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Aromatic Core Modified Decaphyrins with the Largest Two-Photon Absorption Cross-Sections: Syntheses and Characterization

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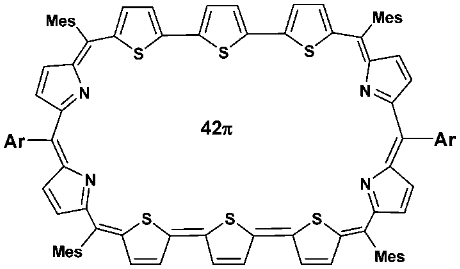
ABSTRACT



Core-modified aromatic decaphyrins with 42π conjugated electrons exhibit the highest two-photon absorption cross-section value (σ_2 = 108 000 GM) known for any organic molecule, suggesting possible device applications in the field of nonlinear optics.

Currently, intense research efforts have been geared toward the development of materials that enhance optical communications, data storage, and optical signal processing. These materials possess nonlinear optical (NLO) properties since light that passes through them is not reflected or refracted with the same energy as that of the incident light.[1] Materials with large third-order optical nonlinearities have recently attracted the attention of chemists.[2] Many π-conjugated organic molecules that exhibit decent two-photon absorption cross-section (TPACS) values have been recently reported.[3] Conjugated polyacetylenes and poythiophenes and various semiconductors are being currently tested for third-order nonlinear properties. Easy processability into thin films, ease of chemical modifications, structural diversity, and bulk optical nonlinearity are some of the advantages of these organic molecules over the conventionally used semiconductors.

Porphyins and expanded porphyrins are one class of organic molecules which has attracted the attention of the organic chemists for nonlinear optical applications. They are exceptionally stable and have large π-conjugated electrons in the aromatic pathway. In this context, several porphyrin geometries have been found to display small to moderate TPACS values.[4] Recent work from this laboratory has shown that increasing number of π electrons in the conjugated pathway can enhance the TPACS values considerably.[5] The enhanced TPACS values are attributed to the large cyclic π-conjugation, more flexible conformation of the macrocycles due to an increase in the number of *meso*-links, and

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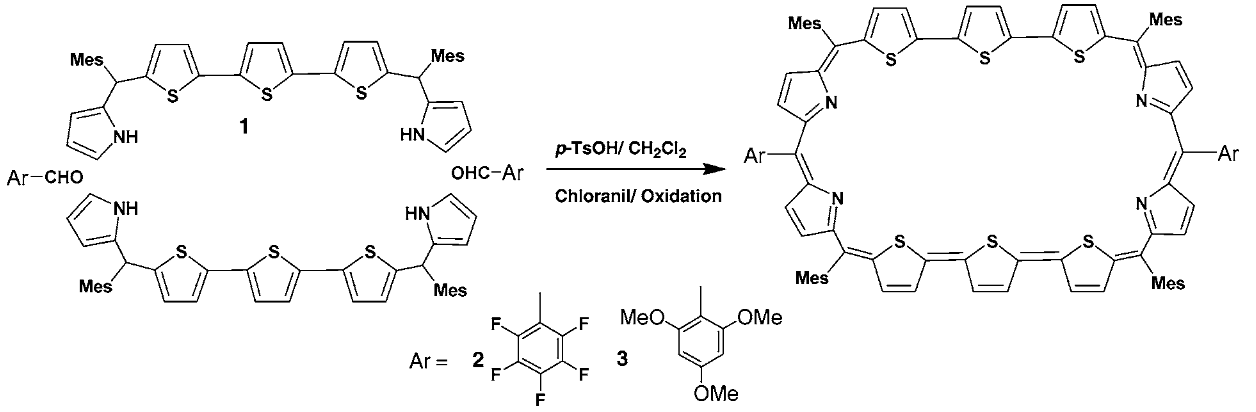
Scheme 1. [5 + 5] Acid-Catalyzed Condensation of Modified Pentapyrranes



an increase in the number of heteroatoms such as sulfur and selenium in the macrocyclic core.

In this context, we wish to report the syntheses of expanded porphyrin macrocycles containing 42π electrons. Expanded porphyrins containing 10 heterocyclic rings in conjugation are termed decaphyrins in the literature. A few decaphyrin systems reported exhibit figure eight conformations, thus losing aromatic character.[6] Hence, synthesis of aromatic decaphyrins is still a synthetic challenge.

The traditional synthetic methodologies known in the literature for expanded porphyrins in all cases lead to various kinds of side products.[7] In this context, our synthetic strategy for expanded core-modified porphyrins bearing six, seven, and eight heterocyclic rings connected through six *meso*-links have the merit of isolation of a single desired product with near-quantitative yield.[8] Thus, to realize this synthetic strategy and to add further a new member to the expanded porphyrin family, core-modified decaphyrins with six *meso*-links **2** and**3** have been achieved via an acid-catalyzed [5 + 5] MacDonald condensation of modified pentapyrrane **1** containing *meso*-mesityl substituents with electron-withdrawing aryl aldehyde-like pentafluorobenzaldehyde and electron-releasing aryl aldehyde-like trimethoxybenzaldehyde (Scheme 1). Under our reaction conditions, when 1 equiv of the modified pentapyrrane was condensed with 1 equiv of the corresponding aryl aldehydes in the presence of 0.5 equiv of p-tolylsulfonic acid catalyst (0.1 equiv of methanesulfonic acid) followed by chloranil oxidation, the desired products, i.e., modified decaphyrins **2** and **3**, were obtained in 11% and 8% yield, respectively.

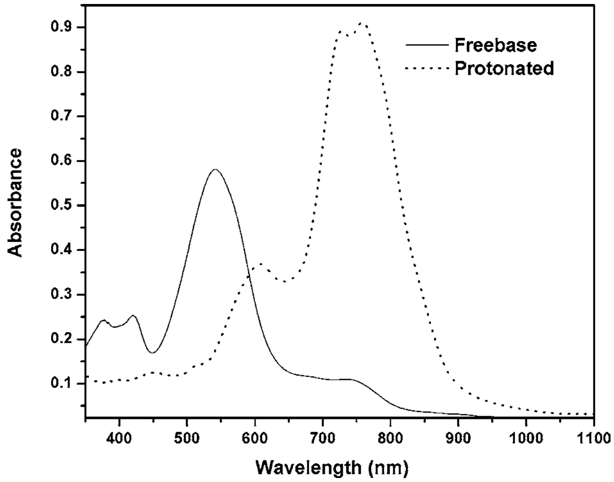


Figure 1. UV−vis spectra of **2** and its protonated derivative.

The characterization of these novel macrocycles has been confirmed from various spectroscopic techniques. The FAB mass spectra show the free base composition of the macrocycles. The UV−vis spectra of these macrocycles show a broad Soret-type band at 542 nm ($\epsilon = 1.01 \times 10^5$ M^{-1} cm^{-1}) and a Q-band like absorption at 750 nm. The broad band indicates non planar nature of the macrocycle. Figure 1 shows the UV−vis spectra of free base and protonated form of **2** as a typical example. A comparison of this spectral observation with its lower congeners, i.e., modified hexaphyrin, heptaphyrin, and octaphyrin analogues,[8] reveals a red shift in absorption clearly depicting an increase in π-conjugation upon going from 26π to 42π. Furthermore, upon complete protonation, there is a 185 nm red shift in the Soret band which is a signature for aromaticity in *meso*-aryl-substituted core-modified expanded porphyrins.[9] All together, these features clearly reveal the porphyrinic nature of the macrocycles. Further insight into the aromatic nature of these macrocycles comes from the ^{1}H NMR spectra for the macrocycle **2**. A fairly well-resolved ^{1}H NMR spectrum was

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obtained upon lowering the temperature to 218 K for this macrocycle in strong support to the well-known fact that larger macrocycles exhibit conformational flexibility; hence, at room temperature, well-resolved peaks could hardly be obtained (see the Supporting Information). The peaks in the region 6−6.5 ppm have been assigned to the phenyl protons of the *meso*-mesityl rings, whereas the peaks in the region 1.8−2.4 ppm have been assigned to the methyl protons of the *meso*-mesityl substituents. The singlets in the region 6.8−12 ppm are mainly due to the β-CH protons of the heterocylic units. substituents. Absence of any correlation in the COSY spectra prevented us from assigning the signals for the respective β-CH protons of the heterocyclic units. But, a $\Delta\delta$ value of 10.8 ppm for the chemical shift difference between the most deshielded proton resonance and the most shielded proton resonance is the strong evidence for the aromatic nature of this macrocycle in the solution.

Our efforts in obtaining a single crystal of X-ray quality were not successful; hence, geometry optimization has been done with the Gaussian 98 suite of programs at the B3LYP/3-21G level of density functional theory.[10] Figure 2 shows the proposed structure with nonplanar geometry taking **2** as typical example. Out of two terthiophene moieties in the macrocycle, two thiophene rings in one of the terthiophene unit are inverted with torsional angle S3−C−C−S2 = 145°.

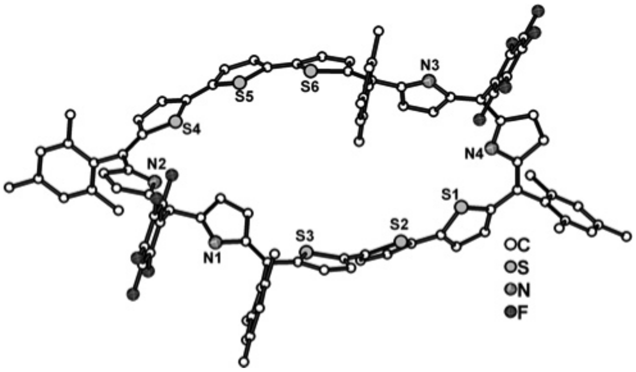

Figure 2. Theoretically optimized structure for **2**.

Recent findings from our laboratory[5] have established that it is possible to enhance TPACS values by increasing the number of π-electrons in conjugation, increasing the number of heteroatoms such as thiophene and selenophene in the core of macrocycle. In this context, core-modified heptaphyrin analogues with six *meso*-links[8c] were found to exhibit 15% lower TPACS values relative to 34π octaphyrins.[5] These core-modified heptaphyrin[8c] and octaphyrin[8b] analogues with six *meso*-links exhibit nonplanar structures in the solid state, whereas the solution state properties unequivocally show aromaticity in these macrocycles. Our core-modified decaphyrin analogues **2** and **3** are found to be nonplanar as judged from theoretically structure optimization, but nevertheless, aromaticity is assured in solution state; thus, these two macrocycles are expected to show still higher TPACS values compared to 34π octaphyrin analogues. The open aperture Z-scan traces for **2** shown in Figure 3 reveal σ_2 values of 108 000 GM for **2** and 106 600 GM for **3** with respect to Rhodamine-6G reference. The measurement technique is exactly the one reported by us.[5] These values represent the largest ever value known for any organic molecules reported to date to the best of our knowledge and are undoubtedly in strong support to our hypothesis for enhancing the absolute TPACS values.

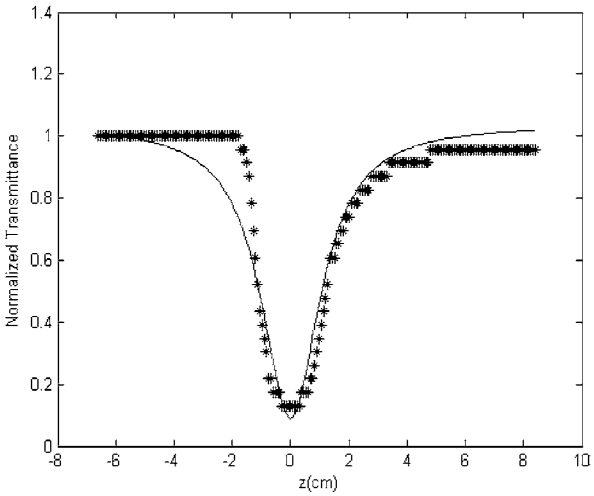

Figure 3. Open aperture Z-scan traces of **2**. The solid line shows the best fitted curves of experimental data.

In conclusion, an analysis of the solid-state structure for 30π heptaphyrins,[8c] 34π octaphyrins,[8b] and the geometry-optimized structure for 42π decaphyrins **2** and **3** reveal interesting correlation. All these macrocycles exhibit typical nonplanar structure in solid state suggesting disruption of the conjugation whereas aromaticity in these macrocycles is assured in the solution state through various spectroscopic analyses. It is thus obvious that there is conformational change on going from the solid state to the solution state due to the flexibility of the macrocycles arising from an increase in number of *meso*-links. Thus, we propose that these macrocycles exhibit a planar structure in solution, facilitating aromaticity and hence resulting unusually large σ_2 values. (We would like to emphasize here that the optimized structure reported here for compound **2** represents the gas-phase geometry and not the exact solid structure. However, our previous experiments on single-crystal X-ray

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crystal structures of such similar molecules reveal that there is little change in structure in solution.) A combination of several such design strategies may provide a better understanding of promising candidates toward effective NLO susceptibility. Several interesting core-modified expanded porphyrins are underway to justify such a hypothesis.

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Supporting Information Available: Experimental procedures and characterization of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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