 (63)	11.8 (36)
505	1.5 (82)	9.6 (18)	1.8 (85)	9.8 (15)
555	2.0 (64)	10.5 (36)	1.9 (55)	9.7 (45)
615		12.5		12.8
690	2.7 (69)	12.7 (31)	2.4 (87)	9.6 (13)
		NicrPc−CuTPPS		
450	1.8 (50)	7.2 (50)	2.0 (54)	7.6 (46)
480	1.7 (73)	8.3 (27)	–	–
570	1.6 (73)	8.9 (27)	2.1 (66)	8.3 (34)
615	–	–	–	14.8
690	2.0 (60)	6.9 (40)	1.9 (72)	8.0 (28)
		CucrPc−NiTPPS		
480	1.8 (43)	191 (57)		
500	1.3 (37)	197 (63)		
700	2.44 (17)	219 (83)		
		CocrPc−FbTCPP		
462	1.76 (86)	7.05 (14)		
475	0.96 (67)	4.23 (33)		
535	0.38 (94)	4.17 (6)		
680	1.30 (47)	7.17 (53)		
745		7.0		

superimposed biexponential fit at 475 nm. Note that the biexponential fit shows an asymptotic value of ca. 0.02 absorbance units. This is due to the presence of residual monomeric free-base porphyrin in the reaction mixture the singlet states of which are generated by the excitation light and which deactivate on nanosecond and longer time scales. The kinetic parameters at selected wavelengths for FbTPPC−CocrPC complex are summarized in Table 1.

FbcrPc−FbTPPs. The previous paper in the series[1] contains the description of the experimental parameters relating to the Fb−Fb complex. It describes the spectral and kinetic data at and beyond 5 ps post-pulse at which time the CT state was completely formed. Spectra taken at earlier times are shown in Figure 10, and time profiles at 480 and 710 nm are shown in the inset to Figure 10. The 10−90% rise time of the former is ca. 300 fs; that of the latter is near to 500 fs, indicating that the bleaching of the ground-state band is somewhat delayed.

Discussion

The excited-state dynamics of the four metal-centered complexes investigated showed many similarities. To simplify the discussion, the NicrPc−NiTPPS system will be examined in detail and used as the paradigm. Detailed discussion of the other complexes will be confined to areas where they differed significantly from the NiNi case.

NicrPc−NiTPPS. Under the concentration conditions of the solution being examined (100 μm NicrPc and 50 μM NiTPPS), the ground-state absorption spectrum showed (Figure 1) the presence of an intense absorption maximum at 412 nm with lesser peaks at 531, 578, and 690 nm. The first three peaks are nearly identical to those found in NiTPPS solutions and correspond to the Soret and Q-bands of this compound; the 690 nm peak corresponds to the CT transition in the complex.[1] Excitation at 400 nm will thus populate a porphyrin-like S_2 state, below which lies a porphyrin-like S_1 state (corresponding to the absorption maxima at 531 and 578 nm). The CT state is the lowest-lying allowed state although it is anticipated that there will be lower-lying, spectroscopically silent Ni-centered states.

The dynamic surface presented in Figure 2 hints at a complex series of spectral and temporal changes that are more clearly visualized with overlapped spectra such as those presented in Figure 3 where the changes in the blue-green spectral region during the first picosecond are represented. The inset to Figure 3 shows the early part of the time profile at 480 nm. The five spectra A−D represent four different delay times between the

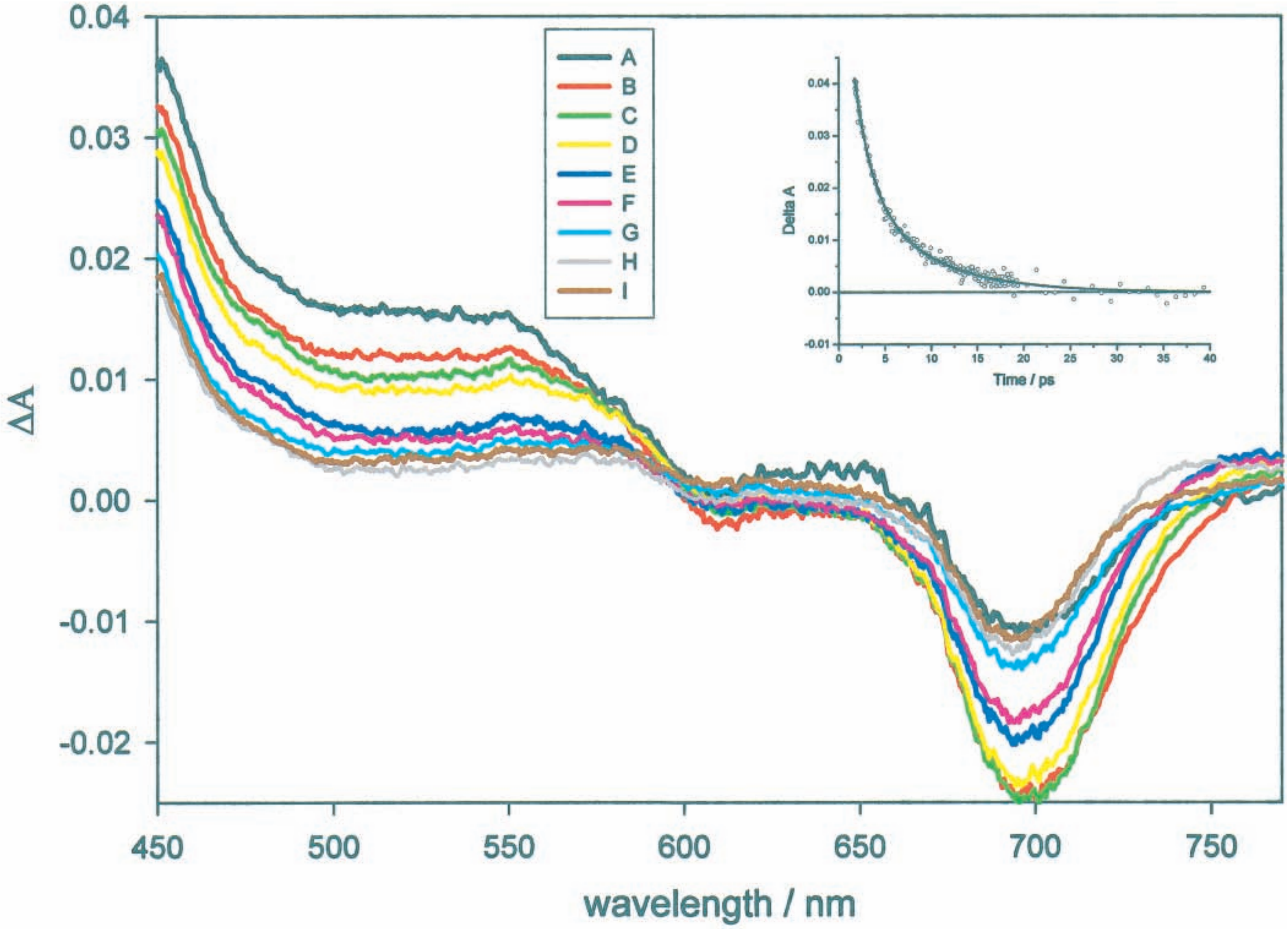

Figure 7. Series of cuts from the NicrPc−CuTPPS dynamic surface obtained with excitation at 400 nm. The range A−I covers nominal times of 3−5 ps. The inset shows the time profile at 450 nm with a biexponential fit superimposed.

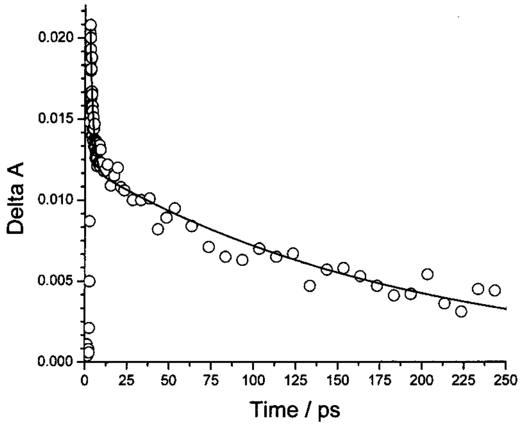

Figure 8. Time profile of the 480 nm absorption of CucrPc−NiTPPS complex in DMSO solution after excitation at 400 nm. The superimposed curve is the result of a biexponential fitting.

arrivals of the pump and probe pulses in the sample. The absolute times corresponding to spectra A through D are nominal because of the effects of chirp, which causes the blue parts of the spectra to be developed before the red parts. Time differences, however, are meaningful, and the total time elapsed between the spectrum A and spectrum D is 0.6 ps. Another thing to note is that the inset to Figure 3 shows that at 480 nm, “time zero” occurs at a delay line setting that corresponds to ca. 1.1 ps. This shifts to later times as the wavelength increases and at 700 nm (see later) the “time zero” occurs at a nominal 2.4 ps. By ca. 3 ps the chirp has moved out of the visible region and thereafter all wavelengths have a common time label. What is clear from Figure 3 is that the spectrum designated as B (1.2 ps) shows a pair of spectral maxima (455 and 480 nm), whereas 0.6 ps later (D) the 480 nm maximum has degenerated into a broad shoulder extending to wavelengths above 520 nm. As indicated in the preceding discussion, the broadening of the shoulder to the red side of the 480 nm maximum is the result of the progress of chirp through the instrument, but the filling in of the 470 nm minimum within ca. 0.6 ps is unlikely to be chirp-related and it is concluded to be a real spectrometric change, caused by the conversion of one chemical species to another. Moreover, as the inset to Figure 3 indicates, the 10−90% rise time of the absorption at 480 nm is ca. 500 fs, significantly longer than the instrument rise time of ca. 250 fs. Thus it is concluded that excitation of this Ni−Ni complex at 400 nm generates a porphyrin-like excited π^* state (absorption peaks at 450 and 480 nm) in the first instance, which converts within a rise time of ca. 500 fs (see Figure 3, inset) to a state having a broad absorption in the blue-green spectral regions (spectrum D in Figure 3). Spectrum D is assigned as arising from the CT state of the co-facial complex and the precursor to this, represented by spectrum B is presumably the porphyrin-like S_1 state, generated by internal conversion (within the instrument response time) from the photogenerated S_2 state. The S_1−CT conversion lifetime is estimated from Figure 3 (inset) as being approximately 300 fs and the process is complete within 600 fs.

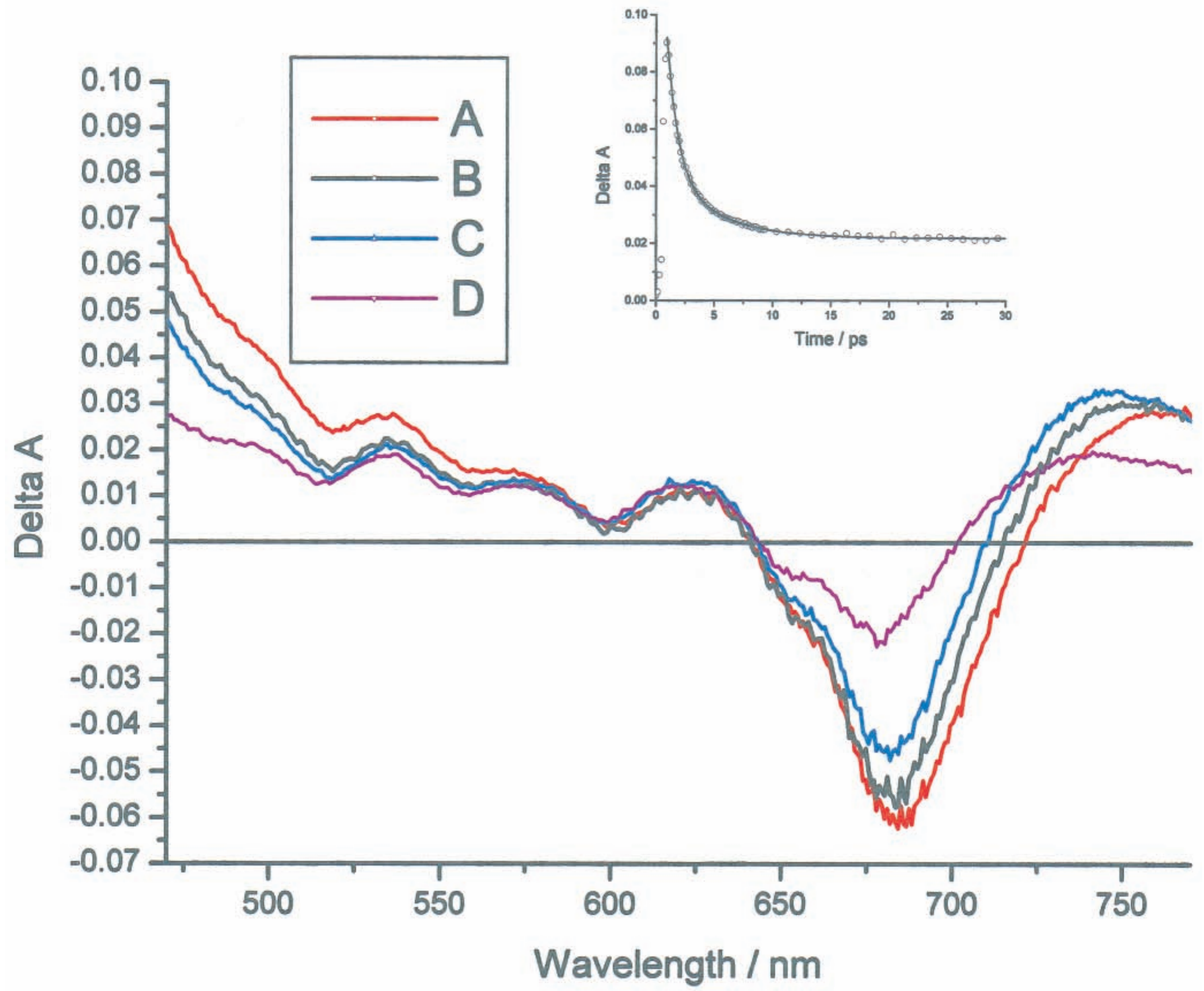

Figure 9. Four cuts extracted from the dynamic surface of CocrPc−FbTCPP in ethanol at nominal times of 1.7 (A), 2.0 (B), 3.0 (C), and 8.0 ps (D) after 400 nm excitation. The inset shows the time profile at 475 nm and a superimposed biexponential decay curve.

The earliest time spectrum presented in Figure 4 (spectrum D) is the same as spectrum D in Figure 3. The series of spectra presented in Figure 4 reveals that the broad blue-green absorption band (identified as arising from the CT state) undergoes rapid spectral narrowing due to loss of absorbance on its long wavelength side. This is manifest as a more rapid loss of absorption intensity in the 500 nm to 550 nm region (ca. 50%) compared to the rate of loss at the 460 nm peak (ca. 16%). This type of behavior is symptomatic of the loss of vibrational energy within an electronic state generated by a stimulated absorption event. For example, when an electric dipole transition causes molecules to be promoted from S_0 ($\upsilon = 0$) to S_1 ($v' = n$), the resulting UV-vis absorption spectrum of the S_1 state arises from transitions from S_1 ($v' = n$) to a higher-lying vibronic state (e.g. S_n). As the molecules in S_1 ($v' = n$) lose vibrational energy, the energy gap corresponding to the absorption transition becomes larger. This process will result in the loss of absorption intensity at the low energy side of the spectrum of the excited state at a rate that reflects the rate of vibrational deactivation within the state from which the absorption transition originates. This argument leads to the conclusion above that the observed spectral narrowing on the complex dynamic surface (Figures 2 and 4) corresponds to the vibrational relaxation within the CT state that was formed as indicated above. An analysis of the temporal profile at 500 nm (Figure 4, inset A) reveals that the cooling process has a lifetime of 1.4 ps, and at the conclusion of this process the vibrationally cold CT state has the absorption spectrum shown as spectrum H in Figure 4. The time elapsed between spectra D and H in Figure 4 is 2.5 ps. To be noted also in this Figure is that as the CT state cools an absorption in the 750−760 nm range grows in over a 2 ps interval. As was discussed in the preceding paper in the issue [1] this is the spectral region where the Pc radical cation absorbs. This lends support to the identification of spectrum H as arising from the CT state.

Further evidence is found by inspecting the rise (inset B in Figure 4) of the negative absorption at 700 nm, the wavelength region that corresponds to the bleaching of the CT band observed in the ground-state spectrum. The time profile reveals that the 10−90% rise of the signal occurs in ca. 700 fs, which is significantly in excess of the instrument response function (ca. 250 fs). Thus, even though molecules in their electronic ground states are being removed from the ensemble at a rate that coincides with the rate of photon absorption, the loss of their spectrum is significantly delayed. This apparent paradox can be resolved if the photoexcitation event initially generates a state that has little or no influence on the CT transition, i.e., if the excited state has an identical CT transition to the ground state. The fact that this could be so is shown in the scheme in

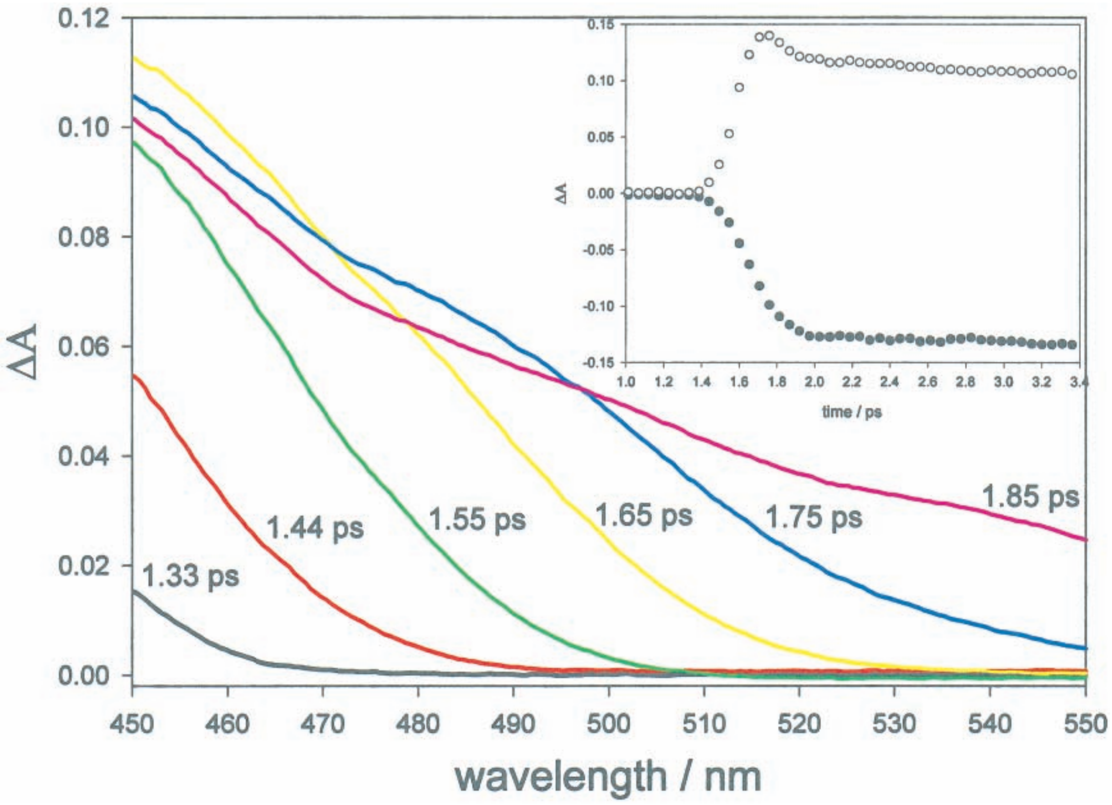

Figure 10. Series of spectra extracted from the dynamic surface of FbcrPc−FbTCPP in ethanol after excitation at 400 nm. The nominal times are as indicated. The inset shows the time profiles for the absorption changes at 480 (upper curve) and 700 nm (lower curve).

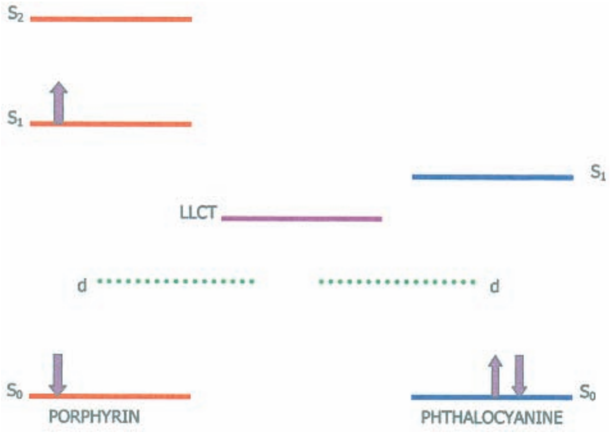

Figure 11. Schematic representation of the energy states of a porphyrin−phthalocyanine complex that has been excited to a porphyrin-like S_1 state showing the continued availability of the LLCT transition from the phthalocyanine ground state (see text).

Figure 11. Here the 400 nm photons carry the system from a porphyrin-like ground state into a porphyrin-like S_2 state from which a porphyrin-like S_1 state is generated within the rise time of the instrument. In Figure 11, we note that the CT transition involves the promotion of an electron from the doubly occupied HOMO of the Pc entity to the state labeled LLCT, lying below the S_1 state of the porphyrin. This transition is available irrespective of the electronic configuration of the porphyrin-like states. As time proceeds, the S_1 state decays, which places an electron in the lower-lying CT state thereby (presumably) perturbing the CT transition and lowering the extinction coefficient. The result is that the bleaching effect becomes manifest and its rate of appearance follows the rate of decay of the porphyrin-like S_1 state into the CT state. It is appropriate to report that when the system was pumped with 690 nm radiation, which directly populates the CT state, the delay in the bleaching signal was not apparent.

The series of spectra displayed in Figure 5 cover an elapsed time of 23 ps and continue the sequence of Figure 4. The spectra show that the cold CT state decays with a concomitant repopulation of the ground-state region. An isosbestic point is discernible in the region around 620 nm, and the spectral band at 760 nm of the CT state undergoes a small blue shift to near 740 nm. Kinetic analysis at the 460 and 560 nm peaks (Table 1) indicates that the signals decay in a biexponential manner with lifetimes of ca. 2.5 and ca. 11 ps.

Excitation of the complex at 690 nm corresponds to the transition into the low-lying charge transfer state; thus, pumping the complex at this wavelength avoids the complications that have been discussed above. Figure 6 shows a series of spectra, the earliest of which (spectrum A) corresponds to a delay of 5 ps post zero (at such a delay the effects of chirp are negligible). The series (A−G) covers an elapsed time of ca. 20 ps. The presence of the large negative transient at 690 nm at 130 ps would appear to refute this assertion. However, this residual signal is due to scattered excitation light picked up in the spectrometer, which simply serves as an irreducible and constant background signal. The positive absorption peaks at 560 and 600 nm (Figure 6) reflect the situation found with 400 nm excitation, and now an isosbestic point at 650 nm is seen. Evidence of spectral activity in the >700 nm range is also discernible. The time profile at the 560 nm peak (Figure 6, inset) shows that the signal is formed within the response time of the instrument and decays in a biexponential manner. The two lifetimes were 1.9 and 9.7 ps. There appears to be little doubt that this 560 nm band, at least at the early times, arises from a transition out of the CT state, which has a 1.9 ps lifetime. The time profile at 600 nm is shown in Figure 6 (inset). Now we see an instantaneous growth followed by a delayed growth (1.9

ps rise time), followed by an exponential decay (12.8 ps lifetime). These observations lead to the conclusion that the instantaneous absorption at 600 nm derives from the CT state which decays with a 1.9 ps lifetime to generate a daughter state that also absorbs at both 560 and 600 nm (and has a band at 740 nm). This sequence implies an isosbestic point between the 560 and 600 nm species within the first few picoseconds after excitation. This is not evident in Figure 6 because at the earliest spectrum displayed (5 ps post zero) the precursor CT state has already decayed to completion. However, such an isosbestic can be discerned in Figure 4 (400 nm excitation). The daughter state into which the CT state converts is likely to be a metal-centered state. Recall from the preceding paper in the series[1] that in the free base−free base complex, the CT state had a lifetime of 3.65 ns and decayed radiatively. The Ni−Ni complex contains two d^8 atoms, and either is capable of becoming electronically excited by energy transfer from the LLCT state. Thus, it is proposed that the CT state decays into a Ni-centered state from which the ultimate ground state is regenerated (with isosbestic point at 650 nm) with a decay lifetime of 10−12 ps. In an earlier publication, it was shown[6] that monomeric NicrPc has an excited metal-centered state that repopulated the ultimate ground state with a decay lifetime of 12.8 ps, very close to that lifetime value found here. Conversely, in a preliminary experiment,[10] we have found that repopulation of the ultimate ground state in NiTPPS monomer occurs with a lifetime of 470 ps. It is therefore concluded that the most likely mode of decay of the LLCT state is to an electronically excited d,d state located on the NicrPc component.

The CucrPc−NiTPPS and the NicrPc−CuTPPS Complexes. Both these complexes showed very similar transient absorption spectra to those of the Ni−Ni variant discussed above. For instance, see Figure 7, which provides a series of spectra recorded after 400 nm excitation of the NicrPc-CuTPPs complex. All assignments made for the Ni−Ni case are carried through to this pair of complexes. Minor differences were evident at early times inasmuch as the absorption at 480 nm and the bleaching at 700 nm grew with a 10−90% rise time of ca. 500 fs compared to the value of ca. 700 fs for the Ni−Ni complex. The CT state had a lifetime of 1.8 ps.

The major item of note from the data in Table 1 is that for the NicrPc−CuTPPS complex the conversion of the metal-centered state to the ground state showed a lifetime of ca. 8 ps (see also Figure 7, inset), whereas for the CucrPc-NiTPPS complex this process had a lifetime of ca. 200 ps (Figure 8). It was argued above that for the Ni−Ni complex the most likely location for the excited metal-centered state was at the Pc component, and on that basis, coupled to the fact of the ca. 8 ps lifetime for the repopulation of the ground state, we argue that the excited metal-centered state in the NicrPc-CuTPPS complex is of the same nature.

The excited metal-centered state in the CucrPc-NiTPPS complex has a lifetime of ca. 200 ps. In an earlier publication from this laboratory, it was shown that following 400 nm excitation of monomeric CucrPc, the ultimate process that repopulated the ground state was $^4T \rightarrow {}^2S$. This was of single-exponential nature with a lifetime of 22 ± 1 ns.[7] There was no evidence for the formation of an excited metal-centered state. It seems reasonable to conclude, therefore, that the 200 ps lifetime in the deactivation sequence of the excited CucrPc−NiTPPS complex is not associated with an excited Cu-centered phthalocyanine state. On the other hand, NiTPPS has a metal-centered excited state that can serve as deactivation pathway. As indicated above, photoexcitation of monomeric NiTPPS generates a metal-centered state that undergoes monoexponential decay with the lifetime of ca. 470 ps, a factor of ca. 2 longer than that observed for the CucrPc−NiTPPS state. It is possible that the lower lifetime in the dimer is connected with the fact that the electronically excited Ni-center is perturbed by the presence of a nearby d^9 Cu center creating spin−spin interactions that enhance the energy-loss process. Kobayashi and Lever have reported[8] that homodimers of CucrPc molecules joined through Cs atoms situated in the crown residues show EPR signals that are different from those of the monomer CucrPc, indicating that Cu−Cu spin interactions occur. It seems not unreasonable to conclude that similar interactions occur when one of the metal centers is an electronically excited Ni.

CocrPc−FbTPPC Complex. As with the Ni−Ni complex, the bleaching of the CT absorption occurred with a 10−90% rise time of ca. 700 fs, indicating that the precursor porphyrin-like S_1 state had a lifetime greater than the instrument response time. Otherwise, as Figure 9 indicates, the spectral features were very similar to those described above for the three other complexes. The spectral dynamics above 700 nm is very clear evidence of a contribution first from the CT state (high absorbance at 760 nm), which rapidly changes to a species having a peak at 730 nm and subsequently decayed to the ground state with a lifetime of ca. 7 ps. The nature of the metal-centered state in this case is interesting. The only possibility is that the state is composed of a Co atom, since the free base component contributes no metal. Earlier work in this laboratory[6] has shown that the excited metal-centered state of monomeric CocrPc has a lifetime of 7.6 ps, a value close to that observed here for the complex. It is therefore concluded that the CT state of the complex deactivates through the metal-centered state located on the phthalocyanine component.

FbcrPc−FbTCPP Complex. The data presented in the previous paper in this series indicates that the CT complex is completely formed within 5 ps and decays (radiatively and nonradiatively) with a lifetime of 3.65 ns. However, as Figure 10 shows, there is evidence of a precursor of the CT state. The blue green absorption at 480 nm is formed within the instrument response time, whereas the bleaching of the CT absorption at 700 nm is clearly significantly delayed. In this respect, the Fb−Fb complex resembles the metal-centered complexes, and the explanation of the delay in the CT band bleach in those cases presumably holds here, viz., that the CT transition is unaffected by excitation into the porphyrin-like states and its loss is only manifest when the LLCT state contains an electron as a result of the decay of the porphyrin-like precursor S_1 state. It is intriguing to note that the early spectra in Figure 10 show none of the spectral features seen in Figures 3 and 4, for example. Thus, referring to Figure 10 (inset), it is seen that at 480 nm the time zero occurs at 1.4 ps, and by 2.4 ps all the rapid dynamic changes are complete and the system is in the CT state from which the ultimate ground state is reached. The lifetime of the promptly formed absorption at 480 nm is estimated to be 430 fs, which corresponds to the rise of the bleaching signal at the CT band maximum (700 nm). In the metal-centered complexes, the subpicosecond process was assigned to be the formation of a vibrationally excited CT state, which cooled with a 1.8 ps lifetime. There are no similar indications of rapid CT state cooling in the Fb−Fb complex.

It is thought to be unlikely that the LLCT state in the Fb−Fb complex cools more rapidly than the metal-centered variants. Indeed, vibrational deactivation of tetrapyrrole macrocycles normally occurs over 10 ps or so[9] and relates to the rate of transfer of vibrational energy from the π-framework to oscillators of the solvent molecules. The NicrPc and CocrPc monomers (in ethanol) were shown[6] to undergo vibrational relaxation with lifetimes of 1.3 ps, similar to those found here for the complexes. There the higher rates in the McrPc's were attributed to an intramolecular transfer from metal-centered oscillators into the oscillators of the π-framework. On these arguments, it appears likely that the cooling of the hot CT state in the Fb−Fb complex is relatively slow (10's of ps) and occurs without any significant extinction coefficient changes and that the ca. 430 fs process is the conversion from the porphyrin-like S_1 state into the (hot) LLCT state.

Concluding Remarks

The spectral and kinetic data obtained for the transition metal containing complexes lead to a general scheme that describes the deactivation pathways after photoexcitation. The LLCT state of the complexes visible in the ground state absorption spectrum can be accessed directly via excitation near 700 nm or indirectly by 400 nm excitation, which populates higher-lying porphyrin-like states. Such states decay into a vibrationally excited LLCT state within ca. 700 fs, significantly slower than the instrument response of ca. 250 fs. The porphyrin-like precursor states have absorption maxima at 450 and 480 nm. The CT state cools rapidly and converts to a metal-centered (d,d) state with lifetime of ∼2 ps. The metal-centered state regenerates the ground state with a lifetime in the 10 to 200 ps range, dependent on the central metal. All the evidence indicated that the LLCT state had McrPc radical cation character.

The absorption spectra of the complex ground states show clearly that porphyrin-like states are present and can be populated by blue-green radiation. The contributions to the spectra from phthalocyanine molecules appear to be limited to the transition to the LLCT state. The reason the act of complexation treats the components in different ways is not yet clear.

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