Core-Modified Rubyrins Containing Dithienylethene Moieties**

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Abstract: *Two stable core-modified rubyrins bearing one and two dithienylethene (DTE) units (**1** and **2**) have been synthesized. With one "closed-form" DTE unit, **1** shows aromaticity associated with its conjugated circuit of 26 π-electrons. In contrast, rubyrin **2** containing one "open-form" DTE unit has nonaromatic properties.*

In recent years there has been a growing focus on the synthesis and characterization of ring-expanded porphyrinoids with both heteroaromatic and nonaromatic π-systems.[1] Aromaticity is a fundamental concept of chemical structure and bonding, which describes the enhanced stability that is derived from the delocalization of π-electrons in cyclic conjugated macrocycles.[2] Although aromaticity cannot be quantified directly by experiment, it can be analyzed by studying the molecular and electronic structures, and the external magnetic field induced diamagnetic ring current. Theoretical calculations such as nucleus-independent chemical shift (NICS) and anisotropy of the current-induced density (ACID) can be used to determine the extent to which a novel macrocycle is aromatic.[3] Typically, porphyrins can be regarded as aromatic molecules following Hückel's

(4N + 2) rule as 18 π-electron are delocalized along the inner ligand perimeter. Porphyrins and their homologues, such as corroles[4] and ring-contracted,[5] core-modified,[6] and ring-expanded porphyrin analogues,[7] provide an ideal platform for developing a deeper understanding of the aromaticity of various compounds. Core-modified and ring-expanded porphyrins have been intensively studied because of their suitability for various applications.[1d,8] The extent of macrocyclic aromaticity is closely related to the number of π-electrons and the topology of the molecular structure. The aromatic character can be fine-tuned through protonation,[9] by modifying the solvent polarity[10] and coordination environment,[11] and by incorporating novel heterocyclic moieties as building blocks.[12]

Dithienylethene (DTE) can exhibit switchable properties in response to certain external stimuli such as light, redox potential, oxidation/reduction, and the presence of ions (Scheme 1). This makes it one of the most interesting building blocks for the fabrication of organic photoswitching and photomemory devices.[13] In the open form of DTE, two thiophene units are linked at their β-positions through a cyclopentene moiety, and thus the conjugation pathway (indicated by alternating single and double bonds) is not planar. In the closed form, the two α-positions of the thiophene units are linked directly, leading to the extension of the π-conjugation system over the entire DTE moiety. The unique structural flexibility inspired us to think about introducing a DTE unit into a macrocycle. Core-modified rubyrins were selected so that the aromaticity of porphyrinoids can be studied further. DTE has previously been used as a building block for the formation of nonconjugated macrocycles,[14] and as a bridging and fused moiety in photochromic porphyrins[15] and phthalocyanines.[16] However, no example of a DTE moiety embedded in a conjugated macrocycle has been reported to date.

Herein, we report the first synthesis and characterization of porphyrinoid macrocycles containing one (**1**) and two (**2**) dithienylethene moieties (Scheme 1). The noteworthy findings were that firstly, even under dark conditions, the embedded DTE moiety of the compound with one DTE moiety exists solely in the closed form, suggesting the formation of a very stable aromatic macrocycle with a 26 π-electron system. Secondly, the optical and redox properties of **1** differ markedly from those of conventional core-modified rubyrins with a 26 π-electron system. Thirdly, due to the constraints imposed by the geometry of the inner perimeter of the macrocycle, the rubyrin with two embedded DTE units (i.e. **2**) contains one closed and one open moiety and retains nonaromatic properties.

The key step in the short synthesis of **1** was the coupling of diol **4** and modified tetrapyrrane **6**[6,18] (Scheme 2, the

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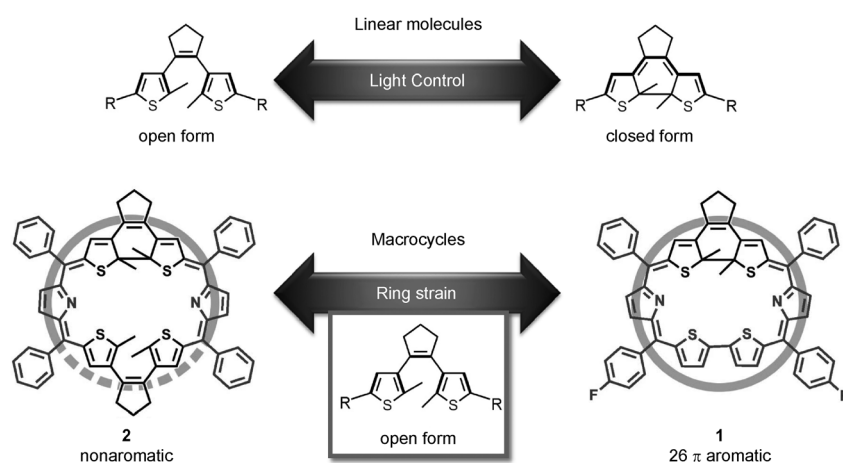Nanjing University, Nanjing, 210093 (China)
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Scheme 1. Schematic representation of the cycloreversion of DTE (top) and structures of rubyrins containing one (**1**) and two (**2**) DTE units (bottom).

torsionally distorted. The bithiophene moiety forms a plane which bends over the DTE plane (C5-C2-C2′-C5′) with a dihedral angle of 34.3°, thus the molecule adopts a J-shaped conformation when viewed from the side. There appears to be a weak intermolecular hydrogen-bonding interaction between a pyrrole β hydrogen atom (H1) and an F atom on a neighboring molecule with a C−H···F distance of 3.508 Å and an angle of 145.7°. As a result, the N1 pyrrole ring has a larger torsion angle (23.8°, relative to the DTE plane) than the N2 ring (6.3°). The C1–C1′ distance (1.532(16) Å) is consistent with that of a typical C−C single bond, which indicates the presence of a "closed-form" DTE moiety in **1**. It is noteworthy that the

experimental details are provided in the Supporting Information). Diol **4** was prepared by the double Grignard reaction of **3**, which was synthesized according to literature procedures.[13] The other coupling component, compound **6**, was obtained by reacting **5**[6b] with excess pyrrole in the presence of trifluoroacetic acid (TFA). Finally, rubyrin **1** was prepared
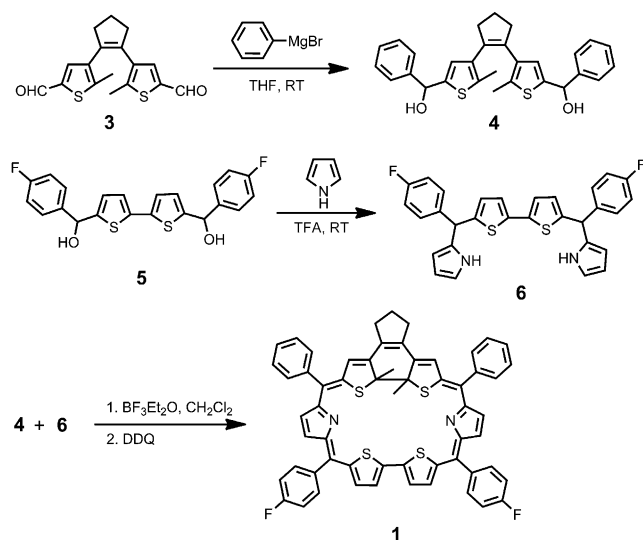
Scheme 2. Synthesis of core-modified rubyrin **1**.

by the reaction of compounds **4** and **6** under Lindsey reaction conditions.[6a,17]

The structure of **1** was unambiguously elucidated by single-crystal X-ray diffraction analysis (Figure 1).[19] Suitable crystals were obtained by the slow diffusion of hexane into a dichloromethane solution at room temperature. The two sulfur atoms and methyl groups of the DTE moiety are disordered. After the final refinement, the occupancies of the two disordered parts were found to be 0.61 and 0.39, respectively. Although the closed form of the DTE moiety adopts a nearly planar conformation, the π-system of **1** is
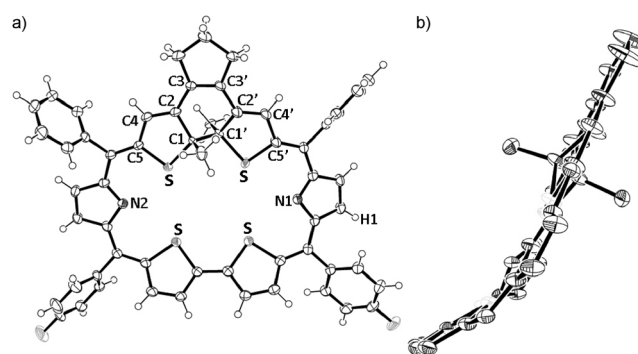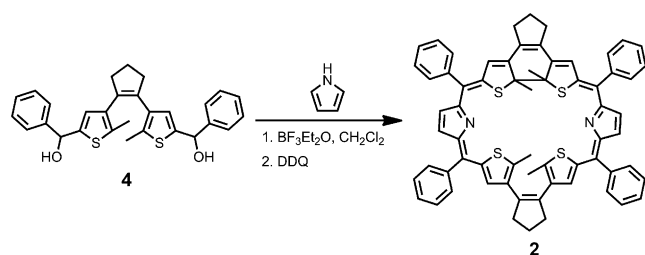

Figure 1. The X-ray crystal structure of rubyrin **1**. a) Top view, b) side view (solvent molecules, hydrogen atoms, and peripheral groups are omitted for clarity).

C4–C2, C3–C3′, and C2′–C4′ distances (1.336(5) Å, 1.325(5) Å, and 1.336(5) Å, respectively) are consistent with C=C double bonds, which differs markedly from the compounds containing "closed-form" DTE units that have been reported previously.[13] It has been reported that the photochromic quantum yields ($\Phi_{O\rightarrow C}$) for DTE cyclization are 10–100 times larger than those for cycloreversion ($\Phi_{C\rightarrow O}$).[13] The presence of only one DTE moiety makes it easy to carry out the conversion from a nonaromatic "open-form" structure to a more stable 26-π aromatic "closed-form" DTE rubyrin. Therefore, we tried to incorporate two DTE moieties into a single macrocycle using the synthetic conditions similar to those used for **1** (Scheme 3).

The chemical structure of the product was found to be consistent with that of **2** based on the HRMS data (m/z: found: 1000.30098; calcd: 1000.30078 [M+] for **2**). The structure of **2** was the only possible structure in this context. In order to estimate the extent of the diamagnetic ring current when an external magnetic field is applied to the molecule, the ¹H NMR spectra of **1** and **2** were recorded in CD₂Cl₂ for comparison (Figure 2). In **1**, the signal of the thiophene methyl protons, which lie inside the conjugated macrocycle, was detected at high field ($\delta = -0.27$ ppm), while the

Scheme 3. Synthesis of core-modified rubyrin 2.

Figure 3. ACID plots of 1 (a) and 2 (b) at an isosurface value of 0.065. The external magnetic field is applied orthogonal to the macrocycle plane with its vector pointing towards the viewer. Current density vectors (green lines and red conics) are plotted onto the ACID isosurface.

thiophene protons of the DTE moiety appeared as a singlet at $\delta = 7.56$ ppm. In 2, the chemical shifts of the thiophene methyl protons ($\delta = 2.01$ (6H) and 2.18 (6H) ppm) and the thiophene
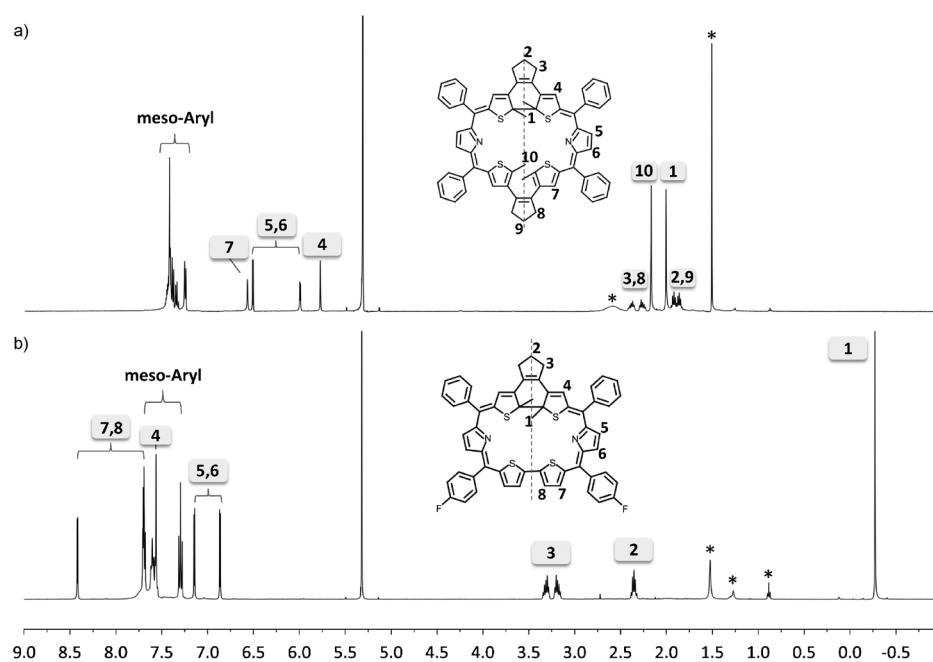

Figure 2. The ^{1}H NMR spectra of a) 2 and b) 1 in CD$_2$Cl$_2$.

the ^{1}H NMR measurements. The π-system of 2 is clearly nonaromatic.

Molecular orbital (MO) and time-dependent (TD)-DFT calculations have been carried out for 1 and 2 (Figures 4 and 5). Although alternating single and double bonds cannot be drawn for the "open-form" structure of 2 (Scheme 1), when viewed in the context of molecular orbital theory, the spectroscopic properties can still be analyzed using theoretical frameworks that have been derived for conjugated macrocycles.[20] First, it is noteworthy that the nodal patterns of the HOMO and HOMO−1 and also the LUMO and LUMO+1 of 1 are consistent with what would be anticipated for a heteroaromatic 26 π-electron porphyrinoid (Support-

protons ($\delta = 5.78$ (2H) and 6.85 (2H) ppm) of the DTE moiety are significantly different from those of 1, indicating that there are two different types of methyl and DTE thiophene protons, as shown in the structure of 2.

In order to disclose the conjugation pathways of 1 and 2, the ACID was calculated at the B3LYP/6-31G* level of theory (Figure 3, Figures S13–S16 in the Supporting Information). There is a distinct diatropic ring current, which is revealed through numerous current density vectors on the isosurface, in the periphery of 1 (red line, clockwise). In contrast, there are only local currents (in benzene, pyrrole, and thiophene rings) in 2. At a higher isosurface value there is a continuous isosurface in 1. In 2, however, the delocalization is interrupted. When this is combined with the bond length data for the 1 macrocycle (see Figure S12 in the Supporting Information), it is clearly evident that 1 has an aromatic 26 π-electron system. In contrast, there is no ring current on the outer ring periphery of 2, as would be anticipated based on
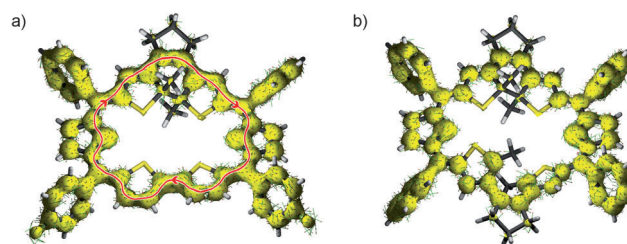

Figure 4. The predicted energies of the frontier π-MOs based on the X-ray structure of 1 and the optimized geometry of 2 at the B3LYP/6-31G* level of theory. Black squares are used to denote occupied MOs. Vertical arrows denote the one-electron transitions associated with the L and B bands of Michl's $4N+2$ perimeter model[21] and the S, N$_{1/2}$, and P$_{1/2}$ bands of the $4N$ perimeter model.[22] The details of the TD-DFT calculations and the angular nodal patterns of the main MOs are provided in the Supporting Information.
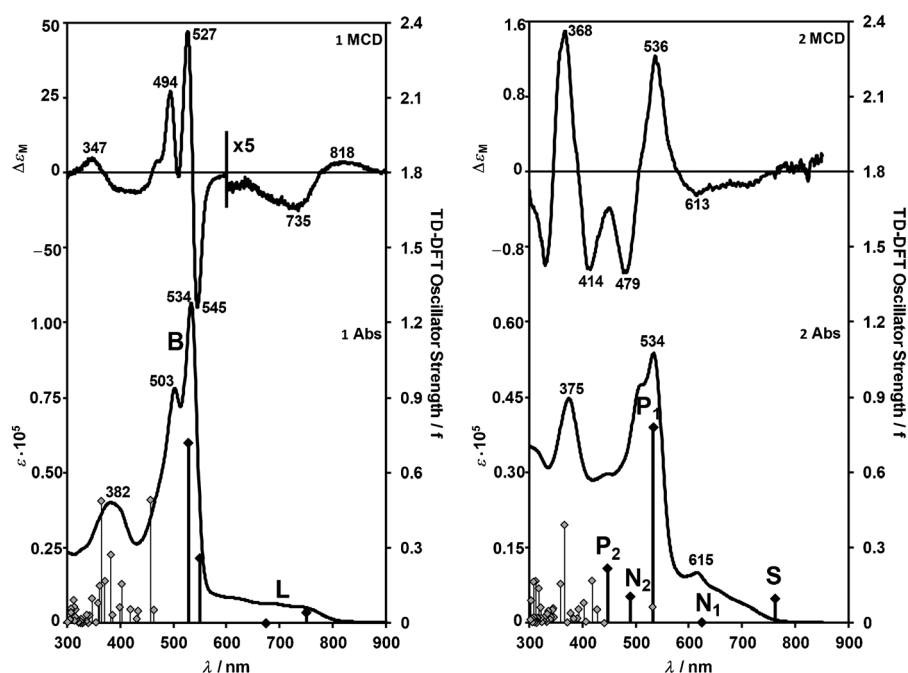
Figure 5. The observed electronic absorption spectra of **1** and **2**, and the calculated TD-DFT (diamonds) oscillator strengths based on the X-ray structure of **1** and the optimized geometry of **2** at the B3LYP/6-31G* level of theory plotted against the primary and secondary vertical axes, respectively. Black and light gray diamonds are used to highlight the L and B bands from Michl's $4N+2$ perimeter model[21] and the S, $N_{1/2}$, and $P_{1/2}$ bands from the $4N$ perimeter model.[22] The details of the TD-DFT calculations and the angular nodal patterns of the main MOs are provided in the Supporting Information.

ing Information), since six angular nodal planes are predicted for the HOMO level and seven for the LUMO level due to an $M_L = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6, \pm 7, \pm 8, \pm 9, \pm 10, \pm 11, \pm 12, 13$ sequence in terms of ascending energy for the MOs derived from a parent $C_{26}H_{26}$ aromatic hydrocarbon perimeter with D_{26h} symmetry. Michl and co-workers have demonstrated that this is the pattern that would normally be anticipated for a heteroaromatic $4N+2$ π-system with 26 atoms and 26 π-electrons.[21] Since only relatively minor energy splittings (the ΔHOMO and ΔLUMO values to use Michl's terminology) are predicted for the four frontier π-MOs derived from the HOMO and LUMO of the parent perimeter, almost fully forbidden L bands and strongly allowed B bands are expected to dominate the UV/Vis absorption spectrum, with pairs of coupled Faraday $\mathscr{B}_0$ terms of opposite signs anticipated in the magnetic circular dichroism (MCD) spectrum in each case. The bands in the 450–600 and 650–850 nm ranges (Figure 5) can be assigned to the B and L transitions based on the TD-DFT calculations and the sign sequences observed in the MCD spectrum.

Due to the presence of the "open-form" DTE unit, the optical properties of the π-system of **2** can be readily interpreted using Michl's $4N$ perimeter model (Figure 4).[22] Six frontier π-MOs derived from the HOMO, SOMO, and LUMO of the parent hydrocarbon perimeter (referred to by Michl as the h−, h+, s−, s+, l−, and l+ MOs) have six, seven, and eight angular nodal planes (Figure S19 in the Supporting Information), respectively, and play the key role in the low-energy singlet electronic states. The intensities of

the MCD bands are an order of magnitude weaker than those of **1**, since the induced excited-state magnetic moments are very weak due to the absence of a heteroaromatic conjugation pathway.[23] The lowest energy band is associated with the s−→s+ transition, which is of an intrashell nature. The absorption and hence also the MCD intensity of the S band is usually predicted to have near-zero intensity. The weak tail of intensity in the 700–850 nm region can be assigned to this transition (Figure 5). The other spin-allowed electronic transitions within the model are intershell, being derived from HOMO→SOMO and SOMO→LUMO one-electron transitions (Figure 4). Two weak (N$_1$, N$_2$) and two strong (P$_1$, P$_2$) electric-dipole transitions are predicted on this basis, which can be readily assigned based on the TD-DFT calculation to the more intense coupled pairs of Faraday $\mathscr{B}_0$ terms in the 450–650 nm range.

In summary, a heteroaromatic core-modified rubyrin bearing one dithienylethene moiety (**1**) has been successfully synthesized and characterized for the first time, along with a nonaromatic macrocycle containing both an "open-form" and a "closed-form" dithienylethene moiety (**2**). An analysis of the MCD spectral data and the TD-DFT and ACID calculations clearly demonstrated that the π-systems of **1** and **2** are aromatic and nonaromatic, respectively. The use of a dithienylethene moiety as a building block, therefore, offers a new vista of opportunities for tuning the aromaticity of ring-expanded core-modified porphyrins. Further research on the incorporation of DTE moieties into larger conjugated macrocycles to form stimuli-active molecules is currently in progress.

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[19] Crystallographic data for **1**: $C_{59.5}H_{41}ClF_2N_2S_4$, $M_r = 985.63$, crystal dimensions: $0.40 > 0.40 > 0.05$ mm^3, monoclinic $C2/c$, $a = 13.741(3)$, $b = 18.160(4)$, $c = 37.729(8)$ Å, $\beta = 95.668(2)°$, $V = 9369(4)$ Å^3, $Z = 8$, $D_{calcd} = 1.398$ g cm^{-3}, $T = 100$ K, 28692 measured reflections, 7662 reflections with $[I > 2s(I)]$. $R = 0.0596$, $R_w = 0.1210$, GOF = 1.152. CCDC 976688 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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