

These observations on the photochemistry of rhodium(III) phthalocyanines show that the primary photoprocesses cannot be described as originating in excited states with acido to metal charge-transfer character. Such a primary photoreactivity can be assigned to reactive $n\pi^*$ states similar to the excited state populated in ultraviolet irradiations of the monomeric copper(II) and cobalt(II) sulfophthalocyanines.^{9,10} Another possibility is the induced oxidation of the solvent when acido to rhodium(III) states are populated. Photoprocesses with this nature, namely, the induced oxidation of the solvent by repolarization of the solvation sphere, have been previously reported for excitations of the acidopentaamminecobalt(III) complexes for acido to cobalt(III) charge-transfer states.^{25,43}

The fact that the photochemistry of the rhodium(III) phthalocyanines is detected at low photonic energies, e.g., $\lambda_{\text{excit}} \approx 400 \text{ nm}$,⁴⁴ is inconsistent with an oxidation of the solvent by repolarization of the solvation sphere. In addition, the charge-transfer states that involve the phthalocyanine ligand, e.g., $\text{CTTM}_{\text{ph} \rightarrow \text{Rh}}$ and $\text{CTTL}_{\text{Rh} \rightarrow \text{ph}}$, are not expected to be able to oxidize the solvent by such a mechanism.

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Registry No. Rh(ph)(H₂O)₂HSO₄, 81725-24-8; Rh(ph)-(CH₃OH)Cl, 81725-25-9; Rh(ph)(CH₃OH)Br, 81725-26-0; Rh(ph)(CH₃OH)I, 81725-27-1.

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Photochemistry of Transition-Metal Phthalocyanines. Monophotonic and Sequential Biphotonic Photochemical Processes of Copper(II) Tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in Nonaqueous Media

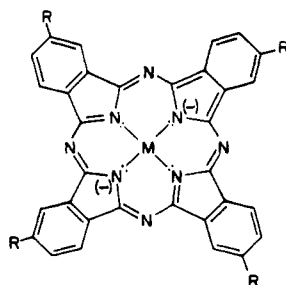
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The photochemistry of dimeric and monomeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in chloroform has been investigated by steady-state, flash and laser flash photolysis. The decay of a low-lying $\pi\pi^*$ triplet-doublet with $k \approx 2 \times 10^7 \text{ s}^{-1}$ was observed in laser flash photolysis. Similar observations were carried out with related complexes. Moreover, long-lived transformations were assigned to the formation of a copper(III) phthalocyanine. Product yields were determined as a function of the excitation wavelength and light intensity. Excitations on the Q band, $\lambda \approx 600 \text{ nm}$, with high intensities from a focused dye laser induce a photochemistry otherwise observed for excitations at $\lambda \leq 350 \text{ nm}$. Mechanisms involving short-lived $n\pi^*$ states and two-photon photochemistry involving a low-lying and long-lived $\pi\pi^*$ triplet-doublet are discussed.

Introduction

The photochemistry of copper(II) tetrasulfophthalocyanine, $\text{Cu}(\text{pts})^{2-}$ (I), has been recently investigated in aqueous so-

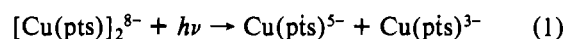


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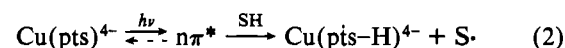
(II) R = SO₂NH-C₁₈H₃₇

(III) R = H

lutions.^{1,2} Ultraviolet irradiations of the dimeric species induce its photodissociation in copper(II) ligand radicals (eq 1). Such



a process was attributed to the population of either $n\pi^*$ excited states or to charge-transfer states, which induce a transfer of charge between units of the dimer.¹ The photochemical properties of the monomeric species lend some support to the possibility of a reactive $n\pi^*$ state. Indeed, the ultraviolet excitation of the monomeric species induces a hydrogen abstraction from appropriate hydrogen donors (eq 2). The



formation of Cu(II) ligand radicals in processes 1 and 2 suggests that the copper(I) and copper(III) complexes are unstable species with respect to the corresponding copper(II) ligand radicals. The photochemical generation of metastable copper(I) and copper(III) complexes has been recently observed in the ultraviolet photolyses of copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine, $\text{Cu}(\text{pts-R})$ (II), in chloroform.³ Although the copper(I) and copper(III) complexes do not transform into the copper(II) ligand radicals, such conversions have been observed with other metastable species. Indeed, one-electron-oxidized cobalt(II) and one-electron-reduced cobalt(III) ligand radicals undergo stabilizing intra-

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(2) G. Ferraudi, *Inorg. Chem.*, **18**, 1005 (1979).

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molecular electron-transfer processes in a microsecond to a millisecond time scale.^{2,4}

The participation of various excited states in the photochemistry of copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine has been investigated in detail in this work.

Experimental Section

Photochemical Procedures. Steady-state irradiations were carried out with apparatus described elsewhere.⁵ A 300-W Varian Eimac xenon lamp coupled with a monochromator and collimating lenses, or a Rayonet Mini-Photoreactor with appropriate lamps were used for quasi-monochromatic photolyses, e.g., band width of the exciting light $\delta\lambda \leq 20$ nm. The light intensity was measured with Parker's actinometer.⁶ Moreover, periodical checks of the intensity were carried out with a thermopile-microvoltmeter setup. The concentrations of the photolytes were selected for absorptions of more than 99.99% of the light at the corresponding exciting wavelength. These solutions were deaerated with streams of solvent-saturated argon or with three freeze-thaw cycles. The homogeneity of the reaction medium was maintained during the irradiations by either passing argon or stirring with magnetic bars.

Also, solutions of the copper complexes were irradiated with high intensities by using a Candela flash-lamp pumped-dye laser. The laser light, with pulses of ~ 200 ns produced with a repetition rate of ~ 25 pulses/min, was focused on the photolyte solution with appropriate lenses. Volumes of the photolyte solutions between $(3.5 \times 10^{-2}) - (7.1 \times 10^{-2})$ cm³ were irradiated in these experiments. An average intensity was determined from measurements before and after the irradiation. Such measurements were carried out with a thermopile-microvoltmeter.

The apparatus used for conventional and laser flash photolysis have been previously described.^{7,8} However, some of their general features are described below. Two xenon flash lamps, Xenon Corp. FP-8D-100C, were fired in series at stored electrical energies between 250 and 60 J/pulse in our flash photolysis experiments. The transient response of the monitoring setup was, first, stored and digitized in a Biomation 805 waveform recorder and, second, processed in a Digital PDP-8L computer. Laser flash experiments were carried out by exciting the samples with light pulses from a Moletron 400 nitrogen laser. Transients were monitored with the focused light of a 500-W Xe lamp that was pulsed to around 10^4 times the steady-state intensity. The data points were stored in a Tektronix R7912 transient digitizer and processed in a Digital PDP-11 computer.

Analytical Procedures. Dichloromethane together with the solvent was distilled under vacuum and analyzed by gas chromatography. Blanks were prepared with solutions maintained in the dark.

Chloride ions were determined with a HNU ion-selective electrode after extraction from the organic solution with 0.1 M NaNO₃. A similar treatment was applied to the blanks. Moreover, a calibration curve was obtained with solutions containing a known concentration of chloride ions.

Materials. The copper(II) phthalocyanine, III, and the sodium salt of the copper(II) tetrasulfophthalocyanine were purchased from Eastman and recrystallized three times from appropriate solvents, namely, H₂SO₄ and H₂O, respectively.¹ Copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine was prepared by the method of Zickendraht.⁹ The crude compound was recrystallized several times from chloroform until the spectral properties agreed well with those reported in the literature.¹⁰

Chloroform was purified before it was used in photochemical experiments. A 1:1 mixture of concentrated sulfuric acid and chloroform was distilled in an all-glass apparatus provided with a 40-theoretical-plate fractionating column. The liquid, collected within ± 0.1 °C of the chloroform boiling point, was first washed with distilled water, then dried over anhydrous Na₂SO₄, activated alumina, and molecular sieves, and finally stored under argon.

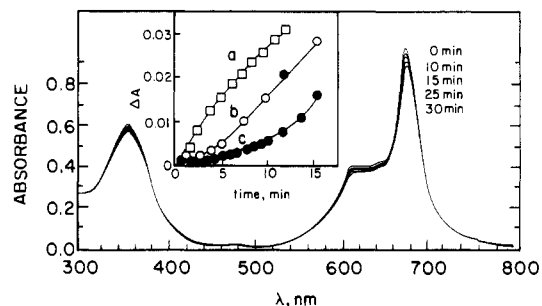


Figure 1. Spectral transformations induced in 280-nm photolysis of 1.1×10^{-4} M copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in deaerated chloroform. Spectra were determined with a 1-mm optical path. The inset shows the time dependence of the 425-nm absorbance change, ΔA , measured in a 1-cm optical path: (a) $[\text{Cu(pts-R)}] = 1.3 \times 10^{-4}$ M, 10% 2-propanol + 90% CHCl₃; (b) $[\text{Cu(pts-R)}] = 1.3 \times 10^{-4}$ M, 10^{-2} M CH₃CO₂H, 10% 2-propanol + 90% CHCl₃; (c) $[\text{Cu(pts-R)}] = 1.2 \times 10^{-4}$ M, 100% CHCl₃.

Table I. Chloride Yields Obtained in Photolyses of Copper(II) Tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in Deaerated CHCl₃

λ_{excit} , nm	I_0 , einstein/(L min)	ϕ_{Cl}
350	1.6×10^{-4}	$(2.4 \pm 0.2) \times 10^{-3}$
320	2.0×10^{-5}	$(1.8 \pm 0.3) \times 10^{-3}$
300	2.2×10^{-5}	$(1.8 \pm 0.2) \times 10^{-2}$
300	1.1×10^{-4}	$(1.8 \pm 0.3) \times 10^{-2}$
280	2.1×10^{-5}	$(1.3 \pm 0.3) \times 10^{-2}$

Results

Steady-State Irradiations. Ultraviolet irradiations of dimeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in deaerated chloroform produce spectral transformations with a complex dependence on the irradiation time (Figure 1). Also, the spectral transformations are largely dependent on medium conditions and have been related, in part, to a photoinduced decomposition of the complex (see below). This behavior made it difficult to estimate quantum yields from the absorbance changes induced by irradiation. Analysis of the reaction products reveals the formation of CH₂Cl₂ and Cl⁻. Quantum yields for the production of chloride ions were determined at various excitation wavelengths and light intensities (Table I). Photochemical transformations were not observed for excitations in the near-infrared region, e.g., 650–700 nm, with the usual light intensities, e.g., $I_0 \leq 10^{-4}$ einstein/(L min). However, irradiations in the region 575–600 nm with large intensities, namely, those obtained with a focused-flash pumped-dye laser, induce the same photochemical transformations observed for the near-ultraviolet excitations (see above). These irradiations in the Q band produce chloride ions with yields that are linearly dependent on the intensity of the laser pulse (see Figure 2 and the Appendix). These yields also exhibit the expected dependence on the concentration of copper(II) complex (Figure 2).

Flash Photolysis. A transient growth of the absorbance was observed in the $400 \text{ nm} \leq \lambda_{\text{obsd}} \leq 550 \text{ nm}$ region for flash irradiations of dimeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in deaerated chloroform (Figure 3). The same transients were detected for excitations in different spectral regions, namely, at $\lambda_{\text{excit}} \geq 280 \text{ nm}$ and $\lambda_{\text{excit}} \geq 320 \text{ nm}$, in the near-ultraviolet.

The difference spectrum of the species that is produced in the slow process that follows the irradiation exhibited a maximum absorption at 400 nm (Figure 3). Moreover, a precursor of such long-lived species can be detected at zero reaction time (see inset a in Figure 3). Indeed a finite absorbance can be observed in the trace at zero reaction time (Figure 3). The rate of the absorbance growth presents a

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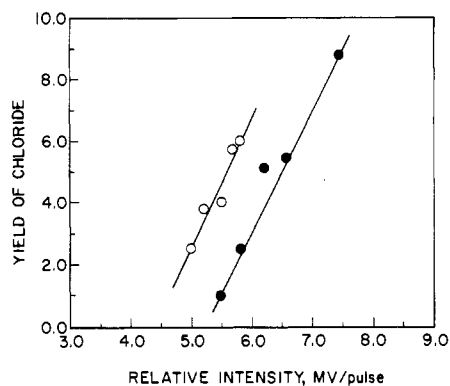


Figure 2. Linear dependence of the relative chloride yields on the intensity of the laser pulse for two different concentrations of dimeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in deaerated CHCl_3 : solid circles, $[\text{Cu}(\text{pts-R})] = 1.5 \times 10^{-4} \text{ M}$; open circles, $[\text{Cu}(\text{pts-R})] = 3.0 \times 10^{-4} \text{ M}$. The intensity is indicated as the average voltage generated by a given number of laser pulses in a thermopile-microvoltmeter setup. Individual yields were obtained as yield = $[\text{Cl}^-]/((\text{number of pulses})(\text{average pulse energy}))$.

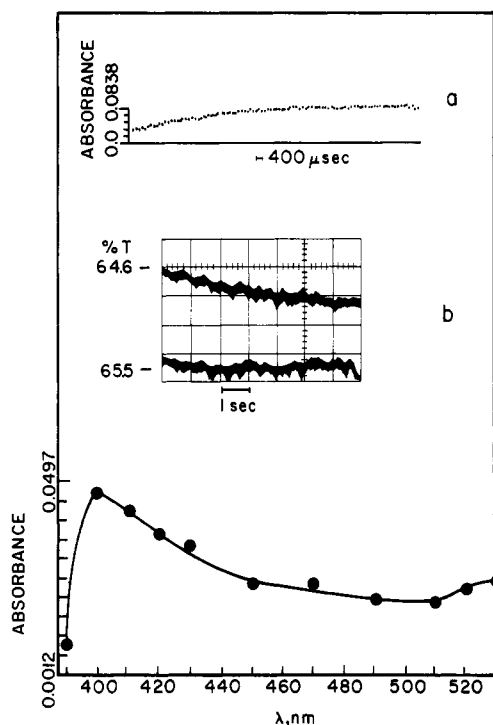


Figure 3. Transient spectrum observed in flash irradiations of the dimeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in deaerated CHCl_3 . Excitations are with 250 J/pulse and $\lambda_{\text{excit}} > 280 \text{ nm}$. The insets show (a) the 400-nm absorbance growth in a short time scale and (b) the decay that follows at a long reaction time. Observations are at $\lambda_{\text{obsd}} = 390 \text{ nm}$.

first-order dependence on the concentration of the precursor, namely, in the absorbance change at zero reaction time, and is independent of the phthalocyanine concentration. A rate constant $k = 1.3 \times 10^2 \text{ s}^{-1}$ was obtained from these measurements. The decay of the long-lived species in deaerated chloroform was observed with $t_{1/2} \geq 5 \text{ s}$ (see inset b in Figure 3). Such a decay is accelerated by 2-propanol.

Although flash irradiations of the dimeric complex do not generate detectable concentrations of copper(II) ligand radicals with $\lambda_{\text{max}} \approx 500 \text{ nm}$,¹¹ such transients can be observed in flash

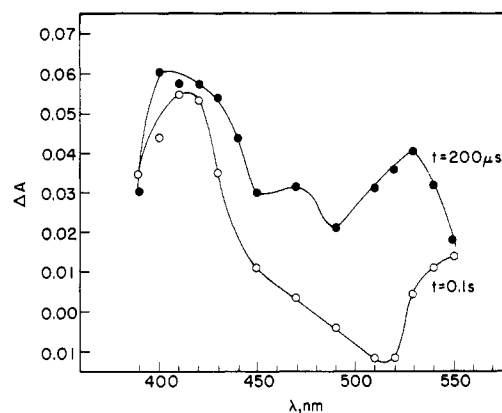


Figure 4. Spectral transformations observed in flash irradiations of monomeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in a deaerated 10% 2-propanol-90% CHCl_3 mixture. Excitations with 250 J/pulse flashes at $\lambda_{\text{excit}} \geq 280 \text{ nm}$.

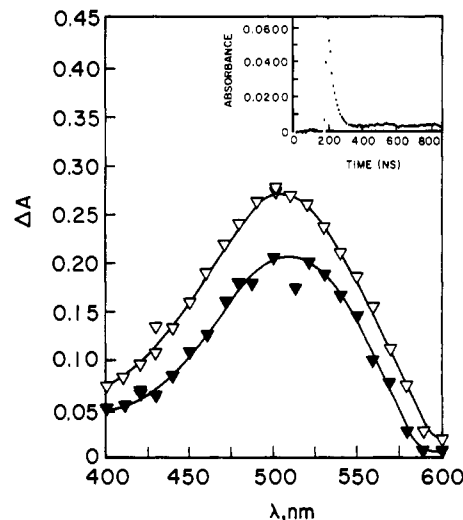


Figure 5. Laser flash irradiations of copper(II) phthalocyanines. The transient spectrum is generated in photolyses of copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in deaerated CHCl_3 (solid triangles) and in deaerated 10% 2-propanol-90% CHCl_3 mixtures (open triangles). The inset shows a typical trace obtained in laser photolysis of the sulfamoyl complex.

photolysis of the monomeric species. Indeed, flash irradiations of the monomer, $\lambda_{\text{excit}} \geq 280 \text{ nm}$, in a deaerated mixture of 10% 2-propanol in chloroform produce a transient spectra with some of the features reported for the one obtained in flash irradiations of the dimer (Figure 4). In addition such spectra show maxima characteristic of the copper(II) ligand radical at $\lambda \approx 500 \text{ nm}$ (Figure 4). The rate of decay of the transient spectra exhibited a second-order dependence on transient concentration. A ratio of the second-order rate constant to the extinction, $k/\epsilon = 5.7 \times 10^4 \text{ cm}^2/\text{s}$, was measured at 520 nm. Flash irradiations of the monomeric complex in methanol-chloroform mixtures produce similar transient spectra.

Laser Flash Photolysis. Laser flash irradiations, $\lambda_{\text{excit}} \approx 337 \text{ nm}$, of dimeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in deaerated chloroform produce transient spectra with $\lambda_{\text{max}} \approx 510 \text{ nm}$ (Figure 5). Such spectra disappear with a rate that has a first-order dependence on transient concentration, namely, $k = 2.0 \times 10^7 \text{ s}^{-1}$. The transient species seems to be unreactive with donors and acceptors of electrons, e.g., triethylamine, dimethylaniline, *o*- and *p*-dinitrobenzene, and ascorbic acid in concentrations equal

(11) One-electron reduced or oxidized ligand radicals of transition-metal phthalocyanines with λ_{max} in the 500-nm region have been previously generated by electrochemical,¹² chemical,¹³ and photochemical means.¹²

(12) L. D. Rollman and R. T. Iwamoto, *J. Am. Chem. Soc.*, **90**, 1455 (1968).

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Table II. Properties of the ${}^1\text{d}\pi\pi^*$ State^{17,18} Generated in Laser Flash Photolysis of Copper(II) Phthalocyanines

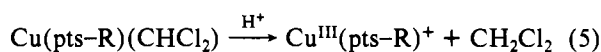
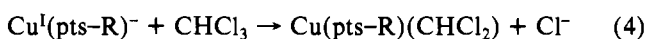
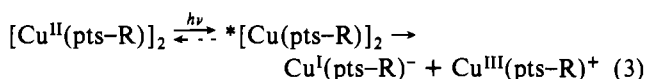
compd/medium	λ_{max} , nm	$10^{-7}k$, s ⁻¹
Cu(pts-R)/CHCl ₃	513	2.0 ± 0.2
Cu(pts-R)/10% 2-propanol in CHCl ₃	506	2.6 ± 0.2
Cu(pts)/H ₂ O	480	4.6 ± 0.3
Cu(pts)/Me ₂ SO	510	2.0 ± 0.1

to or smaller than 0.1 M. Moreover, the same transient spectrum was observed in laser irradiations of monomeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine in 10% methanol–90% chloroform or 10% 2-propanol–90% chloroform mixed solvents.

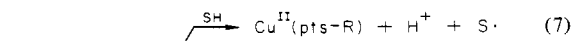
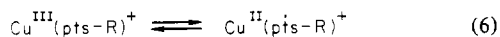
Complexes related to copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine were also investigated. Laser flash irradiations of the monomer copper(II) tetrasulfophthalocyanine in deaerated aqueous solutions produced a short-lived transient, $t_{1/2} = 15 \pm 5$ ns, with $\lambda_{\text{max}} \approx 480$ nm. Moreover, a transient with $\lambda_{\text{max}} \approx 510$ nm and $t_{1/2} \approx 35$ ns was detected in laser flash irradiations of copper(II) phthalocyanine in deaerated Me₂SO (Table II).

Discussion

The results presented above show that the photochemical behavior of dimeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine is markedly different from that reported for dimeric copper(II) tetrasulfophthalocyanine.¹ Indeed, the ultraviolet irradiations of the dimeric species produce only minor concentrations of the copper(II) ligand radicals that were previously detected in photolyses of copper(II) tetrasulfophthalocyanine.^{1,11} In this regard, the species with $\lambda_{\text{max}} \approx 400$ nm, observed in the photodissociation of the dimer in CHCl₃, can be more properly described as metal oxidized and metal reduced complexes (eq 3). The other photoproducts, namely, CH₂Cl₂ and Cl⁻, can be produced in a reaction between the metal reduced species and solvent molecules (eq 4 and 5). The spectral transformations, ob-

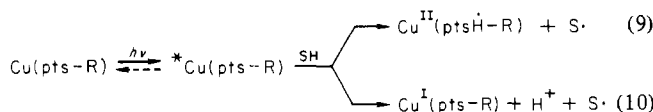


served in continuous-wave photolysis, show that the copper(III) complex (eq 3 and 5) decomposes in a long time scale, e.g., ~5 s. Such a decay probably involves a degradative oxidation of tetrakis(*N*-octadecylsulfamoyl)phthalocyanine macrocycle to various open-cycle products, namely, phthalimide. A mechanism (eq 6–8) similar to that observed with copper(III) macrocyclic complexes¹⁴ can be operative in the case of copper(III) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine.



Mechanistic differences can also be observed between the photochemistries of the monomeric derivatives of the phthalocyanine. Although both complexes, namely, copper(II) tetrasulfophthalocyanine and copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine, oxidize hydrogen donors, there is only a minor formation of copper(II) ligand radicals with the sulfonamide derivative (eq 9 and 10). Such processes are

likely mediated by a reactive $n\pi^*$ excited state, $*\text{Cu}(\text{pts-R})$, as it was previously proposed for copper(II) tetrasulfophthalocyanine.^{1,2}



The photochemical generation of metal oxidized and metal reduced species instead of copper(II) ligand radicals suggests that the mono and tripositive states of copper have achieved some sort of stabilization with respect to the corresponding copper(II) ligand radicals. However, no interconversion between the metal oxidized and reduced species and the ligand radicals has been observed in CHCl₃, suggesting that a thermodynamic stabilization of the products determines their formation from the excited state. Such stabilization can be provided by either a change of the substituents, namely, from sulfonic acid to sulfamoyl or solvation effects that modify the energy gap between metal-centered orbitals and π orbitals of the phthalocyanine or both.^{15,16} This is supported by Gouterman's calculations,¹⁶ which show that departures from a D_{4h} symmetry can introduce a considerable stabilization of the HOMO, mainly a $d_{x^2-y^2}$ metal-centered orbital, with respect to the LUMO, mainly a π^* ligand-centered orbital.

The primary photoprocess observed with monomeric copper(II) tetrakis(*N*-octadecylsulfamoyl)phthalocyanine (eq 9) has been attributed to redox reactions involving a $n\pi^*$ excited state. The same is valid for the dimeric complex. However, the modifications that dimerization introduces in the UV–vis absorption spectrum of the phthalocyanine suggest a strong interaction between the π electronic density of the phthalocyanine ligands in the dimer. This interaction can introduce charge-transfer excited states, namely, states that involve a transfer of charge between units of the dimer, at appropriate photonic energies. However, the monomeric and dimeric species give the same response to laser flash excitations and have close threshold energies for photochemistry, suggesting that they have a common reactive state. A number of $n\pi^*$ states have been assigned to the spectrum of the monomeric copper(II) phthalocyanine in the region $(20 \times 10^3) - (42 \times 10^3)$ cm⁻¹.^{15,16} Our yields show a threshold for photochemistry at $\bar{\nu} = 29 \times 10^3$ cm⁻¹ inside of the B band where Henriksson et al. predicted an $n\pi^*$ excited state involving lone pairs from the nitrogen bridges.¹⁵ Moreover, the transients observed in laser flash experiments can be assigned to the same $\pi\pi^*$ triplet–doublet phosphorescent state, namely, ${}^1\text{d}\pi\pi^*$, that has been previously observed by using both emission¹⁷ and absorption techniques¹⁸ and excitations in the Q band of the phthalocyanine complexes. Differences in the excited-state lifetimes and maxima positions of the tetrakis(sulfamoyl) and the tetrasulfonated complexes can be attributed to perturbations from the substituents and solvent effects and variations in the distribution between the triplet–doublet and triplet–quartet. Such a behavior is in agreement with the observed disparity in their photochemical properties. The detection of the low-lying triplet–doublet state for excitations at 337 nm suggests that such a state achieves population from upper lying states, e.g., the reactive $n\pi^*$ state and/or various $n\pi^*$ and $\pi\pi^*$

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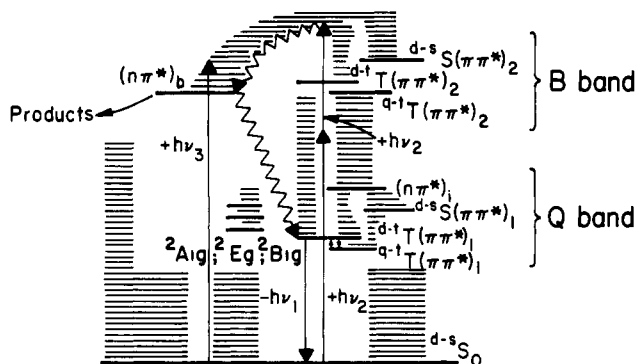


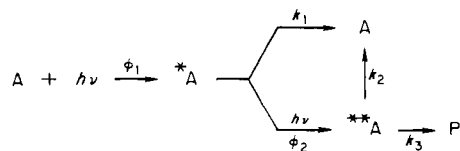
Figure 6. Simplified Jablonski diagram for copper(II) phthalocyanines. The $\pi\pi^*$ levels are split in singlet–doublet, $^s\text{-}^d\pi\pi^*$, triplet–doublet, $^d\text{-}^t\pi\pi^*$, and triplet–quartet, $^t\text{-}^q\pi\pi^*$, as indicated in the text and ref 17 and 18. An arbitrary ordering has been given to low-lying dd metal states $^2\text{A}_{1g}$, $^2\text{E}_g$, and $^2\text{B}_{1g}$. The reactive $(n\pi^*)_b$ involving nonbonding orbitals of bridge nitrogens and lower lying $(n\pi^*)_i$ involving nonbonding orbitals of inner nitrogens have been represented by a single level for simplicity. Straight arrows indicate the population of the $(n\pi^*)_b$ state by a single-photon excitation, $h\nu_3$, or double-photon excitation, $h\nu_2$, to the band B. Charge-transfer states^{15,16,20} and nonradiative paths to ground state have been omitted for simplicity.

states in the region of the B and Q bands (Figure 6). That the low-lying $\pi\pi^*$ states are unreactive is suggested by the irradiation at wavelengths of the Q band with normal laser intensities. Moreover, the photochemistry observed for laser excitations at $\lambda_{\text{excit}} \approx 600$ nm can be attributed to a biphotonic process (see the Appendix). It is feasible that the reactive $n\pi^*$ state can be populated by photolysis of the long-lived triplet–doublet state (Figure 6).¹⁷ In this regard the scheme in Figure 6 shows that the favorable competition of the internal conversion to the low-lying triplet–doublet with the reaction mode of the $n\pi^*$ state must result in a low photoreactivity. Hence it is possible that the reason for the low product yields obtained with copper(II) tetrakis(*N*-octadecylsulfamoyl)-phthalocyanine is related to such a competition.

In conclusion the actual evidence in the single-photon photochemistry of the phthalocyanines shows that the photoprocesses can be associated with the population of $n\pi^*$, $\pi\pi^*$, and various charge-transfer states involving the phthalocyanine ligand.²⁰ However, the absence of long-lived transients that one can relate with CT states in copper(II) phthalocyanines shows that, at least in our conditions, the charge-transfer states do not achieve a significant population for their participation in photochemical processes.

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Scheme I



Appendix

Biphotonic processes have already been reported for the high-intensity-laser excitation of cobalt(III) complexes.¹⁹ We have interpreted our results, obtained in similar experiments, according to Scheme I. A long-lived excited state *A absorbs light in competition with its relaxation to the ground state. The secondarily generated excited state $^{**}A$ can undergo a chemical transformation into a product or relax to the ground state. These transformations can be described by rate equations (11)–(13), where I_A is the light intensity absorbed by

$$\frac{\partial[P]}{\partial t} = k_3[^{**}A] \quad (11)$$

$$\frac{\partial[^{**}A]}{\partial t} = -(k_3 + k_2)[^{**}A] + \phi_2 I_A \approx 0 \quad (12)$$

$$\frac{\partial[^*A]}{\partial t} = \phi_1 I_A - k_1[^*A] - \phi_2 I_A \approx 0 \quad (13)$$

A and I_A absorbed by *A . Moreover we have used eq 14 and 15 in order to obtain explicit expressions for the ab-

$$I_A \approx I_0(1 - e^{-\alpha_A[A]}) \quad \alpha_A = 2.303\epsilon_A l \quad (14)$$

$$I_A + I_{^*A} = I_0(1 - e^{-(\alpha_A[A] + \alpha_{^*A}[^*A])}) \quad (15)$$

$$\alpha_{^*A} = 2.303\epsilon_{^*A} l$$

sorbed light intensities. Such expressions, based on Beer's law, introduce the dependence on the incident light intensity, I_0 , the optical path, l , and the corresponding extinctions, ϵ_A and $\epsilon_{^*A}$, of the species A and *A . The yield of the product P (eq 16) was deduced by combining eq 11–15. Two limiting cases

$$\phi_P = \frac{1}{I_0} \frac{d[P]}{dt} = \phi_1 \phi_2 \left(\frac{k_3}{k_3 + k_2} \right) \left(\frac{I_0 \alpha_{^*A} (1 - e^{-\alpha_A[A]}) e^{-\alpha_A[A]}}{k_1 + I_0 \phi_2 \alpha_{^*A} e^{-\alpha_A[A]}} \right) \quad (16)$$

must be analyzed. The first case corresponds to $k_1 > I_0 \alpha_{^*A} e^{-\alpha_A[A]}$. A product yield with a linear dependence on the light intensity (eq 17) is obtained under such approximation.

$$\phi_P \approx \phi_L I_0 \alpha_{^*A} (1 - e^{-\alpha_A[A]}) e^{-\alpha_A[A]} / k_1$$

$$\phi_L = \phi_1 \phi_2 \left(\frac{k_3}{k_2 + k_3} \right) \quad (17)$$

The second case, deduced under the condition $k_1 < I_0 \alpha_{^*A} e^{-\alpha_A[A]}$, corresponds to a yield that is independent of the light intensity (eq 18). The linear dependence of the chloride yield on light

$$\phi_P \approx \phi_L (1 - e^{-\alpha_A[A]}) \quad (18)$$

intensity (Figure 2) is in agreement with our first approximation as indicated in eq 17.

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