# Excited-State Photophysics of Donor-Appended Cobalt(II) Porphyrins from Picosecond Transient Absorption Spectroscopy

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Picosecond absorption spectra, obtained with 4-ps pump and probe pulses, are reported for the Co(II) complex of octaethylporphyrin (OEP) and of octaelkylporphyrins with single meso substituents: phenyl, N,N,N',N'tetramethyl-p-phenylenediamine (TMPD), dimethylaniline-N,N,N',N'-tetramethyl-p-phenylenediamine (DMA-TMPD), or a phenyl-TMPD. The donor substituents were attached in order to investigate the possibility of transferring charge to the putative Co<sup>(I)</sup>P<sup>+</sup> species transiently formed in the excited-state deactivation of cobalt-(II) porphyrins, thereby increasing the lifetime of a Co(I) phototransient. The substituents shifted the porphyrin ground-state absorption bands only slightly, and the redox potentials of the constituent parts of the constructs were essentially unaffected by the substitution. For all of the cobalt(II) porphyrins, photoexcitation produced transient bleaching of the ground-state Soret band and an induced absorption at ca. 410 nm. Ground-state recovery was complete within 50 ps in all cases. The lifetime of the phototransient was determined to be 12  $\pm$  4 ps for OEP, as well as all the *meso*-substituted octaalkylporphyrins. For the TMPD- and DMA-TMPDappended porphyrins, the transient absorption spectrum in the red region showed a single band at ca. 577 nm, identical to that observed for OEP. The absence of a band at 606 nm excludes significant involvement of oxidized TMPD; from the known absorptivity of TMPD cation, the extent of electron transfer was estimated to be less than 10%. Yet the 12-ps lifetimes should have been sufficient to support electron transfer, judging from rates and driving forces in analogous systems. It is therefore concluded that the observed phototransient is not the  $Co^{(1)}P^+$  charge-transfer (CT) state, as had previously been supposed, but rather a dd excited state. Deactivation of CT states via lower-lying dd states is likely to be a general phenomenon for first transition row metalloporphyrins. Stabilization of transiently reduced or oxidized metal centers via electron transfer from or to porphyrin peripheral substituents may, however, prove fruitful for second or third transition row metalloporphyrins, in which the available dd states may be raised above accessible CT states.

## Introduction

Porphyrins are widely used in research on photo-induced electron transfer and on catalysis. Straightforward to synthesize and stable, porphyrins have an extended aromatic  $\pi$ -electron system that supports reversible electron transfer at accessible redox potentials. The HOMO-LUMO gap is in the visible region, making photoexcitation convenient. A wide range of metal ions can be inserted into the porphyrin macrocycle, forming robust complexes that still have axial coordination sites available for facile ligand chemistry. A variety of stoichiometric and catalytic reactions of metalloporphyrin ligands have been explored.

In view of these properties, the possibility arises that photoexcitation of the porphyrin  $\pi\pi^*$  electronic transitions might be harnessed to useful catalytic reactions via transient reduction or oxidation of the central metal. Transition metals can introduce d orbitals at energies within the HOMO-LUMO gap, resulting in the availability of ligand  $\rightarrow$  metal charge transfer (CT), metal  $\rightarrow$  ligand CT, and/or dd excited states at energies below the lowest  $\pi\pi^*$  state, and therefore accessible to photoexcitation via the strongly allowed  $\pi\pi^*$  transitions. The CT states have metal ions that are transiently reduced or oxidized, while the porphyrin is transiently oxidized or reduced. Redox reactions of coordinated ligands can therefore be envisaged for CT states of metalloporphyrins. Unfortunately, because the recombination between redox partners in intimate contact is facile, such states are usually shortlived.

Much recent work has been directed toward establishing the determinants of intramolecular electron transfer using covalentlyattached electron donor and acceptor molecules. Porphyrins have been at the center of this research because of the convenience of photoexcitation in initiating electron transfer.<sup>1-4</sup> Donor and acceptor groups have been attached to the periphery of the porphyrin ring, and porphyrin-based molecular triads, tetrads, and pentads have been created, which support quite long-lived charge-separated states.<sup>3,5,6</sup> Much of this work has been inspired by the idea of building molecular electron relay devices, using the reaction center of photosynthetic bacteria and plants as a model. It occurred to us that the same idea could be used to build molecules in which the excited-state lifetime available for transient redox reactions could be significantly extended. By covalently attaching one or more donors or acceptors in a relay arrangement, it might be possible to further transfer the electron or hole localized on the porphyrin in a CT state before it recombines with the hole or electron on the metal ion. The resulting charge-separated state should have an extended lifetime, during which the transiently reduced or oxidized metal might be made to undergo useful chemistry.

We were drawn to cobalt porphyrins to test this idea. Co(I) is a strong nucleophile, and cobalt(I) porphyrins have been shown to undergo alkylation reactions and to reduce protons in water.<sup>7</sup> Considerations of redox potentials (see Discussion) as well as extended Hückel calculations<sup>8</sup> indicate that the ligand  $\rightarrow$  metal Co<sup>(I)</sup>P<sup>+</sup> (P = porphyrin) CT state lies well below the lowest-lying Co<sup>(II)</sup>P  $\pi\pi^*$  excited state, and should therefore be accessible as an intermediate in the excited-state deactivation of Co<sup>(II)</sup>P. In fact, Tait and Holten detected a phototransient absorption spectrum for cobalt(II) octaethylporphyrin (Co<sup>II</sup>OEP), which they attributed to this CT state.<sup>9</sup> The transient decayed very rapidly, with a lifetime of 10–20 ps, indicating efficient recom-

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#### SCHEME I





bination of the putative electron-hole pair. This lifetime is much too short to support bimolecular solution chemistry, but it is not too short for electron transfer at close range; recent literature on covalently modified porphyrins suggests that directly appended acceptors or donors can transfer electrons or holes on a subpicosecond time scale if an adequate driving force is provided.<sup>10</sup> To see if the Co(I) lifetime could be extended by a suitable donor, we appended the N, N, N', N'-tetramethyl-p-phenylenediamine molecule (TMPD), to a single meso carbon atom of an OEP-like porphyrin, hexaethyldimethylporphyrin (HEDM-T; Scheme I). TMPD has ample reducing power for the purpose at hand. As a control, we appended a phenyl group instead of TMPD (HEDM-P, Scheme I), to check the effect of a single bulky substituent on the photophysical properties of the cobalt(II) porphyrin. We also inserted an aniline ring between the TMPD and the porphyrin (TETM-AT-a slightly different porphyrin, tetraethyltetramethylporphyrin was used for synthetic convenience), with the aim of producing a donor relay. Aniline is capable of reducing a porphyrin cation, and the aniline cation is reducible by TMPD. The resulting extended charge separation should further increase the lifetime of photogenerated Co(I).

The photophysical properties of these donor-appended porphyrins in their free base form are described in the preceding study.<sup>11</sup> In this paper we report the transient absorption spectroscopy of the cobalt(II) porphyrin-donor complexes. The principle result is that all of the phototransient spectra look very much like that of Co<sup>II</sup>OEP and decay with similar lifetimes. TMPD is *not* oxidized during the phototransient lifetime, whether it is attached directly to the porphyrin ring or indirectly through the aniline. From this behavior we conclude that the phototransient is probably not the Co<sup>IP+</sup> CT state but rather a more rapidly formed dd excited state. It seems likely that CT states are quenched by lower-lying dd states for most first transition row metalloporphyrins and that for useful CT photochemistry one should generally look to second and third transition row metalloporphyrins, with larger dd splittings.

#### Materials and Methods

Synthesis of Cobalt(II) Porphyrin Complexes. All chemicals were obtained from Aldrich Chemical Co. (Milwaukee, WI) and

used as received, unless otherwise specified. Cobalt(II) OEP (Midcentury Chemical Co., Posen, IL) was used as received. Tetrahydrofuran (THF) was distilled over lithium aluminum hydride before use. NMR measurements were taken on a General Electric 300-MHz or a JEOL 270-MHz NMR spectrometer. A Kratos MS50 RFA high-resolution mass spectrometer was utilized for all mass spectroscopic measurements.

[2,5-(N,N,N',N'-Tetramethyldiamino)-1-(2,3,7,8,13,17-hexaethyl-12,18-dimethylporphyrin-5-yl)benzene]cobalt(II) Complex ( $Co^{II}HEDM$ -T). 2,5-(N,N,N',N'-Tetramethyldiamino)-1-(2,3,7,8,13,17-hexaethyl-12,18-dimethylporphyrin-5-yl)benzene free base<sup>11</sup> (2 mg, 0.003 mmol) is mixed with cobalt(II) acetate (5 mg, 0.02 mmol) and refluxed in N,N-dimethylformamide (5 mL) for 30 min under argon. The solvent is removed under reduced pressure and the residue redissolved in dichloromethane. Chromatography is performed on a silica preparative TLC plate, eluting with a dichloromethane/methanol (10:1) solution.

l-[(2,3,7,8,13,17-Hexaethyl-12,18-dimethylporphyrin-5-yl)benzene]cobalt(II) Complex (Co<sup>II</sup>HEDM-P). (2,3,7,8,13,17hexaethyl-12,18-dimethylporphyrin-5-yl)benzene free base<sup>11</sup> (2mg, 0.003 mmol) is mixed with cobalt(II) acetate (5 mg, 0.02mmol) and refluxed in N,N-dimethylformamide (5 mL) for 30min under argon. The solvent is removed under reduced pressureand the residue redissolved in dichloromethane. Chromatographyis performed on a silica preparative TLC plate, eluting with adichloromethane/methanol (10:1) solution.

[2',5'-(N,N,N',N'-Tetramethyldiamino)-4-(2,3,7,8,13,17-hexaethyl-12,18-dimethylporphyrin-5-yl)biphenyl]cobalt(II) Complex (Co<sup>II</sup>HEDM-PT). 2',5'-(N,N,N',N'-Tetramethyldiamino)-4-(2,3,7,8,13,17-hexaethyl-12,18-dimethylporphyrin-5yl)biphenyl free base<sup>11</sup> (2 mg, 0.003 mmol) is mixed with cobalt(II) acetate (5 mg, 0.02 mmol) and refluxed in N,N-dimethylformamide (5 mL) for 30 min under argon. The solvent is removed under reduced pressure and the residue redissolved in dichloromethane. Chromatography is performed on a silica preparative TLC plate, eluting with a dichloromethane/methanol (10:1) solution.

[N-(4-(3,7,13,17-Tetraethyl-2,8,12,18-tetramethylporphyrin-5-yl)phenyl)-N'-(4'-(dimethylamino)phenyl)piperazine]cobalt(II) Complex (Co<sup>II</sup>TETM-AT). N-(4-(3,7,13,17-Tetraethyl-2,8,12,18-tetramethylporphyrin-5-yl)phenyl)-N'-(4'-(dimethylamino)phenyl)piperazine free base<sup>11</sup> (2 mg, 0.003 mmol)is mixed with cobalt(II) acetate (5 mg, 0.02 mmol) and refluxedin N,N-dimethylformamide (5 mL) for 30 min under argon. Thesolvent is removed under reduced pressure and the residueredissolved in dichloromethane. Chromatography is performedon a silica preparative TLC plate, eluting with a dichloromethane/methanol (10:1) solution.

Electrochemical Measurements. Reagent quality tetrabutylammonium perchlorate (Fluka) was recrystallized three times from ethanol and dried in a vacuum oven prior to use. o-Difluorobenzene (Aldrich, 99%) was either filtered through activated alumina or fractionally distilled and then stored over activated molecular sieves before use. Cyclic voltammograms were taken in a three chambered cell, with the counter, working, and reference electrodes arranged in a linear fashion, separated by glass frits. All potentials were referenced to a saturated sodium chloride/ calomel electrode, with a 1-cm<sup>2</sup> platinum working electrode and a platinum wire counter electrode. The platinum electrodes were soaked in acid and heated on an open flame until red hot prior to each use to remove water and ensure a fresh surface. Measurements were performed with a Princeton Applied Research (Princeton, NJ) programmable potentiostat. Each cyclic voltammogram was internally calibrated with the known redox couple of decamethylferrocene (-0.059 V vs SCE).

**Picosecond Absorption Spectroscopy.** The picosecond transient apparatus has been previously described.<sup>11</sup> Briefly, the second



Figure 1. Background-free autocorrelation trace of the 552-nm laser pulses from the synchronously-pumped dye laser with fluorescein 548; the width is  $1.5 \pm 0.2$  ps. The fluorescein dye laser had a 1-plate birefringent filter.

harmonic of a Coherent Antares continuous wave (cw), modelocked Nd:YAG laser synchronously pumped a Coherent 702 dye laser tuned to 552 nm. Background-free autocorrelation traces of the dye laser pulses are shown in Figure 1. Amplification of this pulse in a three-stage, excimer-pumped dye amplifier yielded pulses of 80-100  $\mu$ J. The output of the amplifier was split into two beams to generate the pump and probe by utilizing a 70%R/ 30%T partial beam splitter. For the probe beam, 30% of the amplified pulse was directed through an optical delay line and focused into a 10-cm cell containing either ethylene glycol or chloroform/carbon tetrachloride (4:6) to generate a continuum. A portion of the continuum was selected using a 380-500 bandpass filter (Oriel Corp.) or a 560-nm long-pass filter (Corning Glass Co.) and then split into two beams using a 50%T/50%R beam splitter. The pump beam was focused to a 1.5-mm-diameter spot at the sample with a 1000-mm lens. One of the probe beams and the pump beam were crossed at the sample. The crosscorrelation width at the sample was found to 4.5 ps with ZnTPP as previously described.<sup>11</sup> Lengthening of the pulse width in the time domain probably occurs as a result of dispersion in the continuum generating cell and dye amplifier. The other probe beam passed through an unexcited part of the sample. The transmitted probe beams were collected by a bifurcated fiber optic cable connected to a single, 0.32-m, f/4.8 single monochromator (Instruments SA) coupled to a dual diode array optical multichannel detector (Princeton Instruments). Rejection of the pump beam from the spectrometer was accomplished by an identical 380-500-nm band-pass or 560-nm long-pass filter placed after the sample.

Sample solutions were prepared under a nitrogen atmosphere to a final concentration of ~45  $\mu$ M assuming an extinction coefficient of 229 000 cm<sup>-1</sup> M<sup>-1</sup> at the Soret maxima for the 350-480-nm region experiments and ~250  $\mu$ M assuming an extinction coefficient of 27 500 cm<sup>-1</sup> M<sup>-1</sup> at the Q<sub>0</sub> maxima for the 560-660-nm region experiments.<sup>12</sup> o-Difluorobenzene (99+%, Aldrich) was deoxygenated as above and was used as the solvent for all transient absorption experiments. Solutions were placed in a 1-mm path length cuvette. No evidence of irreversible photochemistry was observed in a comparison of probe-only spectra taken before and after photolysis or in a comparison of bulk absorption spectra taken before and after the experiment. Experiments were repeated on two samples. Spectra were calibrated with Hg emission lines and reported wavelengths are accurate to ±2 nm.

# Results

The results of electrochemical measurements on the cobalt-(II) porphyrins are given in Table I. All cyclic voltammogams exhibited good resolution and excellent signal-to-noise ratios between -2.0 and +1.2 V vs SCE.13 Adding a meso substituent lowers the porphyrin ring oxidation potential slightly, 0.03-0.12 V, from the 0.88 V observed for OEP (the previously reported 1.00 V was for a butyronitrile solution,<sup>35</sup> whereas the current measurements are in o-difluorobenzene.) The Co(II)/(I) reduction potentials are all within 0.05 V of 1.05 V. The TMPD oxidation potential is 0.30-0.35 V, whether the TMPD is attached directly to the porphyrin or separated by a spacer, and is similar to the value reported for TMPD in isolation, 0.22 V in acetonitrile.<sup>14</sup> Likewise the aniline oxidation potential, 0.63 V, is close to that reported previously for unappended dimethylaniline. 0.74 V in acetonitrile.14 Thus, covalent attachment has very little effect on the electron-transfer energetics of the constituent parts of the molecules.

Absorption spectra of the cobalt(II) porphyrins are shown in Figure 2. Both the Soret and Q-bands red-shift 5 nm upon addition of a phenyl group at a single *meso* position (Co<sup>II</sup>HEDM-P vs Co<sup>II</sup>OEP). This red shift is also seen in free base HEDM-P and is attributed to a combination of steric and electronic effects.<sup>11,15</sup> The additional 5–6-nm red shift of the Soret and Q<sub>0</sub> bands and 3-nm red shift of the Q<sub>1</sub> band upon changing the *meso* substituent from a phenyl group to a more electron-rich substituent in the cobalt<sup>II</sup>HEDM-T, -HEDM-PT, and -TETM-AT porphyrins probably arises from increased electron density in the porphyrin ring induced by the amino groups.<sup>16</sup> The perturbation on the energy levels is very small, ca 0.02–0.04 eV. Thus the porphyrin  $\pi\pi^*$  states are only weakly affected by the substitutions.

Picosecond transient absorption difference spectra of the cobalt-(II) porphyrins in the 350-480-nm region are shown in Figures 3-7. All of the cobalt(II) porphyrins show bleaching of the ground-state Soret band together with an induced absorption on the low-energy side of the ground-state Soret band. The band shapes are the same, within experimental error, except that CoII-OEP also exhibits some induced absorption on the high-energy side of the ground-state Soret band. The nature of the phototransient species is not easily deduced from these data. The spectrum of the putative CoIP+ state is not known, of course. The radical cation Co<sup>II</sup>OEP+ absorbs mainly at 376 nm,<sup>17</sup> but this wavelength might be shifted by the Co(II) reduction; Co<sup>I</sup>OEP shows absorption bands both above and below the Co<sup>II</sup>OEP Soret band, at 352 and 413 nm.<sup>18</sup> The fact that the induced absorption is mainly to the red of the ground-state Soret band is also consistent with a dd excited state, as discussed below.

A rough estimate of the ground-state recovery kinetics can be obtained from the Soret bleach in Figures 3–7. In all cases the ground-state recovered completely within 50 ps. First-order kinetic analysis of the Soret bleach recoveries of the cobalt(II) complexes yielded lifetimes of  $12 \pm 4$  ps for OEP, HEDM-P, HEDM-PT, HEDM-T, and TETM-AT. Tait and Holten had estimated the Co<sup>II</sup>OEP phototransient lifetime to be 10–20 ps,<sup>9</sup> but, in view of the 35-ps pulse width of their laser, the difference is probably not significant; the different solvents, toluene vs o-difluorobenzene used in this study, might, however, have an effect on the relaxation rates. The magnitude of the absorption changes at "0 ps" is variable in Figures 3–7, because of the inherent imprecision of overlapping the 4.5-ps pulses; there is no evidence for a measurable picosecond rise time.

Figures 8 and 9 show transient absorption difference spectra in the 560–660-nm region for the Co(II) complexes of HEDM-T and TETM-AT. This region was selected to probe for the characteristic two-banded signature of TMPD<sup>+</sup> radical cation, at 565 and 606 nm. This signature is not observed (vide infra). Rather an induced absorption is seen at 577 nm, somewhat to the red of the ground-state  $Q_0$  band (560 nm, Figure 2) and similar

TABLE I: Redox Potentials (V) for Cobalt(II) Porphyrins<sup>a</sup>

porphyrin	$\Delta \epsilon_{P^+/P}$	$\Delta \epsilon_{T^{+}/T}$	$\Delta \epsilon_{A^+/A}$	$\Delta \epsilon_{Co(II)/(I)}$	$-\Delta U_{cs1}^{b}$	$-\Delta U_{cs2}{}^c$	$-\Delta U_{ca3}{}^d$
Co <sup>II</sup> OEPe	1.00			-1.04	0.18		
Co <sup>II</sup> OEP	0.88			-1.02	0.32		
Co <sup>II</sup> HEDM-P	0.85			-1.00	0.37		
Co <sup>II</sup> HEDM-T	0.83	0.30		-1.08	0.31	0.53	
Co <sup>II</sup> HEDM-PT	0.81	0.33		-1.00	0.41	0.48	
CollTETM-AT	0.76	0.35	0.63	-1.05	0.41	0.13	0.28

<sup>a</sup> The values in the first four columns are measured half-wave potentials from cyclic voltammograms obtained in o-difluorobenzene, unless otherwise indicated. From left to right, the potentials correspond to porphyrin oxidation, TMPD oxidation, aniline oxidation, and cobalt reduction, respectively. <sup>b</sup> Exothermicity of the photoinduced charge transfer from porphyrin to cobalt(II) calculated from  $-\Delta U_{col} = E_{Sl} - E_{P'/P} + E_{Co(II)/(I)}$  with  $E_{Sl} = 2.22$ eV (558 nm). <sup>c</sup> Exothermicity of the charge transfer from TMPD to the porphyrin cation for cobalt(II) HEDM-T and HEDM-PT. Exothermicity of the charge transfer from aniline to the porphyrin cation for cobalt(II) TETM-AT. Calculated from  $-\Delta U_{col} = -E_{P'/P} - E_{T^*/T}$  (or  $E_{A^*/A}$ ). <sup>d</sup> Exothermicity of the charge transfer from TMPD to the aniline cation for cobalt(II) TETM-AT. Calculated from  $-\Delta U_{col} = E_{A^*/A} - E_{T^*/T}$ . <sup>c</sup> From ref 35. The porphyrin oxidation was performed in 0.1 M TBAP in butyronitrile, and the cobalt(II) reduction was performed in 0.01 TBAP in DMSO. <sup>f</sup> Measured in THF.



#### Wavelength (nm)

Figure 2. Ground-state absorption spectra of the indicated cobalt(II) porphyrins. The Q-band region from 490 to 650 nm has been expanded by a factor of 6. Addition of a phenyl group on one of the *meso* positions of octaalkylporphyrin red-shifts the Soret and both Q-bands by 5 nm. Additional 3-5-nm red shifts are seen for porphyrins with TMPD-derived substituents.

to the induced absorption reported by Tait and Holten for Co<sup>II</sup>-OEP.<sup>9</sup> Tait and Holten reported a significant narrowing of the absorption in the first few picoseconds,<sup>9</sup> and this phenomenon can also be seen in our Co<sup>II</sup>HEDM-T spectra; the 5-ps spectrum is conspicuously broad.

## Discussion

**Co(I) and the Electron-Transfer Pathway.** The motivation for this study was to harness the photophysics of the porphyrin chromophore to the redox chemistry of the central metal ion, using charge-transfer (CT) excited states in which the metal is transiently oxidized or reduced. Cobalt(II) porphyrins support reduction to Co(I) at potentials more positive than those required to reduce the porphyrin, and therefore have accessible CT excited states. The potential drop from the initially excited porphyrin S<sub>1</sub> state to the Co<sup>IP+</sup> CT state is given by the difference between the S<sub>1</sub> energy, 2.22 eV for the cobalt(II) porphyrins in this study (obtained from the Q<sub>0</sub> band center, 556 nm), and the difference between the redox potentials for the porphyrin/porphyrin cation couple, ca +0.8 V, and Co(II)/(I) couple, ca. -1.0 V. This potential drop is therefore ca. 0.4 eV (Table I).

The participation of a  $Co^{I}P^{+}$  CT state in the excited-state deactivation of cobalt(II) porphyrins has been suggested in results from picosecond transient absorption spectroscopy. Tait and Holten assigned the observed  $Co^{II}OEP$  phototransient spectrum



Figure 3. Transient absorption difference spectra, at the indicated probe delays, for  $Co^{II}OEP$  in benzene, obtained in the Soret region. Excitation was at 552 nm. The continuum extended from 350 to 460 nm.



Figure 4. As in Figure 3, but for Co<sup>II</sup>HEDM-P in o-difluorobenzene, with a 330-450-nm continuum.

to this CT state.<sup>9</sup> In cobalt(II) tetraphenylporphyrin (Co<sup>II</sup>TPP), a CT state was also suggested as one possible reason for the rapid S<sub>1</sub> excited-state deactivation.<sup>19</sup> With our 4.5-ps pulses, we are able to obtain a value of  $12 \pm 4$  ps for the lifetime of the observed transient. The same lifetime was obtained for our control molecule



Figure 5. As in Figure 3, but for Co<sup>II</sup>HEDM-T in o-difluorobenzene, with a 330-455-nm continuum.



Wavelength (nm)

Figure 6. As in Figure 3, but for  $Co^{II}$ HEDM-PT in o-diffuorobenzene, with a 360–470-nm continuum.

Co<sup>II</sup>HEDM-P, showing that a non-electron donor, *meso*-phenyl substituent does not affect the photophysics on this time scale.

The 12  $\pm$  4-ps lifetime of photoexcited Co<sup>II</sup>OEP should be long enough to support reduction of the CT state by TMPD when it is directly attached to the porphyrin ring, as in Co<sup>II</sup>HEDM-T. The driving force for this process is 0.53 eV, the difference between the reduction potentials for the porphyrin and TMPD cations (Table I). Our previous study of free-base HEDM-T gave an upper limit of 1.5 ps to the lifetime for charge transfer from the TMPD to the photoexcited porphyrin, a process with a 0.25-eV driving force.<sup>11</sup> In a study of porphyrins with directly appended quinone acceptors by Wasielewski et al. a similar decrease in driving force from 0.53 to 0.25 eV was found to decrease the charge separation rate by almost an order of magnitude.<sup>20</sup> Thus, the Co<sup>IP+</sup> state should oxidize directly appended TMPD in roughly 0.15 ps, a time much shorter than the lifetime of the Co<sup>II</sup>OEP phototransient. When a phenyl spacer was inserted between the porphyrin and the TMPD, in HEDM-PT, the fluorescence lifetime of the free base was found to increase to 1.3 ns, reflecting 3 orders



Figure 7. As in Figure 3, but for Co<sup>II</sup>TETM-AT in *o*-difluorobenzene, with a 360–470-nm continuum.



Figure 8. Transient absorption spectra in the red region for  $Co^{II}$ HEDM-T. Excitation was at 552 nm. The continuum extended from ~570 to 660 nm.

of magnitude slowing of the electron-transfer rate.<sup>11</sup> Thus, no electron transfer is expected within the CT-state lifetime for the Co(II) complex. It is therefore not surprising that the ground-state recovery rate is the same for Co<sup>II</sup>HEDM-PT as for Co<sup>II</sup>-HEDM-PT as for Co<sup>II</sup>-HEDM-PT as for Co<sup>II</sup>-HEDM-PT.

The use of free-base data to estimate the charge separation rate for the cobalt systems ignores the possible difference in reorganizational energy. This difference should be small, however, since the critical electron-transfer step involves the same orbitals in the two cases. The acceptor species is Co<sup>I</sup>P<sup>+</sup> in one case and the excited singlet state, 1P\*, in the other. However, the electron is transferred from the TMPD to the hole in the porphyrin HOMO in both cases. The inner shell reorganizational energy should therefore be the same, and the outer shell reorganizational energy, which depends on the electron-transfer distance and on the static and optical dielectric constants, is unlikely to differ appreciably. Wasielewski et al. have shown that the quinone-appended porphyrin free bases and zinc(II) complexes lie on the same free energy diagram, suggesting that electrochemical measurements are sufficient to account for any potential changes in solvent reorganizational energy as a result of the substitution of a metal ion for protons in the porphyrin center.<sup>20,21</sup>



Figure 9. As in Figure 8, but for Co<sup>II</sup>TETM-AT, with a  $\sim$  560–680-nm continuum.

The situation is less clear-cut for aniline as a donor. The porphyrin TETM-AT was constructed in order to provide an electron relay; the aniline can reduce the porphyrin cation formed in the Co<sup>IP+</sup> CT state and in turn be reduced by the TMPD. In free-base porphyrins, the P-A+ CT state is higher in energy than the  $S_1$  state and is therefore not accessible.<sup>11</sup> Aniline, though, is a strong enough reductant to subsequently reduce the porphyrin cation. But the driving force is low, 0.13 eV (Table I), and the electron-transfer rate may be insufficient to compete with collapse of the CT state. If the electron is transferred, then the next step, reduction of the aniline cation by the attached TMPD, has substantial driving force, 0.28 eV. Our measured ground-state recovery time for  $Co^{II}TETM$ -AT is  $12 \pm 4$  ps, essentially identical to that of Co<sup>II</sup>OEP and Co<sup>II</sup>HEDM-P. Within experimental error, the same lifetime was measured for Co<sup>II</sup>HEDM-T. These times are surprisingly short, if the process being monitored is charge recombination from Co(I) to the oxidized donor. For free-base HEDM-T, we obtained a 26-ps lifetime for charge recombination between TMPD<sup>+</sup> and the porphyrin anion, a process with a 1.73-eV driving force.<sup>11</sup> For the states Co<sup>I</sup>HEDM-T<sup>+</sup> and Co<sup>I</sup>TETM-AT<sup>+</sup>, the driving force for recombination is 1.38 and 1.40 eV, respectively (Table I). These large potential differences are probably in the "inverted region" of the Marcus rate relation,<sup>22</sup> and for equal distances of transfer the Co(I) to TMPD<sup>+</sup> recombination may be faster than the porphyrin anion to TMPD+ recombination. But the distances are clearly not equal. The porphyrin anion and TMPD<sup>+</sup> are connected by a single bond in the free-base HEDM-T charge-separated state, while for Co<sup>I</sup>-HEDM-T<sup>+</sup> the neutral porphyrin ring intervenes between the charge centers, and in Co<sup>I</sup>TETM-AT<sup>+</sup>, the diethylaniline ring provides an additional spacer. It is quite implausible that the recombination rate from Co(I) to oxidized TMPD<sup>+</sup> should be the same for Co<sup>II</sup>TETM-AT as for Co<sup>II</sup>HEDM-T, or that they should be twice as fast as the P- to TMPD+ recombination in free-base HEDM-T. The rates are therefore inconsistent with charge separation in the cobalt porphyrin excited states.

Conclusive evidence against charge separation is provided by the picosecond absorption spectrum of photoexcited  $Co^{II}HEDM$ -T and  $Co^{II}TETM$ -AT in the 550–650-nm spectral region (Figures 8 and 9). The absorption spectrum of TMPD<sup>+</sup> is well-known<sup>23</sup> to have two strong bands in this region, at 565 and 606 nm. We obtained the same two bands for  $Co^{II}HEDM$ -T<sup>+</sup> prepared by electrochemical oxidation (in *o*-difluorobenzene). The absorption spectra of the  $Co^{II}HEDM$ -T and  $Co^{II}TETM$ -AT phototransients, however, have a single band at 577 nm. The absorbance at 606 nm is very low. From the TMPD<sup>+</sup> extinction coefficient at this wavelength<sup>23</sup> (12 000 cm<sup>-1</sup> M<sup>-1</sup>) we estimate an upper limit of 10% for the fraction of photoexcited molecules that could contain TMPD<sup>+</sup>.

Reassignment of the Cobalt(II) Porphyrin Phototransient. Since the directly attached TMPD should be oxidized by porphyrin radical cation well within the  $12 \pm 4$ -ps lifetime of the Co<sup>II</sup>-HEDM-T phototansient, we infer that the phototransient does not involve the Co<sup>I</sup>P<sup>+</sup> CT state to a significant extent. Nevertheless, the phototransient absorption spectrum is very similar to that of Co<sup>II</sup>OEP. Tait and Holten were led to assign this spectrum to the Co<sup>I</sup>P<sup>+</sup> state from the observation that the photoinduced absorption band narrows significantly in the first few picoseconds;9 this narrowing is also seen in our Co<sup>II</sup>HEDM-T spectrum (Figure 8). (The narrowing is not apparent in the Co<sup>II</sup>TETM-AT data (Figure 9), because the 5-ps time point was missed). Radical cation absorption bands are known to be somewhat narrower than absorption bands of singlet or triplet  $\pi\pi^*$  states. The early process was attributed to decay of a  $\pi\pi^*$  excited state (postulated to be the tripdoublet state <sup>2</sup>T, populated via intersystem crossing from the singdoublet state  ${}^{2}Q$  to the Co<sup>I</sup>P<sup>+</sup> state.

A plausible alternative assignment is available for the cobalt-(II) porphyrin phototransients, however. They could arise from a dd excited state. The energy differences among the Co(II) d orbitals are expected to be smaller than the HOMO-LUMO energy gap. Indeed the Co(II) porphyrin energy level scheme of Antipas and Gouterman, based on IEH calculations, suggests a d orbital excitation ( $d_{\pi}$  to  $d_{z^2}$ ) at ca. 0.3 eV.<sup>8</sup> Determination of the d-orbital energies and low-lying excited states from ESR data of cobalt(II) porphyrins also suggest that up to seven possible dd states may lie below 1.24 eV, well below the lowest-lying singlet and postulated Co<sup>I</sup>P<sup>+</sup> CT state.<sup>24</sup> Also, photoproduction of dd excited states is expected to be extremely rapid. In the case of nickel(II) porphyrins, for example, conversion of the initially excited  $\pi\pi^*$  state to a low-lying dd excited state has been estimated to occur in 0.35 ps.<sup>25</sup> Interestingly, the nickel(II) porphyrin phototransient absorption bands also narrow significantly during the first few picoseconds. This narrowing has been attributed to vibrational cooling of the dd excited state,<sup>25</sup> a likely explanation as well for the narrowing of the Co(II) phototransient spectra. The absorption spectrum for a metalloporphyrin dd excited state should show the same Q and B bands as the ground state, but with shifted energies. For nickel(II) porphyrins the B and Q bands are red-shifted in the dd excited state. The cobalt(II) porphyrin phototransient bands at 410 and 577 nm are likewise assignable to the B and Q bands of a dd excited state, red-shifted from their ground-state counterparts. For all these reasons, a dd assignment is indicated for all the cobalt(II) porphyrin picosecond phototransients.

This reassignment leads to the proposed photoexcitation scheme shown in Figure 10. The  $\pi\pi^*$  states are rapidly deactivated by conversion to a dd state, which decays to the ground state with a ca. 10-ps time constant. Since the CT state lies between the ground and S<sub>1</sub> states, it can also be on the deactivation pathway, but it cannot live for an appreciable fraction of 5 ps; otherwise Co<sup>I</sup>HEDM-T<sup>+</sup> would have been detected. The similarity of the phototransient absorption spectra and kinetics of all the cobalt-(II) porphyrins indicate that the processes of photodeactivation are the same.

Implications for Photoinduced Metal Redox Chemistry. In retrospect, it is not surprising that charge-transfer photochemistry in a first transition row metalloporphyrin would be short circuited by low-lying dd states. The gaps among d orbitals in divalent metal ions of the first transition row are of the order of 1.5 eV or less, well below the porphyrin  $\pi\pi^*$  states. Because of large metal-ligand bond length changes associated with d orbital population changes, radiationless transitions to and from the dd excited states are rapid. This is the reason that open shell



Figure 10. Schematic diagram of cobalt(II) porphyrin excited-state energetics and decay pathways, showing rapid deactivation to a low-lying dd state, which decays in ca. 10 ps. Additionally, a  ${}^{2}T_{1}$  tripdoublet state may be involved in the excited-state deactivation has been predicted to lie between the  $S_1$  and  $Co^{I}P^+$  CT states (See text).

metalloporphyrins of the first transition row generally have extremely weak luminescence.

Competition between CT and dd excited states is a welldeveloped theme in inorganic photochemistry. The photochemistry is determined by which state lies lowest in energy. For example, for pentaamineruthenium(II) heterocycle complexes in water, the energy of the metal-ligand charge-transfer (MLCT) state has been shown to control the photochemistry.<sup>26</sup> When the MLCT absorption is to the blue of ca. 460 nm, then photoexcitation leads to ligand replacement by water via a lower-lying dd excited state. For longer-wavelength MLCT absorptions, the photosolvation yield drops sharply, the MLCT state now falling below the photoactive dd state.26

Applying this lesson to metalloporphyrins, it is clear that utilizing CT photochemistry will require careful attention to the dd energies. Only when the lowest-lying dd excitation requires more energy than the CT excitation of interest, is it likely that the CT state can be utilized. This requirement rules out most first row transition metalloporphyrins. The second and third row transition metals, having larger d orbital splittings, are much likelier candidates. In addition, the larger spin-orbit coupling of the heavier transition metals gives access to longer-lived CT states, by mixing in triplet character. This is the main factor in the popularity of  $Ru(bpy)_3^{2+}$  as an inorganic photosensitizer.<sup>27</sup> It has a particularly long-lived (650- $\mu$ s) CT triplet excited state, in this case involving charge transfer from metal to ligand. Likewise, some ruthenium(II) porphyrins have well-characterized MLCT excited states, with lifetimes in the tens of nanoseconds.<sup>28</sup> These states can be circumvented by binding a CO molecule to the Ru(II) ion, thereby stabilizing the donor d-orbitals and raising the energy of the MLCT state above that of the triplet.<sup>28</sup> It should be noted that the MLCT state is not deactivated by dd states, which lie too high in energy. The MLCT state of ruthenium(II) porphyrins is Ru<sup>III</sup>P-. Unfortunately, Ru(III) is not expected to be a reactive metal center<sup>29</sup> and holds little promise for catalysis. Ruthenium(V) and ruthenium(VI) porphyrins have shown a great deal of promise as oxygen-transfer catalysts,<sup>30</sup> but these oxidation states have never been achieved photochemically. Rhodium porphyrins, however, have a rich array of redox chemistry<sup>31</sup> and show promise as catalysts for a variety of chemical processes. 32-34 They may also have low-lying LMCT states, 8 which could be accessed photochemically. It is possible that rhodiumbased photochemistry could be developed in useful directions with the aid of covalently modified porphyrins.

#### Conclusions

Covalently attached TMPD is not oxidized by photoexcited cobalt(II) porphyrin, although the ca. 12-ps lifetime should be ample for supporting electron transfer if the phototransient were

Co<sup>I</sup>P<sup>+</sup>, as has previously been thought. Instead the phototransient is assigned to an excited dd state of Co<sup>II</sup>P. Utilization of metalloporphyrin CT states via covalently attached donors or acceptors will require tuning the (dd) states to higher energy, probably by exploiting the properties of second and third transition row metals.

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#### **References and Notes**

(1) Wasielewski, M. R. Chem. Rev. 1992, 92, 435-461.

(2) Hoffman, B. M.; Natan, M. J.; Nocek, J. M.; Wallin, S. A. Struct. Bonding (Berlin) 1991, 75 (Long-range Electron Transfer in Biology), 85-108.

(3) Gust, D.; Moore, T. A.; Moore, A. L.; Makings, L. R.; Seely, G. R.; Ma, X.; Trier, T. T.; Gao, F. J. Am. Chem. Soc. 1988, 110, 7567-7569.

(4) Sakata, Y.; Tsue, H.; Goto, Y.; Misumi, S.; Asahi, T.; Nishikawa,
 S.; Okada, T.; Mataga, N. Chem. Lett. 1991, 1991, 1307-1310.

(5) Wasielewski, M. R.; Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P. J. Am. Chem. Soc. 1990, 112, 4559-4560.

(6) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L. I.; Wasielewski, M. R. Science 1992, 257, 63-65

(7) Kellett, R. M.; Spiro, T. G. Inorg. Chem. 1985, 24, 2373-2377. (8) Antipas, A.; Gouterman, M. J. Am. Chem. Soc. 1983, 105, 4896-4901

(9) Tait, C. D.; Holten, D. Chem. Phys. Lett. 1983, 100, 268-272.

(10) Wasielewski, M. R. In Photoinduced Electron Transfer, Part A-Conceptual Basis; Fox, M. A., Chanon, M., Eds.; Elsevier, New York, 1988; pp 161-206

(11) Loppnow, G. R.; Melamed, D.; Spiro, T. G. J. Phys. Chem., preceding paper in this issue

(12) Smith, K. Porphyrins and Metalloporphyrins; Elsevier: New York, 1975; p 910. (13) The cyclic voltammogram of free base TETM-AT was found to be

irreversible in o-difluorobenzene but was reversible in THF11 and has been attributed to possible polymerization of the dialkylaniline moiety.

(14) Reed, R. C.; Wightman, R. M. In Encyclopedia of Electrochemistry of the Elements; Bard, A. J., Lund, H., Eds.; Dekker, New York, 1984; pp 1-165.

(15) Gouterman, M. J. Chem. Phys. 1959, 30, 1139-1161.

(16) Meot-Ner, M.; Adler, A. D. J. Am. Chem. Soc. 1972, 94, 4763–4764.
(17) Salehi, A.; Oertling, W A.; Babcock, G. T.; Chang, C. K. J. Am. Chem. Soc. 1986, 108, 5630–5631.

(18) Lexa, D.; Momenteau, M.; Mispelter, J.; Saveant, J.-M. Inorg. Chem. 1989, 28, 30-35.

(19) Dzhagarov, B. M.; Timinskii, Y. V.; Chirvonii, V. S.; Gurinovich, G. P. Dokl. Biophys. 1979, 247, 138-140.

(20) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. J. Am. Chem. Soc. 1985, 107, 1080-1082

(21) Wasielewski, M. R.; Niemczyk, M. P. J. Am. Chem. Soc. 1984, 106, 5043-5045.

(22) Marcus, R. A.; Sutin, N. Biochim. Biophys. Acta 1985, 811, 265-322

(23) Albrecht, A. C.; Simpson, W. T. J. Am. Chem. Soc. 1955, 77, 4454-4461.

(24) Lin, W. C. Inorg. Chem. 1976, 15, 1114-1118.

(25) Rodriguez, J.; Holten, D. J. Chem. Phys. 1989, 91, 3525–3531.
 (26) Malouf, G.; Ford, P. C. J. Am. Chem. Soc. 1977, 99, 7213.

(27) Kalyanasundaram, K. Photochemistry of Polypyridine and Porphyrin Complexes; Academic Press: New York, 1992; p 626.

(28) Holten, D.; Gouterman, M. In Optical Properties and Structure of Tetrapyrroles; Blauer, G., Sund, H., Eds.; de Gruyter: New York, 1985; p 63.

(29) Brown, G. M.; Hopf, F. R.; Ferguson, J. A.; Meyer, T. J.; Whitten, D. G. J. Am. Chem. Soc. 1975, 97, 5939-5942.

(30) Groves, J. T.; Quinn, R. J. Am. Chem. Soc. 1985, 107, 5790-5792. (31) Kadish, K. M.; Yao, C.-L.; Anderson, J. E.; Cocolios, P. Inorg. Chem.

1985, 24, 4515–4520. (32) Wayland, B. B.; Ba, S.; Sherry, A. E. J. Am. Chem. Soc. 1991, 113, 5305-5311.

(33) Wayland, B. B.; Poszmik, G.; Fryd, M. Organometallics 1990, 11, 3534-3542.

(34) Bosch, H. W.; Wayland, B. B. J. Chem. Soc., Chem. Commun. 1986, 900-901.

(35) Felton, R. H. In The Porphyrins; Dolphin, D., Ed.; Academic Press: New York, 1978; p 53.