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Photochemically-Induced Radical Reactions of Zinc Phthalocyanine

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Direct measurements of the radical reaction products following the electrochemical and photochemical oxidation and reduction of a metallophthalocyanine π-ring are reported. Electrospray mass spectrometry was used to detect the presence of the anion zinc(II) (1,4,8,11,15,18,22,25-octafluoro, 2,3,9,10,16,17,23,24-octaperfluoroisopropylphthalocyanine chloride, $[ZnperF_{64}Pc(-2)\ (Cl)]^-$, and its π ring anion radical species, $[ZnperF_{64}Pc(-3)(Cl)]^{2-}$. This paper describes the use of ESI-MS techniques to determine the products of an on-line, photochemical radical oxidation, using CBr_4 as a sacrificial photoinduced oxidizing agent, which oxidized the radical, $[ZnperF_{64}Pc(-3)(Cl)]^{2-}$ species to $[ZnperF_{64}Pc(-2)(Cl)]^-$, where the complete reaction was detected directly by the mass spectrometer. This study makes use of electrospray mass spectrometry to detect the presence of an anion radical as the key component in the ring-reduced species and to monitor the immediate products of the important class of photochemical reduction and oxidation reactions in which radicals of the Zn Pc are formed in situ.

Introduction

Ring oxidation and reduction reactions of the natural chlorins and porphyrins play a critically important role in a large number of biological systems. These reactions have been exploited with synthetic porphyrins in applications from solar energy collectors to photocatalysts. Important roles of photoinduced radical reactions of ring-substituted and peripherally substituted porphyrins and phthalocyanines are the key mechanistic steps in photodynamic therapy (PDT) of tumors.[1] Redox reactions of synthetic porphyrins and phthalocyanines are a significant factor in their use as catalysts.[2] While it is well-known that many of the reaction pathways of the porphyrins and phthalocyanines involve radical species formed following chemical, electrochemical, and photochemical oxidation and reduction,[3] in most instances, the identity of all the photochemical products cannot be obtained,[3d,g,4] and in many cases absolute determination of the presence of a ring oxidized or ring reduced species cannot be made because the optical data are not clear. Typically, optical techniques have been used to characterize the redox states of porphyrin and phthalocyanine rings, but often the limited life of these species in solution reduces the utility of the optical data so that mechanisms that involve transient radical species cannot be elucidated. In particular, while ring oxidation in many cases results in the appearance of readily identifiable spectral signatures, in both phthalocyanines and porphyrins (even in proteins), the anion radicals are not nearly as well-characterized. Indeed, the optical data of very few ring-reduced species have been described in detail, yet the ring-reduced porphyrins and phthalocyanines hold promise as the next generation of electron-donor-based catalysts.

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We report here the determination of an anion-radical-based, photochemically dependent reaction mechanism for a zinc phthalocyanine using coupled electrospray ionization mass spectrometry[5] (ESI-MS) and absorption spectrometry to probe the redox state of the ring following the redox reactions. These results show that the ESI-MS technique will allow identification of the transient products of photochemical reactions of porphyrins and phthalocyanines that take place through radical mechanisms. Previously, Van Berkel's group has reported extensively on the use of ESI-MS in analyzing porphyrins and the mechanisms that take place during the ESI-MS analysis.[6] Arakawa and co-workers have laid down the foundation for the use of on-line ESI-MS techniques, including designing flow-through optical cells for use prior to ionization.[7] There have been a number of reports concerning the mechanisms of reactions that take place during ESI-MS analysis[8] with some applications related to porphyrins but none related to the redox chemistry of phthalocyanines.[8a] In this paper, we report the identification of both the photochemically formed anion radical of perfluoro(octaperfluoroisopropyl)phthalocyanine,[9,10] [Zn(II)perF_{64}Pc(−2)], and analysis of the photochemical oxidation of a metal phthalocyanine anion complex. [Zn^{II}perF_{64}Pc(−2)] readily forms the anion radical, [Zn(II)perF_{64}Pc(−3)]$^-$, a species that is stabilized by the electron-withdrawing properties of the 64 peripheral fluorines. The data described here show that ESI-MS can be used to investigate the formation of short-lived intermediate species following reactions that involve complicated electrochemical and photochemical pathways similar to those involved in PDT and catalysis with direct application to novel porphyrin and phthalocyanine chemistries.

Experimental Methods

Materials. [Zn^{II}perF_{64}Pc(−2)]^0 was synthesized and purified at Brown University by Sergei Gorun's research group. Spectrograde DMF (Fischer Scientific), hydrazine hydrate (Aldrich), and CBr_4 (Kodak) were used directly from the bottle.

Methods. Room temperature absorption spectra were recorded from degassed, argon saturated DMF solutions using a Cary 5 spectrophotometer (Varian, Inc.) controlled by the Cary WinUV software. Electrospray ionization mass spectrometry (ESI-MS) was carried out using a Perkin-Elmer Sciex API 365 mass spectrometer calibrated using a standard solution of PPG (polypropylene glycol). Solutions were introduced using a Hamilton 250 μL microsyringe employing a Harvard Apparatus syringe pump. The mass spectrometer was run in the negative ion mode with the ion source at −5400 V at the ionization tip. The infusion rates were 2 μL/min. MALDI-TOF-MS data were acquired on a Micromass TofSpec 2E mass spectrometer (Wythenshawe, Manchester, U.K.) in the negative ion mode. The sample for MALDI-TOF-MS analysis was dissolved in 100% acetone to give a solution of approximately 1 mg/mL. A 10 mg amount of α-cyano-4-hydroxycinnamic acid (α) was dissolved in 1 mL of 99:1 acetone:0.1% TFA to form the matrix solution. Sample and matrix were mixed 1:1 prior to application onto the target. The samples were analyzed in the reflectron mode, and MS spectra were externally calibrated with a peptide mix (bradykinin, angiotensin I, renin substrate, and ACTH18-39). The photochemical reactions were carried out under anaerobic conditions, using a 300 W tungsten−halogen Kodak projector lamp, featuring a Pyrex filter. The photoreduction reaction was carried out using a 1% (v/v) solution of hydrazine hydrate as the electron donor in dimethylformamide (DMF; eq 1).[3d]

$$[M^{II}Pc(-2)][Cl^-]^{-1} + N_2H_4{\cdot}H_2O + h\nu \rightarrow [M^{II}Pc(-3)][Cl^-]^{-2} + \text{hydrazine radical products} \quad (M = Zn) \quad (1)$$

The photochemical oxidation of the radical anion of this molecule was carried out using a 0.1 M solution of CBr_4 in DMF and irradiating the sample with visible light. The use of CBr_4 as a sacrificial electron acceptor has been well-documented in our laboratory[3g] (eq 2).

$$[M^{II}Pc(-3)][Cl^-]^{-2} + CBr_4 + h\nu \rightarrow [M^{II}Pc(-2)][Cl^-]^{-1} + Br^- + \text{other radical products} \quad (M = Zn) \quad (2)$$

Results and Discussion

Figure 1 shows the MALDI-TOF MS spectrum for [Zn^{II}-perF_{64}Pc] in the negative ion mode. We observe peaks centered on 2064 *m*/*z* and 2101 *m*/*z*. The species responsible are assigned as the [Zn^{II}perF_{64}Pc(−3)]$^-$ radical anion at 2064 amu and the [Zn^{II}perF_{64}Pc(−2)(Cl)]$^-$ anion at 2101 amu. The calculations of the isotopic distributions expected for the two species observed in A and C are shown as B and D, respectively, and indicate very close alignment of the patterns

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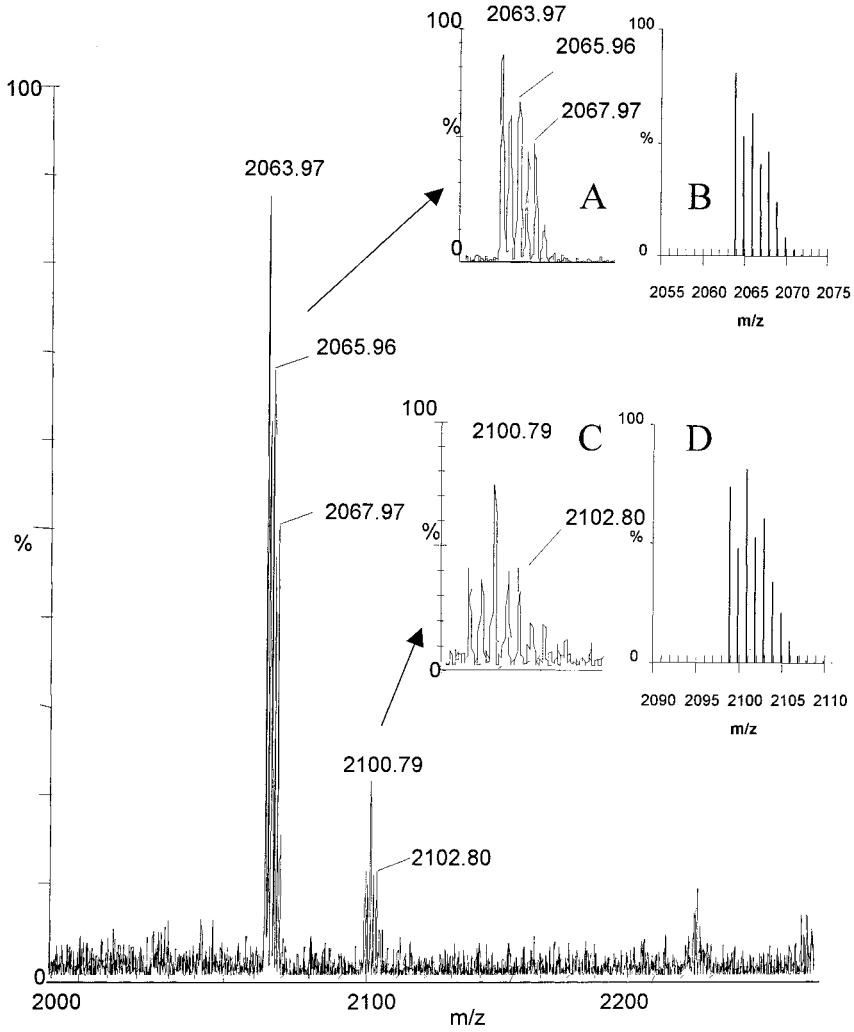

Figure 1. MALDI-TOF mass spectrum of $Zn^{II}perF_{64}Pc$. The four insets (A−D) show the expanded experimental data at 2064 amu (A) for $[Zn^{II}perF_{64}Pc]^-$ (2063.97, 2065.96, and 2067.97) and 2101 amu (C) for $[Zn^{II}perF_{64}PcCl]^-$ (2100.79 and 2102.80), and the corresponding calculated isotopic distribution patterns B (2063.85, 2064.85, 2065.85, 2066.85, and 2067.85 *m*/*z*) and D (2098.82, 2099.82, 2100.83, 2101.83, and 2102.83 *m*/*z*), respectively.

in each region, confirming the identification. In this MALDI-TOF-MS experiment, only anions can be detected, and we propose that the Pc(−2) ring is detected because of the ligation of chloride to the $Zn^{II}perF_{64}Pc$ species and that this accounts for the negative charge on the complex. The radical anion is formed following the photochemical ionization process also leading to an anionic species.

Figure 2 shows two sets of data, a series of mass and absorption spectra, for separate solutions of Zn(II)$perF_{64}Pc$ dissolved in DMF under different experimental conditions. The first set of data illustrates the case where the sample is simply dissolved in DMF (Figure 2A,A′). We can clearly see from both data sets that there is a mixture of two different species, following dissolution. Figure 2A shows the mass spectral pattern obtained for the crystalline [Zn(II)$perF_{64}$-Pc(−2)] dissolved in DMF in the absence of any redox active agent. In Figure 2A, the peak at 1050 *m*/*z* is due to the ring-reduced species, $[Zn^{II}perF_{64}Pc(-3)Cl]^{2-}$, and the peak at 2101 *m*/*z* is due to the chloride ligated neutral species, $[Zn^{II}$-$perF_{64}Pc(-2)Cl]^-$. The absorption spectrum, Figure 2A′, is clearly a mixture of both the solutions in Figure 2B′,C′, that is, a mixture of the neutral and ring-reduced species. The coexistence of these two species shows that an unusual equilibrium is established between the neutral complex and the ring-reduced complex, which we interpret as being due to the presence of the peripheral, electron-withdrawing fluorines that provide a stabilization of the negative radical charge. There are two mechanisms for the radical anion in this initial solution, (i) adventitious photoreduction from the laboratory lighting that takes place even under aerobic conditions, which is observed in the absorption spectrum, and (ii) an additional source of ring reduction in the mass spectral data arises from the negatively charged capillary tip of the ESI spectrometer inlet. Previous reports of cation radical formation in the ESI mass spectrum have shown electrochemical oxidation occurring at this step with detection of the positive ion in the mass spectrometer.[8a] The $[Zn^{II}$-$perF_{64}Pc(-2)]$ is detected as the chloride anion $[Zn^{II}perF_{64}$-$Pc(-2)Cl]^-$ with a total mass of 2101.0 under the low resolution ESI-MS experimental conditions. Zinc phthalocyanines typically bind one chloride ion at the fifth position, and the synthesis of many MPc's involves using the metal chlorides. We observe the isotopic distribution contributed by the bound chloride ion using MALDI-TOF MS (inset

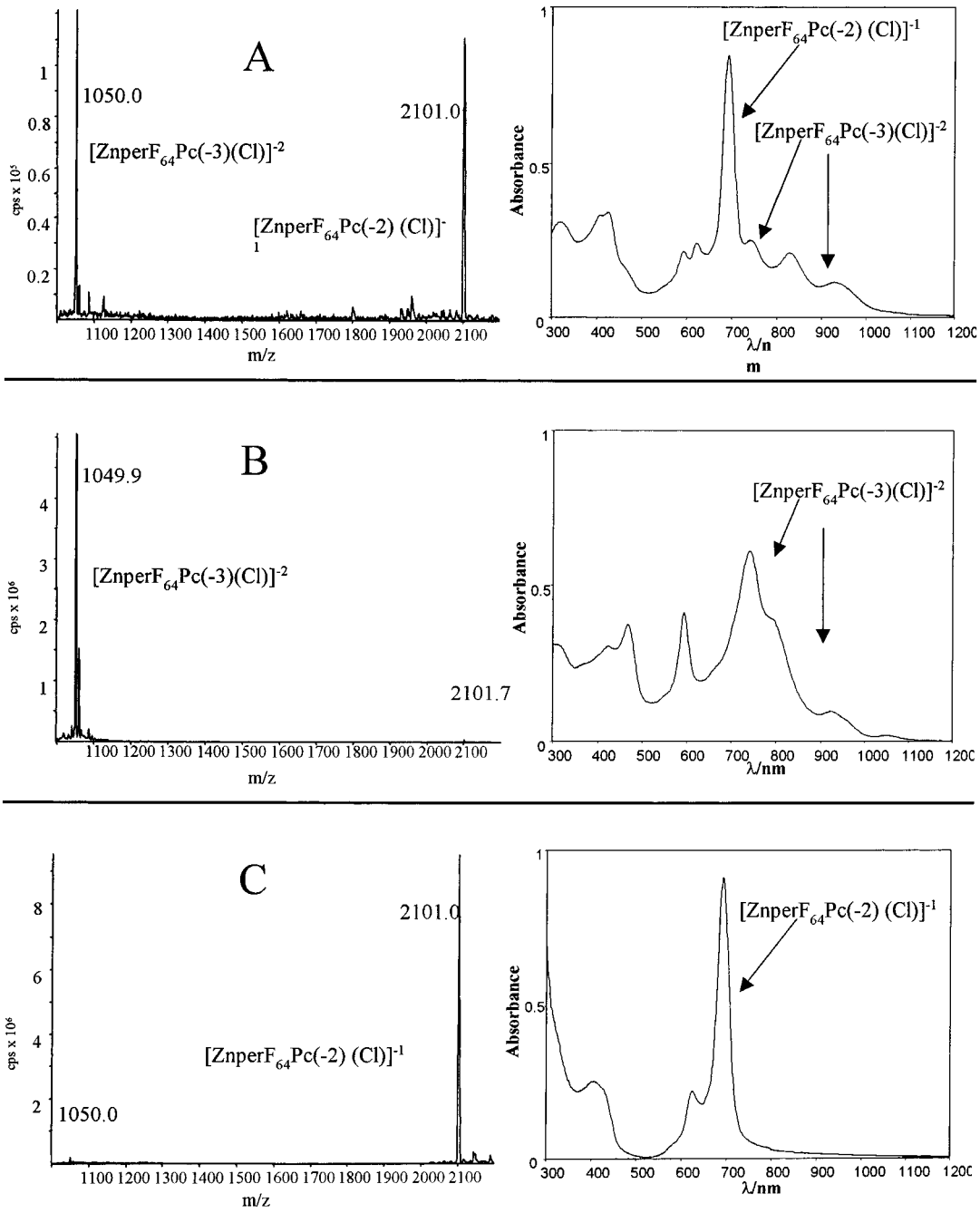

Figure 2. ESI-MS and absorption spectra of $[Zn^{II}perF_{64}Pc(-2)Cl]^-$ in DMF: (A) in solution under Ar, (B) following photoreduction of A, and (C) following photooxidation of A. The mass spectra were obtained by integrating the signal during infusion of the solution for varying periods of time up to 5 min, which gave signal intensities of the order 10^6−10^7 counts/s. The associated absorption spectra were recorded from the same stock solution (top right, A′). Photoreduction of the stock solution (A′) in the presence of hydrazine hydrate gives the spectrum of the ring-reduced π anion radical (middle right, B′), and photooxidation of the stock solution (A′) with CBr_4, resulted in conversion of all species to the neutral $Zn^{II}perF_{64}Pc(-2)$ with its characteristic Q-band at 692 nm (bottom right, C′).

Figure 1C,D) at ca. 2101 *m*/*z*. While the predominant species with a mass of ca. 2064 in the MALDI experiment is without the chloride, the ESI-MS data in Figure 2 confirm that the chloride is bound to all of the Zn(II) in solution.

We have shown previously for ZnPc(−2) and MgPc(−2) that photoreduction using visible-region light results in quantitative formation of the ring-reduced, radical anion species.[3d] The $[Zn^{II}perF_{64}Pc(-2)Cl]^-$ species was dissolved in DMF containing 1% (v/v) hydrazine hydrate (the solution used in Figure 2A, A′) and photolyzed with visible-region light. This resulted in the complete loss of the neutral phthalocyanine and quantitative conversion to the ring-reduced, anion radical, $[Zn^{II}perF_{64}Pc(-3)]^-$, Figure 2B,B′ according to eq 1.[3d] The major peak in the ESI-MS (Figure 2B) at 1049.9 *m*/*z* is assigned as the radical anion chloride, $[Zn^{II}perF_{64}Pc(-3)Cl]^{2-}$ with a mass of ca. 2101 amu. The absorption spectrum (Figure 2B′) shows a complete loss of the Q-band at 692 nm and replacement with bands at 740, 597, and 470 nm, bands associated with the radical anion.[3j] So, while the predominant species in the MALDI data is

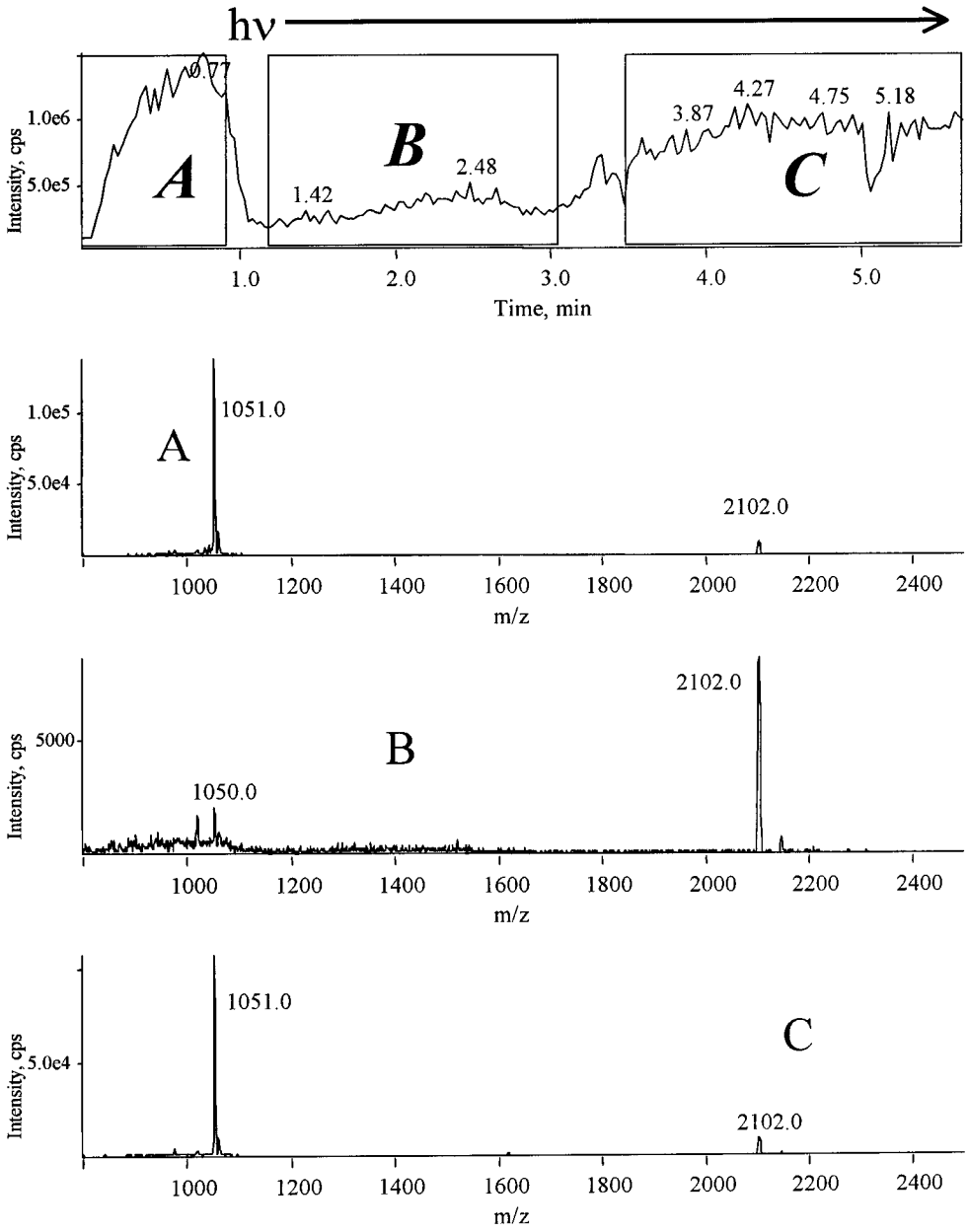

Figure 3. Time-resolved mass spectra. Total ion counts as a function of time during infusion of the solution of $[Zn^{II}perF_{64}Pc(-3)Cl]^{2-}$ in DMF formed off-line by photoreduction using hydrazine hydrate. CBr_4 (photooxidant) was added anaerobically to the solution before infusion. There are three regions: (A) that starts at 0 min, (B) that starts at 0.75 min, and (C) that starts at 3 min. The boxes show the integration range used to extract the mass spectral data plotted below. (A) Infusion of the photochemically reduced $[Zn^{II}perF_{64}Pc(-3)Cl]^{2-}$ begins at 0 min. (B) Photooxidation begins at 0.75 min, using CBr_4 as the electron acceptor and the resultant species is detected as $[Zn^{II}perF_{64}Pc(-2)Cl]^{-}$. (C) At 3 min, the CBr_4 is exhausted and the anion radical re-forms, resulting in detection of the ring-reduced anion radical $[Zn^{II}perF_{64}Pc(-3)Cl]^{2-}$.

the chloride-free ring with a mass ca. 2064 amu, the ESI-MS data confirm that the chloride is generally bound to the Zn(II) in solution to give a mass of 2101 amu.

We have reported previously that main group porphyrins and phthalocyanines can be photooxidized with visible-region light to the ring-oxidized MP(−1) or MPc(−1) species using CBr_4 as an irreversible photooxidation agent;[3g] however, we have not previously applied this powerful and highly selective method to the photooxidation of ring-reduced radical species. CBr_4 was added anaerobically to a solution of the radical anion $[Zn^{II}perF_{64}Pc(-3)Cl]^{2-}$ formed photochemically. Subsequent irradiation with visible-region light formed the species that exhibited a mass of 2101 *m/z* in the mass spectrum (Figure 2C,C′). Clearly, one-electron photooxidation of the ring-reduced anion radical species took place, resulting in quantitative formation of the chloride complex of the neutral phthalocyanine, $[Zn^{II}perF_{64}Pc(-2)Cl]^{-}$, with no indication of degradation. Even though the use of CBr_4 has been demonstrated previously by optical methods, the exact nature of the products of the CBr_4 photooxidation reaction, eq 2, have not previously been reported nor has the lack of photodegradation product been established. When the solution used in Figure 2A′ was photochemically oxidized using CBr_4 as the acceptor, only the chloride ion complex of the neutral phthalocyanine, $[Zn^{II}perF_{64}Pc(-2)Cl]^{-}$, was observed, with a mass of 2101 *m/z*, Figure 2C.

The set of mass spectral data shown in Figure 2 display a novel series of data in which each of the major components in the photoredox cycle has been identified from the dilute solution. While these data and previous reports have described the redox states of stable species, in many cases, the redox intermediates in redox reactions involving ring-based redox chemistry are not stable and are converted to other species before spectroscopic analysis is complete, resulting in ambiguous information. The products of photochemical oxidation and reduction reactions determined dynamically are of greatest importance for applications where the reactions take place under conditions that rapidly quench the photochemically formed radical species. One such example is the detection of the compound **I** intermediate in the cytochrome P_{450} enzymatic cycle (a proposed iron(IV)−porphyrin cation radical with an overall oxidation state of 3+ above the neutral $Fe^{II}P(-2)$). We address such conditions in the reaction described in the mass spectral data shown in Figure 3. The reactions described here form a complete cycle in which photoreduction is followed by in situ photooxidation. The key features are that the data in Figure 3 show how the complete redox cycle can be achieved—that is $Pc(-2) \rightarrow Pc(-3) \rightarrow Pc(-2) \rightarrow Pc(-3)$ − photochemically.

In the course of Figure 3 we show real-time data obtained during photooxidation of a solution of a radical anion preformed by visible-light photochemical reduction using hydrazine hydrate as the electron donor. An aliquot of 0.01 M CBr_4 in DMF solution was then added to the reduced $[Zn^{II}perF_{64}Pc(-3)Cl]^{2-}$ species anaerobically and the mixed solution infused into the ESI mass spectrometer at a rate of 2 μL/min. At this stage, the total ion current grows in intensity (Figure 3A) as the infusion begins to fill the atmospheric pressure interface (API) with phthalocyanine anions; $t = 0$ min marks the beginning of the infusion. The total ion data were recorded over a period of 5.5 min. The time-resolved data in Figure 3 were separated into three stages (A−C) and the *m*/*z* spectra extracted from the total ion chromatogram by integrating within the time limits defining the stage and plotted as the corresponding mass spectra.

During the first stage, the radical dianion, $[Zn^{II}perF_{64}Pc(-3)Cl]^{2-}$, observed at 1051 *m*/*z*, is the sole species for the first 0.75 min, Figure 3A. After 0.77 min the solution was illuminated through the glass syringe with visible light, which, in the presence of CBr_4, initiated a photooxidation reaction inside the glass syringe. Photolysis resulted in 100% oxidation of the radical anion to the neutral species with a mass of 2101 *m*/*z* being detected in stage (Figure 3B).

As the photooxidation reaction proceeds, the CBr_4 is consumed, so that by the 3 min point no unreacted CBr_4 remains and the excess hydrazine hydrate present allows the continued illumination to initiate photoreduction of the ring back to the anion radical. The predominant species in time region C in the presence of the light, Figure 3C, is observed as the peak at 1051 *m*/*z*. MS spectra recorded simultaneously in the 70−90 *m*/*z* region show the appearance of the isotopic masses 79 and 81 from Br^- during the initial illumination reaction. These results represent the first simultaneous detection of the photooxidized, ring-based Pc species and the Br^- product of the irreversible photoreduction reduction of the CBr_4.

These data provide dramatic evidence of the photooxidation of a radical anion in the presence of reagents that will allow subsequent photoreduction. This experimental sequence will allow on-demand reversible photoredox chemistries—reactivity at the rate of the photochemical reaction—triggered by a discrete number of photons. The number of photons depends on the molar ratio of the CBr_4 added—so that there is a mechanism for integrating a process in the following way. CBr_4 is used as the product of a calculation or process and can be added quantitatively to the reduced solution of the ZnPc—laser photolysis can determine the number of photons required to exhaust the CBr_4 and return to the reduced species. In this study, the ESI-MS experiment provided the real-time identity of the intermediate radical products. In future experiments we will examine the response to flash photolysis as a means of determining rates and initial products of redox reactions carried out in dilute solutions and the subsequent appearance of other species following ring oxidation or ring reduction in porphyrins and phthalocyanines. We will also begin study of the short-lived reaction intermediates in the peroxidase and catalase enzymatic cycles to detect all species that take part in these reactions. The detection of all products of the photochemical activating reaction and the tuning of the quantum yield represent major tasks in PDT research.

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