π-Conjugated macrocycles from thiophenes and benzenes†

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π-Conjugated macrocycles consisting of thiophenes and benzenes exhibit benzenoid features for 4*n*π macrocycles, whereas (4*n* + 2)π macrocycles are annulenoid due to rapid interconversion between quinoid and Kekule canonical forms in the benzene units.

Large π-conjugated macrocycles are attractive synthetic targets due to their structural features, optical properties and as a synthetic challenge. The electronic properties of such macrocycles are dependent on the delocalization of the π electrons. Annulenoid macrocycles exhibit diatropic or paratropic ring current effects depending on the number of π electrons in the system. Cyclophanes[1] and porphyrins[2] are examples of such annulene type macrocycles. A few conjugated macrocycles do not display significant ring current effects and are considered benzenoid in nature. For example, α-conjugated cyclo[*n*]thiophenes exhibit benzenoid[3] characteristics. In general the macrocyclic property can be tuned by the nature of a π sub-unit involved in conjugation. A benzene in an annulenoid can adopt a Kekule or a quinoid cannonical form, while contributing to the overall delocalization of π electrons. Even though such a possibility has been discussed,[4] a quinoid-type benzene in air-stable aromatic macrocycles are typically unknown in literature. Herein, we report a straightforward synthesis of air-stable non-pyrrolic porphyrin type macrocycles, **1** and **2**. Both **1** and **2** have a blend of thiophene and benzene π sub-units, wherein one of the benzene rings can be forced to adopt a quinoid form in the 30π aromatic framework of **2**. Such a quinoid form is not essential to maintain conjugation with the 20π network in **1** (Chart 1).

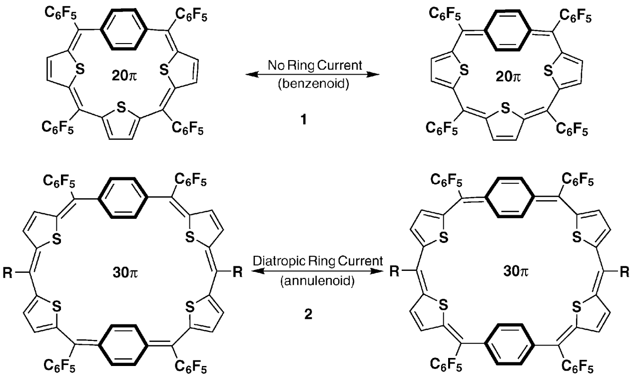
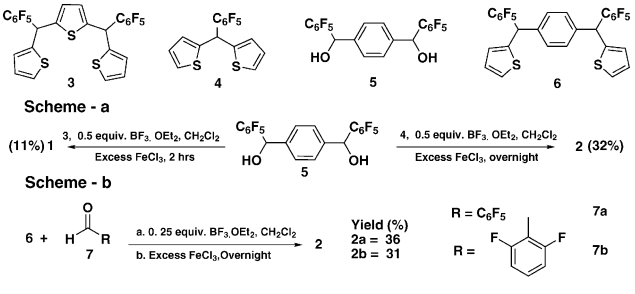


Chart 1

1 and **2** were synthesized from thiophene and benzene derivatives (Scheme 1(a)). 1,4-bis[(pentafluorophenyl)(hydroxy)-methyl]benzene, **5**, was condensed with 2,5-bis[(pentafluorophenyl)(thiophen-2-yl)methyl]thiophene, **3**, in equimolar concentrations, with $BF_3{\cdot}OEt_2$ as the catalyst. Further, oxidation by $FeCl_3$ and column chromatographic purification yielded **1** in 11% yield. In an identical procedure 5-pentafluorophenyl-dithienylmethane, **4**,[5] was condensed with **5** to obtain **2a** in 32% yield. **2a–2e** can be synthesized in better yields (Scheme 1(b)) by the acid catalyzed condensation of 1,4-bis[(pentafluorophenyl)(thiophen-2-yl)methyl]benzene, **6**, with aryl aldehydes, **7a–7e**, such as pentafluorobenzaldehyde (**7a**) and 2,6-difluorobenzaldehyde (**7b**). We were also successful by using other electron-withdrawing aldehydes such as *p*-nitrobenzaldehyde (**7c**), 2,6-dichlorobenzaldehyde (**7d**) and 2-chloro-6-fluorobenzaldehyde (**7e**) (ESI†).

The composition of all the macrocycles were confirmed from mass spectrometric analysis (ESI†). The electronic absorption spectrum (Fig. 1) of **1** shows a strong band at 398 nm ($\varepsilon = 4.4 \times 10^4$) followed by two weaker absorptions at 543 nm (0.6×10^4) and 569 nm (0.6×10^4). **2a** shows a split absorption at 520 nm (30×10^4) and 540 nm (31×10^4) followed by low energy absorption at 613 nm (4.9×10^4), 664 nm (6.9×10^4) and 721 nm (13×10^4). Replacing the *meso*-pentafluorophenyl substituent by 2,6-difluorophenyl did not change the absorption pattern, as depicted in Fig. 1. **1** and **2** have formal 20π and 30π electron counts, respectively, along their conjugated pathway. The red shift in absorptions for **2** is attributed to the extended conjugation and the higher intensity is due to the aromatic nature of the macrocycle as compared to **1**.



Scheme 1 Synthesis of **1** and **2**.

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† Electronic supplementary information (ESI) available: Details of synthesis, UV-Vis, FAB mass, VT NMR for **1** and **2a**, and F···F non-bonded interactions in **2b**. See DOI: 10.1039/b715553k

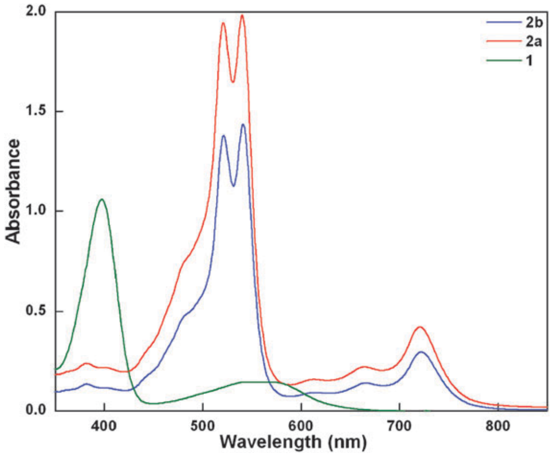

Fig. 1 Electronic absorption spectrum of **1** (10^{-5} M), **2a** (10^{-6} M) and **2b** (10^{-6} M) in CH_2Cl_2.

The effect of π-electron delocalization in **1** and **2** could be well understood from their ^{1}H NMR spectra. The phenylene protons of **1** appear as a singlet at δ 7.53 ppm. Due to C_2 symmetry, the thiophene protons resonate as a singlet at 6.47 ppm and as two doublets at 6.69 and 6.59 ppm. The δ values for **1** signify neither diatropic nor paratropic ring current effects and hence appear to be benzenoid in nature. On the other hand, **2a** and **2b** show diatropic ring current effects as illustrated by the upfield shift of phenylene protons and downfield shift of thiophene protons. The phenylene protons of **2a** resonate at 4.74 ppm, an upfield shift of more than 3 ppm compared to an unsubstituted benzene.[6] The thiophene protons appear as two doublets at 8.82 and 8.76 ppm, revealing a downfield shift of nearly 2 ppm with respect to an unsubstituted thiophene.[6] **2b** also exhibits a similar NMR pattern with a singlet for phenylene protons at 4.53 ppm and two doublets for the thiophenes at 9.0 and 8.9 ppm. In both, **1** and **2**, the rapid flipping of the phenylene ring cannot differentiate shielding and deshielding effects on its protons at room temperature. Even upon lowering the temperature to 178 K for **2a** (223 K for **1**) the ^{1}H NMR spectrum does not show any significant difference (ESI†). In **2**, additionally, the effective π-electron delocalization hastens the exchange between the canonical forms (Kekule ⇔ quinoid) in both the phenylene rings. These two process are too fast compared to the NMR time scale and hence the phenylene protons appear as a singlet even at low temperatures.

Further confirmation of the proposed structure comes from single-crystal X-ray diffraction analysis.‡ **2b** shows a bowl type conformation in the solid state (Fig. 2). The deviation from planarity is attributed to the tilting of the four thiophene rings and the two phenylene rings from the mean plane defined by the six *meso* carbons. The two phenylene rings (A and B) deviate by 27.24 and 17.19°, while the four thiophene rings (containing S1, S2, S3 and S4) deviate by 25.76, 14.99, 22.63 and 27.51°, respectively from the mean macrocyclic plane. The bond lengths between the adjacent carbon atoms along the conjugated pathway vary from 1.34 to 1.45 Å, indicative of aromatic delocalization throughout the macrocycle. The distance between the *meso* carbon and paraphenylene carbons (C17–C14; C10–C11) for ring A was equal and found to be 1.418 Å, while it is 1.421 Å (C28–C27) and 1.448 Å (C34–C31) for ring B. This shows the bond distances between *meso* carbons and ring B are more towards single bond nature than those of ring A.[7] This crystallographic observation shows preferential benzenoid and quinoid sites in the structure. The above argument do not purport to say that one side of the molecule in the crystal structure is always having benzenoid form, and quinoid form on the other side, but it shows that there is more probability for the benzenoid form in ring B and quinoid form in ring A. Due to full resonance within rings A and B, they are indistinguishable from each other. This is consistent with the proton NMR results. Further analysis of the crystal packing revealed intermolecular interactions through C–H···F hydrogen bonds.[8] Two C–H···F interactions (C39–H39···F15 (symm: x, $2.5 - y$, $1/2 + z$) 2.55 Å, 154° and C25–H25···F5 (symm: x, $1 + y$, z) 2.58 Å, 134°) are strong enough for the formation of a two-dimensional supramolecular architecture (Fig. 3). Apart from hydrogen bonds three different F···F non-bonded interactions[9] (F8···F5, F12···F19, F17···F21) were also observed in the crystal lattice (ESI†). The distance between the corresponding fluorine

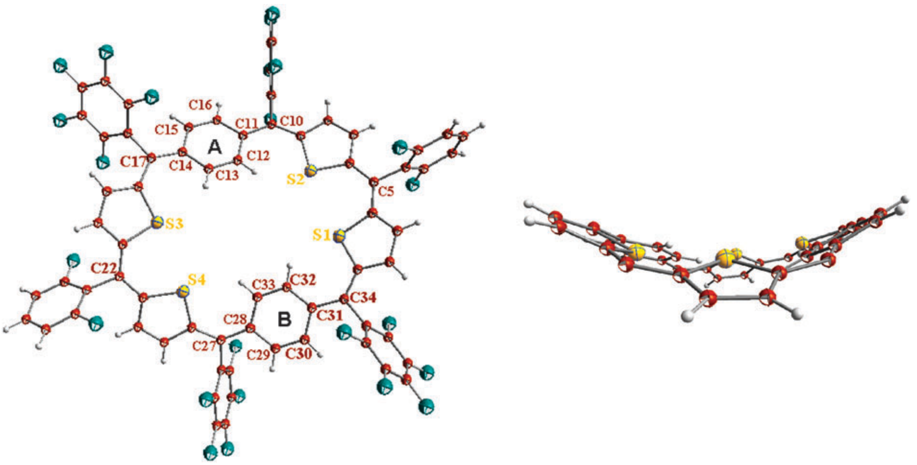

Fig. 2 X-Ray crystal structure of **2b**. Thermal ellipsoids are drawn to 50% probability. Solvent molecules are omitted for clarity. Top view (left) and side view (right) (*meso*-aryl rings are omitted in the latter view for clarity).

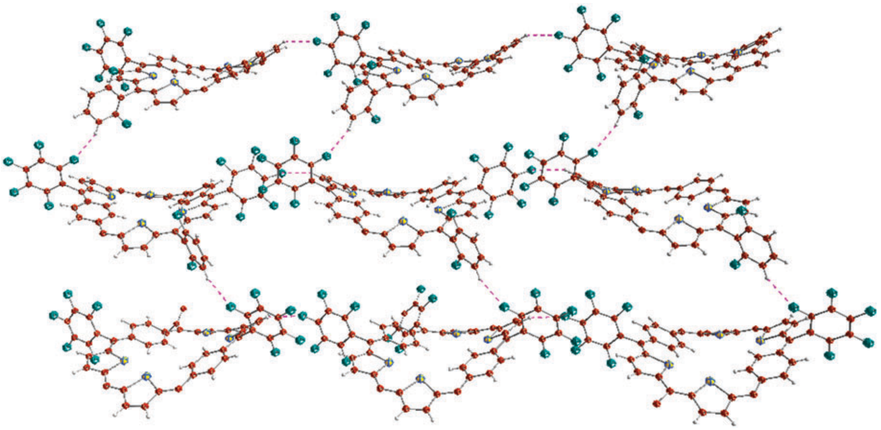

Fig. 3 Supramolecular architecture of **2b** due to C–H···F intermolecular H-bonds as specified by dotted lines. *Meso*-aryl rings which are not involved in hydrogen bonding are omitted for clarity.

atoms are in the range of 2.69 to 2.82 Å, which positions them within the range of a non-bonded interaction (van der Waals radius for fluorine is 1.47 Å).

In conclusion, we have devised a simple and ring-size selective one-pot synthesis of benzene incorporated macrocycles **1** and **2**. The extended delocalization of the macrocycle, **2**, has a profound effect on the benzene aromaticity, thereby complying the 6π arene ring current to be a part of the 30π macrocyclic diatropic ring current. Therefore, one of the two phenylene rings in **2** should exist in quinoid form to sustain the 30π ($4n + 2$ rule) aromaticity. To the best of our knowledge, **2** represents the first such example of having a quinoid form for benzene in a π-conjugated macrocycle.

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Notes and references

‡ Crystals were grown by slow evaporation of *n*-hexane into a chloroform solution of **2b**. *Crystallographic data* of **2b**: $C_{70}H_{22}F_{24}S_4$, M_r = 1447.15, monoclinic, space group $P2_1/c$, a = 19.7374(4), b = 19.0689(4), c = 22.0885(5) Å, β = 114.818(10)°, V = 7544.6(3) Å^3, Z = 4, D_c = 1.589 g cm^{-3}, T = 173 K, $R1$ = 0.0720, $wR2$ = 0.1932. CCDC 663304. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715553k

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