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Communication

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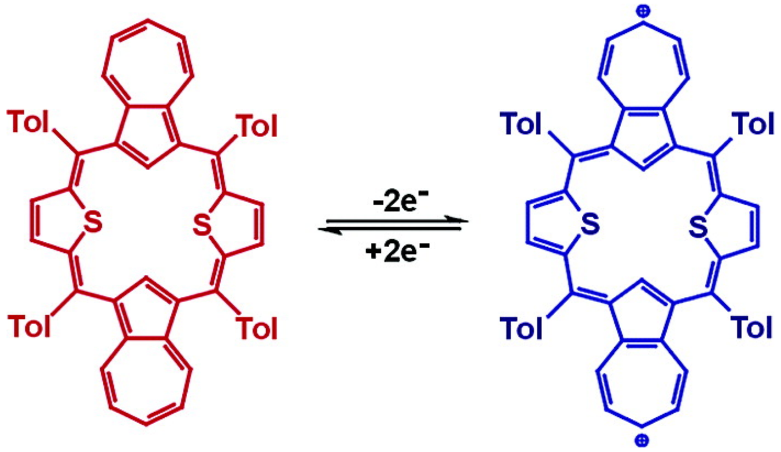

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Dithiadiazuliporphyrin: Facile Generation of Carbaporphyrinoid Cation Radical and Dication

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Carbaporphyrinoids are porphyrin analogues that possess at least one CH unit replacing a pyrrolic nitrogen in the coordination core. This "internal" carbon atom normally belongs to a carbo- or heterocyclic ring substituting one of the pyrroles.[1] Introduction of an azulene moiety to the porphyrinoid framework is of particular interest because of the unusual electronic properties of this bicyclic system. Exploration of this concept led to the synthesis of azuliporphyrin and its heteroanalogues, which exhibit borderline macrocyclic aromaticity and unusual reactivity pathways.[2,3]

Here we report on a high-yielding synthesis of hybrid thiophene−azulene macrocycles and their redox chemistry. Combination of the azulene π system with the heteroporphyrin-like macrocyclic skeleton results in a three-state redox switchable chromophore with a potential for electrochromic (including a near-IR region)[4] or molecular conductivity applications.[5] The molecular framework presented herein is potentially amenable to diverse structural modifications (substitutions of *meso*-aryls or azulene, a choice of heteroatom).

Porphyrinogen **1** is obtained in a modification of the synthesis described for tetraaryl-21,23-dithiaporphyrins.[6] This method relies on the known suitability of azulene as a substrate for Rothemund-type condensation (Scheme 1).[2,7]

Compound **1** is formed as a mixture of stereoisomers in remarkable 95% yield. One of the isomers, possessing effective C_{2h} symmetry, has been characterized by X-ray crystallography (Figure 1). **1** adopts a chair-like conformation in the solid state. The thiophene rings are coplanar, whereas the dihedral angle between each of the azulene moieties and the C_4 plane (defined by the four *meso* carbons) equals 71°. Bond lengths in the azulene and thiophene fragments of **1** are similar to those in isolated molecules.

Oxidation of **1** with varying amounts of DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone) leads to mixtures of the porphyrin analogue **2**, its radical cation $\mathbf{2}^{\bullet+}$, and dication $\mathbf{2}^{2+}$. These three species constitute a multielectron redox system with no precedence in carbaporphyrinoid chemistry. Tetrathiaporphyrin and its oxa-congener are the only other porphyrin analogues for which two different oxidation states (isophlorin and dication) could be isolated.[8] X-ray quality crystals of **2** were obtained directly from the reaction mixture. In the solid state, **2** adopts a saddle conformation, with the azulene and thiophene rings tilted in opposite directions (Figure 2). There is an appreciable effect of the conjugation on the thiophene fragment. The bond distances within the thiophene ring are altered in accord with the valence bond structure of **2**. Thus the $C_\alpha-C_\beta$ bond lengths (1.43−1.45 Å) are longer than the $C_\beta-C_\beta$ distances (1.35 Å), whereas the reverse is true for porphyrinogen **1**. Similarly, the $C_{meso}-C_\alpha$(thiophene) bonds (1.37−1.38 Å) reflect some double-bond character, while the $C_{meso}-C_\alpha$(azulene) distances (1.47−1.49 Å) approach the single-bond limit for $C(sp^2)-C(sp^2)$. The geometry of azulene moieties remains largely unaltered, suggesting that they are not conjugated with the macrocycle.

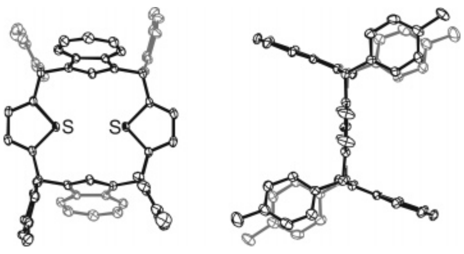
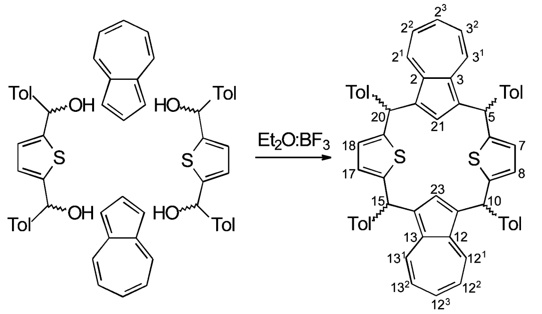


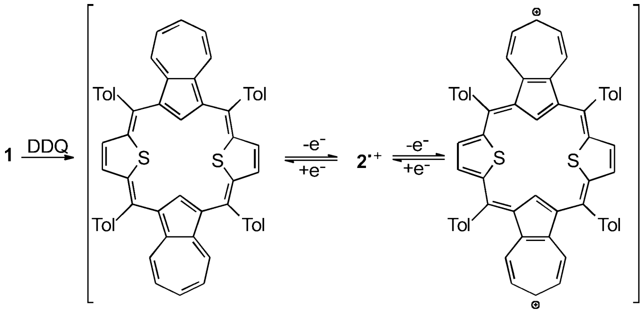
Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Fragments pointing away from the viewer are shown in gray.

Scheme 1. Synthesis of Porphyrinogen **1** (5,10,15,20-tetra-*p*-tolyl-22,24-dithiadiazuliporphyrinogen)



1

Scheme 2. Formation of **2** and Its Oxidized Forms $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{2+}$



2

$\mathbf{2}^{2+}$

The redox system comprising **2**, $\mathbf{2}^{\bullet+}$, and $\mathbf{2}^{2+}$ was further investigated using chemical and physical methods. Addition of an excess of DDQ leads to exclusive formation of the dication $\mathbf{2}^{2+}$. It is quantitatively reduced to **2** by $SnCl_2$ in THF. Systematic titration of **2** with Br_2 followed by UV−vis spectroscopy (Figure 3) reveals the presence of an intermediate, assigned as $\mathbf{2}^{\bullet+}$ on the basis of the ESR data. The solution of $\mathbf{2}^{\bullet+}$ (dichloromethane/1% THF, 298 K) exhibits a single line at $g = 2.0031$, consistent with the cation radical electronic structure. During oxidation, the color of the solution changes from dark red (**2**), through purple ($\mathbf{2}^{\bullet+}$), to navy blue ($\mathbf{2}^{2+}$).

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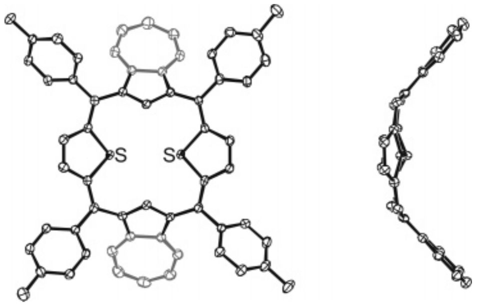

Figure 2. Molecular structure of **2**. Solvent molecules and hydrogen atoms are omitted for clarity. Fragments pointing away from the viewer are shown in gray. In the side view, tolyl groups are omitted.

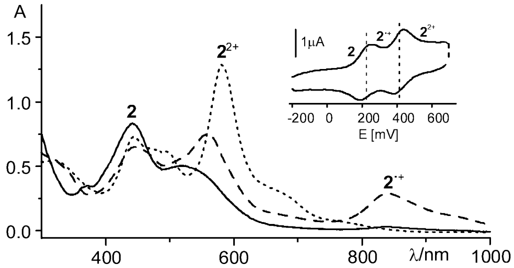

Figure 3. UV−vis absorption spectra (CH_2Cl_2, 298 K) of **2** (solid line), $\mathbf{2}^{\bullet+}$ (dashed line), and $\mathbf{2}^{2+}$ (dotted line). The spectra were obtained by titrating **2** with Br_2. The inset shows a cyclic voltammogram of **2** (CH_2Cl_2 solution, supporting electrolyte TBAP; working electrode, glassy carbon disk; reference electrode, Ag/AgCl; $E_{1/2}$ for ferrocene +553 mV).

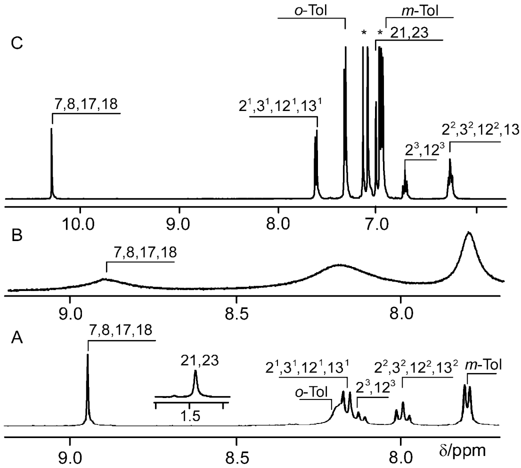

Figure 4. ^{1}H NMR spectra of (A) $\mathbf{2}^{2+}$ (acetonitrile-d_3, 298 K), (B) $\mathbf{2}^{2+}$ with a small amount of $\mathbf{2}^{\bullet+}$ (chloroform-d, 298 K), and (C) **2** (toluene-d_8, 298 K).

Cyclic voltammetry (inset of Figure 3) demonstrates that **2** undergoes two consecutive, reversible one-electron oxidations with half-wave potentials of (1) +227 mV and (2) +420 mV, yielding $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{2+}$, respectively. These potentials are very low, which accounts for the easy accessibility of the oxidized forms.

Well-resolved ^{1}H NMR spectra of **2** and $\mathbf{2}^{2+}$ can be obtained under carefully controlled conditions. In each case, the presence of even a minute amount of the radical $\mathbf{2}^{\bullet+}$ leads to significant line broadening and shortening of T_1 relaxation times, confirming fast electron exchange between differently oxidized forms of **2**.[9] The equilibria are solvent dependent: $\mathbf{2}^{2+}$ yields narrow lines in more polar solvents, such as acetonitrile (Figure 4, trace A), whereas in chloroform the spectrum is very broad (trace B). Conversely, poor solubility of the charged forms $\mathbf{2}^{\bullet+}$ and $\mathbf{2}^{2+}$ in toluene results in the desired sharpening of the spectrum of **2** in this solvent (trace C).

^{1}H chemical shifts observed for $\mathbf{2}^{2+}$, in particular the peculiar upfield position of the inner 21,23-H protons (1.48 ppm), show that a diatropic ring current is present in the macrocycle. In fact, $\mathbf{2}^{2+}$ can be viewed as a 21,23-dicarba-22,24-dithiaporphyrin with two fused tropylium rings. In the spectrum of **2**, the 21,23-H resonance is located at 7.02 ppm, confirming the absence of macrocyclic aromaticity.

In conclusion, the newly designed dithiadiazuliporphyrin **2** is the first example of a non-nitrogenous carbaporphyrinoid in general which is easily oxidizable to its cation radical and dication. Thanks to their hybrid structure, the new systems can be linked into multielement conductive arrays using technologies developed for both azulenes[10] and porphyrins.[11]

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Supporting Information Available: Synthetic procedures, UV−vis and NMR data, and crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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