Triphyrins(n.1.1)

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# Synthesis and Switching the Aromatic Character of Oxatriphyrins(2.1.1)**

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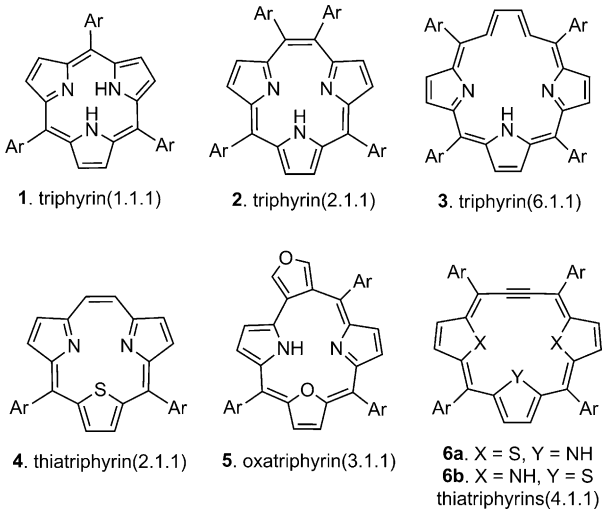
***Abstract:*** *Triangularly shaped, contracted porphyrinoids belong to a group of molecules where the geometry significantly modifies the observed electronic properties. The need for a controllable, effective, and widely applicable approach to triphyrins drives extensive research towards macrocyclic materials that act as potential controlling motifs by switching their aromaticity. Two isomeric thiophene-fused triphyrins-(2.1.1) were synthesized by applying an innovative approach. Spectroscopic techniques (NMR, UV/Vis) show that both macrocycles are aromatic and quantitatively convert into anti-aromatic structures after reduction with a zinc amalgam. The reduced forms were stabilized through boron(III) coordination, thereby allowing the observation of anti-aromatic 16π delocalization within a contracted porphyrin.*

Porphyrins, or more broadly porphyrinoids, are regarded as an elementary motif for fundamental studies in several scientific fields,[1] including for medicinal applications[2] and modern optoelectronics.[3] Attention focuses on the search for organic alternatives of currently, widely explored inorganic molecular devices.

Triphyrins(*n*.1.1) (Scheme 1) are a new class of porphyrinic macrocycles with a reduced number of donors compared to porphyrins and are created by the removal of at least one pyrrole subunit. The rational approach for the synthesis of boron(III) triphyrin(1.1.1) **1**-B,[4] boron(III) subporphyrazines,[5] and boron(III) subphthalocyanines,[6] involves a templating effect. The formation of free-base subpyriporphyrin[7] and several triphyrins(*n*.1.1) (Scheme 1), where *n* varies from 2 to 6,[8] required a stepwise strategy. The triphyrin(*n*.1.1) subgroup is rather small and there are only a few examples of such macrocycles (Scheme 1). Nevertheless, they reveal intriguing properties, including the topology-dependent aromaticity switching of triphyrin(6.1.1) **3** on coordination.[9] The boron(III) triphyrin(1.1.1) complexes **1**-B have demonstrated a variety of optoelectronic properties, such as nonlinear optical absorption and high emission quantum yields, that are directly related to the 14π aromatic delocalization path.[10] An alternative route to tune the properties of triphyrins is a modification of their coordination unit by replacing nitrogen atom(s) with other heteroatoms to yield aromatic thiatriphyrin(2.1.1) **4**,[8d] oxatriphyrin(4.1.1),[8i] and thiatriphyrins(4.1.1) **6**,[8h] as well as non-aromatic oxatriphyrin(3.1.1) **5**.[8g] On the other hand, the aromatic character of triphyrins(*n*.1.1) has not been explored to date, and research concentrates on an unmodified 14π electron circuit. All the above-mentioned aspects of triphyrin chemistry stimulate the intensive search for nontrivial synthetic routes that lead to controllable triphyrin scaffolds with appropriately defined functionality.




***Scheme 1.*** Triphyrins(*n*.1.1).

Here we report on the synthesis of two isomeric thiophene-fused oxatriphyrins(2.1.1) by a coherent method involving the use of precisely crafted synthons. Both macrocycles are aromatic with alternative delocalization and undergo reduction to afford anti-aromatic structures that can be stabilized as boron(III) complexes.

The reported rational approach to form meso-substituted triphyrins(2.1.1) **11** and **13** requires an effective synthesis of the synthons **8** and **10**. Suzuki–Miyaura coupling was applied to achieve this demanding task (Scheme 2) under conditions adapted from those previously reported for heterocycles.[11] The formation of **7** and **9** has been accomplished in yields of 80 and 85%, respectively, starting from commercially available substrates. Both substituted thiophenes **7** and **9** are stable and can be stored without any degredation for several weeks. The deprotection step required the thermal removal of the

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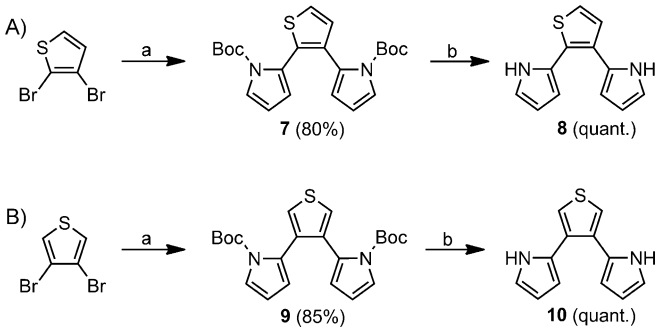



***Scheme 2.*** Formation of thiophene synthons. Conditions: a) *N*-Boc-2-pyrroleboronic acid (3 equiv), $Pd(OAc)_2$ (2% per halogen), SPhos (4% per halogen), $K_3PO_4$ (4 equiv), *n*BuOH, 100 °C, 4 h; b) $HOCH_2CH_2OH$, reflux, inert atmosphere, 1 h).

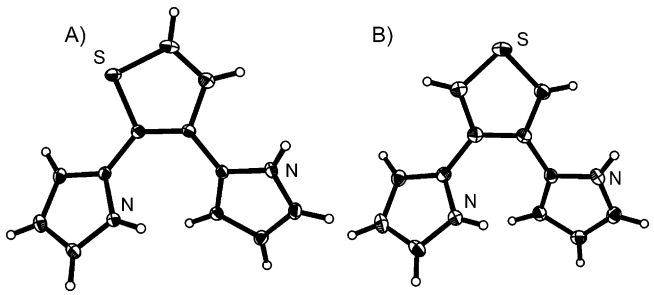
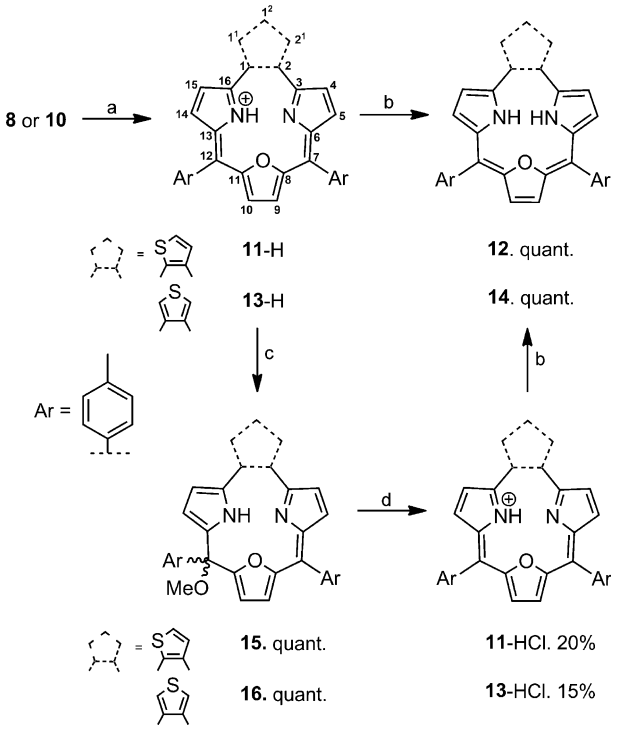



***Figure 1.*** X-ray structures of **8** (A) and **10** (B).




***Scheme 3.*** Formation and reduction of oxatriphyrins(2.1.1). Conditions: a) 2,5-bis(*p*-tolylhydroxymethyl)furan (1 equiv) $CH_2Cl_2$, $BF_3{:}Et_2O$, DDQ (3 equiv); b) Zn/Hg, $CDCl_3$; c) $MeOH/Et_3N$; d) $CH_2Cl_2$/HCl. DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

*tert*-butyloxocarbonyl (Boc) group in refluxing ethylene glycol and led to the quantitative formation of **8** and **10**. Formation of the desired products was confirmed by spectroscopic analysis (see the Supporting Information) as well as X-ray analysis (Figure 1).[12] The substitution affects the C–S bond lengths in **8** and **10**. The unsymmetrical substitution of thiophene in **8** causes a difference within the C–S bonds (1.704(3) Å and 1.678(1) Å), while the lengths of the C–S bonds in the fully symmetric **10** are equal (1.705(2) Å and 1.701(2) Å). The deprotected reagents are less stable and need to be condensed without any extended storage.

The formation of target oxatriphyrin(2.1.1) **11** was achieved by condensation of **8** and 2,5-bis(*p*-tolylhydroxymethyl)furan[8g] in an equimolar ratio under standard Lindsey conditions (Scheme 3). The macrocycle was isolated solely as the monoprotonated form **11**-H. An unidentified counterion obtained during condensation was subsequently replaced by a chloride ion (see the Supporting Information). The anion x exchange process involves a quantitative conversion of the isolated macrocycle into a phlorin-like skeleton followed by acidification with HCl (Scheme 3, paths c and d), thereby resulting in the final formation of **11**-HCl in 20% overall yield. **11**-HCl has aromatic character, as proven by the features in the $^1$H NMR spectrum. The rather large and planar part of the final macrocycle—a thiophene and two pyrrole moieties—results in the high degree of aggregation observed in the NMR spectra. A nicely resolved spectrum was obtained after the addition of 1% TFA (Figure 2A), which increases the solubility and prevents aggregation (see the Supporting Information).

The lack of symmetry in **11**-HCl is reflected by the presence of eight β-H heterocyclic signals in the aromatic region ($\delta = 9.2$–$8.3$ ppm). The full assignment given in Figure 2A was made on the basis of 2D experiments (NOESY, COSY), taking an NOE contact between H($2^1$) and H(4) as the starting point. In contrast to other aromatic porphyrinoids, the resonance of the inner hydrogen atom in **11**-HCl is strongly downfield shifted ($\delta = 11.5$ ppm). This peculiar shift reflects a deshielding contribution from a strong intramolecular N···HN hydrogen bond acting within the cavity, which dominates the typical shielding influence of a diatropic ring current. The effect resembles one reported previously for an N-fused porphyrin[13] and other triphyrins(*n*.1.1).[7,8f,g] The aromaticity of **11**-HCl can be accounted for by the 14 π path of $\mathbf{11}^2$, which is typical for triphyrins(2.1.1). This interplays, however, with the alternative 18 π delocalization route of $\mathbf{11}^3$, which is imposed by 2,3-thiophene fusion (Figure 3). To shed additional light on the control of the electronic structure, a thiophene ring was fused to the oxatriphyrin(2.1.1) backbone at its β positions, with the aim of limiting the 14 π electron route in favor of the "extended" 18 π electron one, albeit with involvement of the sulfur atom on the perimeter.

By following the synthetic approach applied for **11** (Scheme 3), synthon **10** was condensed with 2,5-bis(*p*-tolylhydroxymethyl)furan to eventually form monoprotonated oxatriphyrin(2.1.1) **13**-HCl in 15% yield. An unidentified counterion obtained during condensation was replaced with

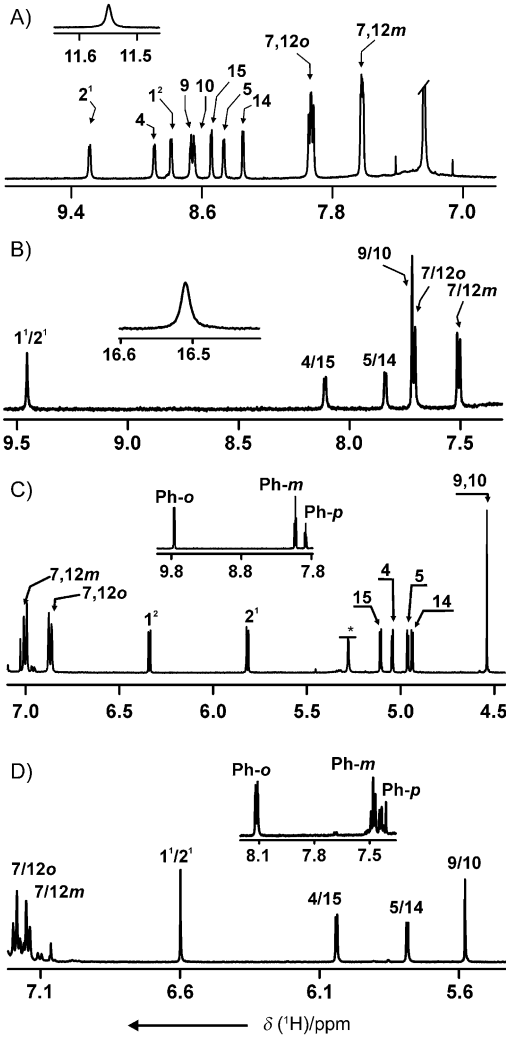



***Figure 2.*** $^1$H NMR spectra. A) **11**-HCl ($CDCl_3$ + 1% TFA, 300 K), B) **13**-HCl ($CDCl_3$ + 1% TFA, 300 K), C) **17** ($CDCl_3$, 300 K), D) **18** ($CDCl_3$, 300 K). The insets show a downfield region of the NH protons (A, B) and axial phenyl group (C, D).

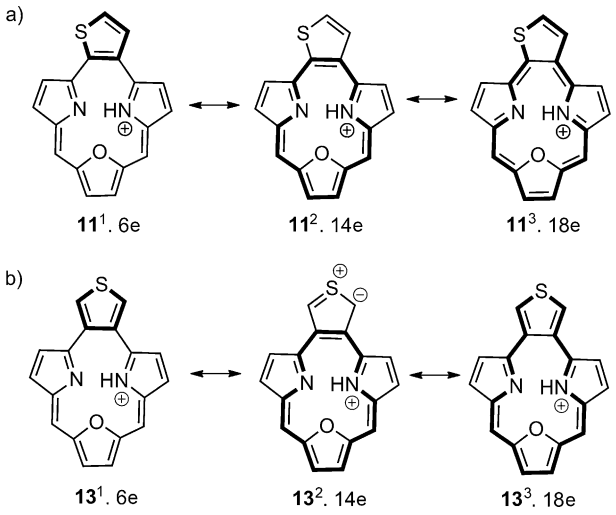



***Figure 3.*** Resonance contributors for **11**-H (A) and **13**-H (B).

a chloride by using the same procedure as reported for **11**-HCl (see the Supporting Information). **13**-HCl behaves similarly to **11**-HCl and requires the use of trifluoroacetic acid to minimize the aggregation. The $^1$H NMR spectrum (Figure 2B) reveals the diminished macrocyclic aromaticity compared to **11**-HCl. The α-H thiophene resonance is observed at $\delta = 9.32$ ppm, whereas the pyrrole and furan resonances are located at $\delta = 8.0$–$7.8$ ppm. The resonance contributors for **11**-H and **13**-H are presented in Figure 3. **11**$^3$ and **13**$^3$ include the sulfur atom in the aromatic conjugation.

The difference in the aromatic character between **11**-H and **13**-H is related to the relative participation of the principal aromatic contributors, which implies 14π (**11**$^2$) and 18π (**11**$^3$, **13**$^3$) delocalization pathways. The 6π involvement (**11**$^1$ and **13**$^1$) in both compounds is insignificant (Figure 3). Thus, the 14π electron path is essential in **11**-H, but negligible in **13**-H. The 18π route (**13**$^3$) is solely responsible for the aromatic character of **13**-H.

DFT optimization of oxatriphyrin(2.1.1) monocations showed a planar structure stabilized by an N···HN hydrogen bond within the internal cavity (Figure 4). The N-N distances

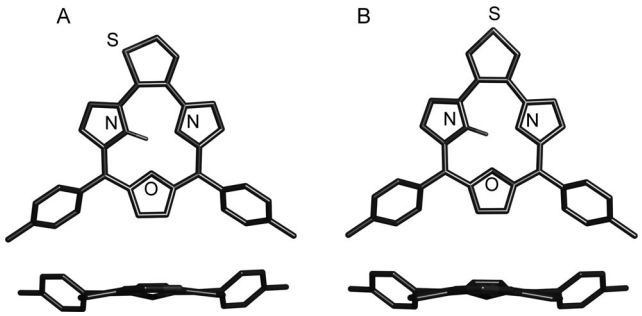



***Figure 4.*** DFT-optimized structures of **11**-H (A) and **13**-H (B).

(2.57 Å **11**-H 2.60 Å **13**-H) significantly increased in the neutral forms (2.70 for **11** and 2.75 Å for **13**; see Figure S26 in the Supporting Information). The bond lengths within the frameworks of **11**-H and **13**-H are consistent with those expected for aromatic macrocycles. In particular, the aromaticity of **11**-H and **13**-H is clearly demonstrated by the equalization of the $C_\alpha$–$C_{meso}$ distances (**11**-H: C(6)-C(7) 1.406 Å, C(7)-C(8) 1.431 Å; **13**-H: (C(6)-C(7) 1.404 Å, C(7)-C(8) 1.432 Å). The macrocyclic aromaticity has a relatively small effect on the thiophene moieties. The $C_\beta$–$C_\beta$ bonds are characteristically longer than the $C_\alpha$–$C_\beta$ bonds, closely resembling the pattern found in thiophene or tetrathiaporphyrinogen. The reverse is true for thiaporphyrinoids,[16] where the thiophene is built into the macrocyclic ring at two $C_\alpha$ positions. An elongation of the C(1)–C(2) bond of **11**-H is evident. The observed aromaticity is consistent with NICS values calculated for the cation **11**-H ($\delta = -11.4$ ppm) and the neutral form **11** ($\delta = -9.4$ ppm), and are similar to that of simple oxatriphyrin(2.1.1) ($\delta = -13.8$ ppm). The lower aromatic character of **13**-H was also confirmed by NICS ($\delta = -3.7$ ppm).

The presence of"porphyrinic" patterns in the UV/Vis electronic spectra of **11**-H and **13**-H confirm the aromaticity.

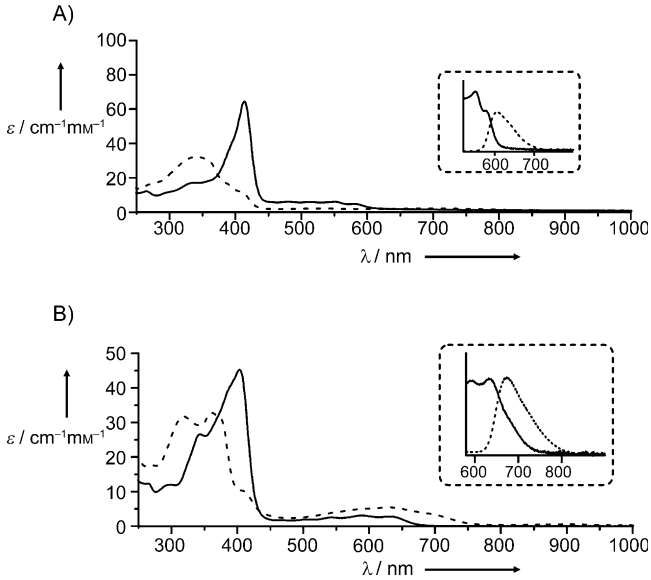
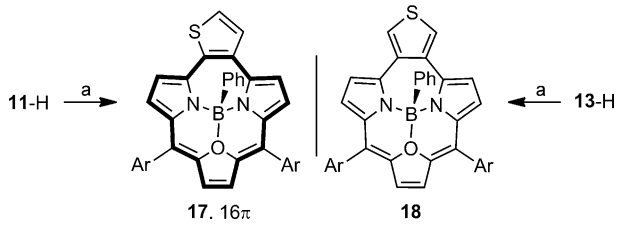



***Figure 5.*** Absorption ($CH_2Cl_2$, 298 K) and emission ($CH_2Cl_2$, 298 K dotted, insets) spectra for: A) **11**-HCl (solid line) and **17** (dashed line) and B) **13**-HCl (solid line) and **18** (dashed line).




***Scheme 4.*** Formation of boron(III) complexes. Conditions: a) $PhBCl_2$, $Et_3N$, toluene, reflux). Ar = *p*-Tol.

The spectra were measured in a solution of methanol/1% trifluoroacetic acid to avoid the possible aggregation observed in dichloromethane solutions (see the Supporting Information). The Soret-like band (B-band) detected at 411 (**11**-H) and 409 nm (**13**-H) is accompanied by a set of four Q-bands (480–650 nm; Figure 5). The macrocycles show a photoluminescence with a maximum at 602 nm (**11**-HCl, $\Phi = 0.038$) and 660 nm (**13**-HCl, $\Phi = 0.012$) and a Stokes shift of 30–40 nm, as observed previously for triphyrins.[4,8]

Cyclic voltammetric studies (see Figures S24 and S25 in the Supporting Information) demonstrate that **11**-HCl and **13**-HCl undergo two consecutive, semireversible one-electron reductions with half-wave potentials for **11**-H of (1) −718 mV and (2) −1186 mV and for **13**-H (1) −698 mV and (2) −1128 mV (versus $Fc/Fc^+$ in $CH_2Cl_2$). Reduction with a zinc amalgam (Zn/Hg) has been used to test the possibility of transforming diatropic **11**-H and **13**-H into paratropic forms. The two samples were prepared in an inert atmosphere in deuterated chloroform and treated with an excess of zinc amalgam to give two-electron reduced compounds **12** and **14,** respectively, with a changed aromatic character (see Figures S23 and S27 in the Supporting Information). The NICS values ($\delta = +14.9$ ppm and $\delta = +4.9$ ppm, respectively) obtained for the two macrocycles confirmed the formation of anti-aromatic circuits.

The reaction of **11**-H or **13**-H with an excess of phenylboron(III) dichloride gave complexes **17** or **18**, where both triphyrins act as dianionic ligands (Scheme 4). Reduction of both ligands during the insertion ($Et_3N$ used as a reducing agent) significantly modifies the observed properties. All the β-resonances of **17** are located in the $\delta = 4.5$–5.1 ppm range (Figure 2C), noticeably upfield compared to those of **11**-H, but also to those of relevant porphodimethenes[14] resembling weakly anti-aromatic 22-oxybenziporphyrin[15] and [16]thiaethyneporphyrin,[16] and in the range previously observed for a 16π path in porphyrin.[17b] Evidently the fused thiophene ring of **17** is not involved in 20π delocalization, and the final complex prefers the 16π anti-aromatic path proven by the NMR spectra and NICS value of $\delta = +17.9$ ppm. A strongly downfield shift of the *ortho* protons of the axial phenyl group ($\delta = 9.85$ ppm, Figure 2C (inset), compared to phenylboronic acid, $\delta = 7.8$ ppm) proves a deshielding influence of the paratropic current observed above (below) the macrocycle plane. Thus, the presence of the axial phenyl group creates another spectroscopic probe that can quantify the anti-aromatic character not shown before. The opposite direction of the observed effect is a complement to the well-established upfield shift recorded for substituents located above (below) the plane of an aromatic compound (a strong shielding effect). The UV/Vis spectrum of **17** confirms its anti-aromaticity (Figure 5A).[18] In addition, **17** remain absolutely silent in fluorescence experiments.

In contrast to **17**, the paratropicity of **18** (NICS = +1.4 ppm) is less noticeable (Figure 2D), which indicates that the 20π contributor involving the external sulfur atom is less essential. Nevertheless, the *ortho* protons of the axial phenyl group resonate at $\delta = 8.11$ ppm, which is slightly downfield shifted. **18** does not show any fluorescence over the whole tested region.

In conclusion, an efficient synthetic approach leading to thiophene-fused oxatriphyrins(2.1.1) has been developed. The generality of the method has been proven by the formation of two feasible isomers. Both macrocycles are aromatic and extend the aromatic delocalization over the external sulfur atom of the rigid $C_2$ bridge derived from the specifically linked-in thiophene ring. Both fused macrocycles can be reduced, and the reduced forms were entrapped as stable boron(III) complexes, thus making them easier to manipulate. A paratropic current (16π) was observed for the very first time in a triphyrin skeleton.

The thiophene-fused oxatriphyrins(2.1.1) represent unique and stable heterotriphyrins and are part of the group of triphyrins(2.1.1)—a promising material for effective absorbers and emitters through modification of the electronic structure by the triangular geometry significantly changing the dipole distribution. On the other hand the observed ability to switch between aromatic/non-aromatic/anti-aromatic structures opens another aspect of exploration for compounds capable of acting as controlling motifs.

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