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Photophysical and Photochemical Investigation of a Dodecafluorosubphthalocyanine Derivative

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The photochemical and photophysical behavior of (dodecafluorosubphthalocyanaoto)boron(III) chloride was examined in room-temperature solutions. The lowest energy absorption maximum of the complex is 570 nm, and the luminescence mirrors the absorption with a maximum at 586 nm (Stokes shift = 480 cm^{-1}). The emission is strong, with a quantum yield in deaerated acetonitrile of 0.66 and a lifetime of 2.6 ns. The complex exhibits a reversible one-electron reduction in cyclic voltammetry ($E° = -0.53$ V vs SCE), and this, combined with the relatively high singlet energy, indicates the emissive excited state is a strong oxidant. Evaluation of the free energy dependence of the emission quenching with a series of substituted benzene donors yields a value of 1.7 V vs SCE for the excited-state reduction potential, $E(*/-)$. The excited complex also reacts with tertiary amines. Photolysis in the presence of triphenylamine results in photoinduced electron transfer and back reaction. Triethylamine, however, reacts efficiently with the excited subphthalocyanine to yield a permanent photoproduct. The product has been characterized by FAB mass spectrometry as well as ^{1}H and ^{19}F NMR to be an adduct involving B−N bond formation.

Introduction

Subphthalocyanines represent an interesting class of luminescent dyes that show promise as materials for nonlinear optical applications.[1] These conically shaped aromatic heterocycles (a general structure is shown in Figure 1) were initially prepared as precursors in the synthesis of unsymmetric phthalocyanines.[2] All subphthalocyanines reported in the literature have an central boron coordinated to three of the nitrogens of the ring; the boron also has an axial anionic ligand, generally either a halogen or an alkoxy derivative. There have been very few reports of the physical properties of these compounds until very recently when Agullo-Lopez and Torres began to explore the use of subphthalocyanines as materials for nonlinear optical applications.[3] Recent publications from this group have shown that particular subphthalocyanines have very large second-order optical nonlinearities.[3a] In addition, sublimed films of **1** (Figure 1) have third harmonic generation susceptibilities in the 950−2000 nm range approximately 3 times larger than those of phthalocyanines.[3b] This interest in subphthalocyanines for NLO applications has stimulated efforts to expand preparative methods for these materials, and the range of available subphthalocyanine derivatives is growing.[4−8]

A striking characteristic of subphthalocyanines is intense pink luminescence, often observed with ambient light excitation in room-temperature solutions. Several papers discussing preparative methods mention the luminescence, but few details have been reported. Kobayashi and co-workers recently reported the preparation and photophysical behavior of various mono- and bis(subphthalocyanine)s.[8] The tris(*tert*-butylsubphthalocyanine), **5**, exhibits fluorescence at 588 nm (Table 1) and has a quantum yield of 0.61 in benzene (aerated) and a lifetime of 2.1 ns. The very small Stokes shift observed for the fluorescence, combined with the high emission yield, suggests these substances may be useful as sensitizers in solar energy conversion devices. However, Kobayashi also mentions bleaching of the subphthalocyanine absorbance upon prolonged irradiation, but no details of the photoreaction are reported.

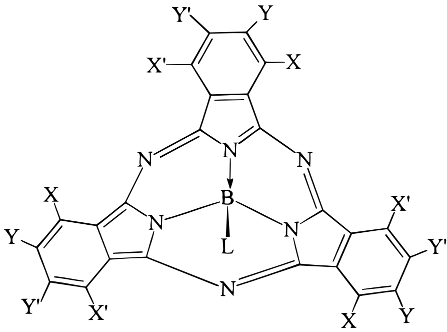

Figure 1. Structures of the subphthalocyanine derivatives.

TABLE 1: Collected Absorption and Luminescence Maxima of Various (Subphthalocyanato)boron(III)(L) Compounds (See Figure 1)

complex	X	X′	Y	Y′	L	λ_{max}^{abs}, nm	λ_{max}^{em}, nm	ref
1	H	H	H	H	Cl	300, 560		3b
2	F	F	F	F	Cl	310, 570	586	this work
3	H	H	H	H	OEt	302, 561		6
4	H	H	H	HC≡C	Cl	345, 583		1a
5	H	H	H	*t*-Bu	Br	305, 567	588	8
6	H	H	H	H	Ph	311, 566		4d
7	H	H	H	I	Cl	314, 574		4b
8	H	H	H	NO_2	Cl	310, 580		1c

In this paper we report the photochemical and photophysical behavior of the perfluorinated subphthalocyanine, **2**. The compound exhibits absorption and emission in the yellow and has a high emission yield and a short lifetime (as reported by Kobayashi for the *tert*-butyl derivative). In addition, the facile one-electron reduction of the subphthalocyanine makes the singlet excited state of **2** a powerful oxidant. The complex undergoes permanent changes upon photolysis in acetonitrile with various amine donors. Isolation and characterization of

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the primary photoproduct with triethylamine indicates substitution of the axial chloride by the amine.

Experimental Section

The (hexafluorosubphthalocyanato)boron(III) chloride, **2**, was obtained from the lab of Professor Harry Ensley.[9] All solvents used were of at least reagent grade quality and, with the exception of acetonitrile, were used without further purification. Acetonitrile was distilled under N_2 from CaH_2 prior to use. Triphenylamine (Aldrich) was recrystallized from ethanol prior to use. Triethylamine (Aldrich) was distilled from KOH immediately before use in quenching and thermal reaction experiments. The substituted benzenes employed in luminescence quenching studies were used as received.

Electrochemistry. Cyclic voltammetry and differential pulse polarography experiments were carried out using an EG&G Versastat controlled by a personal computer. All studies were carried out using N_2 degassed acetonitrile solutions with tetraethylammonium perchlorate (0.1 M) as supporting electrolyte, either Pt or glassy carbon as working electrode, and a Ag/AgCl pseudo reference electrode. Ferrocene was used as an internal reference, and measured potentials are reported relative to the SCE reference ($E°(Fc^+/Fc) = 0.307$ V vs SCE).[21]

Luminescence Spectra and Quantum Yields. Emission spectra were obtained using a Spex Fluorolog I spectrofluorimeter equipped with a 450 W Xe arc lamp for excitation and spectrograph/ CCD (liquid N_2 cooled) detection. Room-temperature spectra were obtained in aerated solutions and were not corrected for wavelength response of the detector. The quantum yield for **2** emission was obtained in CH_3CN solution at room temperature and was measured relative to *meso*-tetraphenylporphyrin in benzene ($\Phi = 0.11$[10]).

Luminescence Lifetimes; Quenching Studies. Luminescence lifetimes were measured by time-correlated single-photon counting using a home-built apparatus previously described.[11] Samples were excited with the 20−40 kHz filtered ($\lambda > 350$ nm) output of an IBH flashlamp, and emitted light was collected at right angles to excitation using a cooled PMT after passing the light through a band-pass filter ($\lambda \pm 5$ nm). The electronics for photon counting and the algorithms for data reduction are described elsewhere.[11]

Stern−Volmer luminescence quenching experiments were carried out on aerated acetonitrile solutions of the subphthalocyanine. Various volumes of stock quencher solution were added to 1 mL of a 30 μM stock solution of **2**, and the final volume was adjusted to 4 mL with acetonitrile. The solutions were mixed well before being capped and stored in the dark until emission spectra were taken. (Excitation was into the blue edge of the Q-band at 500 nm.) Spectra were collected using CCD detection (approximately 1 s exposure) so that irradiation of the solution was kept to a minimum. Quenching rate constants were determined from linear fits to plots of the ratio of the integrated emission intensity in the absence and presence of quencher versus quencher concentration, assuming Stern−Volmer quenching kinetics.

Transient Absorption Spectra. Transient spectra were obtained from single wavelength decays over the 400−700 nm region. Solutions were excited with the doubled output of a Coherent Infinity 40-100 YAG laser; with typical pulse intensities of 10−20 mJ. The transient absorbance was monitored by using the output of a 150 W PTI Xe arc lamp aligned at right angles relative to the excitation pulse. The analyzing light was passed through a CGA McPherson monochromator with PMT detection. Samples were pumped through a flow cell using a peristaltic pump (5 mL/min) to avoid flash excitation of photoreaction products. The dimensions of the flow cell were 0.2 × 0.2 × 1 cm with the probe beam focused into the sample down the long axis. The excitation beam was incident along the entire probe beam path using a cylindrical lens to disperse the excitation light. Samples were bubble degassed with N_2(g), and typical concentrations of **2** and quencher were 10 μM and 55 mM, respectively. A total of 500−2000 laser pulses per wavelength were averaged using a LeCroy 9370 oscilloscope. Data acquisition and analysis was managed using a Gateway computer with a Pentium processor; software for instrument control was written using Labview for Windows.

Photoreactions. Bulk photolyses were carried out using the output of a 150 W Xe arc lamp passed through a 420 nm cutoff filter and 3 in. path of water. Typical photolysis mixtures consisted of acetonitrile solutions containing **2** (30 mg in 600 mL) and a 1000-fold molar excess of either triphenylamine (TPA) or triethylamine (TEA). Solutions were bubble degassed with N_2 prior to photolysis.

Quantum yield measurements for the disappearance of **2** in the presence of TPA were made by photolysis of acetonitrile solutions. Samples were irradiated with the 310 ± 10 nm output of a 450 W Xe arc lamp filtered through a SPEX 0.25 m monochromator. Both aerated and degassed acetonitrile solutions of **2** (5 μM) and the TPA (0.05 M) in quartz cuvettes were irradiated, and the decay of the absorbance of **2** at 578 nm was measured as a function of irradiation time. The lamp intensity was measured using ferrioxalate actinometry.

Results and Discussion

Preparation and Characterization. The tetrafluorophthalonitrile was prepared by methods reported earlier.[12] Synthesis of the subphthalocyanine was accomplished by reaction of BCl_3 and the tetrafluorophthalonitrile in benzene.[9] The corresponding bromo derivative could not be prepared by this approach. The subphthalocyanine is soluble in a wide variety of solvents and is highly soluble in acetonitrile. Solutions of **2** in acetonitrile, acetone, and $CHCl_3$ are stable for long periods (>1 week) when stored in the dark. However, thermal decomposition of the subphthalocyanine occurs in hexanes to yield a light blue product. We have not determined the product(s) of the decomposition. In addition, **2** reacts thermally with triethylamine in solvents in which the subphthalocyanine is stable; the reaction is greatly accelerated by visible light photolysis. Cyclic voltammetry waves used to follow the reaction and the results are discussed below.

Electrochemistry. Very few studies of subphthalocyanine redox chemistry have been published. Kasuga and co-workers reported cyclic voltammetric results for a series of alkoxy-substituted derivatives such as complex **3**.[6] The one-electron oxidation of **3** in CH_2Cl_2 was observed at 1.03 V ($E_{p,a}$) and the reduction at −1.11 vs SCE. The oxidation is quasi-reversible and appears to be accompanied by some decomposition. The reduction appears to be reversible on the cyclic voltammetric time scale (100 mV/s). Very similar results were obtained for the complex having an axial chlorine, **1**.[6]

We examined the dodecafluorosubphthalocyanine, **2,** by cyclic voltammetry in acetonitrile. A typical voltammogram is shown in Figure 2. The complex has a single reversible one-electron reduction at −0.43 V vs SCE. Thus, fluorination of the benzo ring leads to a nearly 700 mV positive shift in the one-electron reduction potential relative to the unsubstituted derivative. The reduction is reversible ($i_{p,c}/i_{p,a} = 1$) at sweep rates as low as 10 mV/s, indicating stability of the anion radical

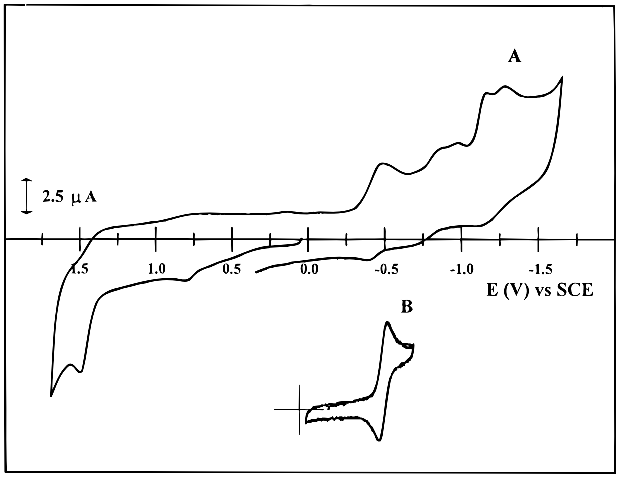

Figure 2. (A) Cyclic voltammogram of **2** in room-temperature CH_3CN having tetraethylammonium perchlorate as supporting electrolyte. (B) The inset shows the reversibility of the first reduction. Both voltammograms were obtained using a sweep rate of 100 mV/s.

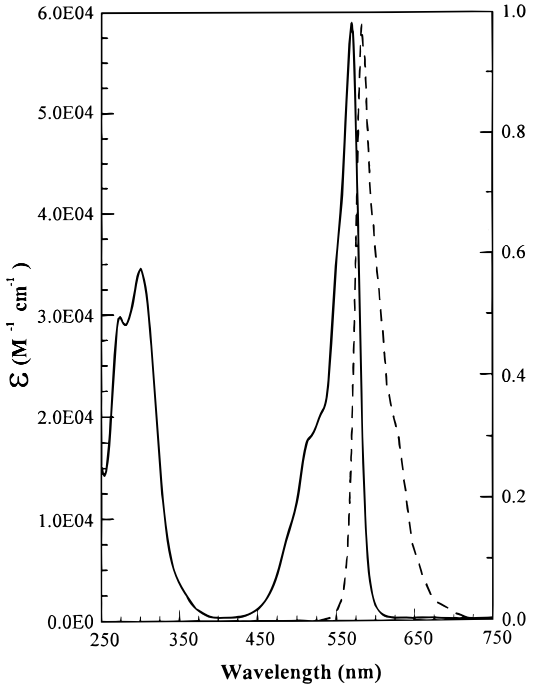

Figure 3. Absorption and emission spectra of **3** in acetonitrile at 298 K.

on the 10−50 s time scale. Because of the stability of the reduced subphthalocyanine, the spectrum of the anion radical was obtained by spectroelectrochemistry. The spectrum has a single maximum in the visible at 490 nm in acetonitrile and is shown in Figure 5A. A single irreversible oxidative wave is observed for **2** with an anodic peak of approximately 1.5 V vs SCE in CH_3CN. Since the average difference between the first oxidation and first reduction observed for the subphthalocyanines **1** and **3** is 2.1 V**,** the approximate potential difference for **2** is slightly lower than that of the other derivatives.

Absorption and Emission Spectra. Table 1 lists ultraviolet and visible absorption maxima for several (subphthalocyanato)boron(III) compounds. The electronic spectra arise from π to π^* transitions associated with the 14-electron Huckel π systems of the subphthalocyanine.[3b,4b] The transitions are analogous to absorption in porphyrins and phthalocyanines and consist of a high-energy B-band (the Soret band) and a lower energy Q-band.

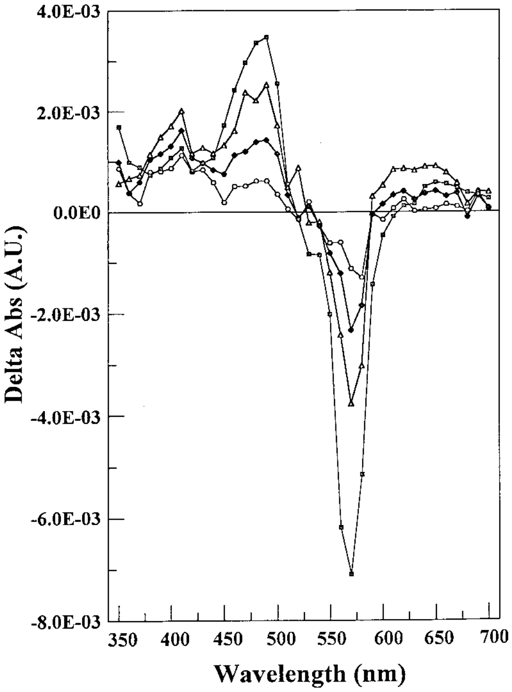

Figure 4. Transient absorption spectrum obtained following nanosecond laser excitation of **2** in acetonitrile containing 0.1 M TPA. Excitation wavelength: 532 nm. Delay times are 4, 25, 50, and 100 μs.

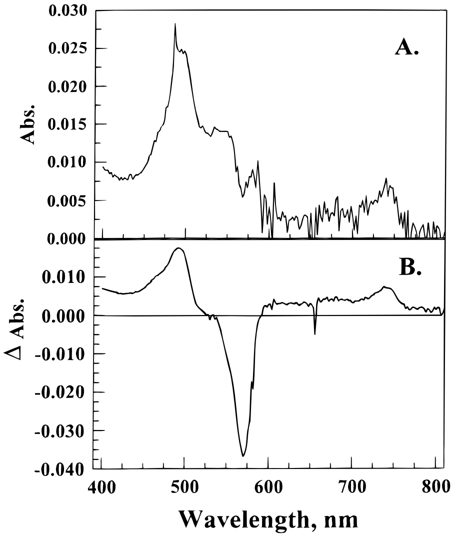

Figure 5. (A) Visible absorption spectrum of the anion radical of **2** generated spectroelectrochemically. (B) The difference of the anion radical spectrum and the ground-state spectrum.

In the subphthalocyanines the B-band is observed between 300 and 310 nm while the Q-band is at 560−580 nm (Table 1). Typical molar absorptivities are 50 000−80 000 M^{-1} cm^{-1} for both transitions. The luminescence of these complexes arises from the singlet state (τ < 5 ns) and exhibits a very small Stokes shift. For the complex **2** the Stokes shift is only ∼500 cm^{-1} and that for the unsymmetric derivative **5** is 600 cm^{-1}, indicating very small distortion of the excited state. Figure 3 shows the absorption and emission spectra of complex **2** in room-temperature CH_3CN, and the maxima for absorption and emission of **2** in various solvents are given in Table 2; the lack of any systematic change in absorption maxima with solvent donor number, Kosower *Z* parameter, or solvent E_t value suggests a negligible dipole moment change between the ground

TABLE 2: Absorption and Emission Maxima of 2 in Various Solvents

solvent	Q-band max, nm	emission max, nm	Stokes shift, cm^{-1}
propionitrile	564	581	519
diethyl ether	568	585	512
methanol	568	586	541
acetone	570	589	566
acetonitrile	570	586	479
ethyl acetate	570	588	537
ethanol	570	585	450
tetrahydrofuran	572	591	562
acetic anhydride	572	588	476
nitromethane	572	588	476
dioxane	572	590	533
benzene	574	595	615
dimethylformamide	574	582	239
N-dimethylacetamide	574	582	239
dimethyl sulfoxide	574	590	472
pyridine	576	588	354
nitrobenzene	578	597	550

state and excited state. In other work it was found that ground-state dipole of the unsubstituted subphthalocyanine **1** was found to be nearly zero.[3b]

The luminescence of complex **2** is very strong in all solvents, and in CH_3CN, the emission quantum yield is 0.6 with a lifetime of 2.6 ns. The only other subphthalocyanine for which luminescence data are reported is **5**, having three *tert*-butyl substituents on the periphery and bromide on the boron.[8] The fluorescence yield and lifetime are very similar, suggesting that excited-state relaxation and intersystem crossing processes are relatively independent of substitution on the benzo ring and changes in the axial halogen.

Excited-State Electron-Transfer Reactions. The combined electrochemical and photophysical behavior of **2** indicates the complex will act as a powerful one-electron oxidizing agent in the singlet excited state. Given the excited-state energy of complex **2** of 2.1 eV[13] and the one-electron reduction potential of −0.4 V, the approach of Rehm and Weller can be used to estimate the excited-state reduction potential to be approximately 1.7 V (vs SCE) (eq 1).[14]

$$[\mathrm{B(subpc)Cl}]^* + e^- \rightarrow [\mathrm{B(subpc)Cl}]^- \qquad E(*/-) \approx 1.7\ \mathrm{V} \tag{1}$$

Indeed, it was found that the luminescence of **2** was quenched in the presence of various alkyl- and arylamines and alkylated benzenes. To examine the products of the quenching reactions, solutions with high concentrations of triphenylamine (TPA) were examined by nanosecond flash photolysis using excitation at 532 nm. Since permanent products are formed upon continuous photolysis of solutions containing **2** and TPA, all flash photolysis experiments were conducted using a flow cell configuration. Figure 4 shows the transient spectrum obtained at several times following excitation. After 1 μs the transient spectrum shows absorption maxima at 410, 480, and 650 nm along with bleaching at 570 nm. The transient observed at 570 nm is associated with bleaching of the ground-state absorption; the transient decay at this wavelength follows equal concentration second-order kinetics. The transient at 410 nm grows in and then decays and is completely gone after 400 μs, as are all observable transients. The spectrum obtained at relatively short times following excitation strongly resembles the spectrum obtained from the difference of the anion radical, obtained from spectroelectrochemical results, and the ground-state absorption spectrum. Figure 5 shows the visible absorption spectrum of the radical anion and the spectrum generated by subtracting the ground-state absorption spectrum from the anion radical spectrum. The calculated spectrum has features similar to the transient spectrum except that the relatively small absorption in the 600−700 nm region, corresponding to TPA^+, and the transient absorbance at approximately 410 nm are missing in the generated spectrum.

SCHEME 1

$$\mathbf{2} \xrightarrow{h\nu} \mathbf{2}^*$$

$$\mathbf{2}^* + \mathrm{TPA} \longrightarrow \mathbf{2}^- + \mathrm{TPA}^+$$

$$\mathrm{TPA}^+ + \mathrm{TPA} \longrightarrow \mathrm{TPA}_2{}^+$$

$$\mathbf{2}^- + \mathrm{TPA}^+ \longrightarrow \mathbf{2} + \mathrm{TPA}$$

$$\mathbf{2}^- + (\mathrm{TPA})_2{}^+ \longrightarrow \mathbf{2} + 2\,\mathrm{TPA}$$

TABLE 3: Rate Constants for Quenching of 2 in Room-Temperature Acetonitrile

quencher	$E(+/0)$, V	k_{obs}, M^{-1} s^{-1}
1,4-dimethoxybenzene	1.34	5.4×10^{10}
2-naphthol	1.42	6.3×10^{10}
hexamethylbenxene	1.59	1.3×10^{10}
2-methylnaphthalene	1.68	2.4×10^{9}
pentamethylbenzene	1.71	1.8×10^{9}
fluorene	1.71	1.6×10^{9}
phenanthrene	1.73	2.6×10^{9}
durene	1.78	3.3×10^{8}
naphthalene	1.8	3.1×10^{8}
1,2,3,4-tetramethylbenzene	1.84	5.4×10^{7}
1,2,4-trimethylbenzene	1.92	1.6×10^{7}

The relatively complex decay behavior associated with the transient at 410 nm is related to the fact that one-electron oxidation of TPA is followed by reaction of the cation radical with TPA to yield the a "dimeric" cation radical. Pulse radiolysis results of Sumiyoshi indicate that the radical cation of TPA reacts with available TPA on the microsecond time scale (for 1 mM solutions of TPA in 1,2-dichloroethane);[15] the initial TPA radical cation has absorption maxima at 550−650 nm, and the "dimeric" product $(TPA)_2{}^+$ has maxima at 400 and 850 nm. The product $(TPA)_2{}^+$ differs spectrophotometrically from the tetraphenylbenzidine cation radical. The results of Figure 4 indicate that $(TPA)_2{}^+$ is formed over the first 30−50 μs following excitation and reacts with the subphthalocyanine anion radical to yield the starting materials. The participating reactions are summarized in Scheme 1; despite the mechanistic complication, the decay of the transient bleach at 570 nm follows equal concentration second-order kinetics, suggesting that back-electron-transfer rate constants are comparable for reaction of $\mathbf{2}^-$ with both TPA^+ and $(TPA)_2{}^+$.

In an effort to more clearly establish the one-electron reduction potential of the excited state of **2**, the free energy dependence of the photoredox reaction of **2** with a series of electron donors was examined. Stern−Volmer quenching constants were determined for reaction of photoexcited **2** with a series of alkylbenzene quenchers in acetonitrile solution by luminescence intensity quenching; rate constants are given in Table 3 (given the excited-state lifetime for **2** of 2.6 ns).

The rate constant for electron-transfer quenching can be expressed in terms of the rate constant for collisional diffusion, k_{diff}, and the product of the equilibrium constant for association of the excited acceptor/donor pair and the rate constant for electron transfer within the encounter complex, k_q (eq 2).[16,17]

$$1/k_{obs} = 1/k_{diff} + 1/k_q \qquad (2)$$

Rate constants for collision were estimated using the Smoluchowski equation for neutral collision pairs.[18] From the calculated rate constants (all approximately 2×10^{10} M^{-1} s^{-1}) and the observed second-order rate constants, values were obtained for k_q. The free energy dependence of the excited-state electron-transfer rate constant can be fit using a classical expression for electron transfer which has the reorganizational energy, λ, the equilibrium constant for association of the reactant pair, K_{DA}, and the excited-state reduction potential, $E(*/-)$, as variable parameters (eq 3).

$$\ln(k_q) = \ln(\nu_{et}K_{DA}) - \frac{\lambda}{4RT}\left[1 - \frac{E(*/-) - E(+/0)}{\lambda}\right]^2 \qquad (3)$$

This approach has been used by others in the estimation of excited-state redox potentials.[16] A fit of the data to eq 3 with $\lambda = 0.4$ eV, $K_{DA} = 0.006$ M^{-1}, and $E(*/-) = 1.7$ V is shown in Figure 6. The results support the redox and spectroscopic data which indicate **2*** is a powerful oxidant.

The reorganizational energy of 0.4 eV is really very small. Using dielectric continuum theory to estimate the solvent reorganizational energy, a value of 0.7 eV is obtained assuming the radii for **2**, the quencher, and the donor/acceptor precursor complex are 6.7, 4.5, and 11 Å, respectively.[17] Since dielectric continuum theory assumes spherical reactants and both the subphthalocyanine and the substituted benzene are better approximated as disks, the theory may have significant errors.[19] In fact, the value of λ from the fit is similar to that found by Bock and co-workers in fits of electron-transfer quenching of $[Ru(bpy)_3]^{2+}$ by a series of arylamines in acetonitrile.[16] Assuming λ is close to the fit value, the implication is that quenching of **2** with very easily oxidized donors (with $E(+/0) \sim 0.1$ V) may lie deep in the Marcus inverted region, and the rate constant for the quenching reaction may be significantly lower than diffusion limited. In general, such behavior is only observed if there are factors limiting electronic coupling between the donor/acceptor pair such that measured rate constants are uniformly below diffusion-limited values.[20] Also, it should be noted that the classical expression for evaluating the electron-transfer rate constant in these systems, eq 3, is not likely to appropriately describe electron-transfer reactions in the inverted region. We are presently exploring the possibility of observing inverted region behavior with readily oxidized electron donors.

Thermal and Photochemical Reactions of 2 with Amines. Steady-state visible photolysis ($\lambda > 420$ nm) of dilute solutions of **2** in the presence of triphenylamine (~10 mM) results in a disappearance of all absorption in the visible. The quantum yield for the process was low (measured to be <0.001), and the products of the reaction were not characterized. The reaction is not observed in solutions stored in the dark at room temperature. It may be that the dihydrotetraphenylbenzidine cation observed in flash photolysis, $(TPA)_2^+$ in Scheme 1, is capable of providing protons for the subphthalocyanine radical anion (below, TPB = tetraphenylbenzidine).

$$(TPA)_2^{+} \rightarrow (TPA)_2^{\bullet} + H^{+}$$

$$(TPA)_2^{\bullet} - e^{-} \rightarrow TPB + H^{+}$$

The subphthalocyanine reacts much more readily with triethylamine (NEt_3), both irradiated and in the dark. Absorption spectral changes for unirradiated solutions are shown in Figure 7. Isosbestic points are observed at 510 and 590 nm, and the product has broad absorption throughout the visible with maxima at 480 and 660 nm. The thermal reaction was also followed by observing changes in the reductive cyclic voltammogram. As can be seen from Figure 8, the first reduction wave of **2** ($E_{p,c} = -0.53$ V) gives way to a reduction at more negative potentials ($E_{p,c} = -0.65$ V). The absence of clear isoelectric points could be the result of changes in the background current over the time span required for the changes.

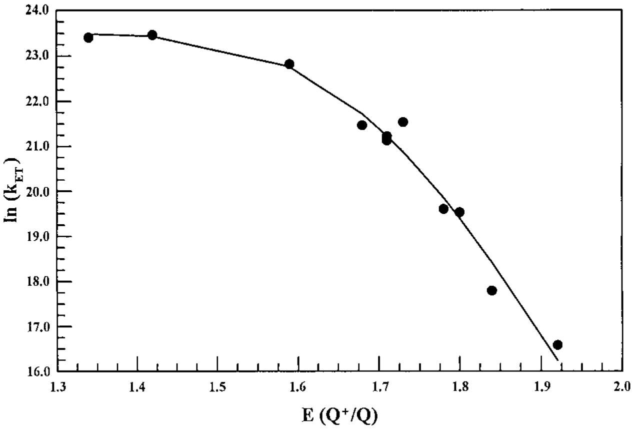

Figure 6. Dependence of the rate constant for electron-transfer quenching of **2*** on the one-electron oxidation potential of the quenching species, $E(Q^+/Q)$. The solid line represents the fit of the data to eq 3 with K_{DA}= 0.006, $\lambda = 0.4$ eV, and $E(*/-) = 1.7$ V.

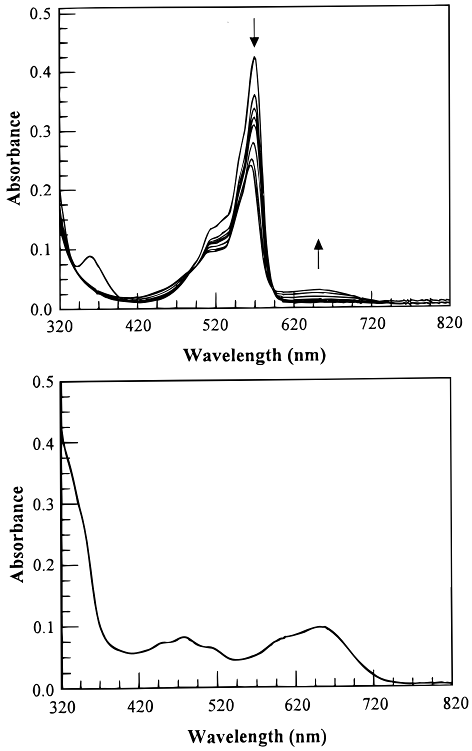

Figure 7. (top) Absorption spectra taken following preparation of a solution containing 7 μM **2** and 0.07 M NEt_3 in acetonitrile (without photolysis). Times are 0, 1, 3, 5,7, 15, 40, and 80 min following mixing. (bottom) Spectrum taken after 24 h.

Visible photolysis ($\lambda > 420$ nm) of solutions having approximately the same concentrations of **2** and NEt_3 results in very rapid conversion to products; the reaction was complete in approximately 3 min using broad-band photolysis with a 150 W Xe arc lamp focused onto a stirred solution of the reactants. Photolysis of **2** with NEt_3 under preparative conditions yields three distinct products. The major product (>50%) has an

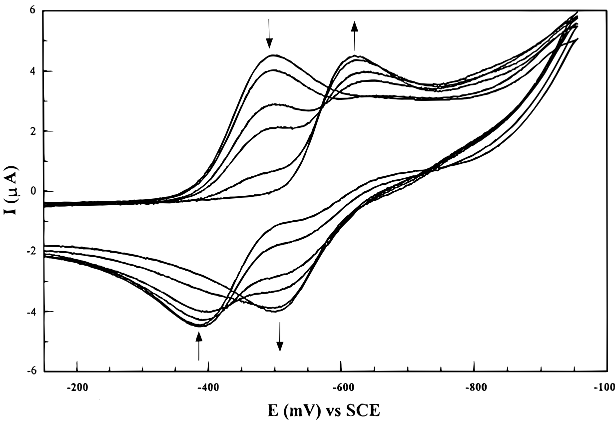

Figure 8. Cyclic voltammograms of **2** obtained at different times following addition of NEt_3 to CH_3CN solutions.

absorption spectrum identical to the thermal product. FAB mass spectra obtained for this product have peaks at *m*/*z* of 726.8 (**2** + NEt_3 − HF), 709.5 (**2** + NEt_3 − 2F), and 628.5 (**2** − F + H). The two higher mass peaks are consistent with formation of an adduct of **2** with NEt_3 in which HF and two F atoms have been eliminated. While no higher mass ions are observed, it cannot be said with certainty that the highest mass peak observed is the parent ion. ^{1}H spectra of the major photoproduct exhibit resonances consistent with addition of NEt_3. The ^{19}F NMR spectrum of the photoproduct has two doublets of doublets (−59.3 and −66.0 ppm relative to trifluoroacetic acid in acetone). The starting complex, **2**, also has two doublets of doublets with one different chemical shift (−59.3 and −69.8 ppm). The fact that the product has only two types of ^{19}F resonances suggests that the product is of high symmetry and indicates a likely structure is an amine adduct of the type $[(Et)_3NB(subpc)Cl]$.

It is not entirely clear how photolysis accelerates the observed rate of formation of a product like that shown above. Steady-state luminescence measurements clearly show that NEt_3 quenches the emission of **2**, and the most likely quenching mechanism certainly involves oxidation of the NEt_3. Transient absorption spectra were obtained for mixtures of **2** and NEt_3 using flow cell conditions to ensure flash excitation of fresh solution; the spectra show only bleaching of the ground-state absorption with the initial bleached signal decaying to a final bleach over approximately 15 μs. The anion radical of **2** is *not* observed in the transient spectrum. This result suggests the amine radical cation (or the deprotonated amine α carbon radical) reacts with the subphthalocyanine anion radical without separation of the initial photoproducts. Since such a recombination reaction would be expected to be on a time scale much faster than the decay of the observed transient (15−20 μs), assignment of the transient is not clear. We are presently investigating thermal and photoreactions of alkyl- and arylamines with subphthalocyanines in greater detail.

Conclusions

The subphthalocyanine **2** has a highly luminescent singlet excited state which proves to be a powerful one-electron oxidant. Measured rate constants for quenching with a series of substituted aromatic hydrocarbon quenchers yields an excited-state reduction potential, *E*(*/−), of 1.7 V vs SCE. Laser flash photolysis of **2** in the presence of triphenylamine illustrates that quenching of the singlet luminescence results in electron-transfer products. The complex reacts thermally with triethylamine to produce a permanent color change. The reaction is greatly accelerated by photolysis. Spectroscopic analysis of the product indicates that triethylamine either substitutes for the axially bound chloride or adds to the boron to form a zwitterion.

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