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Photophysical Properties of a Series of Free-Base Corroles

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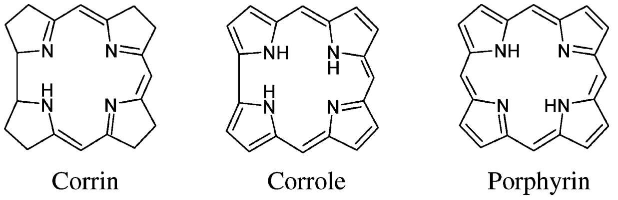
Four free-base corroles with electron-donating or electron-withdrawing groups on the para or 2 through 6-positons of the meso phenyl rings were prepared via either Paolesse or Gross conditions and investigated for their absorption and emission properties. The triaryl corroles 5,10,15-triphenylcorrole, 5,10,15-tris(pentafluorophenyl)corrole, 5,10,15-tris(*p*-nitrophenyl)corrole, and 5,10,15-tris(*p*-methoxyphenyl)corrole were examined. Absorption, steady-state, and time-resolved fluorescence measurements were performed on all compounds in both nonpolar (dichloromethane) and polar (dimethylacetamide) solvents. The experimental evidence points to hydrogen bonding with an internal N−H group as the most likely factor in the solvent-dependent photophysical behavior of these corroles, that is also highly dependent upon substitution.

Introduction

The chemistry and photophysics of normal porphyrins have been heavily explored, in large part due to their relevance to biological active sites and as components of advanced materials.[1] While the optical and electronic properties of porphyrins are reasonably well understood, the properties of analogues and isomers of porphyrins remain open areas of investigation. Over the past decade, new and improved syntheses have resulted in the facile production of a number of similar macrocycles, or porphyrinoids, including porphyrin isomers such as N-confused porphyrin[2,3] and N-fused porphyrin,[4] core-modified rings such as carbaporphyrin,[5] and expanded polypyrroles such as octaphyrin.[6] One example of a porphyrin analogue is the aromatic tetrapyrrole corrole,[7] which is a contracted macrocycle where one meso position has been eliminated resulting in a direct pyrrole−pyrrole bond. The structure of corrole represents an intermediate between porphyrin and the corrin ring in the B_{12} cofactor (Chart 1). The first investigation on corrole was carried out by Johnson and Kay[8] in the late 1960s when the macrocycle was produced as a byproduct during the synthesis of B_{12}. Investigations into this porphyrinoid have recently increased with the synthetic work of the groups of Paolesse[9] and Gross,[10] who each reported a one-pot synthesis of triarylcorroles. Developments into the directed synthesis of corrole macrocycles are currently an active area of research, with recent contributions from the groups of Bruckner,[11] Gryko,[12] Collman,[13] and Geier.[14]

While investigations into the syntheses of free-base and metal corroles[15] have blossomed in recent years, the photophysical properties of corrole remain largely unexplored and poorly understood.[16] Investigation of these properties is crucial for the potential use of these compounds as sensors,[17] light-harvesting molecules,[18] or photodynamic therapy candidates.[19] In addition to uncovering new potential applications, research into the photophysical properties of corroles provides important insight into the electronic structure of the macrocycle (which has been found to stabilize high valent oxidation states in metals)[15] as well as contrast with the well understood properties of normal porphyrin.

CHART 1: Structures of Corrin, Corrole, and Porphyrin



In this report, we present data from four free-base corroles **1**−**4** (Figure 1) that were prepared via Paolesse's[9] and Gross's[10] conditions: 5,10,15-triphenylcorrole (**1**), 5,10,15- tris(pentafluorophenyl)corrole (**2**), 5,10,15- tris(*p*-nitrophenyl)corrole (**3**), and 5,10,15- tris(*p*-methoxyphenyl)corrole (**4**). By generating corroles with either electron-withdrawing or -donating groups on the meso phenyl ring, these four variants provide us an opportunity to study the substituent effects on the photophysical properties. In addition, we have examined the properties of these porphyrinoids in both polar and nonpolar solvents since corroles exhibit strikingly solvent-dependent absorption and emission behavior.

Experimental Section

Synthesis. All reagents and solvents were purchased from Aldrich and used as received. **1**, **3**, and **4** were prepared by using the synthetic protocol developed by Paolesse et al.[9] **2** was prepared by using the synthetic methodology reported by Gross et al.[10] Absorption experiments were carried out on a Hitachi 3100 single monochromator spectrophotometer. Flash chromatography was carried out on silica gel (230−400 mesh) or basic alumina (60−325 mesh). Thin-layer chromatography (TLC) was carried out on silica gel TLC plates (250 u) or basic alumina (200 μm).

High-Resolution Mass Spectrometry Experiments were performed on an electrospray ionization time-of-flight (ESI-TOF) mass spectrometer equipped with an orthogonal electrospray source (Z-spray) operated in positive ion mode. Sodium

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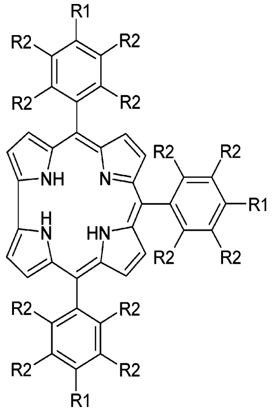


1 $R_1 = R_2 = H$
2 $R_1 = R_2 = F$
3 $R_1 = NO_2, R_2 = H$
4 $R_1 = OMe, R_2 = H$

Figure 1. Structures of free-base corroles **1**−**4**.

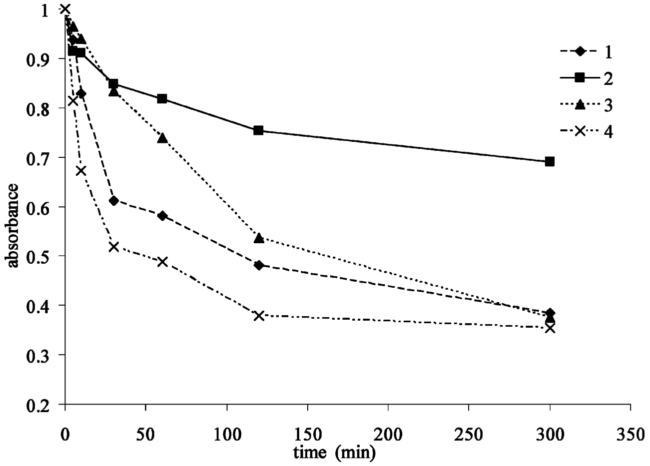


Figure 2. Absorbance of the Soret band as a function of time for dilute solutions of corroles **1**−**4** in CH_2Cl_2 in the presence of ambient light. The λ_{max} of the Soret band of **4** shifted from 418 to 402 nm during the experiment. Both **1** and **4** showed a diminished and broadened Soret band after 5 h of exposure to air and light.

iodide was used for mass calibration for a calibration range of *m/z* 100−2000. Samples were prepared in a solution containing 50% methanol and 1% acetic acid infused into the electrospray source at a rate of 5−10 μL min^{-1}. Optimal ESI conditions were with a capillary voltage of 3000 V, a source temperature of 110 °C, and a cone voltage of 40 V. The ESI gas was nitrogen, and all ions transmitted into the pusher region of the TOF analyzer were scanned over *m/z* 700−1200 with a 1-s integration time. Data were acquired in continuum mode until acceptable average data was obtained.

Steady-State Fluorescence Spectra were collected using argon-saturated solutions by exciting at the Soret maxima of optically matched samples (OD 0.20) in S/R mode, with a correction also used for changes in the lamp output intensity. TLC was carried out to provide freshly purified materials for the fluorescent experiments. Quantum yield measurements were made relative to H_2TPP and were run multiple times. For the excitation spectra, slits were set to 1.3 mm for the entrance, 1.7 mm for the intermediate, and 1.3 mm for the exit and for the emission spectra 1.9 mm for the entrance, 2.2 mm for the intermediate, and 1.9 mm for the exit. Methylene chloride (CH_2Cl_2) and dimethylacetamide (DMAc) were spectrophotometric grade and were used without further purification. In none of the experiments was any fluorescence observed for the corresponding free-base porphyrin. Excitation spectra were found to match the absorption spectra.

Time-Correlated Single-Photon Counting Spectra were collected utilizing the pulses from a Coherent 702 dye laser pumped by the 527-nm output of a Quantronix 4217 mode-locked Nd:LYF laser. Emission signals in this system are detected at 55° with an emission polarizer and depolarizer using a Hamamatsu R3809U-51 red-sensitive multichannel plate detector. Data collection and analysis are accomplished with an Edinburgh Instruments data collection system. The time-resolution of this system is estimated at ~10 ps after reconvolution.

Results and Discussion

Synthesis. The syntheses of compounds **1**, **3**, and **4** were carried out by using the acidic condensation conditions described by Paolesse. The crude products were purified by column chromatography on silica gel for **1** and **3** and on basic alumina for **4**. Compound **2** was produced by using Gross's protocol and purified via column chromatography on silica gel. The purification of corroles can be very tedious due to its similar elution characteristics with normal porphyrin and is hampered by the lack of stability of free-base corroles in solution toward light and air.[14] In part, this lack of stability results from the reduced aromaticity of corrole and the deformation of the macrocycle from planarity due to the steric bulk of the three interior hydrogens.[20] Corroles in aerobic solution under ambient light tend to break down to open chain structures, which we found under certain circumstances can rearrange to form the more thermally stable regular porphyrin.[14,21] Figure 2 shows the breakdown of compounds **1**−**4** in methylene chloride exposed to air and ambient room light by comparing the absorption of the Soret band (normalized) vs time. All four macrocycles show significant decomposition over the course of an hour, although **1** and **4** exhibit the most rapid breakdown. The most thermally stable of the four corroles was the perfluorophenyl variant **2**, but even this macrocycle decomposes appreciably during the hour.

The instability of corrole makes investigations into its photochemistry problematic. High-purity material is essential because normal porphyrin and linear polypyrroles exhibit significant fluorescence. While we were able to confirm purity of our corroles via high resolution mass spectrometry, we still found that it was essential to purify the corroles immediately prior to any experiment, which we achieved through TLC. One method for stabilizing corroles is via metalation (as shown by Gross); however for the free-base corroles, great care must be taken to obtain reproducible spectra.

Absorption Spectroscopy. Since corroles are macrocycles closely related to porphyrins (they are essentially porphyrins contracted by one meso carbon), their absorption properties parallel their tetrapyrrolic parents. By analogy to regular porphyrins, we assign the absorption bands in the 440-nm region to the Soret-type transitions, and those at lower energies (i.e., 500−700 nm) to Q-band type transitions. At this point, we cannot assign specific UV−visible transitions in corroles other than to use the empirical designations of "Soret" and "Q-bands" due to the obvious electronic and structural similarities to porphine. The absorption spectra of corroles are dominated by $\pi-\pi^*$ transitions analogous to those of normal porphyrins, with an intense and broader Soret band (B band) near ~400 nm and lower intensity Q-bands higher than 500 nm. The four corroles presented in this report are readily correlated with the corresponding tetraphenyl porphyrins. The absorption spectra of corroles do, however, exhibit two important differences from porphyrins. First, there is greater change in the optical bands upon variation of the substitution on the phenyl group in the

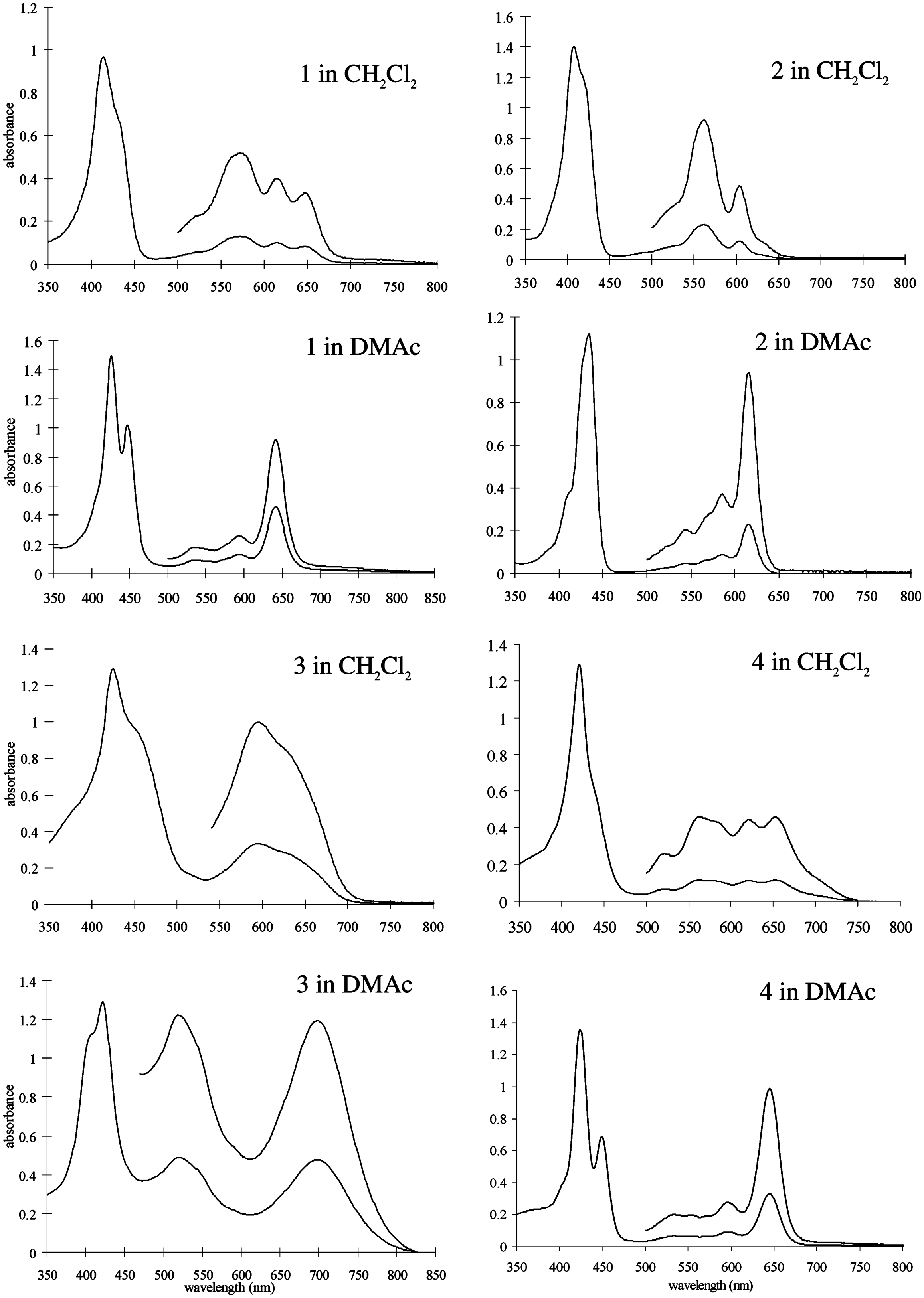


Figure 3. Absorption spectra of **1** (top left), **2** (top right), **3** (bottom left), and **4** (bottom right). In all cases, the spectra in CH_2Cl_2 is shown on the top and in DMAc on the bottom. Extinction coefficients for these transitions can be found in Table 1.

corroles than in the corresponding porphyrins. Second, corroles exhibit very significant solvent-dependent absorptions in contrast to the small shifts typically seen in normal porphyrins.

In general, the Soret bands of the free base triaryl corroles are red shifted from those of the corresponding tetraphenylporphyrins.[22−24] Figure 3 shows the spectra of compounds **1**−**4** in both nonpolar (CH_2Cl_2) and polar (DMAc) solvents. The absorption bands of compounds **1**−**4** are presented in Table 1, while the bands for the corresponding free-base tetraphenylporphyrins are summarized in Table 2.[22−24] The spectra of the four tetraphenylporphyrins have Soret bands ranging from 410 to 424 nm, and the spectrum of H_2TPP in toluene is representative

TABLE 1: Summary of UV−Vis Absorption Bands and Extinction Coefficients for Compounds 1−4

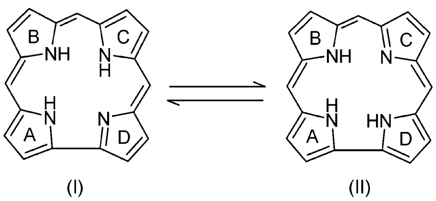
corroles	solvent	Soret (nm)		Q-bands (nm)			
1	CH_2Cl_2	414		524	572	615	647
		5.43×10^4		3.20×10^3	7.29×10^3	5.61×10^3	4.66×10^3
	DMAc	424	447	536	593	642	
		2.91×10^4	2.05×10^4	1.79×10^3	2.57×10^3	9.21×10^3	
2	CH_2Cl_2	407		523	561	604	632
		3.20×10^4		1.97×10^3	5.23×10^3	2.77×10^3	6.40×10^3
	DMAc	434		543	569	586	615
		2.98×10^4		1.25×10^3	1.73×10^3	2.36×10^3	6.14×10^3
3	CH_2Cl_2	425		455	595	633	
		5.79×10^4		4.19×10^4	1.49×10^4	1.22×10^4	
	DMAc	422		519	697		
		6.28×10^4		2.38×10^4	2.32×10^4		
4	CH_2Cl_2	419		520	563	620	652
		2.74×10^4		1.40×10^3	2.46×10^3	2.40×10^3	2.46×10^3
	DMAc	424	448	536	557	596	645
		3.82×10^4	1.93×10^4	1.86×10^3	1.83×10^3	2.62×10^3	9.28×10^3

TABLE 2: Summary of Primary Soret and Q Absorption Bands of Free-Base Tetraphenyl Porphyrins[22−24]

	absorption (nm)				
compound	B(0,0)	$Q_y(1,0)$	$Q_y(1,0)$	$Q_x(1,0)$	$Q_x(0,0)$
H_2TPP	419	514	549	592	647
H_2TFPP	417	508	541	586	640
H_2TNPP	424	516	552	592	649
H_2TMPP	424	488	555	595	653

of aryl porphyrins in nonpolar solvents, with the Soret band at 419 and four Q-bands at 514, 549, 592, and 647 nm.[22] In CH_2Cl_2, the Soret band of triphenyl corrole **1** is blue shifted to 414 nm, is broader, and has a smaller extinction coefficient than H_2TPP. The Q-band structure is also quite different, with three primary bands observed at 572, 615, and 647 nm, all of which have larger extinction coefficients than H_2TPP. The Soret band of the pentafluorophenyl corrole **2** in methylene chloride is similarly blue-shifted to 407 nm, in contrast to the analogous band at 417 nm for H_2F_{20}TPP in toluene.[22] The Q-band structure is significantly different from either **1** or H_2F_{20}TPP, with two primary bands at 561 and 604 nm and shoulders at 523 and 632 nm, respectively. The absorption spectrum of the methoxyphenyl corrole **4** is similar to that of **1**, and has a Soret band at 419 nm and four Q-bands at 520, 563, 620, and 652 nm. The nitrophenyl corrole **3** has a red-shifted Soret band at 425 nm that has a shoulder to the red at 455 nm. The Q-band region is dominated by a single intense absorption at 595 nm that has a prominent shoulder at 633 nm. The general blue-shift observed in the Soret bands of three of the four corroles is expected since the symmetry of the ring is reduced. Corrole has a similar 18-electron π system as a normal porphyrin,[25] but the reduced symmetry is expected to induce a splitting of the e_g lowest-unoccupied molecular orbitals. To a first-order approximation, this change in orbital energy results in lower-energy transitions for some of the Q-bands and a higher-energy transition for the Soret band. The increase in the relative extinction coefficients of the Q-bands vs the Soret can also be attributed to the decrease in symmetry observed in corroles relative to porphyrins. The reduction in symmetry does increase the extinction coefficients of the Q-bands (and lowers the Soret) because of the reduction of alternancy symmetry.[26] In a normal porphyrin, the Q-band transition dipole vectors are nearly the same in magnitude and parallel in orientation, leading to a pseudoparity forbidden transition. The opposite is true for the Soret, which increases in intensity. This effect is partially turned off by the change in symmetry of the ring in corrole, resulting in a Soret/Q-band ratio that is closer to unity. The nature of the "split" Soret band in **3** is unclear at this point.

CHART 2: Two Tautomers of Corrole Where NH Protons Are Assigned to Different Rings



Normal porphyrins typically exhibit small solvent-dependent shifts in their absorption bands. Unlike normal porphyrins, the absorption spectra of corroles **1**−**4** are all highly solvent dependent and in polar media have very different spectra than those described above. In DMAc, the Soret bands of **1**, **2**, and **4**, are red shifted to 424, 434, and 424 nm, respectively, and a split Soret band is observed for **1** and **4**. Nitrophenylcorrole **3** has a Soret band blue-shifted from the analogous band in CH_2Cl_2 (422 nm). More strikingly, the Q-band region in all the corroles is affected by the change in solvent. In compounds **1**, **2**, and **4**, the polar solvent results in an altered Q-band structure, with the most intense band in each compound also the lowest energy absorption (642, 615, and 645 nm, respectively). The spectrum of **3** changes more drastically, with an apparent splitting of the Q-bands to a higher-energy transition at 519 nm with a shoulder at 540 nm and a lower-energy transition at 697 nm.

The solvent-dependent absorption of the corroles could result from one of three contributing factors. First, NH tautomerization is thought to readily occur for corroles, where the inner NH protons migrate around the ring as shown in Chart 2.[27] Because of the asymmetry of the tetrapyrrole ring, the two tautomeric forms are distinct and are structurally quite different.[20] However, since both tautomers are similarly nonplanar, exchange is probably rapid,[27] and because both tautomers presumably have similar energies, it is unlikely that this is the primary contributor to the solvent-dependent absorption properties. The second potential factor that could affect the spectra of the corroles is deprotonation of the macrocycle in polar solvents. As reported by Gross, the pK_a of the pyrrolic nitrogens is increased by the steric crowding and lack of planarity in the macrocycle.[28] The conjugate base resulting from deprotonation is expected to be planar and exhibit a significantly different absorption spectrum. There is indirect evidence supporting this premise: in the presence of an excess of triethylamine in methylene chloride, all of the corroles presented in this report show an identical spectrum to the analogous corrole in DMAc (Figure 4). However, this interpretation has two problems. First, the nature

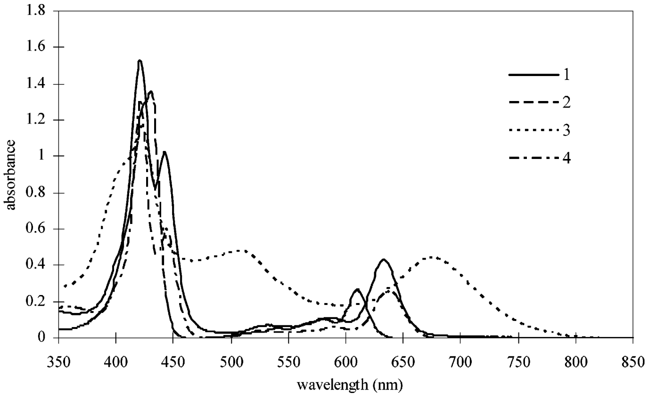


Figure 4. Absorption spectra for corroles **1**−**4** in CH_2Cl_2 in the presence of excess TEA.

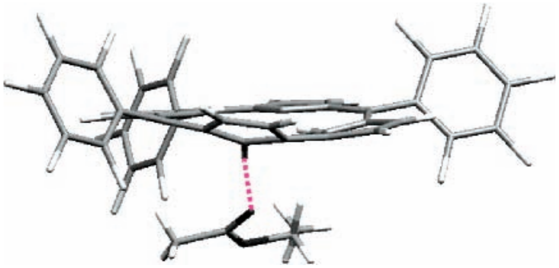


Figure 5. Crystal structure of H_3TPFC in ethyl acetate. The hydrogen bonding to solvent via an internal N−H group is indicated by the dashed bond.[20]

of the base in polar media is unclear. While a small amount of water may be in our steady state absorption experiments in DMAc, the spectrophotometric grade solvents we used do not contain significant concentrations of potential proton acceptors such as dimethylamine. In addition, samples of all of the corroles dissolved in freshly dried and purified dimethylformamide (DMF) obtained from a PureSolv solvent purification system exhibit the same spectra as "wet" DMF. Second, while the pK_a of corroles is lower than that of normal porphyrin, it is not low enough to react completely with solvents such as DMAc or DMF so that only the deprotonated form is observed in solution.

A third interpretation is that hydrogen bonding with an internal N−H group induces the solvent dependent changes. This interpretation explains the spectroscopic changes without invoking a deprotonation of the macrocycle, can occur readily with nearly any polar solvent, and is consistent with the triethylamine experiment. Hydrogen bond induced changes in absorption spectra have been observed in nonplanar porphyrins,[29−31] and due to the lack of planarity in corroles, similar internal N−H hydrogen bonding to solvent can take place. In previous structural work on corroles,[20] we found that in the X-ray structure for the perfluorophenyl corrole **2** isolated from ethyl acetate (Figure 5), a hydrogen bond between a pyrrolic N−H and a solvent molecule in the crystalline lattice void space was observed. Although this experiment is a solid-state observation, we believe that a similar sort of interaction occurs in polar solvents and gives rise to the solvent dependent optical properties.

Fluorescence Spectroscopy. The fluorescence spectra of free-base corroles **1**, **2**, and **4** in both CH_2Cl_2 and DMAc are characterized by strong emission bands. The steady-state fluorescence of these three corroles in CH_2Cl_2 and DMAc relative to H_2TPP are shown in Figure 6, and the corresponding fluorescence maxima (λ_{max}) and fluorescence quantum yield (Φ_F) are summarized in Table 3. In the corroles studied in this report, these compounds all exhibit exceptionally large Stokes shifts relative to their analogous porphyrins.[22,29] For example, the Stokes shift in H_2TPP ranges from 25 cm^{-1} in methylcyclohexane to 120 cm^{-1} in 2-methyltetrahydrofuran,[22] while that for **1** in CH_2Cl_2 is 574 and 285 cm^{-1} in DMAc. Similarly, in H_2TFPP the observed Stokes shift is 75 cm^{-1} in toluene,[22] whereas in the case of **2** this value is 271 cm^{-1} in CH_2Cl_2 and 234 cm^{-1} in DMAc. The $Q_x(0,0)$ emission bands in DMAc are all blue-shifted from the analogous bands in CH_2Cl_2, resulting in smaller Stokes shifts by a factor of nearly two. The larger Stokes shifts provide evidence that the electronic structures of the emitting excited states are much different from the initially prepared Franck−Condon states in corroles.

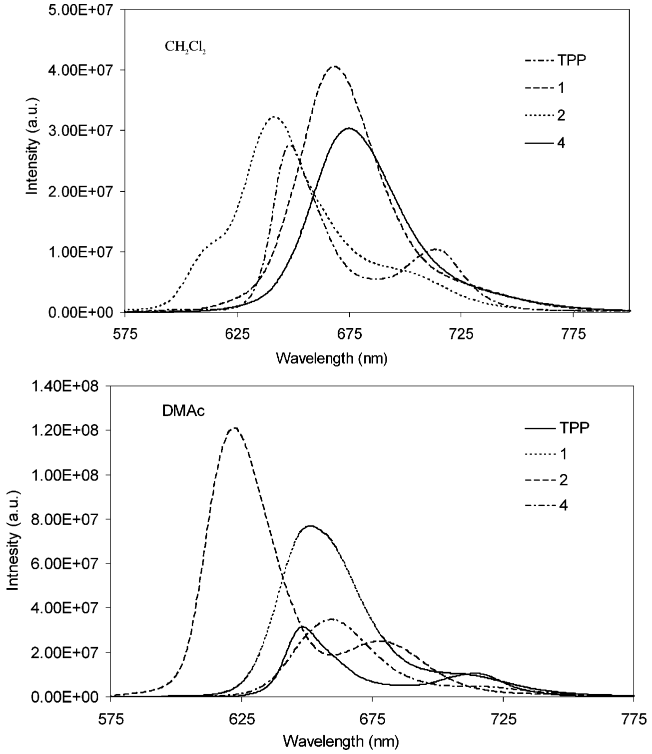


Figure 6. (a) Fluorescence spectra of H_2TPP and compounds **1**, **2**, and **4** in CH_2Cl_2 (top) and in DMAc (bottom).

The fluorescence quantum yields of the substituted corroles examined here are in general higher than the analogous porphyrin derivative (Table 3). The Φ_F values obtained in CH_2Cl_2 are similar for **1** (0.19), **2** (0.14), and **4** (0.16). The quantum yield for **3** is smaller than the others by a factor of 5. The values of Φ_F are significantly higher in DMAc for **1** and **2** than in CH_2Cl_2, while that of **4** is nearly identical in both solvents (∼0.16). A reliable quantum yield for **3** in DMAc could not be obtained. Paolesse and Smith[16] recently reported a very low quantum yield of fluorescence for **3** that was attributed to charge-transfer transitions from the corrole macrocycle to one of the nitrophenyl groups. Time-correlated single photon counting (TCSPC) experiments on **1**, **2**, and **4** yielded a long-lived decay (∼3.3−3.9 ns) component in either solvent. A second minor component in these experiments ranged from 252 ps to 1.5 ns. These observations are in agreement with the lower time resolution data recently published by Paolesse and Smith.[16] The fluorescence lifetime obtained for **3** in CH_2Cl_2 was significantly shorter than the other corroles, with a major component of ∼128 ps (74.7%) and smaller components of 4.9 ns (10.8%) and 22 ps (14.6%). These values mirror the steady-state data, which showed a significantly smaller quantum yield for **3** than the other corroles. Similar to the steady-state results, we were unable to obtain an acceptable lifetime for **3** in DMAc, probably

TABLE 3: Summary of Fluorescence Data for Compounds 1−4

corroles	solvent	Soret (nm)	emission maxima (nm)[a]	Φ_{fl}[b]	Stokes shift (cm^{-1})	τ_1	τ_2	τ_3
1	CH_2Cl_2	414	672, 721	0.19 ± 0.02	551	3.8 ns (97%)	1.5 ns	
	DMAc	417	654, 711	0.30 ± 0.03	237	3.98 ns (99%)	324 ps	
2	CH_2Cl_2	407	643, 700	0.14 ± 0.02	1059	3.7 ns (98%)	1.1 ns	
	DMAc	434	624, 682	0.41 ± 0.03	208	3.99 ns (99%)	1.5 ns	
3	CH_2Cl_2	427	657, 716	0.027 ± 0.005	1058	128.7 ps (74.7%)	4.9 ns (10.8%)	21.97 ps (14.6%)
	DMAc	405	651, 715					
4	CH_2Cl_2	419	681, 742	0.164 ± 0.006	747	3.3 ns (97%)	590 ps	8.05 ps
	DMAc	424	661, 719	0.163 ± 0.002	399	3.9 ns (98%)	252 ps	

[a] Excited at the Soret bands (the most strongly absorping band) to minimize solution concentration to avoid aggregation. [b] Relative to the fluorescence of H_2TPP. Quantum yields were calculated using standard methods.

because of sample instability, although all measurements indicated a very short lifetime.

The fluorescence data indicate similar excited-state behavior for **1**, **2**, and **4** in nonpolar solvents, where we observe similar values of Φ_F and τ_F. Changing solvents to the more polar solvent DMAc leads to an approximately 3-fold increase of the quantum yields for **1** and **2**, while Φ_F for **4** remains constant. The fact that the fluorescence lifetimes of **1** and **2** do *not* increase with the change to a polar solvent (and increase in Φ_F) leads us to postulate that hydrogen bonding decreases k_{IC} (or k_{ISC}) in corroles **1** and **2**, possibly as a result of the corrole ring becoming relatively more rigid from the hydrogen bonding interactions. In the case of **4**, the electron-donating properties of the methoxy groups in **4** decrease the acidity of the N−H groups, decreasing their ability to hydrogen bond. The ramification of decreased hydrogen bonding is a higher rate constant for internal conversion, resulting in fluorescence lifetimes for **1**, **2**, and **4** that are nearly identical, but where the quantum yield of **4** does not change with the change to a more polar solvent and the value of Φ_F is the same in both CH_2Cl_2 and DMAc. This interpretation is also consistent with the steady-state absorption data for **4**, for which a much smaller variation between the Soret and Q-band positions in both solvents is observed compared to **1** and **2**. In the case of **3**, the electron-withdrawing nature of the nitro group leads to a tendency for charge-transfer in the excited state, an effect that is exacerbated in polar solvents where, in addition to promoting hydrogen bonding, the increased dielectric constant of the solvent stabilizes the charge-transfer state. An increase in hydrogen bonding effectively makes the corrole macrocycle more prone toward charge transfer because of increased electron density (partial negative charge) on the corrole N−H nitrogens. Thus, the quantum yield for **3** in CH_2Cl_2 is significantly smaller than those of **1**, **2**, and **4** and is too small to accurately measure in DMAc.

Conclusions

While globally similar to their tetrapyrrolic parents, the absorption and emission characteristics of the corroles exhibit several marked differences from normal porphyrins. First, all of the corroles examined in this report exhibit striking solvent-dependent behavior, consistent with hydrogen bonding in polar media. We believe that this solvent dependence results from hydrogen-bonding interactions that form in polar media rather than from deprotonation or tautomerization effects. In addition, the effect of substituents on the optical properties of corroles is significantly larger than in normal porphyrins, leading to a diversity of absorption differences upon simple substitution. Finally, corroles can be very emissive, with high quantum yields of fluorescence. The above observations lead to the conclusion that corroles could be excellent candidates for sensor applications; however, the instability of these contracted porphyrinoids would limit the effective usefulness of these compounds. We are continuing this work investigating the electronic structure of free base corroles and are extending this work to metal complexes.

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Supporting Information Available: High-resolution TOF-MS data of free-base corroles **1**−**4** are available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Publication. This article was released ASAP on July 30, 2005. In the first sentence of the abstract, 5-positions was changed to 6-positions. The correct version was posted on August 4, 2005.

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