

Synthesis Design

Synthesis, Characterization, and Electronic Structures of Porphyrins Fused with Polycyclic Aromatic Ring Systems

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Abstract: A series of porphyrins fused with acenaphthylene, phenanthroline, and benzofluoranthene polycyclic aromatic rings were prepared by means of a 3+1 porphyrin synthesis approach and subsequent retro-Diels–Alder reaction of bicyclo[2.2.2]octadiene-fused precursors. Analysis of the magnetic circular dichroism spectra and the results of time-depen-

dent DFT calculations are used to identify the reasons for the trends observed in the wavelengths and relative intensities of the Q bands of the products. Michl's perimeter model is used as a conceptual framework to explain the changes in the relative energies of the frontier π -molecular orbitals.

Introduction

There has been considerable interest in the expansion of the π systems of porphyrins for applications such as light-emitting displays, thin-film transistors, solar cells, and photosensitizers for photodynamic therapy.^[1] Expansion of the porphyrin π system has been achieved by fusion of aromatic rings either on the periphery of the pyrrole moieties or through the introduction of aryl substituents at the *meso*-positions. These strategies are effective methods for modifying the electronic structures and optical properties of porphyrins. Pyrroles fused with polycyclic aromatics, such as acenaphthylene, phenanthrene, or phenanthroline, are readily prepared by the Barton–Zard reaction of nitroarenes. These pyrroles are useful starting materials for the synthesis of π -expanded porphyrins, which have been studied to identify the best strategies for tuning the absorption band wavelengths.^[2–4] For example, although the B (or

Soret) band of octaethylporphyrin lies at $\lambda \approx 400$ nm, those of *meso*-free tetraacenaphthoporphyrin, and its *meso*-phenyl and *meso*-alkynyl derivatives are redshifted to $\lambda = 528$ (trifluoroacetic acid (TFA)/CHCl₃), 556, and 604 nm (CHCl₃), respectively. On the other hand, linearly π -expanded porphyrins, such as [2,3]naphthoporphyrins, could not be obtained by this method owing to the selectivity or reactivity of the nitration and Barton–Zard reactions.

The synthesis of π -expanded porphyrins has also been achieved through the aromatization of a suitable precursor. Two approaches were reported almost simultaneously, in this regard. First, the oxidative dehydrogenation of porphyrins fused with partially saturated rings with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ).^[5] The other approach, which was developed by the Ono group, has been the synthesis of a series of linearly π -expanded porphyrins through a retro-Diels–Alder strategy of bicyclo[2.2.2]octadiene (BCOD)-fused porphyrins.^[6,7] This approach afforded tetra[2,3]naphtho-,^[6a] tetra[2,3]anthra-,^[6b] and benzofluoranthene-fused porphyrins.^[7] Intense absorption bands were observed in the near-infrared (NIR) region for anthracene- and benzofluoranthene-fused porphyrins. However, the linearly π -expanded tetra[2,3]naphtho- and tetra[2,3]anthraporphyrins are relatively unstable. Their instability towards oxidation and reduction has been predicted by molecular orbital (MO) calculations.^[8] Benzofluoranthene-fused porphyrins **1** and **2** (Figure 1) are stable and have intense Q bands with large molar absorption coefficients of over $10^5 \text{ m}^{-1} \text{ cm}^{-1}$ at $\lambda = 651$ and 740–760 nm, respectively. The fusion of the porphyrin chromophore to a fluoranthene moiety with a BCOD ring afforded the target compounds, **1** and **2** (Figure 1), in nearly quantitative yields after heating in vacuo. This strategy provided an effective strategy for controlling the wavelengths of the main spectral bands. It is important to predict the structure to achieve specific electronic properties. Recently, we reported the synthesis of a series of core-modified

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