Electrochemical Syntheses of Cyclo[*n*]pyrrole

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Abstract: Cyclo[8]pyrrole was obtained efficiently when 3,3′,4,4′-tetraethylbipyrrole was subjected to bulk electrolysis, with yields spanning a range from close to 0% with tetra-*n*-butylammonium fluoride as the electrolyte, to almost 70% when tetra-*n*-butylammonium hydrogensulfate was used for this purpose. These observations are consistent with the conclusion that the reaction is controlled by anion-related factors such as a specific templating effect. Note that cyclo[8]pyrrole was the only detectable macrocyclic product obtained from 3,3′,4,4′-tetraethylbipyrrole under the conditions of the electrochemical oxidation. When similar electrolyses were performed by using 3,4-diethylpyrrole as the starting material, two products could be isolated, which were identified as being the cyclo[7]pyrrole and cyclo[8]pyrrole, respectively. Detailed analyses of the oxidized forms of cyclo[7]pyrrole and cyclo[8]pyrrole revealed that under the conditions of the electrolysis these latter species are not stable.

Keywords: anions · electrochemistry · electrolysis · oxidative coupling · pyrroles

Introduction

Expanded porphyrins have emerged in recent years as an attractive class of porphyrin analogues, with interesting anion-binding properties,[1,2] unusual metal complexation properties,[3] and potential utility in the area of molecular electronics device construction.[4,5] Owing to the absence of *meso* carbon atoms in their cyclic frameworks, one set of expanded porphyrins, the cyclo[*n*]pyrroles, represented by structures [**1**H$_6$]$^{2+}$, [**2** H$_7$]$^{2+}$, and [**3**H$_8$]$^{2+}$ (Scheme 1), were found to be amenable to chemical synthesis through the oxidative coupling of 3,3′,4,4′-alkyl substituted 2,2' bipyrroles.[6,7] In a broader sense, chemically driven oxidative coupling reactions between aryl fragments have been extensively employed in the preparation of numerous compounds including polycyclic aromatic hydrocarbons,[8] fused porphyrin arrays,[9] natural products,[10] and porphyrin analogues.[11,12] However, harsh reaction conditions or expensive organometallic reagents are often required. This has made the use of electrochemical methods attractive as possible alternatives.[13–21]

Although widely employed to produce conducting or insulating amorphous polymeric structures[22,23] including polythiophene or polypyrrole, recent findings have provided support for the highly appealing suggestion that porphyrins and porphyrin analogues could be prepared directly by using electrochemical methods. Such an approach was pioneered by Smith and co-workers who described the first electrosynthesis of porphyrins from a,c-biladienes.[24,25] More recently, an N-substituted cyclo[6]pyrrole was produced from a sterically constrained hexapyrrolylbenzene by using a covalently templated electrochemical procedure.[26] In the context of our own efforts to develop electrochemical oxidations as a potentially clean and straightforward complement to chemical-based oxidative procedures, we have reported the electrochemically driven ring-closure of a linear hexapyrrole to give a [24]hexaphyrin(1.0.1.0.0.0).[27] We have also described the electrolyte-assisted electrochemical oxidative conversion

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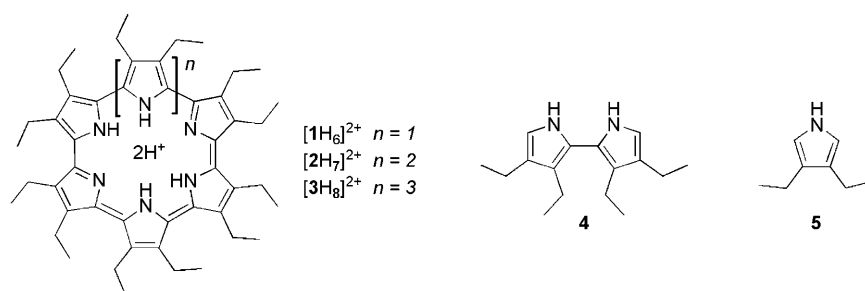
Scheme 1.

of 3,3′,4,4′-tetraethyl-2,2′-bipyrrole (**4**, Scheme 1) into the corresponding cyclo[8]pyrrole (e.g., [**3H$_8$**]$^{2+}$).[28]

In our hands the electrochemical-based strategy not only gave yields that were competitive with those obtained by using the best chemical oxidation methods,[29,30] it also allowed us to avoid the use of harsh conditions, such as 1 N acid and iron(III) or chromium(VI) salts, that are a hallmark of these chemical methods. Another appealing aspect of electrochemical-based methods is that they allow the reaction conditions to be varied easily. For instance, under conditions of electrolysis it is possible to adapt the oxidation potentials to suit specifically the redox properties of a given pyrrolic precursor and to study the effects of various potential templating agents. The study of possible templating effects is of particular interest in the case of cyclo[n]pyrroles. This is because cyclo[8]pyrrole [**3H$_8$**]$^{2+}$ proved to be the exclusive product when the chemical oxidation was carried out under conditions of chemical oxidation in the presence of H$_2$SO$_4$; in contrast, a mixture of cyclo [6]-, cyclo[7]-, and cyclo[8]pyrrole (i.e., [**1H$_6$**]$^{2+}$, [**2H$_7$**]$^{2+}$, and [**3H$_8$**]$^{2+}$, respectively) was obtained when HCl was used.[6] We thus set out to explore the electrochemical oxidation of bipyrrole **4** and pyrrole **5** (Scheme 1) and to investigate the possible templating effects of various electrolytes. Specific motivation for this study came from an appreciation that 1) acids other than H$_2$SO$_4$ and HCl failed to give isolable quantities of any cyclo[n]pyrrole when bipyrrole **4** was subject to chemical oxidation and 2) attempts to effect the direct conversion of pyrrole **5** to cyclo[n]pyrrole likewise failed completely. As detailed below, these limitations are relaxed when electrochemical methods are employed.

Results and Discussion

Electrochemical oxidation of 3,3′,4,4′-tetraethyl-2,2′-bipyrrole (4): In our initial studies, we found that cyclo[8]pyrrole, specifically [**3H$_8$**](SO$_4$), was obtained efficiently when bipyrrole **4** was subjected to bulk electrolysis. However, the effect of putative anion templates was not investigated, even though such effects were thought to account for the roughly 3-fold reduction in yield of [**3H$_8$**]$^{2+}$ seen when H$_2$SO$_4$ was replaced by HCl under conditions of chemical oxidation.[6] A primary goal of the present study was thus to test the

effect various anions might have on the electrochemical conversion of bipyrrole **4** into cyclo[n]pyrrole.

Before considering the problem of synthesis, the effect of anions on the redox potentials of **4** was assessed by using cyclic voltammetry. Initially, two cyclic voltammograms (CVs), corresponding to the oxidation of **4** with Br$^-$ and BF$_4^-$ (both as the tetrabutylammonium, TBA, salts) as the electrolytes, were recorded. As can be seen from an inspection of Figure 1, the effect of anions is significant. Although both CVs are qualitatively alike,
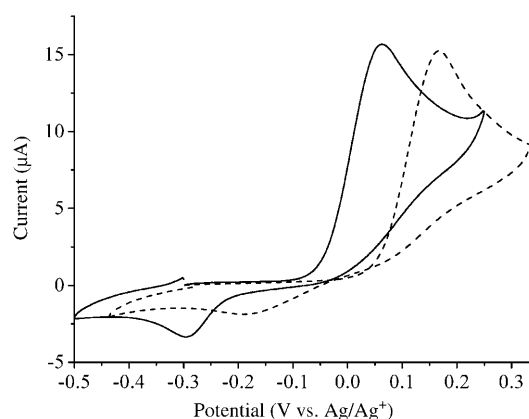

Figure 1. CVs corresponding to the oxidation of **4** (1.5×10^{-3} M) in CH$_2$Cl$_2$ in the presence of two different supporting electrolytes tetra-*n*-butylammonium bromide (——— = 0.15 M TBABr) and tetra-*n*-propylammonium tetrafluoroborate (----- = 0.11 M TPABF$_4$). Pt electrode, $\varnothing$ = 2 mm, 100 mV s^{-1}.

with an irreversible oxidation and a reduction wave of weak intensity in the reverse scan being observed at all accessible scan rates (attributed to the formation and reduction of an electro-generated quaterpyrrole radical cation),[31] an approximately 100 mV difference in both signals is clearly evident.[32,33]

The influence of organic and inorganic anions on the polymerization of pyrrole has been investigated by several authors and it has been shown, for instance, that the favorable action of tosylate anions in promoting polypyrrole formation can be accounted for in large measure by homogeneous processes involving ion pairing and hydrogen bonding.[34] The significant potential shift (≈ 100 mV; see above) observed between the Br$^-$ and BF$_4^-$ curves can thus reasonably be attributed to strong anion binding effects. Specifically, a tightly bound (hydrogen-bonded, ion-paired) electron-rich anionic species would increase the overall electron density on **4** and **4**$^{+\cdot}$ and thus shift the corresponding oxidation to a less positive value.[35] A similar anion effect has been

previously noticed by Zotti et al.[34] in the context of studying the anodic coupling of 2,2′-bipyrrole in acetonitrile.

To assess the affect of anions in the context of the electrochemical conversions to cyclo[n]pyrroles, several electrolyses involving bipyrrole **4** were carried out in dichloromethane in the presence of various supporting electrolytes (TBA salts containing different anions) by using a platinum working electrode. The data obtained from these analyses are summarized in Table 1.

Table 1. Yields corresponding to the electrochemical synthesis of $[3H_8]^{2+}$ from **4** in the presence of different supporting electrolytes. The thermochemical radii of each anion are those of Roobottom.[36] Peak potentials correspond to the pyrrole-centered irreversible oxidation wave.

Supporting electrolyte	Yield [%]	Anion radii [nm][b]	Oxidation potential [V][a]
TBAF	≈ 0	0.126	0.080
TBACl	17	0.168	–
TBABr	33	0.190	0.065
TBANO$_3$	54	0.200	0.080
TPABF$_4$	55	0.205	0.165
TBAHSO$_4$	68	0.218	0.350
TEAClO$_4$	11	0.225	–

[a] Irreversible oxidation: the values are the peak potentials measured at a scan rate of $0.1\,V\,s^{-1}$ (Pt electrode, E vs. Ag/Ag$^+$). TBA = tetra-n-butylammonium, TPA = tetra-n-propylammonium, TEA = tetraethylammonium. [b] Thermochemical radii were used for complex anions; see text for details.

It is apparent from these results that the choice of anionic species within the supporting electrolyte has a major effect on the oxidation potentials and on the efficiency of the cyclization process. Specifically, yields of $[3H_8]^{2+}$ were found to vary from close to 0 % when the electrolysis was carried out in the presence of TBAF, to almost 70 % with TBAHSO$_4$. Notable is the factor of four reduction in yield when the electrolysis was effected in the presence of Cl$^-$ instead of HSO$_4^-$. This correlates well with the threefold decrease seen under conditions of chemical oxidation. Although this is not proof, such an observation is consistent with the intuitively appealing conclusion that the reaction in both cases is controlled by anion-related factors such as a specific templating effect.[6]

Given the above observation, we have attempted to correlate the cyclization yield with two key parameters, namely, the size and basicity of the anions in question. Both of these factors would be expected to affect the strength of the NH–anion interaction both in the starting bipyrrole **4** and in the final cyclo[8]pyrrole $[3H_8]^{2+}$. Although other factors, including the strength of the hydrogen bonds and the ability to form ion pairs in solution, could also play important roles in regulating the yield, this analysis was expected to provide a first-order insight into the role anions could be playing in terms of mediating the conversion of two-pyrrole fragment **4** into cyclic octapyrrolic product $[3H_8]^{2+}$.

Unfortunately, experimental data for the ionic radii of complex anions such as BF$_4^-$ and HSO$_4^-$ are scarce. Thus, we chose to use the semi-empirical thermochemical radii, as

computed from crystal structure data.[36] Although these values may not represent the actual size of each anion, they nevertheless reflect accurately the relative size of the anions involved in our experiments. Therefore, by using these values, plots of yield versus size were constructed (Figure 2).
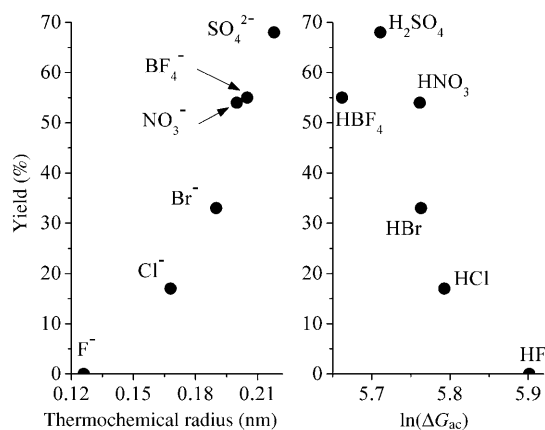

Figure 2. Plots of the yield of $[3H_8]^{2+}$ obtained through electrochemical oxidation of **4** against (left) the size of the anion[36] and against (right) the logarithm of the gas-phase acidity of the conjugate acid of the anion in question.[37–39]

In agreement with theoretical calculations predicting that dicationic pyrrole oligomers tend to wrap around anions,[40] the resulting graph provides support for the notion that appropriately sized anions, specifically ones that can fit well into the pocket of $[3H_8]^{2+}$, act as templates and help drive the electrochemically driven C−C coupling process towards the cyclo[8]pyrrole product. The trend is quite consistent and shows that ions with very similar sizes such as BF$_4^-$ and NO$_3^-$ afford similar yields.

Another important factor that could account for the observed electrolyte versus cyclo[8]pyrrole yield data is the basicity of the anionic species. It is well known from a wide range of solid-state structures that cyclo[n]pyrroles, as well as linear polypyrroles, in their protonated forms can bind anions.[41,42] As a general rule, more basic anions are expected to bind more strongly. However, if the anionic species in question is too basic, deprotonation can occur. During electrolyses, the α,α-coupling process generates free protons (Scheme 2). However, if the electrolyte is relatively basic, as is true for F$^-$, the anion template effect, relying on hydrogen bonds and electrostatic interactions, could be inhibited as the result of deprotonation and formation of well-recognized species such as HF and F$_2$H$^-$ anions. Depending on the extent to which this occurs, the α,α coupling process might not proceed or follow unproductive pathways with regard to cyclo[8]pyrrole formation.[43]

The experimental basicities of anions in CH$_2$Cl$_2$ are not well established. Therefore, for the purposes of comparison, we used the gas-phase acidities of the corresponding conjugate acids, either experimental (HX) or calculated (HNO$_3$, H$_2$SO$_4$, HClO$_4$, and HBF$_4$).[37–39] By using these values, a
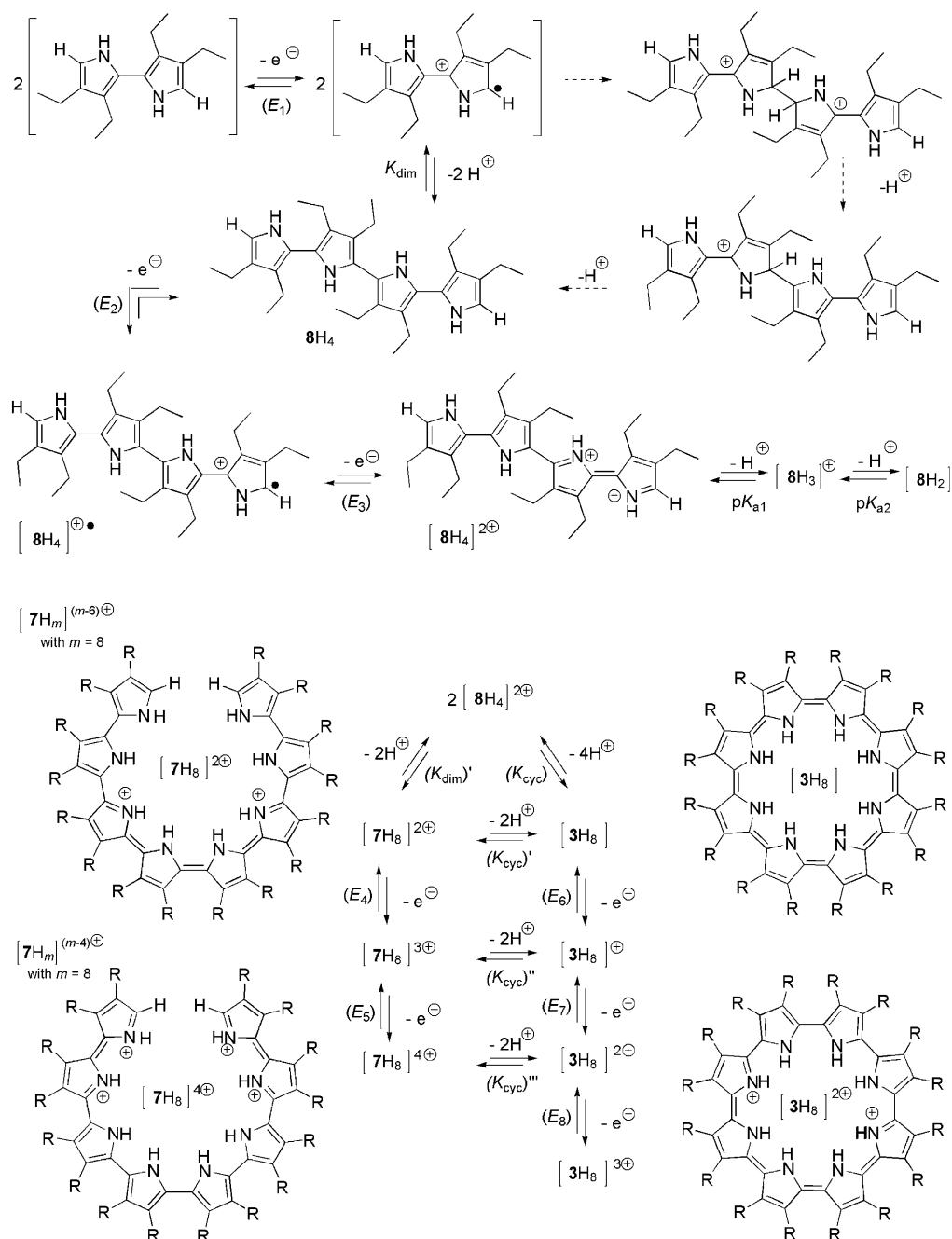
Scheme 2. Possible mechanism leading to the cyclo[8]pyrrole $[3H_8]^{2+}$ from four molar equivalents of bipyrrole **4**. The final steps from **8** to **3** have been detailed from $[8H_4]^{2+}$ but similar coupling processes could potentially be considered from $[8H_3]^+$, $[8H_2]$, or $[8H_4]^+$.

plot of yield versus inferred basicity (specifically the log of the gas-phase acidity) was constructed (Figure 2). In comparison with what was seen in the analogous plot relating the product yield with the size of the anion template (also given in Figure 2), the correlation is less clear. For instance, BF_4^- (which is a weaker base than HSO_4^-) gives a lower yield, whereas NO_3^- and Br^- (two anions that have almost identical basicities) produce very different yields. On the other hand, if we restrict the discussion to the three halide anions in which complicating factors such as disparities in

anion geometry can be more safely ignored, then the yield follows the anion basicity, with F^- (which is a rather strong base in CH_2Cl_2) falling at the extreme limit of the plot. Presumably, this better correspondence reflects the fact that in this solvent system there is a good correlation between halide anionic radius and effective basicity.

Note that cyclo[8]pyrrole $[3H_8]^{2+}$ was the only macrocyclic product obtained from **4** under the conditions of the electrochemical oxidation. Specifically, no smaller analogues of cyclo[8]pyrrole, namely, $[1H_6]^{2+}$ or $[2H_7]^{2+}$, were ever

identified, even in trace amounts. This was true for all of the electrolyses that we performed even when nonideal anions such as chloride and fluoride were used to make up the electrolyte. This finding stands in marked contrast with what is seen under conditions of chemical oxidation in the presence of HCl. For instance, when bipyrrole **4** was subject to oxidation with $FeCl_3$ in HCl (1 M), isolable quantities of cyclo[6]-pyrrole $[1H_6]^{2+}$ and cyclo[7]pyrrole $[2H_7]^{2+}$ were obtained.[6] The formation of these latter species through chemical synthesis must necessarily reflect the specific reaction conditions, which involve the use of 1) a relatively strong iron-(III)-based oxidant, 2) a biphasic reaction set-up, and 3) a strongly acidic aqueous phase (1 M HCl). Presumably, these conditions influence the anion–pyrrole interactions as well as, possibly, the bipyrrole–bipyrrole coupling process.[43] Interestingly, in the absence of strong acid, isolable quantities of cyclized product were not obtained when bipyrrole **4** was treated with $FeCl_3$. Left undetermined by these observations is whether the high proton concentration used under the chemical conditions is needed to increase the activity of the iron(III) reagent or to create protonated intermediates that would be more likely to undergo cyclization. Although it is difficult to ascertain directly the effective pH under either the biphasic chemical conditions or the purely organic ones used for the electrolyses, it is safe to assume that the proton concentration is lower under the latter conditions. This is certainly true at the beginning of the electrolyses because no added acid is present. Although unlikely to rise to the level provided by contact with a biphasic aqueous HCl (1 M) layer, it is important to appreciate that the proton concentration does increase throughout the electrolysis process. This is because protons are released as the result of the successive C−C couplings. This proton release will displace the various equilibria towards fully protonated species. This chemistry is shown in Scheme 2 for the quaterpyrrole intermediates such as $[8H_4]^{2+}$, which are assumed to form at the working electrode through oxidative coupling of two bipyrrole precursors (see below). This, in turn, will shift the oxidation potential of the fragments in question towards more positive values. In a less acidic environment such as that expected to operate during the early stages of the electrolysis, the formation of neutral and thus easier to oxidize intermediates such as $[8H_2]$ could lead to a different reactivity profile and product distribution than that operative under the conditions of chemical oxidation.

Strong evidence of the effect of acidity on pyrrole–oligomer electrochemistry has been put forward recently by Kadish and co-workers.[44] Specifically, these researchers showed that an α-protected tetrapyrrole derivative analogous to **8** could be protonated in the presence of a large excess of TFA in CH_2Cl_2 and that this protonation, in turn, affects quite dramatically the electrochemical activity of this particular open-chain tetrapyrrolic species. Unfortunately, pyrrole and oligopyrroles such as **8**, which are not α-protected can polymerize spontaneously in the presence of Brönsted or Lewis acids. Thus, we were unable to carry out electrochemical oxidations of **4** under acidic conditions directly

analogous to those used in the case of the iron(III)-mediated oxidative coupling.[45] Nevertheless, we feel that one key to the present electrochemical approach is that it allows coupling to take place under lower proton concentrations than those required for chemical coupling.[46]

At present, it is not possible to formulate a detailed mechanism for the reactions involving the conversion of bipyrrole **4** to the isolated cyclo[8]pyrrole product $[3H_8]^{2+}$. However, as detailed below (and summarized in Scheme 2), considerable insights into the details of the process have been obtained. The unambiguous first step of the process is the irreversible oxidation of the bipyrrole **4** to form a cation radical **4**$^{+•}$. This radical is then expected to evolve spontaneously towards the quaterpyrrole $8H_4$ as the result of a C−C coupling with the concomitant release of two protons. Although this latter species will be easier to oxidize than the starting material **4**,[31] the resulting radical $[8H_4]^{+•}$ is expected to be far less reactive than its shorter precursor **4**$^{+•}$,[47] leading us to propose that the dimerization of **4**$^{+•}$ (producing quaterpyrrole $8H_4$) proceeds more quickly than various competing processes.

Consistent with this hypothesis is our failure to observe the formation of hexa- or heptapyrrolic products (e.g., $[1H_6]^{2+}$ or $[2H_7]^{2+}$) under the conditions of electrochemical cyclization, even when templating anions of small size such as chloride are employed. This excludes the involvement of terpyrrolic or pentapyrrolic intermediates. These same observations also rule out any pathways that would require the coupling of quaterpyrrole species such as **8** or its radical forms with bipyrrole precursors such as **4** or **4**$^{+•}$ as being significant. On the other hand, the observed anion-mediated effects are fully consistent with the coupling of bipyrrole **4** to form a tetrapyrrolic intermediate, which then couples with yet another tetrapyrrole to produce the cyclo[8]pyrrole product $[3H_8]^{2+}$. What is less clear, however, is the oxidation state and degree of protonation of the intermediates in question, $8H_4$, $8H_4^{2+}$, $8H_3$, and $8H_2$.

One possibility is that a π dimer[48] is formed between two tetrapyrrolic radicals such as $[8H_4]^{+•}$, and that such a species would be the intermediate giving rise to the final cyclic product. To the extent that this occurs, it would lead to the direct (and exclusive) formation of the final cyclo[8]pyrrole product $[3H_8]^{2+}$. It is known that oligopyrrole radical cations tend to form π dimers,[33, 49] and the production of such species would certainly be consistent with the exclusive formation of cyclo[8]pyrrole under conditions of electrolysis. However, such a π dimer is likely to have its geometry set by orbital interactions; therefore, its transformation into $[3H_8]^{2+}$ is unlikely to be affected to a significant degree by the nature of the anion present in the electrolyte. However, the anions do play a critical role (see above), and we believe that at least one nonradical tetrapyrrolic species is involved in the final coupling step. In fact, based on spectroelectrochemical analyses (see below), and on existing data that show that the (unsubstituted) tetrapyrrole radical cation has a rather low π-dimerization equilibrium constant (≈ 70 L mol^{-1}),[33, 49] we conclude that such dimeric species

are not important intermediates in the conversion of **4** into $[3H_8]^{2+}$.

To rule out the significant participation of intermediates other than those related to **4** and **8**, a bulk electrolysis experiment involving bipyrrole **4** and tetra-*n*-butylammonium hydrogensulfate as the electrolyte was carried out in dichloromethane. The results of this electrolysis reaction was followed in situ by using a 1 mm UV/Vis immersion probe (Figure 3). The signature spectral feature growing in the
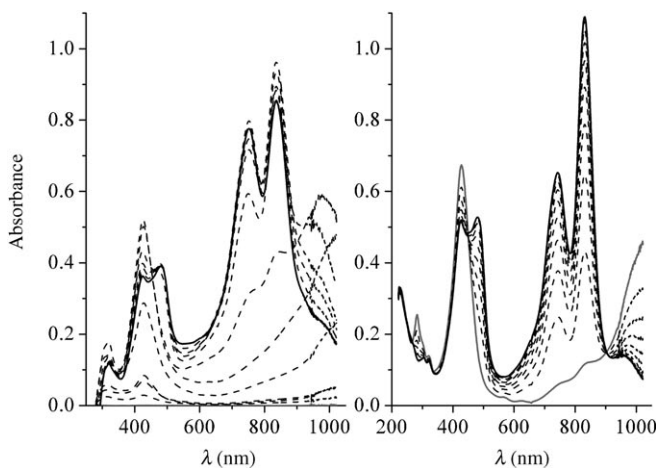

Figure 3. Left: Electrolysis of a solution of **4** (5.10^{-4} M) followed by UV/Vis spectroscopy ($l = 1$ mm; $CH_2Cl_2 + TBAHSO_4$ (0.25 M); $E_{app} = 0.3$ V vs. Ag/Ag⁺; Pt plate working electrode; the initial spectrum is virtually indistinguishable from the *x*-axis). Right: Electrolysis of a solution of $[3H_8]SO_4$ ($1.25\ 10^{-4}$ M) followed by UV/Vis spectroscopy ($l = 1$ mm; $CH_2Cl_2 + TBAHSO_4$ (0.25 M); $E_{app} = 0.2$ V vs. Ag/Ag⁺; Pt plate working electrode; —— = initial and —— = final).

first stage of the experiment, namely, a broad band above 900 nm and a narrower one at 425 nm, was attributed to the targeted cyclo[8]pyrrole $[3H_8]^{2+}$, which evolves at the end of the electrolysis towards the mono oxidized species $[3H_8]^{3+}$. This assignment is based on the finding that a species with an identical spectral signature is observed when isolated cyclo[8]pyrrole is subject to oxidation under spectroelectrochemical conditions (Figure 3). The spectroelectrochemistry experiments shown in Figure 3 are thus fully in accord with the efficient formation of $[3H_8]SO_4$ without the formation of significant quantities of any open-chain oligopyrrolic intermediates containing more than four pyrrolic subunits.

A similar conclusion was reached from analogous experiments carried out by using a thin-layer spectroelectrochemical cell (an electrochemical cell with a 1 mm optical path), which also failed to reveal spectral features ascribable to nonbipyrrolic or nontetrapyrrolic intermediates. In fact, sequential UV/Vis spectra recorded during the course of single CVs carried at sweep rates of either 50 mV s⁻¹ or 500 mV s⁻¹ revealed features that matched what was observed during the first stages of the bulk electrolysis experiments described above. Specifically, a broad band above 900 nm was seen, as well as a narrower feature at $\lambda_{max} =$

425 nm. Although the absence of unambiguous evidence leaves the issue of mechanism unresolved, our failure to observe higher-order intermediates during the course of obtaining cyclo[8]pyrrole $[3H_8]^{2+}$ leads us to suggest that this product is formed through an anion-assisted cyclization process. Specifically, we propose that $3H_8$ is formed from first bipyrrolic and then tetrapyrrolic species, without the involvement of higher-order oligopyrrolic species such as **7**.

Electrochemical oxidation of 3,4-diethylpyrrole: To the extent that the above mechanism is correct, any process that produces bipyrrolic species such as **4** would be expected to generate cyclo[8]pyrrole, as long as side reactions are kept to a minimum. Unfortunately, all efforts to produce cyclo[8]pyrrole $[3H_8]^{2+}$ directly from 3,4-diethylpyrrole (**5**) through chemical oxidation have so far failed. Presumably, this reflects the fact that highly oxidizing conditions are needed to oxidize the monopyrrole to the corresponding bipyrrole, which allows for side reactions to occur that can compete with the subsequent coupling to produce the requisite tetrapyrrole.

In contrast, the relatively mild nature of the electrolysis conditions used to produce $[3H_8]^{2+}$ led us to consider that such an approach could be employed to convert 3,4-diethylpyrrole **5** directly to cyclo[8]pyrrole. The advantage of this putative electrochemical process is that it would prevent the need to synthesize a β-substituted bipyrrole such as **4**. Bipyrroles of this type, although convenient building blocks for expanded porphyrin construction, are typically obtained in four steps from 3,4-diethylpyrrole ethyl ester through a copper-mediated Ulmann coupling and are not routinely available on a large scale.[50–52] On the other hand, β-alkylated pyrroles such as **5** are easier to prepare and, not surprisingly, they have already been studied as precursors of polymeric materials. However, to the best of our knowledge, none of the investigations involving polymerization led to the identification and/or isolation of well-defined cyclic species.[53–57] In support of our assumption that **4** and subsequently cyclo[*n*]pyrrole might be produced electrochemically from 3,4-diethyl pyrrole **5**, we note a recent contribution from Kita and co-workers,[58] wherein **4** was produced directly from **5** through the oxidative coupling of the corresponding cation radicals formed in situ by treatment with phenyliodine bis(trifluoroacetate) (PIFA) and bromotrimethylsilane.

As above, prior to carrying out the electrolysis reactions, the electrochemical properties of 3,4-diethylpyrrole were analyzed. In agreement with previous studies,[53,55–57] the CV of **5** recorded in CH_2Cl_2 containing $TBAHSO_4$ (0.1 M; Figure 4) revealed the characteristic irreversible wave of pyrrole oxidation at approximately 0.95 V. Owing to its limited conjugation pathway and lower number of electron-donating β-alkyl groups, the pyrrole-centered oxidation process is observed at a much more positive potential in **5** than in **4**. This is very much as expected and is fully consistent with the failure to obtain cyclo[8]pyrrole from **5** through chemical oxidation; the required conditions simply appear too harsh.
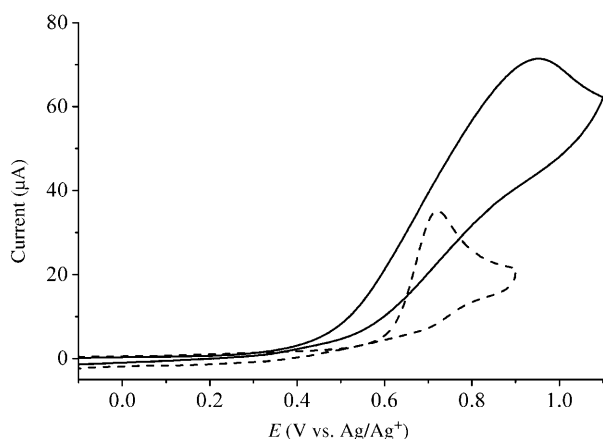
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Figure 4. CV of **5** in $CH_2Cl_2 + TBAHSO_4$ (0.2 M; $\approx 4.5 \times 10^{-3}$ M; ——) and $CH_2Cl_2 + TBAClO_4$ (0.1 M; $\approx 2.5 \times 10^{-3}$ M; -----). Pt electrode, $\emptyset = 2$ mm, 100 mV s^{-1}.

Importantly, under the conditions used for our CV analysis (CH_2Cl_2; TBAHSO$_4$ (0.1 M)), no evidence of polymer film being deposited onto the electrode was observed; this was true even after repetitive cycling. Although no polymeric materials were evidently formed under the conditions of cyclic voltammetry, the irreversibility of the oxidation wave is consistent with the species produced on oxidation, **5**$^{+\cdot}$, evolving quickly towards soluble oligomers by successive coupling reactions. The rather large difference between the peak potentials measured on both irreversible curves shown in Figure 4 (≈ 0.95 V for the TBAHSO$_4$ electrolyte compared with 0.72 V for the TBAClO$_4$ electrolyte)[59] also serves to highlight a significant anion effect, similar to what was observed when bipyrrole **4** was subject to electrooxidation. This led us to consider that appropriate anion-templating conditions could be found, which would allow for the direct formation of **3** from **5**.

A preparative-scale electrooxidation of **5** was conducted in CH_2Cl_2 by using a large platinum electrode (see the Experimental Section for details). In this study, the current was maintained at < 0.15–0.20 mA cm^{-2} and a relatively low concentration of **5** (< 10 mM; typically 4–4.5 mM) was employed. Under these conditions the electrolysis usually yielded almost exclusively soluble products with very little polymer being deposited onto the electrode. At higher concentrations of **5** (> 10 mM) the formation of an insoluble polymer film on the platinum electrode became clearly visible.

Because it is known that poly(**5**) usually exhibits low conductivity[59] and that, therefore, even thin films would serve to passivate the working electrode, special care was taken to minimize polymerization. It was found that the easiest way of avoiding polymer formation was to oxidize **5** at an initial concentration of 4–5 mM by potential cycling starting at low potentials (at the foot of the oxidation wave) and gradually increasing the lower and upper limits as **5** was consumed (see the Experimental Section for details).

Following the protocol detailed in the Experimental Section, electrolyses were performed by using **5** as the starting

material. Two products could be isolated after workup, which were identified as being the cyclo[7] and cyclo[8]pyrrole products **[2H$_7$]$^{2+}$** and **[3H$_8$]$^{2+}$**, respectively. Unfortunately, the yields for these two species were found to range from 1 to 3%, with the best reproducible yield of **[3H$_8$]$^{2+}$** (2.5% isolated yield) being obtained for a charge corresponding to 1.5 electrons per pyrrole equivalents. In the case of **[2H$_7$]$^{2+}$**, the best yield (3% isolated) was obtained when the electrolysis was stopped after passing a charge corresponding to 0.5 electrons per pyrrole units. Unfortunately, all efforts to increase the yields (such as changes in electrolyte, solvent, and temperature) met with failure.[60] Nevertheless, it is important to appreciate that, to the best of our knowledge, the present study defines the first time wherein stable and clearly defined cyclic expanded porphyrin species have been isolated as products from the electrolysis of a simple pyrrole derivative.

Spectroelectrochemical investigations of [2H$_7$]$^{2+}$ and [3H$_8$]$^{2+}$: Because the yields in **[2H$_7$]$^{2+}$** and **[3H$_8$]$^{2+}$** turned out to be low, we questioned the stability of their oxidized forms generated in situ as the result of the electrosyntheses. Table 2 summarizes the reversible oxidation and reduction potentials recorded for **[2H$_7$]$^{2+}$** and **[3H$_8$]$^{2+}$**.[6]

Table 2. Summary of the electrochemical data for **[2H$_7$]$^{2+}$** and **[3H$_8$]$^{2+}$** in $CH_2Cl_2 + TBAP$ (0.1 M). Irreversible oxidation waves are also observed with both species at approximately 0.7 V.

	[2H$_7$]$^{2+}$	[3H$_8$]$^{2+}$
$E^{0'}_{ox1}$	0.08 (1 e$^-$)	0.37 (1 e$^-$)
$E^{0'}_{ox2}$	0.35 (1 e$^-$)	–
$E^{0'}_{red1}$	−0.53 (2 e$^-$)	−0.41 (2 e$^-$)

Species **[3H$_8$]$^{2+}$** shows two reversible one-electron oxidation waves. Moreover, bulk oxidation of **[3H$_8$]$^{2+}$** carried out at 0.200 V induced drastic changes in the UV/Vis signature, with intense absorption bands growing in between 700 and 900 nm and a clear splitting of the Soret-like band at approximately 400 nm likewise occurring (Figure 5). These latter spectral features were attributed to the oxidized form **[3H$_8$]$^{3+}$**, a species that proved to be stable on the time scale of the electrolysis as evidenced by the fact that the spectral signature of the starting material **[3H$_8$]$^{2+}$** could be quantitatively recovered after a back-reduction was performed at 0 V.

The evolution of the UV/Vis spectrum of **[3H$_8$]$^{2+}$** observed as oxidation was performed at 0.525 V, conditions in which the doubly oxidized species **[3H$_8$]$^{4+}$** should be formed, is shown in Figure 5. The spectrum recorded after removing 2 e$^-$ per molecule is quite similar to that of **[3H$_8$]$^{3+}$**,[28] with intense bands being observed at 743 and 831 nm. It is thus concluded that **[3H$_8$]$^{3+}$** is formed as an intermediate. However, three new bands can also be seen at 297, 360, and 600 nm, the intensities of which increase as the columbic charge is raised. After passing 6 e$^-$ per molecule, a point at which the signature features of **[3H$_8$]$^{3+}$** were still
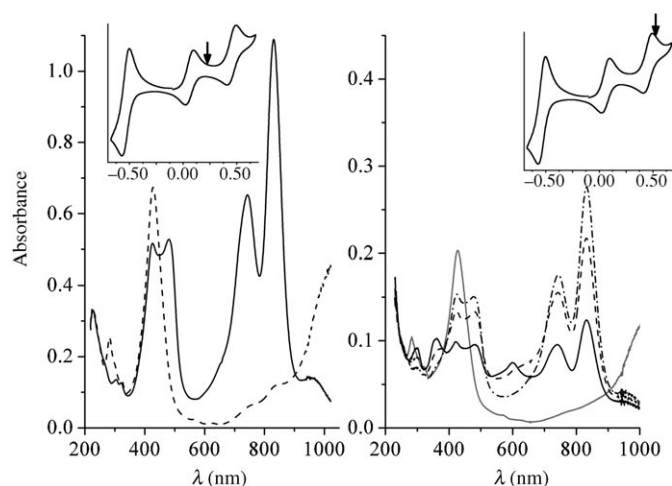
Figure 5. Left: UV/Vis absorbance spectra recorded for a solution of $[3H_8]^{2+}$ in CH_2Cl_2 (1.25×10^{-4} M) + TBAHSO$_4$ (0.25 M) before (-----) and after (——) bulk oxidation conducted at 0.200 V. The arrow in the inset CV points to the 0.200 V value. Right: Electrooxidation of $[3H_8]^{2+}$ in CH_2Cl_2 (4×10^{-5} M) + TBAHSO$_4$ (0.15 M) at 0.525 V under nitrogen (in a dry-box). The arrow in the inset CV points to the 0.525 V value; —— = initial, –·–·– = 1 e$^-$ per molecule, ----- = 2 e$^-$ per molecule, and —— = 6 e$^-$ per molecule.

clearly visible, the working electrode potential was set to −0.10 V to effect reduction.

The spectrum was then recorded after full reduction and was compared to the initial spectrum of $[3H_8]^{2+}$ (Figure 6). The bands at 297 and 360 nm are still clearly visible, with the band at 600 nm converted into a shoulder. A new band is also observed at approximately 570 nm. On this basis it is concluded that roughly half of the initial starting material $[3H_8]^{2+}$ is lost over the course of this bulk oxidation/reduction process. It is thus inferred that $[3H_8]^{4+}$, although stable enough to permit the recording of CV scans, is not stable on the time scale of a normal electrolysis reaction.
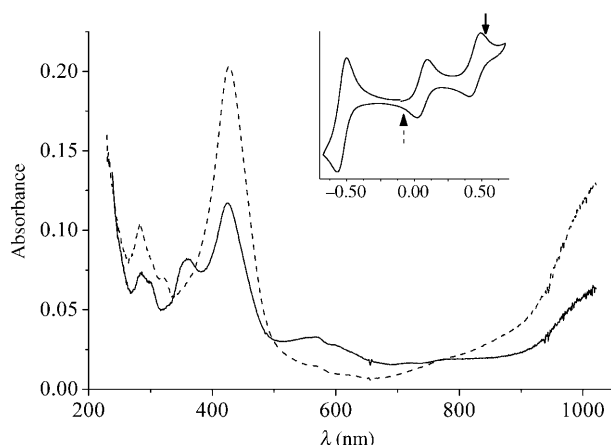

Figure 6. Comparison between the initial absorbance (-----) of $[3H_8]^{2+}$ and the spectrum of the solution after its oxidation at 0.525 V and re-reduction at −0.10 V (——). The arrows in the inset CV point to the 0.525 V (solid arrow) and −0.10 V (dotted arrow) values.

Figure 7 shows the evolution of the UV/Vis spectrum of $[2H_7]^{2+}$ recorded during a bulk oxidation conducted at 0.400 V. The trend is similar to what was observed during
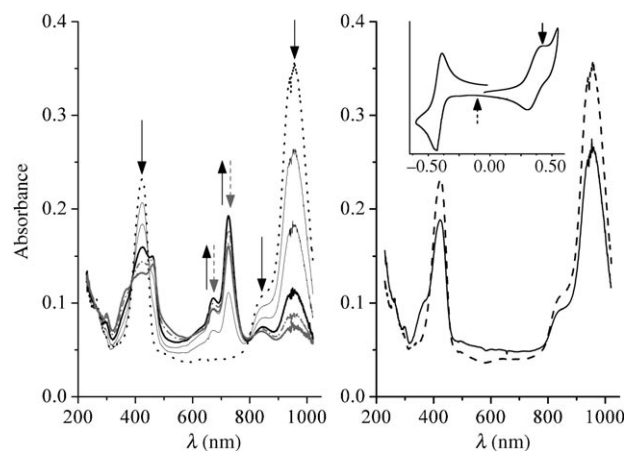

Figure 7. Left: Electrooxidation of $[2H_7]^{2+}$ in CH_2Cl_2 (5×10^{-5} M) + TBAHSO$_4$ (0.15 M) at 0.400 V under nitrogen (in a dry-box). Right: Comparison between the initial absorbance (•••••) of $[2H_7]^{2+}$ and the spectrum of the solution after its oxidation at 0.400 V and re-reduction at −0.1 V (—— = 0.6 e$^-$ per molecule and —— = 1.0 e$^-$ per molecule). The arrows in the inset CV point to the 0.400 V (solid arrow) and −0.100 V (dotted arrow) values.

the oxidation of $[3H_8]^{2+}$ to $[3H_8]^{3+}$ with the initial band at 425 nm splitting into two less-intense signals centered at 425 and 459 nm.[28] As the electrolysis proceeds, the shoulder at 845 nm and the intense band at approximately 950 nm almost disappear, and two new bands (attributed to $[2H_7]^{3+}$ by analogy to $[3H_8]^{3+}$) appear at 673 and 725 nm. However, these changes occur monotonically only up to about 0.6 e$^-$ per molecule; afterwards, the newly formed bands start to decrease and a new band at 370 nm starts to grow in.

After passing 1 e$^-$ per molecule, the solution was subject to reduction by setting the electrode potential at −0.100 V (Figure 7, right). After reduction, analysis of the UV/Vis spectrum revealed that about $\frac{1}{3}$ of the initial $[2H_7]^{2+}$ was lost (as inferred from changes in the spectral intensity). On the other hand, the band at 370 nm is still visible as a shoulder. We thus conclude that $[2H_7]^{3+}$ is not stable on the time scale of the electrolysis, at least under our experimental conditions. The fact that neither this species nor $[3H_8]^{2+}$ is stable at the high oxidation potentials used to effect macrocycle synthesis provides a reasonable explanation for why the yields of the cyclic product obtained from **5** are low.

Conclusion

In summary, we have established that appropriately sized anions act as templates that favor the electrochemical oxidative conversion of 3,3′,4,4′-tetraethyl-2,2′-bipyrrole into the corresponding cyclo[8]pyrrole. For the first time we have also isolated cyclic expanded porphyrins, namely, cyclo[8]

and cyclo[7]pyrrole, as products from the electrolysis of a simple pyrrole derivative. This approach, relying on the use of a monomeric heterocyclic building block 3,4-diethylpyrrole, still needs to be developed further if preparatively useful quantities of the cyclic products are to be obtained. Our current efforts are aimed at effecting this optimization and to generalizing the present electrochemical-based strategy such that viable quantities of new and extant expanded porphyrin-type macrocycles can be obtained from cheap and readily available starting materials.

Experimental Section

General methods and materials: Pyrroles **4**[50] and **5**[61] were synthesized according to procedures reported in the literature. The solvents used for chromatography (chloroform (HPLC grade, Carlo Erba) and methanol (SDS, anhydrous)) were used as received. The solvents used for electrochemical and spectroelectrochemical analyses (dichloromethane (SDS, anhydrous), dichloroethane (98%), acetonitrile (Rathburn, HPLC grade), and nitromethane (Acros Organics, 99+%)) were used as received. Tetrabutylammonium fluoride trihydrate (TBAF, Fluka, 98%), tetrabutylammonium chloride (TBACl, Fluka, 99%), tetrabutylammonium bromide (TBABr, Fluka, >98%), tetrabutylammonium nitrate (TBANO$_3$, Fluka, 97%), tetrabutylammonium hydrogensulfate (TBAHSO$_4$, Fluka, 99%), and tetraethylammonium perchlorate (TEAClO$_4$, Fluka, 97%) were used as received.

Tetrapropylammonium tetrafluoroborate (TPABF$_4$) was prepared by neutralizing tetrapropylammonium hydroxide (TPAOH) with an aqueous solution of HBF$_4$ (49.5–50.5%, Aldrich). The white precipitate obtained in this way was collected by filtration, washed three times with small amounts of water, and dried. The white solid that remained was dissolved in a minimum amount of chloroform and the resulting solution was then passed through a filter and evaporated to dryness. The resulting white powder was dried for two days by using a vacuum pump at room temperature and it was used without further purification.

All electrochemical data discussed in this report were obtained by using platinum working electrodes. These had either a large area (55 cm^2) in the case of the electrolyses, or consisted of a small disk (CH-instrument, 2 mm diameter) for the collection of cyclic voltammetry data. All electrolyses were carried out on a PAR 273 potentiostat, whereas cyclic voltammetry data were obtained by using a CHI model 620 electrochemical workstation. Spectroelectrochemical data were recorded by using a PAR 173 potentiostat-galvanostat and a Zeiss MCS 500 UV/NIR spectrometer.

Typical experimental details for the electrochemical oxidation of 3,4-diethylpyrrole: In a magnetically stirred three-compartment electrolysis cell, 30–35 μL (≈27–32 mg) of **5** were dissolved in CH$_2$Cl$_2$ (≈60 mL) + TBAHSO$_4$ (0.2 M; ≈4.5 mM of **5**). The solution was purged with argon for approximately 20 min prior to pyrrole addition (argon was bubbled continuously until the end of the electrolysis). A large (≈55 cm^2) platinum mesh was used as the working electrode in the anodic compartment with a carbon foam as counterelectrode in the cathodic compartment. A double-junction Ag/AgNO$_3$ (10^{-2} M) in CH$_3$CN + tetrabutylammonium perchlorate (0.1 M) reference electrode was used in all experiments (all potentials are referred to it). This reference electrode was placed in the anodic compartment as close as possible to the working electrode to minimize the ohmic drop. After the addition of **5**, the potential of the working electrode was scanned (50 mV s$^-$) from 0.4 to 0.75 V, with a waiting time of 3–12 s at the upper potential limit. The potential limits and waiting times were gradually increased during the electrolysis (the upper value was limited to 0.95 V) as **5** is consumed and the current drops. After passing the required charge, the contents of both the anodic and middle compartments (some mixing between these compartments occurs during electrolysis) were collected and the solvent evaporated. The re-

sulting solid was washed with 2×60 mL aqueous solution of H$_2$SO$_4$ (0.1 M) to remove the supporting electrolyte, filtered, and finally rinsed with approximately 25 mL of distilled water. The dark insoluble solid was recovered and dissolved in CH$_2$Cl$_2$. The solution was then dried over anhydrous Na$_2$SO$_4$, filtered, and the solvent was evaporated off to afford a dark solid. Chromatography over silica gel by using CH$_2$Cl$_2$+CH$_3$OH (1–5%) as the eluent allowed for the isolation of crude fractions containing [3H$_8$]$^{2+}$ and [2H$_7$]$^{2+}$, respectively. The crude fractions were further purified by using silica-gel column chromatography that used CHCl$_3$+CH$_3$OH (1%) as the eluent for [5H$_8$]$^{2+}$ and CHCl$_3$+CH$_3$OH (4%) as the eluent for [2H$_7$]$^{2+}$.

Electrochemical oxidation of 3,3′,4,4′-tetraethyl-2,2′-bipyrrole: A similar approach was used for experiments involving the oxidation of bipyrrole, except that the potential was not scanned. Rather, the potential was maintained initially at −0.1 V and then slowly increased up to 0.025–0.05 V.[35] A typical experiment involved approximately 20–25 mg of **2** in approximately 60 mL of the solvent mixture (CH$_2$Cl$_2$+supporting electrolyte (0.15 M, or 0.11 M in the case of TPABF$_4$)). The concentration of **2** was thus approximately 1.5 mM. After passing the required charge (2.4–2.5 e$^-$ per molecule), the reaction was worked up by using a procedure similar to the one employed in the case of the electrooxidation reactions involving **5** (see above). The supporting electrolyte was removed by washing with a dilute (≈0.1 M) aqueous solution of the corresponding acid, except for the TBABr and TBAF, in which an aqueous solution of H$_2$SO$_4$ (≈0.05 M) was used. In all other cases, care was taken to avoid any contact with sulfate anions (e.g., drying was achieved by adding large amounts of pentane followed by azeotropic distillation of water).

The yields of [2H$_7$]$^{2+}$ and [3H$_8$]$^{2+}$, especially in the case of electrooxidations involving **5** in which small amounts of product are recovered (≈1 mg, but in some cases <0.3 mg), were calculated by using data from UV/Vis spectroscopy (i.e., extinction coefficients) rather than weighing. Thus, after isolation, samples of [2H$_7$]$^{2+}$ or [3H$_8$]$^{2+}$ were dissolved in CH$_2$Cl$_2$ to produce solutions that were roughly 10^{-4} M in expanded porphyrin (as calculated from weighing when the quantity of material permitted this) and the UV/Vis spectrum was recorded. The absorbance values at 425 ([2H$_7$]$^{2+}$) and 428 nm ([3H$_8$]$^{2+}$) were measured and the amount of substance in the solution was calculated by using the reported data for the molar absorptivity[6,7] of [2H$_7$]$^{2+}$ and [3H$_8$]$^{2+}$. For the electrolyses involving TBAHSO$_4$, the yield was found to be reproducible within 3% (average of three electrolyses) and only one electrolysis was performed by using the other anions.

Spectroscopic data for [2H$_7$]$^{2+}$: ^{1}H NMR (CDCl$_3$, 400 MHz,): $\delta = -2.18$ (br s; NH), 1.80 (t, $J = 7.28$ Hz, 42H; CH$_2$CH_3), 4.25 ppm (br s, 28H; CH_2CH$_3$); MS (ESI): m/z: 882.5 [MH$_2$Cl]$^+$; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 426 nm (4.63 mol^{-1} dm^3 cm^{-1}). These data are in accord with the published values.[7]

Spectroscopic data for [3H$_8$]$^{2+}$: ^{1}H NMR (CDCl$_3$, 250 MHz, 293 K): $\delta = 1.59$ (t, $^3J = 7.3$ Hz, 48H; −CH$_2$CH_3,), 4.10 ppm (br s, 32H; −CH_2CH$_3$); MS (DCl/NH$_3$): 969 [M+1]$^+$; MS (ESI): m/z: 1065.7 [M+H$_2$SO$_4$]$^+$; UV/Vis (CH$_2$Cl$_2$): λ_{max} (log ε) = 428 nm (4.76 mol^{-1} dm^3 cm^{-1}). These data are in accord with the published values.[6]

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