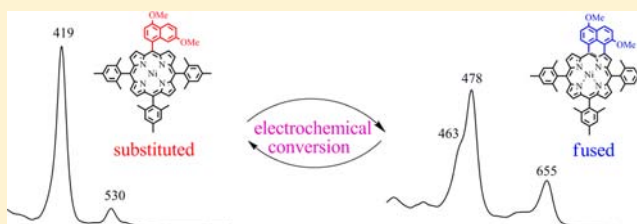


Electrochemically Driven Intramolecular Oxidative Aromatic Coupling as a Pathway toward  $\pi$ -Extended PorphyrinsPing Chen,<sup>†</sup> Yuanyuan Fang,<sup>†</sup> Karl M. Kadish,<sup>\*,†</sup> Jan P. Lewtak,<sup>‡</sup> Dominik Koszelewski,<sup>‡</sup> Anita Janiga,<sup>‡</sup> and Daniel T. Gryko<sup>\*,‡</sup><sup>†</sup>Department of Chemistry, University of Houston, Texas 77204-5003, United States<sup>‡</sup>Institute of Organic Chemistry, Polish Academy of Sciences, 02-784, Kasprzaka 44/52, Poland

## Supporting Information

**ABSTRACT:** A Ni(II) complex of a  $\pi$ -extended porphyrin bearing three mesityl substituents and one electron-rich naphthalene moiety has been prepared via electrochemical oxidation. It was proven that the whole oxidative process starts from electrochemical generation of a radical-cation on the porphyrin core. Electrochemistry and spectroelectrochemistry of both a naphthalenyl-substituted porphyrin and a porphyrin with a fused naphthalenyl group on the  $\pi$ -ring system provide clear distinction between metal- and ring-centered processes. The redox reactivity of the naphthalenyl-substituted metalloporphyrin in nonaqueous media is presented while outlining the most important structural factors which influence the reversible half-wave potentials for oxidation and reduction of this complex and the following chemical reactions which lead to an extended  $\pi$ -system.



## INTRODUCTION

Highly conjugated porphyrins by nature of their electronic and redox properties, have attracted attention as conducting materials, near-IR dyes, nonlinear optical materials, or photosensitizers for photodynamic therapy (PDT) of cancer tissues or in vivo studies.<sup>1,2</sup> Ring extension of the porphyrins will lead to a significant modification of the compound's optical features, redox characteristics and the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

The relationship between the structure of porphyrinoids and their spectroscopic and photophysical properties is a complex issue.<sup>3</sup> Over the past two decades considerable attention has been devoted to studies involving the  $\pi$ -conjugation of porphyrins. These materials display significant changes in their optical and electrochemical properties when compared with native porphyrins. Among other changes,  $\pi$ -extension of a porphyrin chromophore usually leads to a bathochromic shift in its absorption (and hence emission) spectrum.<sup>4</sup> The diverse class of  $\pi$ -extended porphyrinoid molecules has attracted much attention because of their fundamental and theoretical interest, as well as because of the opportunities they offer in technology and medicine that arises from their linear and nonlinear optical properties.<sup>5</sup> The  $\pi$ -electron system of a porphyrin macrocycle can be extended by peripheral substituents at the *meso*-positions, or by the addition of one or more fused polycyclic ring systems.<sup>6</sup> The magnitude of this alteration depends more on the type of conjugation than on the actual number of double/triple bonds or aromatic rings added.<sup>7</sup> In the past years three fundamental papers showed that it is possible to prepare porphyrins fused with other porphyrins or with aromatic

hydrocarbons at both the *meso* and  $\beta$ -positions of the macrocycle.<sup>8</sup> These discoveries have opened up new avenues that were quickly followed by other researchers.<sup>8–10</sup>

Over time, it was observed that the synthesis of  $\pi$ -extended porphyrins via intramolecular oxidative coupling usually requires activation of the aromatic subunits (for example by introducing alkoxy groups).<sup>11</sup>

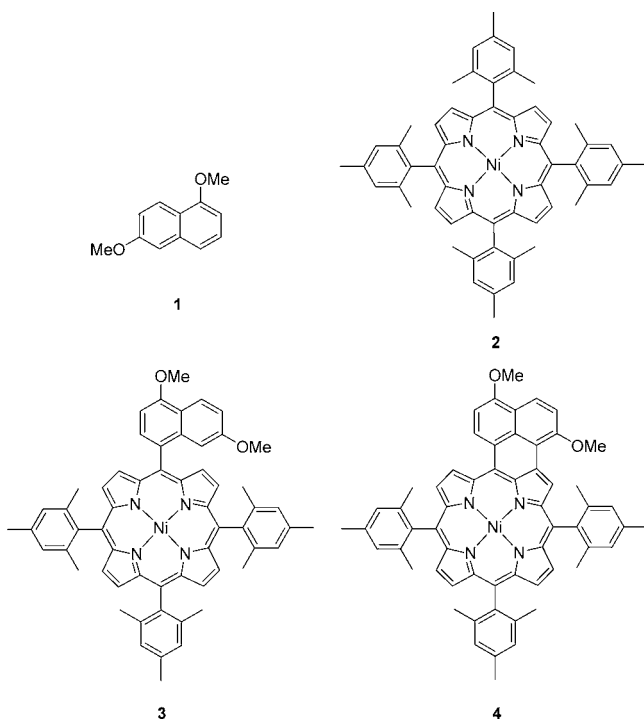
Oxidative aromatic coupling has recently become a popular method for the  $\pi$ -extension of a porphyrin.<sup>12</sup> The first example of a porphyrin fused with naphthalene was reported by Cammidge and co-workers in 2005.<sup>13</sup> In principle, any aromatic unit located at the *meso*-position of a porphyrin and possessing high electron density should be able to form analogous products via oxidative aromatic coupling, which was proven in a seminal contribution by Anderson et al.<sup>14a</sup>

Previous studies<sup>11</sup> (most notably by Osuka and Anderson)<sup>8a,11c–f,12b,dg</sup> and general knowledge of aromatic oxidative coupling both indicate that the planned concept can only be realized if the naphthalene-porphyrin bears an electron-donating substituent at a suitable position.<sup>14,15</sup> In the course of our studies involving an elucidation of relationships between the output of oxidative aromatic coupling reactions, the nature of the oxidizing agent, and the central metal cation we were able to establish a protocol for oxidative coupling leading to a *meso*, $\beta$ -naphthalene-fused porphyrinoid **4** (see Chart 1) in high yield without contamination from chlorinated side-products using Fe(ClO<sub>4</sub>)<sub>3</sub>·H<sub>2</sub>O.<sup>16</sup> Unfortunately, the described procedure is sensitive to solvents and oxidant quality and not general

Received: May 15, 2013

Published: July 29, 2013

Chart 1. Structures of the Investigated Compounds



for diverse *meso*-substituted porphyrinoids. Because of these drawbacks, we were led to consider the use of electrochemical methods as a possible alternative in solving mechanistic issues. Such an approach was pioneered by Smith and co-workers who described the first electrosynthesis of porphyrins from *a,c*-biladienes.<sup>17a,b</sup> Recently an elegant approach toward cyclo[*n*]-pyrroles via electrochemical intermolecular oxidative coupling was presented by Bucher and Sessler.<sup>17c,d</sup> Electrochemically mediated aromatic oxidative coupling has also been applied for other substrates.<sup>17e–g</sup>

Another motivation to perform this study came from the fact that a major road-block to enhancing the synthesis of  $\pi$ -extended porphyrins via intramolecular oxidative coupling requires a better understanding of the mechanism of these reactions. Specifically it is pivotal to know which moiety (porphyrin or the second aromatic system) is first attacked by the oxidant to form an electrophilic radical-cation. An answer to this and similar questions will help explain the apparently contradictory observations such as (a) the participation of units

which are by no means electron rich<sup>18</sup> and (b) the difficulty with carrying out oxidative aromatic coupling on an already partially fused porphyrin<sup>14,19</sup> where product decomposition is observed in cases when multiply electron-rich hydrocarbons are fused with the central macrocyclic ring.<sup>19</sup> Electrochemically mediated aromatic oxidative coupling is the only way to establish these mechanistic details. In our initial study of this problem, we have chosen a Ni(II) porphyrin with an extended  $\pi$  system which was previously prepared using chemical oxidation. We assumed that having such a standard in hand would allow us to unequivocally establish the order of steps in the synthetic process. Herein we report the results of our study.

## EXPERIMENTAL SECTION

The following compounds were prepared according to published procedures: 2,<sup>16</sup> 3,<sup>16</sup> and 4.<sup>16</sup> 2,6-Dimethoxynaphthalene (1) is commercially available.

**Electrochemical and Spectroelectrochemical Measurements.** Absolute dichloromethane ( $\text{CH}_2\text{Cl}_2$ , 99.8%, EMD Chemicals Inc.) was used for electrochemistry without further purification. Benzonitrile (PhCN) was purchased from Aldrich Chemical Co. and distilled over  $\text{P}_2\text{O}_5$  under vacuum prior to use. Tetra-*n*-butylammonium perchlorate (TBAP), used as supporting electrolyte, was purchased from Sigma Chemical or Fluka Chemika Co., recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least one week prior to use.

Cyclic voltammetry was carried out with an EG&G model 173 potentiostat/galvanostat at room temperature. A homemade three-electrode electrochemistry cell was used and consisted of a platinum button or glassy carbon working electrode (diameter = 0.3 mm), a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE.

Thin-layer UV–visible spectroelectrochemical experiments were performed with a home-built thin-layer cell which has a light transparent platinum net working electrode. Potentials were applied and monitored with an EG&G PAR Model 173 potentiostat. Time-resolved UV–visible spectra were recorded with a Hewlett-Packard Model 8453 diode array spectrophotometer. High purity  $\text{N}_2$  from Trigas was used to deoxygenate the solution and kept over the solution during each electrochemical and spectroelectrochemical experiment.

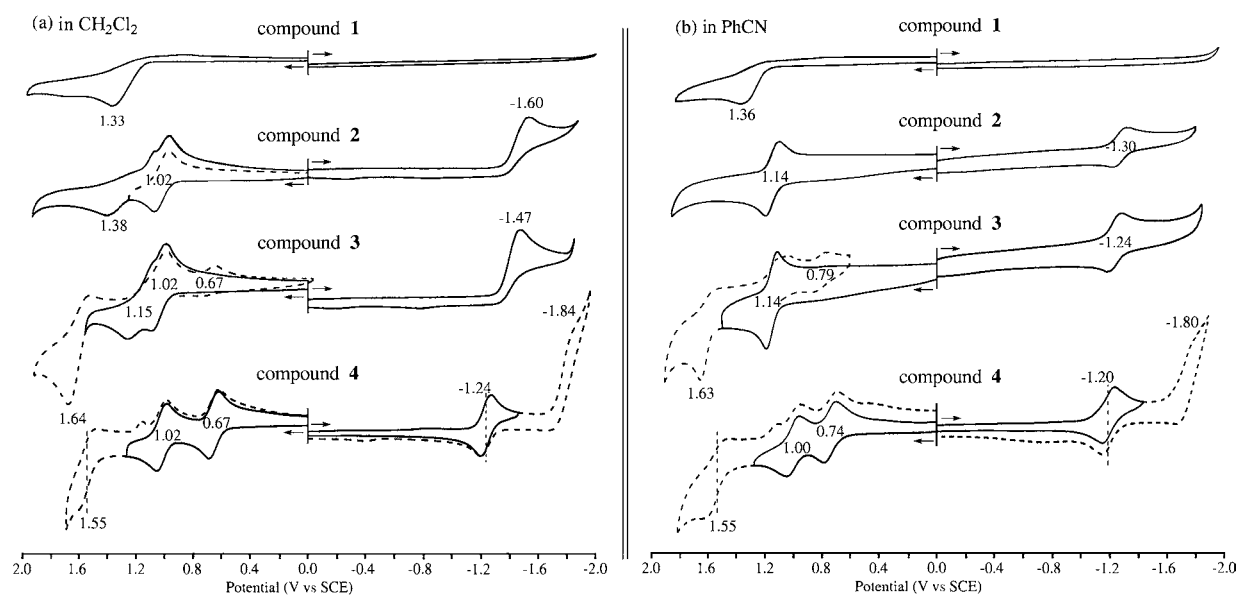
## RESULTS AND DISCUSSION

The investigated compounds 1–4 were examined as to their electrochemical behavior in  $\text{CH}_2\text{Cl}_2$  and PhCN containing 0.1

Table 1. Half-Wave or Peak Potentials (V vs SCE) and Proposed Site of Electron Transfer for Redox Reactions of Investigated Porphyrins in  $\text{CH}_2\text{Cl}_2$  and PhCN Containing 0.1 M TBAP<sup>a</sup>

solvent	cpd #	naphthalene	oxidation			reduction	
			$\text{Ni}^{\text{II/III}}$	ring		ring	
				$E_{1/2}$	2nd	1st	1st
$\text{CH}_2\text{Cl}_2$	1	1.33 <sup>b</sup>					
	2			1.38 <sup>b</sup>	1.02	–1.60 <sup>b</sup>	
	3	1.64 <sup>b</sup>	1.15	1.02	–1.47 <sup>b</sup>		
	4	1.55	1.02	0.67	–1.24	–1.84 <sup>b</sup>	
PhCN	1	1.36 <sup>b</sup>					
	2			1.14	1.14	–1.30	
	3	1.63 <sup>b</sup>	1.14	1.14	–1.24		
	4	1.55	1.00	0.74	–1.20	–1.80 <sup>b</sup>	

<sup>a</sup>Scan rate = 0.1 V/s. <sup>b</sup>Peak potential at a scan rate of 0.1 V/s.



**Figure 1.** Cyclic voltammograms of 1–4 in (a)  $\text{CH}_2\text{Cl}_2$  and (b) PhCN containing 0.1 M TBAP. Scan rate = 0.1 V/s.

M tetrabutylammonium perchlorate (TBAP) and the measured half-wave or peak potentials for reduction and oxidation of each compound are summarized in Table 1. The site of electron transfer for each redox reaction is also given in the table, with assignments being based on the measured spectral changes, measured  $E_{1/2}$  values, and previous assignments of electron transfer site given in the literature for related compounds.<sup>19</sup> Cyclic voltammograms for these compounds are shown in Figure 1.

**Reduction of Ni(II) Porphyrins.** Many Ni(II) porphyrins undergo two one-electron reductions in nonaqueous media to form  $\pi$ -anion radicals and dianions,<sup>20</sup> and this is also the case for compound 4 in PhCN or  $\text{CH}_2\text{Cl}_2$ . However, other Ni(II) porphyrins show just one reduction because of a limited negative potential range of the utilized solvent, the presence of a macrocycle with highly electron-donating substituents, or the occurrence of a chemical reaction between the electroreduced porphyrin and the solvent. The latter situation occurs for compounds 2 and 3 which exhibit just a single reduction which is reversible in PhCN but irreversible in  $\text{CH}_2\text{Cl}_2$ . The singly reduced porphyrins 2 and 3 both react with  $\text{CH}_2\text{Cl}_2$  as was reported for many related nickel porphyrins where the transient formation of a  $\text{CH}_2\text{Cl}$  sigma-bonded species may be generated.<sup>19a,b</sup> In contrast, most singly reduced nickel porphyrins are stable in PhCN, as is the case for the currently investigated compounds where the product can be assigned as a Ni(II) porphyrin  $\pi$ -anion radical.

**Oxidation of Ni(II) Porphyrins.** The first two oxidations of most Ni(II) porphyrins generally lead to a porphyrin  $\pi$ -cation radical and dication, but the absolute potential difference between these two redox processes will be highly variable, and will depend upon the solvent, the substituents on the macrocycle, and the anion of the supporting electrolyte.<sup>20</sup> Two well-separated one-electron oxidations are observed for some Ni(II) porphyrins while others undergo two overlapping one-electron oxidations at the same potential.<sup>20</sup> As seen in Figure 1, these two extremes of electrochemical reactivity are observed for the three nickel porphyrins investigated in the current study. Compounds 2, 3, and 4 exhibit two well-separated one-electron oxidations in  $\text{CH}_2\text{Cl}_2$  while only

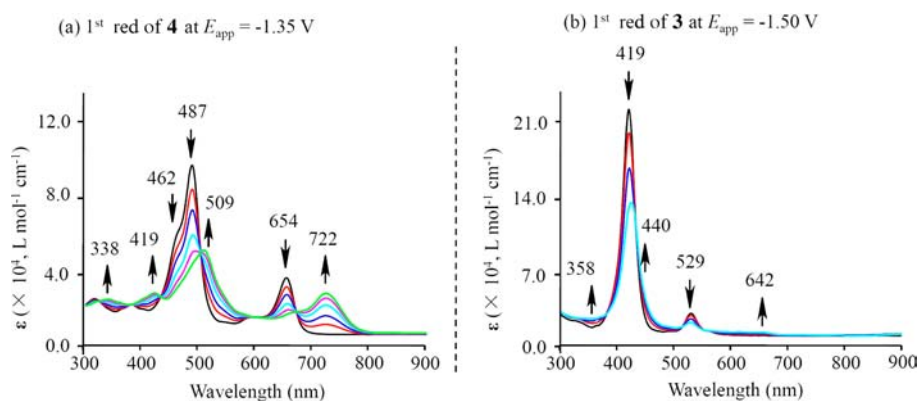
compound 4 displays this behavior in PhCN. In contrast, an overall two-electron oxidation to give the Ni(II) porphyrin dication occurs at  $E_{1/2} = 1.14$  V for compounds 2 and 3 in this solvent.

A third reversible oxidation has been reported for some Ni(II) porphyrins,<sup>20b</sup> and this is also the case for compounds 3 and 4 in both solvents. The third oxidation involves a one-electron transfer and formation of a Ni(III) porphyrin dication. Because of the very positive potential for this metal-centered reaction, it is often hard to detect, but for compound 4, the third oxidation is easily observed and located at  $E_{1/2} = 1.55$  V in both solvents.

All three oxidations of 4, which has  $\pi$ -conjugated system are more facile as compared to the same reaction for compound 3. The magnitude of the potential shift is largest for the first ring-centered reaction which shifts by 350–400 mV (depending upon solvent), smaller for the second oxidation which shifts by 130–140 mV, and smallest for the third, metal-centered process which shifts by only 80–90 mV upon going from compound 3 to compound 4. The absolute potential difference between the reversible second and third oxidations of 4 ( $\Delta|Ox_3 - Ox_2|$ ) ranges from 530 to 550 mV in  $\text{CH}_2\text{Cl}_2$  and PhCN (see Figure 1), and this is consistent with reported 500–730 mV potential differences between similar redox reactions of other nickel porphyrins which exhibit a Ni(II)/Ni(III) process at positive potentials.<sup>20</sup>

The third oxidation of 3, at  $E_p = 1.63$ – $1.64$  V is slightly more difficult than the third oxidation of 4 which occurs at  $E_p = 1.59$  V in PhCN and  $\text{CH}_2\text{Cl}_2$ , and this process is also assigned to generation of a Ni(III) porphyrin. In compound 3 the reaction is irreversible because of the occurrence of a coupled chemical reaction which occurs after the electron transfer. This reaction is related to the electrochemical generation of 4 as discussed in later sections of the paper.

As seen in Figure 1, the irreversible oxidation of 1,6-dimethoxynaphthalene (cpd 1) is located at  $E_p = 1.33$ – $1.36$  V, either by itself (top voltammogram in Figure 1) or in solutions also containing 2 (figure not shown). No oxidations are observed in this potential region for compound 3 in  $\text{CH}_2\text{Cl}_2$  or PhCN, which implies that the naphthalene group shows no



**Figure 2.** UV–visible spectral changes of (a) **4** and (b) **3** during the controlled potential reduction in PhCN containing 0.1 M TBAP.

electrochemical activity when it is attached to the *meso*-position of this Ni(II) porphyrin. This observation proves that the electrochemically generated radical-cation located on the porphyrin macrocycle attacks the neighboring dimethoxynaphthalene unit, forming a C–C bond (and not vice versa)

#### Spectral Monitoring of Reduction in Thin-Layer Cell.

The three Ni porphyrins were also characterized by UV–vis spectroelectrochemistry. Examples of the spectral changes which occur during controlled potential reduction and oxidation of **3** and **4** in PhCN are illustrated in Figures 2 and 3, while the corresponding spectral changes for **2** are given in Supporting Information, Figures S1 and S2.

Figure 2 compares the spectral changes for **3** and **4** during the first one-electron reduction in PhCN. The neutral porphyrin **4** in this solvent is characterized by a Soret band at 487 nm (molar absorptivity,  $\epsilon = 9.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ), a shoulder at 462 nm, and a visible band at 654 nm ( $\epsilon = 3.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The neutral porphyrin **3** has an intense

Soret band at 419 nm ( $\epsilon = 22.6 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and a weak visible band at 529 nm ( $\epsilon = 2.8 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The ring-expanded **4** has a slightly more intense visible band than **3**, but it has a much weaker Soret band than the compound with a nonexpanded porphyrin macrocycle. This is consistent with known spectral characteristics of ring-expanded porphyrins;<sup>22,23</sup> the Soret band becomes weaker while the visible band becomes more intense as the size of the  $\pi$ -conjugated system increases.

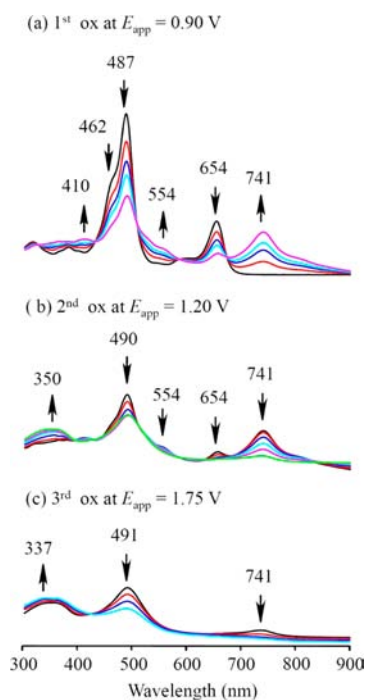
During the first one-electron reduction of **4** (Figure 2a), the bands at 462, 487, and 654 nm decrease in intensity while new bands grow in at 338, 419, 509, and 722 nm. For compound **3** (Figure 2b), the Soret and Q bands of the neutral compound both decrease in intensity as the first reduction proceeds and a new weak, and very broad, band appears at 642 nm. Both sets of spectral changes can be assigned to a ring-centered addition of one electron to form a porphyrin  $\pi$ -anion radical. Of note, however, is the fact that the spectrum of singly reduced **3** does not have an intense band close to 722 nm as does singly reduced **4** (labeled as **4**<sup>-</sup>) and this absorption, in the case of **4**, can then be used as a marker band for the radical anion of the naphthalene-fused Ni(II) porphyrin.

#### Spectral Monitoring of Oxidation in Thin-Layer Cell.

Figure 3 presents the spectral changes which occur during the three stepwise one-electron oxidations of **4** in PhCN (see cyclic voltammogram of the compound in Figure 4). During the first controlled potential oxidation at 0.90 V, the 462, 487, and 654 nm bands all decrease in intensity while a strong new band grows in at 741 nm. The final spectrum after the first one electron oxidation also has a moderate intensity band at 490 nm and two weak, broad, bands at 410 and 554 nm. This spectrum is shown in Figure 3a and corresponds to the porphyrin  $\pi$ -cation radical product of compound **4**. The 741 nm band in the  $\pi$ -cation radical spectrum of compound **4** is not seen in the spectrum of singly oxidized **3** (see Figure 4b) and is assigned as a marker band for the cation radical of the singly oxidized naphthalene-fused Ni(II) porphyrin.

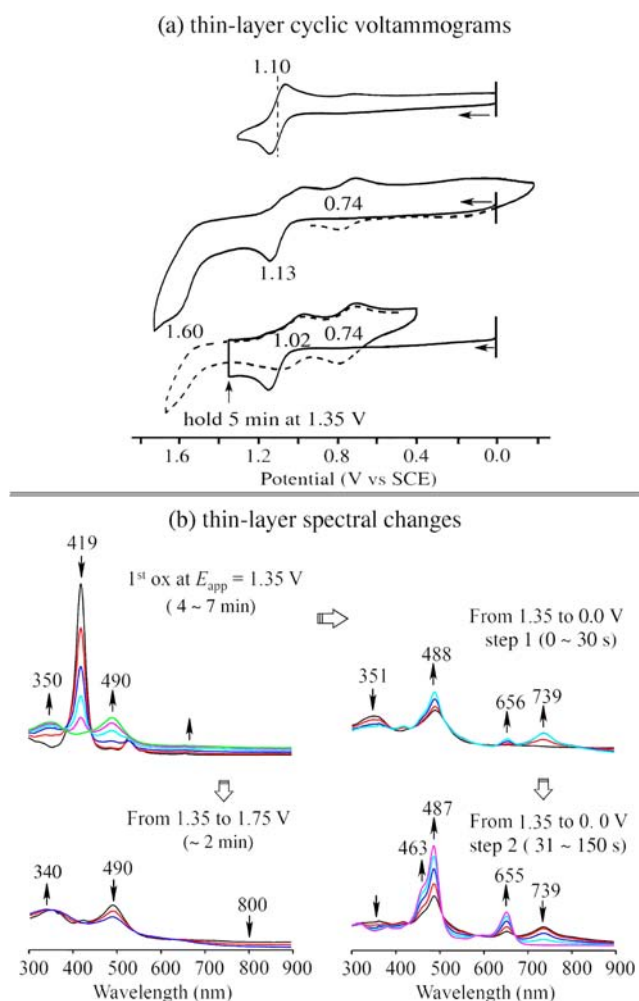
When the potential of singly oxidized **4** was switched from 0.90 to 1.20 V (Figure 3b), the 741 nm marker band of the cation radical disappears, consistent with the formation of a Ni(II) dication in the thin-layer cell. This species is characterized by weak bands at 350 and 491 nm. Finally, the Ni(III) porphyrin dication of **4** was electrogenerated by switching the controlled potential from 1.20 to 1.75 V; this triply oxidized species has two very weak bands at 337 and 491 nm.

The dimethoxynaphthalene group is electron-rich, and the effect of this substituent on half wave potentials for reduction



**Figure 3.** UV–visible spectral changes of **4** during the controlled potential oxidations at (a) 0.90 V, (b) 1.20 V, and (c) 1.75 V in PhCN containing 0.1 M TBAP.





**Figure 4.** (a) Thin-layer cyclic voltammograms of **3** in PhCN containing 0.1 M TBAP at a scan rate of 20 mV/s and (b) stepwise UV–visible spectral changes of **3** during the indicated applied potential under the same solution conditions.

or oxidation of the porphyrin should be similar to that of a compound having only mesityl groups. This can be seen by comparing reversible half wave potentials for the first one-electron oxidation of compounds **2** and **3** in PhCN (see cyclic voltammograms in Figure 1b). When one of the four mesityl groups on the *meso*-positions of compound **2** is replaced by a dimethoxynaphthalene group to form compound **3**, the half wave potential for the reversible two-electron oxidation remains unchanged at  $E_{1/2} = 1.14$  V in PhCN. In contrast, when the dimethoxynaphthalene group is fused onto the porphyrin macrocycle, as in compound **4**, a large negative shift in potential for the first oxidation is observed. This is shown by the cyclic voltammograms in Figure 1 where the initial reversible one-electron oxidation of **4** occurs at  $E_{1/2} = 0.67$  V ( $\text{CH}_2\text{Cl}_2$ ) or 0.74 V (PhCN) (as compared to 1.02 and 1.14 V for oxidation of compound **3** in  $\text{CH}_2\text{Cl}_2$  and PhCN, respectively). The second one-electron abstraction of **4** is also reversible in the two solvents and located at  $E_{1/2} = 1.00$  V in PhCN as compared to  $E_{1/2} = 1.14$  V for the second oxidation of **3** in the same solvent.

In a previous study of Pt porphyrins with  $\pi$ -expanded macrocycles, we reported that ring expansion results in a considerable raising of the macrocycle HOMO levels but induces only small changes in the LUMO levels of the  $\pi$ -ring

system.<sup>22</sup> As a result of the more facile ring oxidations, the measured HOMO–LUMO gap decreases as the size of the  $\pi$ -conjugated system is increased. This is also seen for compound **4** in PhCN where the reversible first reduction potential of  $-1.20$  V is only slightly easier than the reversible first reduction of **3** at  $-1.24$  V and the HOMO–LUMO gap decreases from 2.38 V for **3** to 1.94 V for **4**.

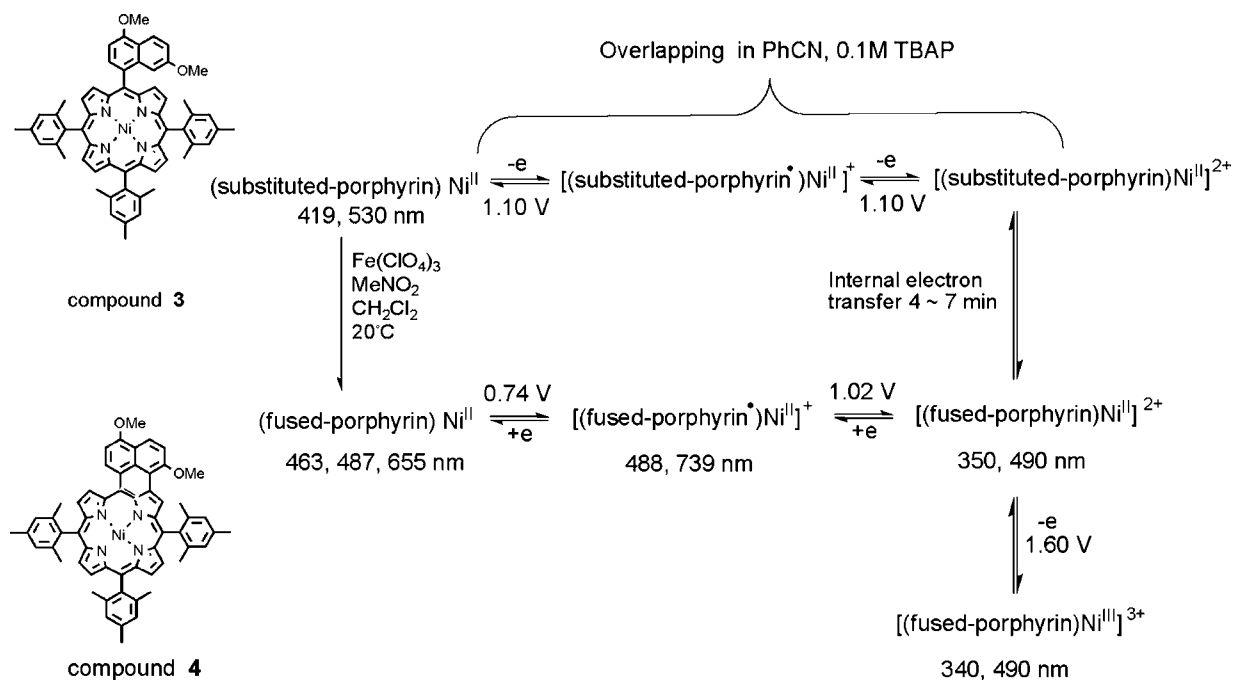
Of critical importance is the fact that compound **3** shows a new reversible redox couple located at  $E_{1/2} = 0.67$  V (in  $\text{CH}_2\text{Cl}_2$ ) or  $E_{1/2} = 0.79$  V (in PhCN), after scanning the potential to values positive of the third oxidation where the Ni(III) porphyrin dication is electrogenerated. The formation of the new peak on the return negative potential scan is shown by a dashed line in the cyclic voltammograms of Figure 1. The  $E_{1/2}$  of 0.67 V for the new peak in  $\text{CH}_2\text{Cl}_2$  is identical to  $E_{1/2}$  for the first oxidation of **4** in this solvent, and similar oxidation potentials are also seen for the relevant processes of **3** and **4** in PhCN. These results prove that a chemical transformation occurs after oxidation of compound **3**, with an oxidized compound **4** being generated as a product of the reaction at the electrode surface. In a previous study<sup>16</sup> we demonstrated that compound **4** could be synthesized by chemically oxidizing **3**, and a similar electro-synthesis of **4** appears to have occurred in the electrooxidation of compound **3**. To further prove this hypothesis and to better understand the electrooxidation processes of **3**, the spectra of each oxidation product was characterized by in situ thin-layer spectroelectrochemistry. The results of these measurements are discussed below.

**Fusion of  $\pi$  Ring System and Conversion of **3** to **4** during Oxidation.** Figure 4a illustrates thin-layer cyclic voltammograms of **3** in PhCN using different potential sweep ranges. As in the case of “regular” cyclic voltammetry, the first two oxidations of **3** occur in a single step two electron transfer at  $E_{1/2} = 1.10$  V. The oxidative coupling reaction occurs when the scan is reversed at 1.35 V, but the new redox couple of **4** at 0.74 V has very small current (top voltammogram of Figure 4a). In contrast, a new well-defined new reduction and reoxidation process is seen at  $E_{1/2} = 0.74$  V when the potential scan in the thin-layer cell is reversed at a more positive potential of 1.75 V (middle CV of Figure 4a). Furthermore, when the positive potential scan was held at 1.35 V for 5 min and then reversed, two reversible redox couples were obtained at  $E_{1/2} = 1.02$  and 0.74 V (lower CV of Figure 3a). As seen in Figure 1 and Table 1, the potentials of the two new redox couples generated in the thin layer cell after the second or third oxidation of **3** are almost identical to half wave potentials for the first two oxidations of **4** in the same solvent/supporting electrolyte system.

Figure 4b shows the UV–visible spectral changes which occur during the stepwise oxidations of **3** at the indicated potentials. The neutral compound **3** in PhCN is characterized by an intense Soret band at 419 nm and a weak band at 530 nm. When the potential is held at 1.35 V for 4–7 min, the initial bands at 419 and 530 nm disappear while two weak new bands of the product grow in at 350 and 490 nm (Figure 4b); further oxidation at an applied potential of 1.75 V leads, after 2 min of electrolysis, to a spectrum having bands at 350 and 490 nm (lower left spectrum in Figure 4b). These latter spectral changes are almost the same as those which occur during the second and the third oxidations of **4** (see Figure 3b).

The reverse spectral changes in Figure 4b unambiguously confirm the formation of doubly oxidized **4** which is then reduced to the neutral compound **4** when a controlled potential

Scheme 1. Proposed Mechanism for the Reversible Conversion between Compound 3 and 4



of 0.00 V is applied to the thin-layer cell. Two electrons are added stepwise during controlled potential reduction of the electrogenerated dication at 0.00 V, giving in the first step a spectrum with bands at 488 and 739 nm and then, in the second step, a final reduction product which is characterized by a split Soret band at 463 and 487 nm and a visible band at 655 nm. A 739 nm band was earlier assigned as a marker band for the radical cation of the naphthalene-fused Ni porphyrin. This band is seen in the first step during reduction at 0.0 V (top right spectrum in Figure 4), and the spectrum of the final product after further reduction is identical to that of the neutral compound 4 (see spectrum in lower right on Figure 4b).

The electrochemical and spectroelectrochemical data are thus self-consistent, indicating that compound 3 is first oxidized to a dication ( $3^{2+}$ ) via two one-electron abstractions, after which  $3^{2+}$  converts to  $4^{2+}$  by an internal electron transfer process. Based on the results obtained from electrochemistry, thin-layer spectroelectrochemistry and the literature,<sup>16</sup> a proposed reaction mechanism in PhCN is presented in Scheme 1. The conversion of 3 and 4 is not limited to PhCN as a solvent, and similar electrochemical and spectroelectrochemical results are also obtained in  $\text{CH}_2\text{Cl}_2$ . These data are given in Supporting Information, Figures S2–S4.

## SUMMARY

In conclusion, an electrochemical approach to synthesis of the  $\pi$ -extended porphyrin 4 allowed us to avoid the use of harsh reaction conditions, such as the need for adding iron(III) or molybdenum(V) salts which are a hallmark of these chemical methods. More importantly, by electrochemical and spectroelectrochemical studies, we have proven that a radical-cation is initially formed on the porphyrin ring, following its reaction with the linked dimethoxynaphthalene moiety. This observation will enable the design of suitable architectures for the future synthesis of  $\pi$ -extended porphyrins by both electrochemical and chemical methods. Another appealing aspect of an electrochemically based synthetic method is that it allows

the reaction conditions to be easily varied. For instance, under conditions of the electrolysis, it is possible to adapt an oxidation potential which specifically suits the redox properties of a given porphyrinic precursor and to also study the effects of various metals placed into the macrocyclic core. In summary, the currently described electrochemical method describes a new and simple way to produce  $\pi$ -extended porphyrins, which should permit control of electronic interactions and thus enable one to more closely control and tune the physical properties of these type macrocycles.

## ASSOCIATED CONTENT

### Supporting Information

Synthetic procedures, and other additional information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [kkadish@uh.edu](mailto:kkadish@uh.edu) (K.M.K.), [dtgryko@icho.edu.pl](mailto:dtgryko@icho.edu.pl) (D.T.G.).

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The authors thank the Robert A. Welch Foundation (K.M.K., Grant E-680) and the Foundation for Polish Science (TEAM 2009-4/3).

## REFERENCES

- (a) Vinogradov, S. A.; Wilson, D. F. *J. Chem. Soc., Perkin Trans. 2* **1995**, 103. (b) Chen, P.; Dvornikov, A. S.; Nakashima, M.; Roach, J. F.; Alabran, D. M.; Rentzepis, P. M. *J. Phys. Chem.* **1996**, *100*, 17507. (c) Chou, J. H.; Kosal, M. E.; Nalwa, H. S.; Rakow, N. A.; Suslick, K. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 6, p 43; (d) Fronczek, F. R.; Hao, E.; Vicente, M. G. H. *J. Org. Chem.* **2006**, *71*, 1233.

- (2) (a) Bonnett, R. *Chem. Soc. Rev.* **1995**, *24*, 19. (b) Boyle, R. W.; Dolphin, D. *Photochem. Photobiol.* **1996**, *64*, 469.
- (3) (a) Anderson, H. L. *Chem. Commun.* **1999**, 2323. (b) Schwab, P. F.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863. (c) Pschirer, N. G.; Kohl, C.; Nolde, F.; Qu, J.; Müllen, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 1401.
- (4) Sessler, J. L.; Seidel, D. *Angew. Chem., Int. Ed.* **2003**, *42*, 5134.
- (5) (a) Nath, M.; Pink, M.; Zaleski, J. M. *J. Am. Chem. Soc.* **2005**, *127*, 478. (b) Sprutta, N.; Swiderska, M.; Latos-Grażyński, L. *J. Am. Chem. Soc.* **2005**, *127*, 13108. (c) Anand, V. G.; Saito, S.; Shimizu, S.; Osuka, A. *Angew. Chem., Int. Ed.* **2005**, *44*, 7244. (d) Khoury, T.; Crossley, M. *J. Chem. Commun.* **2007**, 4851. (e) Lash, T. D.; Colby, D. A.; Idate, A. S.; Davis, R. N. *J. Am. Chem. Soc.* **2007**, *129*, 13800. (f) Esdaile, L. J.; Jensen, P.; McMurtrie, J. C.; Arnold, D. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2090. (g) Boyle, R. W.; Fox, S. *Chem. Commun.* **2004**, 1322.
- (6) (a) Gill, H. S.; Harujanz, M.; Santamaria, J.; Finger, I.; Scott, M. J. *Angew. Chem., Int. Ed.* **2004**, *43*, 485. (i) Fronczek, F. R.; Hao, E.; Vicente, M. G. H. *J. Org. Chem.* **2006**, *71*, 1233. (j) Collins, H. A.; Khurana, M.; Moriyama, E.; Mariampillai, H. A.; Dahlstedt, E.; Balaz, M.; Kuimova, M. K.; Drobizhev, M.; Yang, V. X. D.; Phillips, D.; Rebane, A.; Wilson, B. C.; Anderson, H. L. *Nat. Photonics* **2008**, *2*, 420.
- (7) (a) Chang, C. K.; Bang, N. J. *Org. Chem.* **1995**, *60*, 7030. (b) Fumoto, Y.; Uno, H.; Murashima, T.; Ono, N. *Heterocycles* **2001**, *54*, 705. (c) Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 1, p 45; (d) Wilson, G. S.; Anderson, H. L. *Synlett* **1996**, 1039. (e) Finikova, O.; Cheprakov, A.; Beletskaya, Z.; Vinogradov, S. *Chem. Commun.* **2001**, 261. (f) Ono, N.; Hironaga, H.; Ono, K.; Kaneko, S.; Murashima, T.; Ueda, T.; Tsukamura, C.; Ogawa, T. *J. Chem. Soc., Perkin Trans. 1* **1996**, 417. (g) Lash, T. D.; Chandraseker, P. A.; Osuma, T.; Chaney, S. T.; Spence, J. D. *J. Org. Chem.* **1998**, *63*, 8455. (h) Ito, S.; Ochi, N.; Uno, H.; Murashima, T.; Ono, N. *Chem. Commun.* **2000**, 893.
- (8) (a) Sahoo, A. K.; Mori, S.; Shinokubo, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 7972.
- (9) (a) Tsuda, A.; Furuta, H.; Osuka, A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2549. (b) Sugiura, K.; Matsumoto, T.; Ohkouchi, S.; Naitoh, Y.; Kawai, T.; Takai, Y.; Ushiroda, K.; Sakata, Y. *Chem. Commun.* **1999**, 1957. (c) Yamane, O.; Sugiura, K.; Miyasaka, H.; Nakamura, K.; Fujimoto, T.; Kaneda, T.; Sakata, Y.; Yamashita, M. *Chem. Lett.* **2004**, *33*, 40.
- (10) Diev, V. V.; Hanson, K.; Zimmerman, J. D.; Forrest, S. R.; Thompson, M. E. *Angew. Chem., Int. Ed.* **2010**, *49*, 5523.
- (11) (a) Ahn, T. K.; Kim, K. S.; Kim, D. Y.; Noh, S. B.; Aratani, N.; Ikeda, C.; Osuka, A.; Kim, D. *J. Am. Chem. Soc.* **2006**, *128*, 1700.
- (12) (a) Sanienda, A. Z. *Naturforsch., Teil B: Anorg. Chem., Org. Chem.* **1967**, *22*, 1107–1111. (b) Bucher, C.; Buda, M. In *The Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; World Scientific: Singapore, 2012; Vol. 17, p 240; (c) Anderson, H. L.; Davis, N. L. S.; Pawlicki, M. *Org. Lett.* **2008**, *10*, 3945. (d) Anderson, H. L.; Davis, N. L. S.; Thompson, A. L. *Org. Lett.* **2010**, *12*, 2124. (e) McKeown, N. B.; Makhseed, S.; Msayib, K. J.; Ooi, L. L.; Helliwell, M.; Warren, J. E. *Angew. Chem., Int. Ed.* **2005**, *44*, 7546. (f) Sahoo, K.; Nakamura, Y.; Aratani, N.; Kim, K. S.; Noh, S. B.; Shinokubo, H.; Kim, D.; Osuka, A. *Org. Lett.* **2006**, *8*, 4144.
- (13) (a) Lewtak, J. P.; Gryko, D. T. *Chem. Commun.* **2012**, 48, 10069. (b) Kim, D.; Osuka, A. *Acc. Chem. Res.* **2004**, *37*, 735. (c) Ono, N.; Yamada, H.; Okujima, T. In *The Handbook of Porphyrin Science*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; World Scientific: Singapore, 2009; Vol. 2, p 1; (d) Tsuda, A.; Osuka, A. *Science* **2001**, *293*, 79. (e) Tsuda, A.; Osuka, A. *Adv. Mater.* **2002**, *14*, 75. (f) Pereira, A. M. V. M.; Richeter, S.; Jeandon, C.; Gisselbrecht, J.-P.; Wytko, J.; Ruppert, R. *J. Porphyrins Phthalocyanines* **2012**, *16*, 464–478. (g) Kim, D.; Osuka, A.: Single-molecule photophysical properties of various directly linked porphyrin arrays. In *Multiporphyrin arrays*; Kim, D., Ed.; Pan Stanford Publishing: Singapore, 2012; pp 1–54.
- (14) Hughes, D. L.; Cammidge, A. N.; Scaife, P. *J. Org. Lett.* **2005**, *7*, 3413.
- (15) (a) Whiting, D. A. In *Comprehensive Organic Synthesis*; Pergamon Press: Oxford, U.K., **1991**; Vol. 3, p 659; (b) Dohi, T.; Ito, M.; Morimoto, K.; Iwata, M.; Kita, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 1301. (c) Dwight, T. A.; Rue, N.; Charyk, R. D.; Josselyn, R.; DeBoef, B. *Org. Lett.* **2007**, *9*, 3137. (d) Kalyani, D.; Deprez, N. R.; Desai, L. V.; Sanford, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 7330. (e) Gryko, D. T.; Tasiar, M.; Koszarna, B. *J. Porphyrins Phthalocyanines* **2003**, *7*, 239–248. (f) Wang, K.; Lu, M.; Yu, A.; Zhu, X.; Wang, Q. *J. Org. Chem.* **2009**, *74*, 935. (g) Sarhan, A. A. O.; Bolm, C. *Chem. Soc. Rev.* **2009**, *38*, 2730. (h) Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem., Int. Ed.* **2013**, DOI: 10.1002/anie.201210238.
- (16) Lewtak, J. P.; Gryko, D.; Bao, D.; Sebai, E.; Vakuliuk, O.; Ścigaj, M.; Gryko, D. T. *Org. Biomol. Chem.* **2011**, *9*, 8178.
- (17) (a) Jeyakumar, D.; Snow, K. M.; Smith, K. M. *J. Am. Chem. Soc.* **1988**, *110*, 8562. (b) Wijesekera, T. P.; Dolphin, D. *Chemtracts: Org. Chem.* **1990**, *3*, 375. (c) Buda, M.; Iordache, A.; Bucher, C.; Moutet, J.-C.; Royal, G.; Saint-Aman, E.; Sessler, J. L. *Chem.—Eur. J.* **2010**, *16*, 6810. (d) Bui, T.-T.; Iordache, A.; Chen, Z.; Roznyatovskiy, V. V.; Saint-Aman, E.; Lim, J. M.; Lee, B. S.; Ghosh, S.; Moutet, J.-C.; Sessler, J. L.; Kim, D.; Bucher, C. *Chem.—Eur. J.* **2012**, *18*, 5853. (e) Hammerich, O.; Parker, V. D. *Acta Chem. Scand.* **1982**, *B36*, 519. (f) Schäfer, H. J. Electrolytic oxidative coupling. In *Organic Electrochemistry*, 4th ed.; Lund, H., Hammerich, O., Ed.; Marcel Dekker: New York, 2001; pp 883–967; (g) Kirste, A.; Elser, B.; Schnakenburg, G.; Stecker, F.; Waldvogel, S. R. *J. Am. Chem. Soc.* **2012**, *134*, 3571–3576.
- (18) Eu, S.; Hayashi, S.; Tanaka, M.; Matano, Y.; Umeyama, T.; Imahori, H. *Chem. Commun.* **2007**, 20, 2069.
- (19) (a) Kadish, K. M.; Franzen, M. M.; Han, B.; Araullo-Madams, C.; Sazou, D. *J. Am. Chem. Soc.* **1991**, *113*, 512. (b) Kadish, K. M.; Franzen, M. M.; Han, B.; Araullo-Madams, C.; Sazou, D. *Inorg. Chem.* **1992**, *31*, 4399. (c) Lewtak, J. P.; Węclawski, M.; Gryko, D. T.; unpublished results.
- (20) (a) Kadish, K. M.; Caemelbecke, V. E.; Royal, G. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 8; (b) Kadish, K. M.; Van Caemelbecke, E.; Boulas, P.; D'Souza, F.; Vogel, E.; Kisters, M.; Medforth, C. J.; Smith, K. M. *Inorg. Chem.* **1993**, *32*, 4177.
- (21) Kadish, K. M.; Lin, M.; Van Caemelbecke, E.; De Stefano, G.; Medforth, C. J.; Nurco, D. J.; Nelson, N. Y.; Krattinger, B.; Muzzi, C. M.; Jaquinod, L.; Xu, Y.; Shyr, D. C.; Smith, K. M.; Shelnut, J. A. *Inorg. Chem.* **2002**, *41*, 6673.
- (22) Chen, P.; Finikova, O. S.; Ou, Z.; Vinogradov, S. A.; Kadish, K. M. *Inorg. Chem.* **2012**, *51*, 6200.
- (23) Gouterman, M. *J. Mol. Spectrosc.* **1961**, *6*, 138.