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# [18]/[20]$\pi$ Hemiporphyrazine: A Redox-Switchable Near-Infrared Dye

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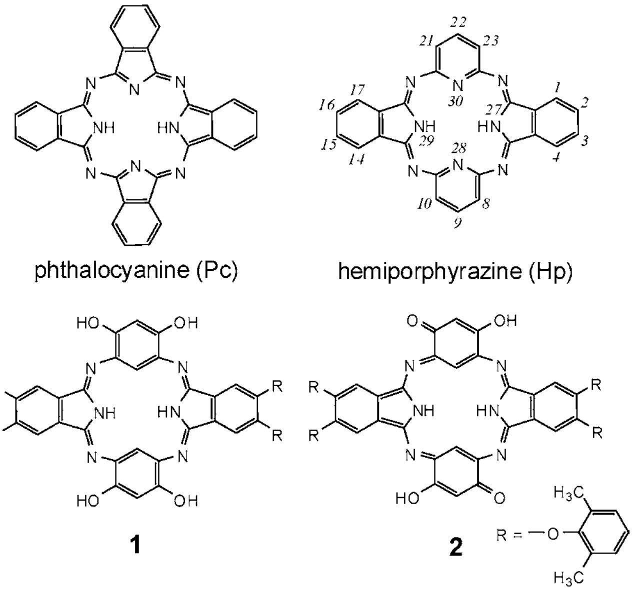
*Supporting Information*

**ABSTRACT:** An aromatic hemiporphyrazine with an $18\pi$-electron structure has been synthesized by oxidizing $20\pi$-electron 8,10,21,23-tetrahydroxy-28,30-dicarba-27*H*,29*H*-hemiporphyrazine with bulky aryl ether substituents. The aromatic nature of the oxidized form was characterized by means of various spectroscopic methods and single-crystal X-ray analysis, with the help of quantum-chemical calculations. The oxidized hemiporphyrazine exhibited an intense absorption at ~850 nm. The redox process was found to be reversible.

Porphyrins and their analogues, such as phthalocyanines, usually have an $18\pi$-electron aromatic system. Hemiporphyrazines are a broad class of phthalocyanine analogues in which two opposing pyrrole units are replaced by other moieties such as pyridine, triazole, or benzene.[1] These compounds do not display aromatic behavior. The bonding in these macrocycles is not delocalized, and they act as Schiff base ligands. The macrocycle has been considered to be formally a $20\pi$-electron system,[2] but little is known about the electronic structures of these compounds. We anticipated that $18\pi$-electron hemiporphyrazines would be formed by two-electron oxidation of the hemiporphyrazine skeleton if hemiporphyrazines do indeed have a $20\pi$-electron system.[3] Modification of hemiporphyrazine $\pi$-electron systems, however, has not been reported to date. Torres and co-workers attempted to oxidize triazolehemiporphyrazines to the corresponding aromatic compounds, but aromatic compounds were not obtained by either chemical or electrochemical methods.[1c,d] In this communication, we report the synthesis and characterization of the first aromatic hemiporphyrazine. Intriguingly, it was found that the hemiporphyrazine is a redox-switchable near-IR chromophore.[4]

In the design of an aromatic hemiporphyrazine, we selected the resorcinol unit as the redox-active moiety of the hemiporphyrazine framework.[5] We designed **1**, a tetrahydroxydicarbahemiporphyrazine[6] with aryl ether substituents. The bulky groups were introduced to increase the solubility and allow easier chromatographic separation. A two-electron-oxidized form of the phenol form **1** can be formally drawn as a quinoidal form, **2** (Chart 1).

**Chart 1. Structures of Phthalocyanine and Hemiporphyrazines**



phthalocyanine (Pc)

hemiporphyrazine (Hp)

**1**

**2**

Scheme 1 shows the synthesis of the aromatic hemiporphyrazine **2**. Diiminoisoindoline was prepared from 4,5-bis(2,6-dimethylphenoxy)phthalonitrile.[7] The reaction of the diiminoisoindoline with diaminoresorcinol dihydrochloride gave dicarbahemiporphyrazine **1** in 79% yield. Upon the addition of 1 equiv of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) to a chloroform solution of **1** at room temperature, the solution showed a marked color change from orange to dark-green. The oxidized product **2** was successfully isolated in 70% yield by silica-gel column chromatography and characterized by NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis [see the Supporting Information (SI)]. Both of the macrocycles **1** and **2** are soluble in common organic solvents such as chloroform, THF, pyridine, and DMF.

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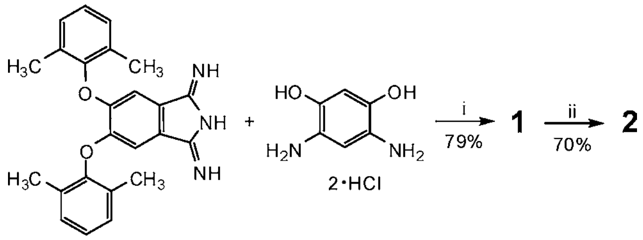
**Scheme 1. Synthesis of Aromatic Hemiporphyrazine 2**[a]



[a](i) $NEt_3$ (2 equiv), EtOH, 80 °C, 24 h. (ii) DDQ (1 equiv), $CHCl_3$, rt, 25 min.

The structures of **1** and **2** were determined by single-crystal X-ray diffraction analysis (Figure 1). The macrocycle of **1** adopts a nonplanar saddle conformation. This type of saddle conformation is often observed in hemiporphyrazines, although tetrahydroxycarbahemiporphyrazine without peripheral substituents has a planar conformation in the X-ray structure.[6] Interestingly, the oxidized form **2** was essentially planar and adopted a zwitterionic form. Thus, the internal pyrrole protons migrated to the meso nitrogen atoms. The O−H···N and N−H···O distances are 2.57 and 2.59 Å, respectively, supporting the presence of intramolecular hydrogen bonds in **2**.

Selected bond distances in the X-ray structures of **1** and **2** are shown in Figure 2. The bond lengths of the phenol form **1** are similar to those of nonaromatic dicarbahemiporphyrazines.[8] Thus, the C(resorcinol)−N(meso) bonds have single-bond character (ca. 1.42 Å), while double-bond character is seen for the C(pyrrole)−N(meso) bond (ca. 1.29 Å). The bond length difference disappeared upon oxidation [1.342(8) and 1.327(8) Å for the nonprotonated C−N bonds]. The bond lengths are consistent with those of regular phthalocyanines.[9] As expected, one C−O distance in each of the resorcinol units was shortened upon oxidation [1.241(8) Å]. The bond distances in the resorcinol moiety of **2** were very similar to those in the X-ray structure of protonated quinonemonoimine.[10]

NMR spectra of **1** and **2** were measured to elucidate the solution structures (see the SI). Broad $^1H$ NMR signals were observed for the phenol form **1**, probably as a result of its flexible skeleton at room temperature. In contrast, a well-resolved $^1H$ NMR spectrum of the quinoidal form **2** was obtained (Figure 3a). The spectrum indicates an apparently symmetrical nature of the structure, so we consider the interconversion between the two tautomers (Figure 3b) to be fast under the experimental conditions used. The broad signal at 11.61 ppm can therefore be attributed to NH and OH protons ($H_a$). Sharpening of the peak was observed when the temperature was lowered (see the SI). The chemical shift of the internal CH protons ($H_e$) was observed in an upfield region at −0.49 ppm, indicating that a diatropic ring current is present in **2**. The isoindoline protons ($H_b$) appeared at 7.66 ppm. Since the signals of the isoindoline protons of octakis(2,6-dimethylphenyl)phthalocyanine are seen at 8.18 ppm,[7] the ring current effect of the present system appears to be somewhat weaker than that in regular phthalocyanines.

Geometry-optimization calculations on **1** and **2** were performed at the B3LYP/6-31G(d,p) level to gain insight into the structures (see the SI). The lengths of the C(resorcinol)−N(meso) and C(pyrrole)−N(meso) bonds of the phenol form **1** were calculated to be 1.40 and 1.28 Å, respectively, whereas those of the nonprotonated C−N bonds of the oxidized form **2** were 1.35 and 1.33 Å, respectively. These features are in good agreement with the X-ray data. Nucleus-independent chemical shift (NICS) indices[11] and $^1H$

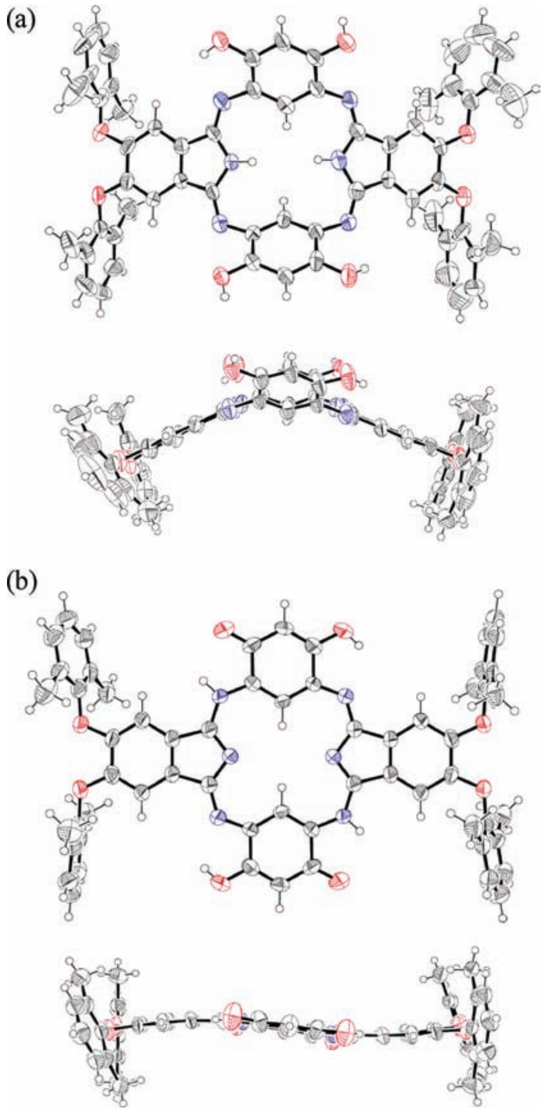


**Figure 1.** X-ray structures of (a) **1** and (b) **2**. The thermal ellipsoids are scaled to the 50% probability level. In both cases, solvent molecules have been omitted for clarity.

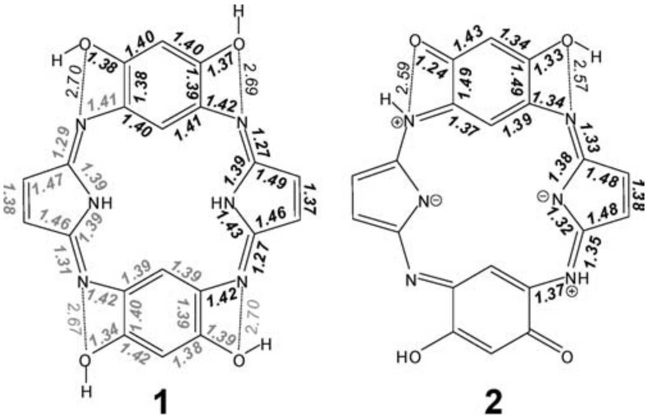


**Figure 2.** Selected bond distances (Å) in the X-ray structures of **1** and **2**.

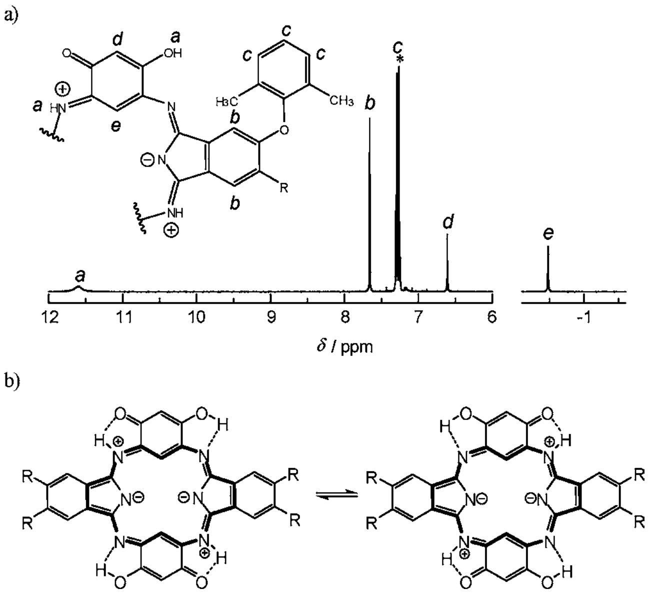


**Figure 3.** (a) Partial $^1$H NMR spectrum of the quinoidal form **2** in $CDCl_3$. Solvent signals were overlapped with signals c. (b) Possible tautomeric forms of **2**. The π-electron conjugation pathway is shown by thick lines.

NMR chemical shifts were calculated for the optimized structures (see the SI).

Figure 4 shows the electronic absorption and magnetic circular dichroism (MCD) spectra of the two forms of the carbahemiporphyrazine in chloroform. The phenol form **1** exhibited an absorption band at ∼400 nm and a weak band at longer wavelengths. The spectral features of the quinoidal form **2** are significantly different from those of the phenol form. The intense absorption bands observed at 852 and 653 nm are attributable to two split Q bands, since coupled Faraday *B* terms were observed for these absorption bands.[12] The MCD pattern of the oxidized form **2** is characteristic of low-symmetry phthalocyanine derivatives.[13]We measured the fluorescence spectra of the macrocycles in chloroform (see the SI). The quinoidal form **2** exhibited a fluorescence peak at 871 nm ($\Phi_F$ = 0.001), while no detectable fluorescence was observed for the phenol form **1**.

Frontier molecular orbitals of the hemiporphyrazines are shown in Figure 5. Obviously, the nodal patterns of the HOMO and LUMO of the phenol form **1** are similar to those of a pair of degenerate LUMOs of the 18π-electron perimeter model. It is noteworthy that the LUMO and LUMO+1 orbitals of the quinoidal form **2** are derived from the HOMO and LUMO of the phenol form **1**, respectively. In addition, the nodal pattern of the HOMO of **2** is analogous to that of one of the degenerate HOMOs of the perimeter model. These features are consistent with those of phthalocyanines having an 18π-electron structure. From these results, it is now clear that the phenol and quinoidal forms of the hemiporphyrazine are 20- and 18π-electron systems, respectively.

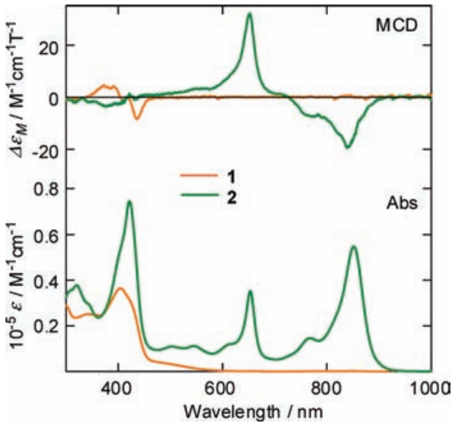


**Figure 4.** (top) MCD and (bottom) electronic absorption spectra of **1** (orange) and **2** (green) in $CHCl_3$ at room temperature.

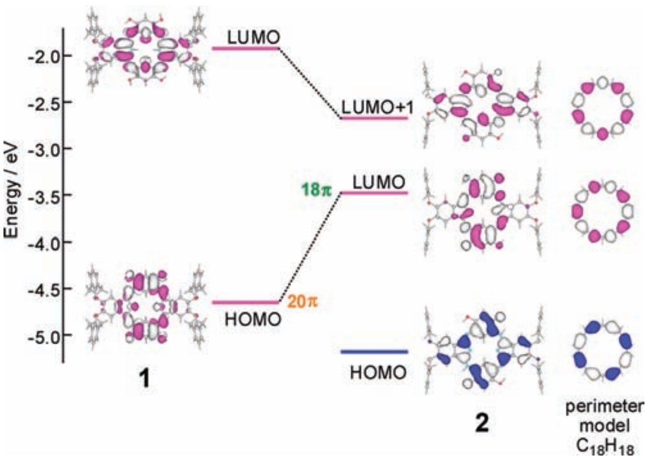


**Figure 5.** Frontier molecular orbitals and energy levels of the optimized structures of **1** and **2** calculated at the B3LYP/6-31G(d,p) level. Isosurface plots of molecular orbitals of the 18π-electron perimeter model are also shown.

The large change in the optical properties of **1** and **2** can be interpreted in terms of the difference in the frontier orbitals. Since the HOMO and LUMO of **1** are derived from a pair of perimeters with equal numbers of angular nodes, the HOMO → LUMO transition is predicted to be electric-dipole-forbidden.[14] The weak absorption band observed in the 450–550 nm region can be assigned to the HOMO → LUMO transition of a [4*n*]π-electron ring system. In the case of the oxidized form **2**, the number of nodes of the HOMO is different from that of the LUMO, so the HOMO → LUMO transition is allowed theoretically. The HOMO–LUMO gap of the quinoidal form (1.70 eV) was calculated to be smaller than that of the phenol form (2.73 eV). Time-dependent density functional theory (TDDFT) calculations support the above interpretation. Thus, the lowest-energy transition of the phenol form **1** (594.9 nm) is associated with the HOMO → LUMO transition, and the oscillator strength was estimated to be zero. In the case of the quinoidal form **2**, two allowed transitions were predicted in the longer-wavelength region (714.7 and 609.5 nm).

Finally, we investigated the reversibility of the redox process between **1** and **2**. The oxidized form **2** was easily reduced with $NaBH_4$ in chloroform at room temperature to give the original phenol form **1**. The oxidized form was recycled at least seven times under our experimental conditions during the redox process (see the SI).

In conclusion, the newly designed carbahemiporphyrazine **2** is the first example of an aromatic hemiporphyrazine with an 18π-electron structure. The hemiporphyrazine was easily prepared in high yield by making use of the resorcinol functionality in the skeleton of dicarbahemiporphyrazine **1**. It was found that the hemiporphyrazine is a redox-switchable near-IR chromophore. We believe that such aromatic hemiporphyrazines offer a new perspective for the design of near-IR-absorbing organic materials for optoelectronic applications.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental procedures, spectral data, crystallographic data (CIF), and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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