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# Core-Modified *meso*-Aryl Hexaphyrins with an Internal Thiophene Bridge: Structure, Aromaticity, and Photodynamics

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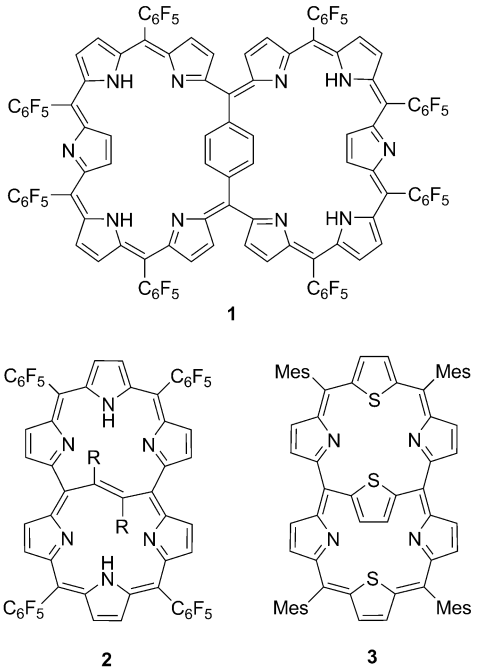
Expanded porphyrins continue to attract the attention of researchers because of their diverse applications.[1–4] Depending on the number of heterocycle/pyrrole rings, the nature of connectivity and the number of π electrons in conjugation, they can be aromatic, antiaromatic and Möbius aromatic in nature.[5] An increase in number of pyrrole rings and *meso* carbon atoms result in conformational flexibility, leading to nonplanar twisted structures.[6] Various synthetic approaches have been followed in the literature to avoid twisting of the structures, leading to planar aromatic 30π, 34π and 42π systems.[7–9] One approach to avoid the twisting of structure is to introduce an internal bridging group linking the *meso* carbon atoms. Using this approach, Osuka and co-workers reported the synthesis of near-planar decaphyrin **1** (Scheme 1) using an internally bridging 1,4-phenylene group.[10] Later, same group also synthesized planar hexaphyrin **2** using an internal vinylene bridge, and these molecules have an interesting electronic structure.[11,5b]

To the best of our knowledge, there are no reports on core-modified analogues of internally bridged expanded porphyrins. This report describes synthesis of core-modified hexaphyrins with an internal bridging thiophene following a simple and efficient synthetic approach. Spectroscopic and structural studies revealed that hexaphyrin macrocycle was planar and aromatic and that the internal bridging thiophene ring deviates from the mean plane of *meso* carbon atoms. For **3**, the deviation is 49°, while it is 73° for **4**. Compound **4** exhibits the expected 26π hexaphyrin electron conjugation, while the conjugation pathway for **3** has a hybrid character with contributions from both the 18π porphyrin-like skeleton and 26π hexaphyrin skeleton in the free-base form. Preliminary photophysical studies indicate an increase in singlet lifetime and two-photon absorption cross-section for the bridged systems.




Scheme 1. Examples of bridged expanded porphyrins.

For the synthesis of the thiophene-bridged hexaphyrins, we adopted the method similar to that used for the synthesis of **1**. The required 2,5-thienylbis(dipyrromethane) **7** was synthesized by condensing 2,5-thiophenedicarboxaldehyde **6a** with pyrrole in the presence of trifluoroacetic acid (TFA) as catalyst to afford **7** in 45% yield. **7** was further condensed with 2,5-bis(mesitylhydroxymethyl) thiophene **8** in the presence of 0.5 equiv of TFA and later oxidized with *p*-chloranil to afford **3** in 4% yield along with two side products, mono-condensed porphyrin (5,10-dimesityl-15,20-dipyrrolyl dithiaporphyrin) and tetramesityldithiaporphyrin (Supporting Information). Increasing the acid concentration led to more acidolysis product and reduced yield of **3**, while decreasing the acid concentration led to more mono-condensed product. By changing the acid catalyst to *p*-toluenesulphonic acid (*p*-TSA), no drastic change in the yield of **3** was observed; however, the amount of acidolysis product was reduced. By using this synthetic route, and varying the acid and its concentration, a maximum 6% yield of **3** was observed at

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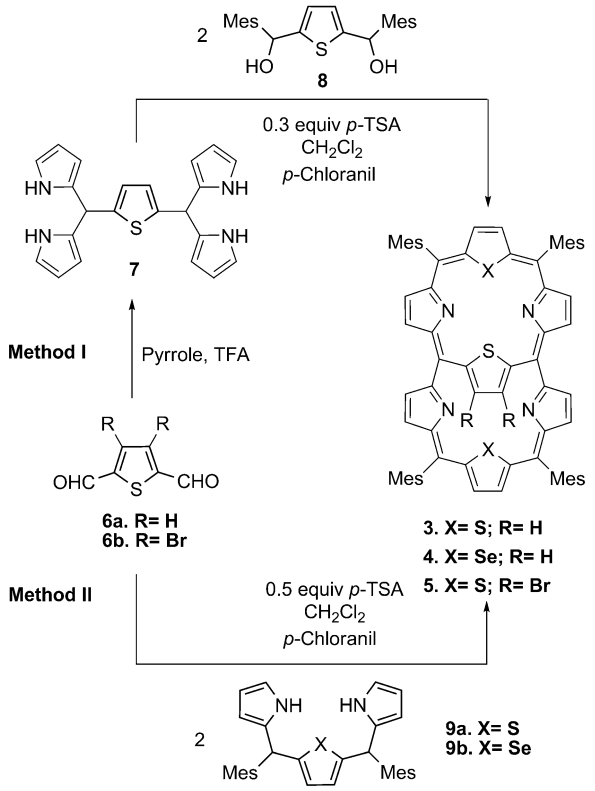
0.3 equiv of *p*-TSA (Scheme 2, method I) with trace amount of side products. To avoid the side-product formation, we adopted the modified synthetic method shown in Scheme 2 (method II). Precursor **9a** or **9b** was condensed with **6a** or




Scheme 2. The synthesis of internally thiophene-bridged *meso* aryl hexaphyrins.

**6b** in the presence of 0.5 equiv of *p*-TSA followed by oxidation with *p*-chloranil to afford the hexaphyrins (**3–5**) in 8–15% yield, while the rest are inseparable polymeric materials. As tripyrranes are less prone to acidolysis, no other side products were detected. All of the macrocycles are soluble in most polar organic solvents.

Mass spectrometry shows parent ion peaks at *m/z* 1051.7947 [M; $H^+$] for **3** and 1146.8234 [$M^+$] for **4**, thus confirming a composition that is consistent with the expected macrocycles (Supporting Information). The electronic absorption spectra of **3** and **4** were characterized by typical strong Soret-like band and weak low-energy Q bands (Figure 1). In the Soret region, **3** exhibits two bands (433 nm and 531 nm). The position of higher-energy band was similar to that found in dithiaporphyrin,[12] while the band at 531 nm has similar features to hexaphyrin.[13] However, **4** has only one Soret band at 567 nm and was found to be 1.6 times more intense than observed for **3**. The position of low-energy Q bands were typical of hexaphyrins. Upon protonation, the band at 531 nm in **3** is red-shifted to 570 nm with a shift value of 39 nm, while the band at 567 nm in **4** is red-

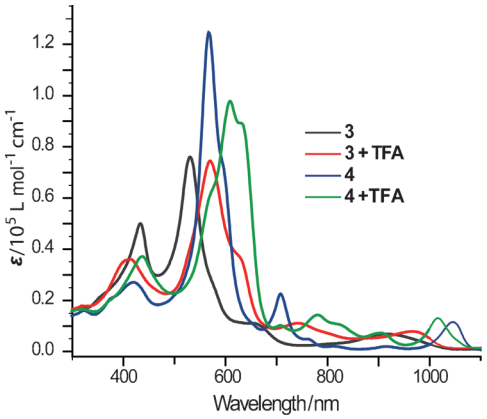



Figure 1. Electronic absorption spectra of **3**, **4** and their protonated forms formed by treatment with TFA.

shifted to 609 nm with a shift value of 42 nm, indicating an extension of the conjugation.

The $^1$H NMR spectrum of **3** in $CD_2Cl_2$ at 298 K is shown in Figure 2. In the downfield region, two doublets and three singlets with equal intensity are observed. The doublets (b

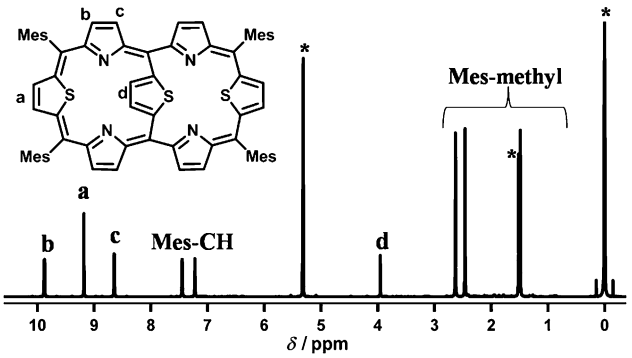



Figure 2. $^1$H NMR spectrum of **3** in $CD_2Cl_2$.

and c) at 9.8 and 8.6 ppm are assigned to four pyrrolic β-CH protons. This was further confirmed by 2D homonuclear correlation spectroscopy (COSY) (Supporting Information). The β-CH protons of the two thiophene rings in the core resonate as a singlet (a) at 9.17 ppm. The remaining two singlets, (Mes-CH) at 7.4 and 7.2 ppm, are assigned to the phenyl protons of the mesityl group. The methyl protons of mesityl resonate as three singlets (Mes-methyl) at 2.6, 2.4 and 1.49 ppm, respectively. The spectrum also contains a singlet (d) at 3.95 ppm, which is assigned to the bridging thiophene β-CH protons. The $\Delta\delta$ value (the shift difference between the bridged thiophene and the macrocyclic core thiophene β-CH protons) of 5.22 ppm shows that the bridging thiophene unit is experiencing an aromatic ring current effect from core porphyrin ring, suggesting that the bridging thiophene unit was not completely orthogonal with respect to the plane of macrocycle. Protonation of **3** using TFA in

$CDCl_3$ leads to small downfield shift in the pyrrole and thiophene β-CH protons in the $^1$H NMR spectrum of **3**. On the contrary, the β-CH protons of bridging thiophene experience shielding of 1.2 ppm upon addition of 2 equiv of TFA. However, excess addition of TFA (4 equiv) leads to downfield of the β-CH protons, and they appear at 4.2 ppm (Supporting Information, Figure S14). These observations clearly suggest that the conformation of the bridging thiophene group is sensitive to protonation, and significant changes occur in the conformation upon protonation.

The protonated inner NH peaks were observed only at low temperature (183 K) (Supporting Information). On adding 2 equiv of TFA, five different NH peaks were observed in the range of −1 to −7 ppm, suggesting the presence of different species that are chemically and magnetically inequivalent. On adding 4 equiv of TFA, a single peak at −4.7 ppm was observed, which indicates the saturation of protonation centers. Furthermore, the increase in the number of *meso*-mesityl methyl and pyrrole peaks (Supporting Information) is attributed to 1) a lack of rotational freedom owing to the internal bridging thiophene; and 2) a lowering of the symmetry, making the *meso*-mesityl rings inequivalent. The $^1$H NMR spectrum of **4** at 298 K shows the similar pattern as **3**. The β-CH protons of the bridging thiophene in **4** are more shielded relative to **3** and resonate at 1.35 ppm.

In an effort to understand the characteristics in the absorption spectra, we calculated molecular orbitals (MO) based on X-ray crystal structures and transition energies by TD-DFT method using Becke's three-parameter hybrid exchange functional and the Lee–Yang–Parr correlation functional (B3LYP) employing the 6–31G basis set for **3** (Figure 3). According to the frontier orbital diagram, the MOs of bridged hexaphyrin consists of the summation of the MOs in which electron density distribution is localized on porphyrin (HOMO−1, HOMO−2) and the MOs in which electron density distribution is localized on hexaphyrins (LUMO). The MOs where electron density distribution of **3** is localized on porphyrin give rise to porphyrin-like transition at 433 nm. Furthermore, the MOs where electron density distribution is localized on porphyrin moiety also affect hexaphyrin-like transition at 917 nm. From these data,

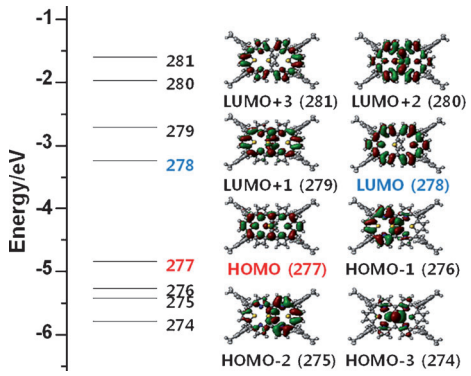



Figure 3. Energy level diagram and molecular orbitals of **3**.

we could assume that the hybrid character of bridged hexaphyrin cause two transitions; one is porphyrin-like transition, while the other is a hexaphyrin-like transition. Based on a comparison of the absorption spectra with the calculated results, we could assume that the peak at 433 nm is originated from porphyrin, that around at 531 nm region is mixed with hexaphyrin and porphyin, and one at 917 nm is caused by hexaphyrin. This hybrid character of **3** is also supported by the AICD plots, which show the 3D image of delocalized electron densities with a scalar field and illustrates the paramagnetic term of the induced current density; aromatic molecules show clockwise current density and antiaromatic species show counter-clockwise current density. The AICD plot shows that the ring currents flow along not only the hexaphyrin frame but also the bridged thiophene (Supporting Information). From this result, we could assume that the overall ring current density consist of the ring current flows, which are mainly localized on hexaphyrin and partially localized on porphyrin. On the other hand, the MO picture for **4** (Supporting Information) indicates that the electron density distribution is mainly localized on the 26π hexaphyrin skeleton and an intense Soret-like band observed at 567 nm is consistent with this conclusion.

For the evaluation of aromaticity, we calculated the NICS(0) values both within the inner porphyrin cavities and outside (Supporting Information). To avoid the local aromatic effect from the bridging thiophene ring, we chose to calculate the NICS values at the centers of two porphyrin-like cavities rather than at the center of the hexaphyrin skeleton. The highly negative NICS(0) values observed (for **3**, −14.0 and −13.3 ppm; for **4**, −18.3 and −17.9 ppm) at the inner cavities and positive values outside strongly suggest the aromatic nature of the bridging hexaphyrins. The reversible/quasi reversible redox waves from the cyclic voltammetric experiments further confirm such a conclusion.

The final confirmation of structures of **3** and **4** came from the single-crystal X-ray structural analyses (Supporting Information). In both **3** and **4**, the molecule is located on a crystallographic two-fold axis. As predicted from the spectral analyses, **3** contains two thiatripyrrin units, while **4** consists of two selenatripyrrin units and both the units are individually bridged by a thiophene moiety and the remaining four *meso* positions are occupied by the mesityl groups (Figure 4a). The bridged thiophene in **3** and **4** is in positional disorder, where two of the thiophene units overlap each other. Analysis of crystal structure reveals that the thiatripyrrin units in **3** (N1-S1-N2) are slightly deviated from the mean plane with deviations of 10.2°, 3.3° and 5.7°, where the selenatripyrrin in **4** (N1-Se1-N2) units are hardly deviated from the plane. However, the bridged thiophene unit in **3** and **4** are deviated by 49° and 73°, respectively (Figure 4b), while the *meso*-mesityl rings in **3** and **4** are almost perpendicular (89.3°; 81.5° for **3** and 83.4°; 78.1° for **4**) to the mean macrocyclic plane. Further, one of the *meso*-mesityl CH groups is in intermolecular hydrogen bonding interaction with *meso*-mesityl π-cloud (C23-H23c···Mes(π)) of the adjacent molecule that was used to generate the one-dimension-

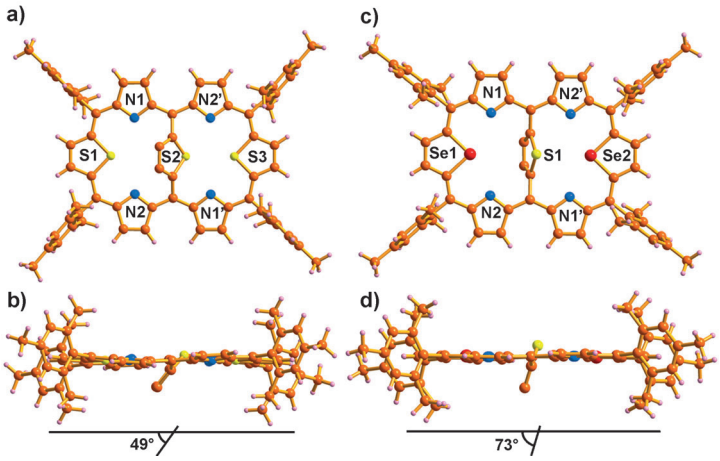



Figure 4. Single-crystal X-ray structures of **3** and **4**. a),c) Top and b),d) side views. Owing to disorder, the bridging thiophene β-CH hydrogen atoms are omitted in both views. C orange, H pink, N blue, S yellow, Se red.

al array in the solid state, with a distance and angle of 3.17 Å and 144°, respectively (Supporting Information).

The participation of bridging thiophene ring in the π electron conjugation pathway and the hybrid character observed for **3** can be rationalized in terms of a smaller tilt angle of 49° of the bridging thiophene ring with respect to mean plane of hexaphyrin skeleton. The observation of 433 nm Soret band (typical of 18π dithiaporphyrin) also supports such a conclusion. However, a near orthogonal tilt angle of 73° of the bridging thiophene group in **4** does not facilitate conjugation through bridging thiophene ring, and thus **4** exhibits a 26π electron conjugation pathway that is typical of hexaphyrins.

A representation of conjugation pathway for **3** before and after protonation is shown in Figure 5. To substantiate the hybrid character observed in **3** further, the hexaphyrin **5**

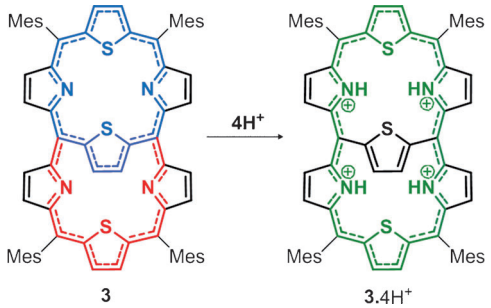



Figure 5. Proposed conjugation pathway of **3** and its protonated form.

was synthesized where heavier bromine atoms were introduced on the bridging thiophene ring. The heavier bromine atoms increase the tilt angle and make the bridging thiophene group almost orthogonal to the hexaphyrin plane. The electronic absorption spectrum of **5** (Supporting Information) exactly resemble that observed for **4**, thus justifying our conclusion.

The hybrid aromatic character in **3** prompted us to use this compound for nonlinear optical applications. The preliminary photophysical studies reveal an increase of singlet lifetime by two times upon introduction of bridge, which is presumably due to increased rigidity of the macrocycle.[9] The two-photon absorption cross-section (TPA) for **3** is 2.6 times higher (1000 GM for dithiahexaphyrin and 2600 GM for **3**), which proves that this class of molecules are promising candidates for NLO applications.

In conclusion, we have demonstrated the syntheses of two new internally *meso* thiophene-bridged core-modified hexaphyrins by a simple and efficient method. Spectroscopic and structural data reveals the aromatic nature of both the hexaphyrins. A comparison of structures of bridged hexaphyrins **3** and **4** with the corresponding hexaphyrins without an internal bridge reveal the following:[13,14] 1) introduction of internal bridging group makes the hexaphyrin skeleton rigid, thus preventing ring inversion of heterocyclic ring; and 2) the hexaphyrin skeleton in the bridged structure are more planar, thus facilitating better a π conjugation pathway and therefore increasing the aromaticity. Such structural changes lead to changes in the electronic structure, which are important from the point of view of their application as nonlinear optical materials. Detailed studies are underway to probe these properties further.

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**Keywords:** aromaticity · bridged systems · core modification · expanded porphyrins · macrocycles

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