## Synthesis, Optical Properties, and Electronic Structures of Fully Core-Modified Porphyrin Dications and Isophlorins

Masaru Kon-no,<sup>[a, b]</sup> John Mack,<sup>[c]</sup> Nagao Kobayashi,<sup>\*[c]</sup> Masahiko Suenaga,<sup>[b]</sup> Kenji Yoza,<sup>[d]</sup> and Teruo Shinmyozu<sup>\*[a]</sup>

**Abstract:** The synthesis, structures, optical properties, and electronic structures of the tetraphenyltetrathiaporphyrin dication ( $S_4TPP^{2+}$ , **6**) and tetrakis(pentafluorophenyl)tetrathiaisophlorin ( $S_4F_{20}TPP$ , **7**) are reported.  $S_4TPP^{2+}$  (**6**) and  $S_4F_{20}TPP$  (**7**) were synthesized by acid-catalyzed condensation of the corresponding hydroxylmethylthiophene, followed by oxidation. The electronic structures of  $S_4TPP^{2+}$  (**6**) and  $S_4F_{20}TPP$  (**7**) were analyzed by using UV/Vis-absorption spectroscopy and by magnetic circular dichroism (MCD) spectroscopy and the bands were assigned by using time-dependent density functional theory (TD-DFT) and ZINDO/s calculations. A red-shift of the Q bands of  $S_4TPP^{2+}$  (6) is observed relative to the spectra of tetraphenylporphyrins because a desta-

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bilization of the HOMO leads to a narrower HOMO–LUMO band-gap. Michl's perimeter model was used to assign the absorption bands and MCD spectra of  $S_4F_{20}TPP$  (7). Current-density maps and nucleus-independent chemical-shift (NICS) calculations of  $S_4TPP^{2+}$  (6) and of a model compound predict marked modification to the diamagnetic ring current, whilst nonaromatic character is predicted for  $S_4F_{20}TPP$  (7).

## Introduction

Porphyrinoid compounds have been widely studied owing to their unique optical properties and rich redox chemistry. The role of porphyrinoid compounds within biochemistry has long inspired the study of synthetic porphyrinoid compounds. Chlorophylls play pivotal roles in photosynthesis during light-harvesting and in the conversion of sunlight into chemical energy.<sup>[1]</sup> Hemes in blood play a key role in oxygen-transport and -storage in aerobic organisms.<sup>[2]</sup> Interest has recently focused on core-modified porphyrins, in

- [a] Dr. M. Kon-no, Prof. T. Shinmyozu Institute for Materials Chemistry and Engineering (IMCE) Kyushu University, 6-10-1 Hakozaki, Higashi-ku Fukuoka 812-8581 (Japan)
   E-mail: shinmyo@ms.ifoc.kyushu-u.ac.jp
- [b] Dr. M. Kon-no, Dr. M. Suenaga Department of Chemistry, Graduate School of Sciences Kyushu University, 6-10-1 Hakozaki, Higashi-ku Fukuoka 812-8581 (Japan)
- [c] Dr. J. Mack, Prof. N. Kobayashi Department of Chemistry, Graduate School of Science Tohoku University, Sendai 980-8578 (Japan) E-mail: nagaok@m.tohoku.ac.jp

[d] Dr. K. Yoza Bruker AXS K. K.
3-9 Moriya-cho, Kanagawa-ku, Yokohama Kanagawa 221-0022 (Japan)

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which one-or-more of the core nitrogen atoms is replaced by another main-group element, because these compounds often have unusual structures, optical- and redox properties, and reactivities.<sup>[3,4]</sup> In recent years, there has been increasing interest in core-modification with Group 16 heteroatoms. Sukumaran, Detty, and co-workers studied tellurium-containing 21- and 21,23-core-modified porphyrins,<sup>[5]</sup> whilst Ono and co-workers have studied the partial core-modification of tetrabenzoporphyrin- and tetraphenyltetrabenzoporphyrin ligands with oxygen- and sulfur atoms.<sup>[6]</sup> Only minor changes were observed in the optical spectra of 21- and 21,23-coremodified tetrabenzoporphyrins<sup>[6d]</sup> because the orbital angular momentum properties of the frontier  $\pi$ -MOs are largely unaffected when the lone pair of a protonated pyrrole nitrogen atom is replaced by that of an oxygen- or sulfur atom. Major modifications to the optical properties were observed upon core-modification of a non-protonated pyrrole nitrogen atom; however, fully core-modified compounds are of considerable interest for practical applications.

The synthesis- and characterization of fully core-modified porphyrins tends to be problematic. The parent tetrathiaporphyrin dication species  $(S_4P^{2+}, 1)$  was first reported by Vogel et al. in 1989 (Figure 1), based on the oxidation of tetrathiaporphyrinogen.<sup>[7]</sup> The X-ray structure and <sup>1</sup>H NMR- and electronic absorption spectroscopic properties in sulfuric



Figure 1. Tetrathiaporphyrin dication  $S_4P^{2+}$  (1).

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acid were consistent with an aromatic  $18\pi$ -electron system.<sup>[7a]</sup> Despite this result, the  $S_4P^{2+}$  species exhibits low solubility and is unstable in common organic solvents. To resolve these solubility problems, the octaethyltetrathiaporphyrin dication ( $S_4OEP^{2+}$ ) was subsequently prepared,<sup>[7b]</sup> but it readily reacted with nucleophiles at the *meso* positions, thus making in-depth spectroscopic studies and their use in practical applications problematic.

Recently, interest has also focused on the core-modification of  $20\pi$ -electron *N*,*N'*-dihydroporphyrin compounds (3), which are commonly referred to as isophlorins. The porphyrin (18 $\pi$ )–isophlorin (20 $\pi$ ) redox system, 2 $\approx$ 3, first proposed by Vogel and co-workers in 1991,<sup>[8]</sup> has been studied as a prime example of the intertwined structural- and chemical relationships of porphyrins and annulenes (Figure 2). Al-



Figure 2. Porphyrin (18 $\pi$ )–isophlorin (20 $\pi$ ) redox system and isophlorin derivatives.

though the possible formation of an isophlorin was noted during the total synthesis of chlorophyll by Woodward in 1960,<sup>[9]</sup> the first synthesis and characterization of an isophlorin derivative, 21,22,23,24-tetramethyloctaethylporphyrin (4), was accomplished by Vogel and co-workers as recently as 1991, based on the chemical reduction of the corresponding dication.<sup>[8]</sup> Isophlorin 4 exhibits a shift in the degenerate  $\pi$ -bond at room temperature. The <sup>1</sup>H NMR spectrum of isophlorin 4 (with localized  $\pi$ -bonds) was observed at -72 °C in [D<sub>6</sub>]toluene, which indicated the existence of a stable structure (4) owing to the spatial demands of the Nmethyl groups. Although a number of ring-expanded isophlorins have subsequently been reported,<sup>[10]</sup> there have only been a few reports of  $20\pi$ -isophlorins because these compounds are usually readily oxidized into 18n-porphyrins.<sup>[11,12]</sup> Recently, several relatively stable isophlorins have been prepared by taking advantage of strong electron-withdrawing substituents on the porphyrin periphery.<sup>[13,14]</sup> Chen and co-workers reported the synthesis of 2,3,12,13-tetrakis-(trifluoromethyl)-5,10,15,20-tetraphenylporphyrin, a relatively stable nonaromatic  $20\pi$ -isophlorin with a non-planar saddle conformation.<sup>[13]</sup> Fully core-modified tetraoxa- and dithiadioxaisophlorins (5a and 5b, Figure 2) were recently reported by Reddy and Anand to have remarkably planar structures and antiaromatic properties.<sup>[14]</sup>

In the context of this study, we adopted a similar approach to study the properties of a tetraaryltetrathiaisophlorin compound, which is likely to be non-planar owing to the larger size of the sulfur atom. The  $18\pi$ -electron 5,10,15,20-tetraphenyl-21,22,23,24-tetrathiaporphyrin dication (S<sub>4</sub>TPP<sup>2+</sup>, 6) and the  $20\pi$ -electron 5,10,15,20-tetrakis-(pentafluorophenyl)-21,22,23,24-tetrathiaisophlorin  $(S_4F_{20}-$ TPP, 7) were selected as target molecules (Figure 3) to enable an in-depth study of the spectroscopic properties of the fully core-modified  $S_4P^{2+}$  and  $S_4P$  parent structures because substitution at the meso positions protects the macrocycles from nucleophilic attack. Elucidation of the electronic structure of porphyrinoids has attracted considerable attention from both an experimental- and theoretical standpoint.<sup>[15-21]</sup> The results of time-dependent DFT (TD-DFT) and ZINDO/s calculations are compared to the observed magnetic circular dichroism (MCD) spectra and the electronic absorption spectra to study the effect of core-modification on the electronic structure. A current-density map and nucleus-independent chemical-shift (NICS) calculations are also used to analyze the aromatic properties of these  $\pi$ systems.



Figure 3. Structures of  $S_4TPP^{2+}$  (6) and  $S_4F_{20}TPP$  (7).

## **Results and Discussion**

**Synthesis**: The synthetic route that we adopted to prepare  $S_4TPP^{2+}$  (6) is shown in Scheme 1. BF<sub>3</sub>·OEt<sub>2</sub> was added to a solution of 2-(1-hydroxy-1-phenylmethyl)thiophene (8)<sup>[22]</sup> in CH<sub>2</sub>Cl<sub>2</sub> at room temperature and the mixture was stirred for



Scheme 1. Synthesis of  $S_4TPP^{2+}$  (6).

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Chem. Eur. J. 0000, 00, 0-0

3 h. Column chromatography on silica gel (CHCl<sub>3</sub>/*n*-hexane) afforded an isomeric mixture of compound **9** in 36 % yield. Further careful separation by using the same approach led to the complete separation of one of the isomers (**9a**), thereby leaving an inseparable mixture of isomers **9b** and **9c** (see the Supporting Information, Figure S7). Dehydrogenation of the tetraphenyltetrathiaporphyrinogen intermediate (**9**) with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in acetic acid at room temperature for 2 h, followed by treatment with HClO<sub>4</sub>, afforded tetrathiaporphyrin dication **6a** (98 % yield) as a dark-green solid. The ClO<sub>4</sub><sup>-</sup>counteranion was exchanged by treatment with lithium *tetrakis*(pentafluorophen-yl)borate, LiB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>, in MeCN to afford S<sub>4</sub>TPP<sup>2+</sup>·2B-(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>-</sup> (**6b**) as dark-green needles.

The synthetic route that was used to prepare  $S_4F_{20}TPP$  (7) is shown in Scheme 2. Reddy and Anand synthesized iso-



Scheme 2. Synthesis of  $S_4F_{20}TPP$  (7).

phlorin **5a** by using a Lewis acid-catalyzed condensation reaction of 2-(1-hydroxy-1-pentafluorophenyl-methyl)furan and subsequent oxidation with FeCl<sub>3</sub>.<sup>[14]</sup> We used a similar approach for the synthesis of compound **7**. 2-(1-Hydroxy-1pentafluorophenylmethyl)thiophene (**11**), which is the key precursor of S<sub>4</sub>F<sub>20</sub>TPP, was prepared by reacting 1-bromothiophene (**10**) with *n*BuLi and then with pentafluorobenzaldehyde. Condensation of compound **11** in the presence of BF<sub>3</sub>·OEt<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>, followed by oxidation with FeCl<sub>3</sub> and purification of the crude product by repeated column chromatography on Sephadex, afforded S<sub>4</sub>F<sub>20</sub>TPP (27%) as a brown solid.

The anticipated parent positive-ion peaks were identified by high-resolution FAB MS at m/z = 684.1073 for compound **6a**  $[M-2 \operatorname{ClO}_4]^+$ , m/z = 684.1058 for compound **6b**  $[M-2B-(C_6F_5)_4]^+$  (calcd for  $C_{44}H_{28}S_4$ : 684.1074), and m/z = 1043.9186for compound **7**  $[M]^+$  (calcd for  $C_{44}H_8F_{20}S_4$ : 1043.9190).  $S_4\text{TPP}^{2+}$  **6a** and **6b** and  $S_4F_{20}\text{TPP}$  (**7**) were found to be stable in air and in organic solvents under neutral conditions. Singlet peaks are observed for the thiophene  $\beta$ -protons in the <sup>1</sup>H NMR spectra of  $S_4\text{TPP}^{2+}$  **6a** (in CD<sub>3</sub>CN) and **6b** (in CDCl<sub>3</sub>) at  $\delta = 9.88$  and 9.84 ppm, respectively. This result is consistent with the presence of an  $18\pi$  diamagnetic ring-current. The corresponding signal of the parent  $S_4P^{2+}$ (**1**) with ClO<sub>4</sub><sup>-</sup> anions has been reported to appear at  $\delta =$  10.52 ppm in  $D_2SO_4$ .<sup>[7a]</sup> The <sup>1</sup>H NMR spectrum of  $S_4F_{20}TPP$ (7) in CDCl<sub>3</sub> exhibits a singlet at  $\delta = 6.19$  ppm for the  $\beta$ -protons, which shows a significant upfield shift compared to the corresponding signals of  $S_4TPP^{2+}$  (6). This value also represents a significant downfield shift relative to the signals for the  $\beta$ -protons of the antiaromatic structure of compound **5b** ( $\delta = 3.33$  and 3.37 ppm in CDCl<sub>3</sub>).<sup>[14]</sup> These <sup>1</sup>H NMR data suggest that the  $\pi$ -system of  $S_4F_{20}TPP$  (7) is nonaromatic. The redox properties are summarized in the Supporting Information.

**Structural properties**: Single crystals of  $S_4TPP^{2+}$  **6b** and  $S_4F_{20}TPP$  (**7**) that were suitable for X-ray crystallographic analysis were obtained by recrystallization (Figure 4 and



Figure 4. Crystal structure of  $S_4TPP^{2+}$  **6b**; thermal ellipsoids set at 50% probability. The B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>-counteranion is omitted for clarity.

Figure 5). The thiophene moieties on the y axis of compound 6b are tilted above and below the plane that is formed by the four meso carbon atoms so that the four sulfur atoms can be accommodated inside the central cavity, whilst the two thiophene rings on the x axis lie within the x/y plane. This feature leads to a marked expansion of the inner perimeter of the  $\pi$ -system so that the distances between neighboring sulfur atoms remain close to those between the pyrrole nitrogen atoms in the structures of tetraphenylporphyrin (H<sub>2</sub>TPP) and zinc tetraphenylporphyrin (ZnTPP; see the Supporting Information, Table S1); this structure is commonly referred to as a wave conformation.<sup>[23-25]</sup> Therefore, the molecular structure of  $S_4TPP^{2+}$  6b is very similar to that of the parent compound  $S_4P^{2+}$  (1),<sup>[7a]</sup> despite the introduction of the phenyl substituents at the meso positions.

In the molecular structure of compound **7**, two thiophene rings are tilted out of the plane that is formed by the four

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Figure 5. Crystal structure of  $S_4F_{20}TPP$  (7); thermal ellipsoids set at 50% probability. Solvent molecules are omitted for clarity.

meso carbon atoms along one axis in a disordered manner with an occupancy factors of 0.50 above and below the meso carbon atoms (see the Supporting Information, Figure S9), whilst the other two thiophene rings are almost coplanar with the rest of the  $\pi$ -system; this structure is referred to as a saddle conformation.<sup>[23-25]</sup> Greater alternation is predicted in the bond lengths on the inner perimeter of the porphyrin macrocycle owing to the nonaromatic character of the  $\pi$ -system (see the Supporting Information, Figure S1), whilst non-alternating bond lengths are observed in the phenyl rings in both structures. The bond-alternation pattern for  $S_4F_{20}TPP$  (7) is consistent with that normally anticipated for an isophlorin. Geometry-optimizations were carried out by using the B3LYP functional of the G03W<sup>[26]</sup> software package with 6-31G(d) basis sets. The B3LYP geometry-optimizations for  $S_4TPP^{2+}$  (6) and  $S_4F_{20}TPP$  (7) are very similar  $\clubsuit$ to their X-ray structures (see the Supporting Information, Table S1).

Absorption- and MCD spectroscopy: The absorption spectrum of the  $D_{4h}$ -symmetric ZnTPP complex contains weak, forbidden Q bands at 547 and 592 nm in the visible-light region and a more-intense B band at 421 nm, with derivative-shaped x/y-polarized Faraday  $A_1$  terms that are aligned with the absorption-band centers in the MCD spectrum (Figure 6). In contrast, the Q-band region of free-base H<sub>2</sub>TPP contains four absorption bands in the absorption spectrum with two coupled pairs of oppositely signed Faraday  $B_0$  terms in the MCD spectrum, owing to the  $D_{2h}$  symmetry that results from the loss of the main four-fold axis of symmetry. The absorption spectrum of  $S_4$ TPP<sup>2+</sup> 6a is broadly similar to that of ZnTPP, with two broad bands at 948 and 733 nm in the near-IR region and a more-intense band



Figure 6. Absorption and MCD data for H<sub>2</sub>TPP, ZnTPP, S<sub>4</sub>TPP<sup>2+</sup>, and S<sub>4</sub>F<sub>20</sub>TPP plotted against energy and wavelength scales. The calculated TD-DFT spectra for the B3LYP-optimized structures of H<sub>2</sub>TPP, ZnTPP, and S<sub>4</sub>F<sub>20</sub>TPP, as well as the X-ray structure of S<sub>4</sub>TPP<sup>2+</sup>, are plotted against a right-hand axis. The main Q- and B bands and bands that are primarily associated with the phenyl substituents and lower-lying porphyrin  $\pi$ -system MOs are denoted with diamonds, triangles, and squares, respectively.

in the visible-light region at 491 nm (Figure 6); each of these bands correspond to a derivative-shaped pseudo- $A_1$  term in



the MCD spectrum, despite the  $C_s$  symmetry. There is a marked red-shift of the main absorption bands of  $S_4TPP^{2+}$ **6a** relative to those in the spectra of H<sub>2</sub>TPP and ZnTPP and the absorption- and MCD bands are less intense by one and two orders of magnitude, respectively, owing to the non-planarity of the  $\pi$ -system. The absorption spectrum of the non-aromatic  $S_4F_{20}TPP$  (7) is markedly different from that of  $S_4TPP^{2+}$  **6a** and contains a single broad band at 411 nm with a weak tail of absorbance that extends out to 800 nm (Figure 6). There is almost no MCD intensity in the 500–800 nm region with extremely weak Gaussian-shaped Faraday **B**<sub>0</sub> terms in the 300–500 nm region.

Many of the key breakthroughs in understanding the electronic structure of porphyrinoids have been obtained by using MCD spectroscopy and are based on information about the ground- and excited-state degeneracies and bandpolarizations, which can be derived from the orbital angular momentum properties that are associated with the magnetic quantum number.<sup>[27]</sup> Analysis of MCD spectra is based on three Faraday terms,  $A_1$ ,  $B_0$ , and  $C_0$ , which arise from the Zeeman splitting of the absorption bands for left and right circularly polarized light into an orbitally degenerate excited state, the field-induced mixing of zero-field states, and Zeeman splitting that is associated with population-adjustment for an orbitally degenerate ground state, respectively. The spectroscopic properties of  $S_4TPP^{2+}$  (6) can be readily assigned by using either Gouterman's 4-orbital model<sup>[28]</sup> or Michl's 4N+2 perimeter model.<sup>[29]</sup> Perimeter-model approaches make use of the fact that the MOs of high symmetry cyclic polyenes, which are referred to as parent hydrocarbon perimeters, retain their nodal patterns, even after symmetry-lowering perturbations. The optical properties of porphyrinoids can be readily understood with reference to a  $C_{16}H_{16}^{2-}$  parent perimeter, with MOs that are arranged in an  $M_{\rm L} = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5, \pm 6, \pm 7, 8$  sequence in ascending energy. The HOMO and HOMO-1 of H<sub>2</sub>TPP, ZnTPP, and S<sub>4</sub>TPP<sup>2+</sup> have  $M_{\rm L} = \pm 4$  nodal properties, whilst  $M_{\rm L} = \pm$ 5 nodal patterns are observed for the LUMO and LUMO+1. The optical spectroscopy of  $D_{4h}$ - and  $D_{2h}$ -symmetric porphyrin π-systems can be assigned by using Gouterman's 4-orbital model,<sup>[28]</sup> based on an allowed  $\Delta M_{\rm L} = \pm 1$ and a forbidden  $\Delta M_{\rm L} = \pm 9$  band, which are associated with the four spin-allowed transitions between the HOMO and LUMO levels of the parent perimeter. These transitions are referred to as the Q- and B (or Soret) bands, respectively. The forbidden Q bands of TPP typically gains intensity through vibronic coupling with the B band.<sup>[30]</sup> As a result, Q<sub>01</sub> vibrational bands are often more intense than the main electronic  $Q_{00}$  bands (Figure 6). The bands at 948, 733, and 491 nm in the absorption spectrum of  $S_4TPP^{2+}$  6a can be assigned as  $Q_{00}$ ,  $Q_{01}$ , and  $B_{00}$  bands, respectively, by analogy with the spectra of H<sub>2</sub>TPP and ZnTPP,<sup>[21,28]</sup> based on the results of TD-DFT and ZINDO/s calculations (Figure 6 and Table 1; also see the Supporting Information, S2).

However, the results of the TD-DFT calculations are somewhat problematic. Only one intense  $A_1$  term (or pseudo- $A_1$  term) is observed in the 400–500 nm region of

the H<sub>2</sub>TPP<sup>[31]</sup> and ZnTPP spectra, despite the fact that TD-DFT calculations predict the presence of two intense x/y-polarized transitions (Table 1). The relatively small structural difference between the X-ray- and B3LYP-optimized structures of  $S_4 TPP^{2+}$  (6; see the Supporting Information, Table S1) results in significant changes in the calculated TD-DFT spectrum, with four sets of intense bands between 350 and 520 nm predicted for the X-ray structure (see the Supporting Information, Figures S2 and S3 and Table S2). In contrast, a single, intense set of B bands is predicted by the ZINDO/s technique for both structures (see the Supporting Information, Figure S3). TD-DFT spectra have previously been reported to predict a greater degree of interaction between the B band and higher-energy  $\pi\pi^*$  states of porphyrinoid  $\pi$ -systems than would be anticipated based on the optical spectroscopy data.<sup>[6a,21]</sup> Reimers and co-workers<sup>[32]</sup> recently demonstrated that calculations that were carried out with the commonly used BP86 and B3LYP functionals underestimate the energy of states that are associated with the  $1b_{2u} \rightarrow 1e_{g}^{*}$  one-electron transition of free-base porphyrins, owing to their charge-transfer character, and that a larger Hartree-Fock component is often required to compensate for this difference.

The differences between the spectra of  $S_4TPP^{2+}$  (6) and those of H<sub>2</sub>TPP and ZnTPP can be readily accounted for based on changes in the relative energies of the four frontier  $\pi$ -MOs (Figure 7 and the Supporting Information, S4). There is a marked destabilization of the 1a' MO of S<sub>4</sub>TPP<sup>2+</sup> (6) relative to the 1a<sub>2u</sub> MO of ZnTPP, because the large MO coefficients on the pyrrole nitrogen atoms are absent in the case of  $S_4TPP^{2+}$  (6; Figure 8 and the Supporting Information, S5). This absence leads to a smaller HOMO-LUMO band-gap and, hence, to a marked red-shift of the Q-band region. The incorporation of the sulfur atoms has a muchsmaller effect on the energies of the other three frontier  $\pi$ -MOs because there is significantly less electron density on the four pyrrole nitrogen atoms. The lifting of the almostdegeneracy of the HOMO and HOMO-1 on moving from  $H_2TPP$  to  $S_4TPP^{2+}$  (6) results in a mixing of the allowed and forbidden properties of the B- and Q bands so the Q-band region becomes significantly more intense relative to the B band. Because there is only a slight lifting of the degeneracy of the LUMO, the MCD spectrum of  $S_4TPP^{2+}$  (6) is broadly similar to that of ZnTPP, with a pseudo- $A_1$  term for each of the main bands. In the absence of the slight non-planarity that is introduced by the steric hindrance between the four thiophene sulfur atoms, the structure of  $S_4TPP^{2+}$  (6) would have four-fold symmetry, as is the case with ZnTPP.

The absorption- and MCD spectra of  $S_4F_{20}TPP$  (7) are clearly different from those of  $S_4TPP^{2+}$  (**6a**; Figure 6). The conventional Q-and-B-band nomenclature that is associated with Gouterman's 4-orbital model<sup>[28]</sup> is no longer applicable because the  $\pi$ -system contains two extra  $\pi$ -electrons and is no longer heteroaromatic. The h-, h+, s-, s+, l-, and l+terminology that is used in Michl's 4N-perimeter model<sup>[33]</sup> for the lower- and higher-energy MOs is derived from the HOMO, SOMO, and LUMO levels of an ideal highly sym-

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Table 1. Calculated TD-DFT electronic excitation spectra for B3LYP geometry optimizations of  $H_2$ TPP, ZnTPP,  $S_4$ TPP<sup>2+</sup> (6), and  $S_4F_{20}$ TPP (7) and the X-ray structures of compounds 6 and 7 that were calculated by using the B3LYP functional with 6–31G(d) basis sets (see Figure 6).

Band <sup>[a]</sup>		Symmetr	ry	Calculate	ed <sup>[b]</sup>	Experin	nental <sup>[c]</sup>	Wavefunction <sup>[d]</sup>
			-		H	$_{2}$ TPP $(D_{2h})$ , H	B3LYP	
Q	1	${}^{1}\mathbf{B}_{2u}$	17.4	575	(0.02)	15.6	641	$64\% \ 1b_{1u} \rightarrow 1b_{3g}^{*}; 40\% \ 1a_{u} \rightarrow 1b_{2g}^{*}; \dots$
Q	2	${}^{1}\mathbf{B}_{3u}$	18.6	537	(0.03)	18.4	544	$58\% 1b_{1u} \rightarrow 1b_{2g}^{*}; 40\% 1a_{u} \rightarrow 1b_{3g}^{*}; \dots$
В	3	${}^{1}B_{2u}$	25.6	391	(0.80)	24.0	416	$35\% 1a_u \rightarrow 1b_{2g}^*; 24\% 2b_{1u} \rightarrow 1b_{3g}^*; 13\% 1b_{1u} \rightarrow 1b_{3g}^*; \dots$
В	4	${}^{1}B_{3u}$	26.5	377	(1.30)			$38\% \ 1a_u \rightarrow 1b_{3g}^{*}; 19\% \ 1b_{1u} \rightarrow 1b_{2g}^{*}; \dots$
-	7	${}^{1}B_{3u}$	28.8	347	(0.22)	-	-	$89\% 2b_{1u} \rightarrow 1b_{2g}^{} ;$
	8	$\mathbf{B}_{2u}$	28.9	346	(0.76)			$68\% 2b_{1u} \rightarrow 1b_{3g}^{*}; \dots$
	1	10	10.7	525	Zi	$\frac{1100}{1100}$	33LYP	520/ 1 1 × 400/ 1 1 ×
Q	1	$^{-}E_{u}$	18.7	535 535	(0.01)	16.9	592	$53\% 1a_{2u} \rightarrow 1e_{gx}^{*}; 42\% 1a_{1u} \rightarrow 1e_{gy}^{*};$
Q B	2		16.7 26.2	387	(0.01)	23.8	421	$35\%$ $1a_{2u} \rightarrow 1c_{gy}$ , $42\%$ $1a_{1u} \rightarrow 1c_{gx}$ , $35\%$ $1b^{N}$ $1e^{-st} 20\%$ $1e^{-st} 12\%$ $1e^{-st} 12\%$
B	4	$\mathbf{L}_{u}$	26.2	382	(0.75)	23.8	421	$33\% \text{ 1b}_{2g} \rightarrow 1e_{gx}^{N}, 20\% \text{ 1a}_{1u} \rightarrow 1e_{gy}^{N}, 12\% \text{ 1a}_{2u} \rightarrow 1e_{gx}^{N}, \dots$ $33\% \text{ 1b}_{2}^{N} \rightarrow 1e^{-s} \cdot 21\% \text{ 1a}_{2} \rightarrow 1e^{-s} \cdot 13\% \text{ 1a}_{2} \rightarrow 1e^{-s} \cdot 12\% \text{ 1a}_{2}^{N}$
-	5	${}^{1}E$	26.9	371	(0.62)	_	_	$55\% 1b_{2g}^{N} \rightarrow 1e_{gy}^{N}$ , 21% $1a_{1u}^{N} \rightarrow 1e_{gx}^{N}$ , 15% $1a_{2u}^{N} \rightarrow 1e_{gy}^{N}$ ,
-	6	Ľu	26.9	371	(0.60)			$58\% 1b_{2g}^{N} \rightarrow 1e_{gy}^{*}; 13\% 1a_{1u} \rightarrow 1e_{gx}^{*}; 9\% 1a_{2u} \rightarrow 1e_{gy}^{*};$
					$S_4$	$\text{TPP}^{2+}(C_{\text{s}}), \text{ I}$	33LYP	
Q	1	${}^{1}\mathbf{A}''$	13.0	772	(0.23)	10.5	948	73 % 1a'→1a''*; 6 % 5a''→1a'*;
Q	2	${}^{1}A'$	13.9	719	(0.26)			$69\% 1a' \rightarrow 1a'^*; 5\% 5a'' \rightarrow 1a''^*; \dots$
-	16	${}^{1}A'$	21.3	470	(0.12)	-	-	$33 \% 4a''^{Ph} \rightarrow 1a''; 26 \% 4a''^{Ph} \rightarrow 1a'''; 11 \% 4a'^{Ph} \rightarrow 1a'';$
D	10	1.4.4	22.4		(0.47)	20.4	101	$9\% 5a'' \rightarrow 1a''*; \dots$
В	18	<sup>1</sup> A'	22.4	447	(0.47)	20.4	491	$27\%$ $5a' \rightarrow 1a'*; 21\%$ $5a'' \rightarrow 1a''*;$
– D	19	<sup>1</sup> A''	22.8	439	(0.12)			$3/\%$ $5a' \rightarrow 1a'^*; 31\%$ $5a'' \rightarrow 1a'^*;$
В	20	A	22.9	437	(0.36)			$29\%$ 5a $\rightarrow 1a\%$ ; 18% 5a $\rightarrow 1a\%$ ; 12% 6a <sup>-11</sup> $\rightarrow 1a\%$ ;
	25	1 . 1	26.6	275	(0.11)			$10\% 3a \rightarrow 1a\%,$
-	23	A 1 <b>A</b> '	20.0	363	(0.11) (0.11)	_	_	$56 \% 0a \rightarrow 1a^{+}, 20 \% 0a \rightarrow 1a^{+},$
_	29	${}^{1}A''$	27.0	355	(0.11)	_	_	$26\%$ $1a' \rightarrow 2a'*; 26\%$ $8a' \rightarrow 1a''*; 13\%$ $6a'' \rightarrow 1a'*;$
					S	$_{4}\text{TPP}^{2+}(C_{s}),$	X-ray	
0	1	<sup>1</sup> A″	13.4	747	(0.28)	10.5	948	75% 1a'→1a''*: 9% 5a''→1a'*:
õ	2	${}^{1}A'$	14.1	708	(0.21)			$73\% 1a' \rightarrow 1a''^*; 11\% 5a'' \rightarrow 1a''^*;$
-	12	${}^{1}\mathbf{A}'$	19.3	517	(0.18)	_	_	$56\% \ 3a''^{Ph} \rightarrow 1a''^*; \ 35\% \ 3a'^{Ph} \rightarrow 1a'^*; \ \dots$
_	15		20.2	495	(0.15)	_	_	$94\% 3a''^{Ph} \rightarrow 1a'^{*};$
В	17	${}^{1}\mathbf{A}'$	21.6	463	(0.26)	20.4	491	$54\% 5a'v \rightarrow 1a''^*; 27\% 5a'^{Ph} \rightarrow 1a'^*;$
В	18	${}^{1}A''$	22.1	453	(0.23)			$48\% 5a'' \rightarrow 1a'^*; 39\% 5a'^{Ph} \rightarrow 1a'^*;$
-	21	${}^{1}A''$	24.9	375	(0.19)	-	-	$34\% 5a'^{Ph} \rightarrow 1a''^*; 34\% 7a' \rightarrow 1a''^*; 21\% 5a'' \rightarrow 1a'^*; \dots$
-	22	${}^{1}\mathbf{A}'$	25.6	363	(0.25)	-	-	$52\% 5a'^{Ph} \rightarrow 1a'^*; 14\% 5a'' \rightarrow 1a''^*; 7a' \rightarrow 1a'^*;$
-	25	${}^{1}\mathbf{A}'$	27.6	355	(0.29)	-	-	$37\% 7a' \rightarrow 1a'^*; 35\% 7a' \rightarrow 1a''^*; \dots$
	29	${}^{1}\mathbf{A}'$	28.7	349	(0.21)	-	-	$41\% \ 6a'' \rightarrow 1a''^*; 28\% \ 7a' \rightarrow 1a'^*; 12\% \ 7a' \rightarrow 1a''^*; \dots$
					S <sub>4</sub> F	$F_{20}$ TPP ( $C_{2v}$ ),	B3LYP	
S	1	${}^{1}A_{2}$	14.7	678	(0.00)	13.3 <sup>[e]</sup>	750 <sup>[e]</sup>	$90\% 1b_2(s-) \rightarrow 1b_1^*(s+); \dots$
$N_1$	2	${}^{1}\mathbf{B}_{1}$	18.9	530	(0.00)	20.0 <sup>[e]</sup>	500 <sup>[e]</sup>	$51 \% 1a_1(h+) \rightarrow 1b_1*(s+); 50 \% 1b_2(s-) \rightarrow 1a_2*(l-); \dots$
$\mathbf{P}_1$	3	${}^{1}\mathbf{B}_{1}$	21.9	457	(0.94)	24.3	411	$34\% 1b_2(s-) \rightarrow 1a_2^*(l-); 33\% 1a_1(h+) \rightarrow 1b_1^*(s+); \dots$
$N_2$	5	${}^{1}\mathbf{B}_{2}$	25.2	396	(0.06)	22.5	444	89% $1a_2(h-) \rightarrow 1b_1*(s+); 7\% 1b_2(s-) \rightarrow 1a_1*(l+);$
-	6	${}^{1}\mathbf{B}_{1}$	27.0	371	(0.44)	-	-	$88\% 2a_1 \rightarrow 1b_1^*(s+); \dots$
<b>P</b> <sub>2</sub>	7	${}^{1}\mathbf{B}_{2}$	28.0	357	(0.23)	28.1	356	$85\% 1b_2(s-) \rightarrow 1a_1^*(l+); 4\% 2a^*(h-) \rightarrow 1b_1^*(s+); \dots$
					S <sub>4</sub> 1	$\mathbf{F}_{20}\mathbf{TPP}\ (C_{2v}),$	X–ray	
S	1	${}^{1}A_{2}$	0.71	14000	(0.00)	13.3 <sup>[e]</sup>	750 <sup>[e]</sup>	$16\% \ 1b_2(s-) \rightarrow 1b_1*(s+); \dots$
$N_1$	2	${}^{1}\mathbf{B}_{1}$	7.77	1290	(0.00)	$20.0^{[e]}$	500 <sup>[e]</sup>	56 % $1a_1(h+) \rightarrow 1b_1*(s+); 54 \% 1b_2(s-) \rightarrow 1a_2*(l-);$
$\mathbf{P}_1$	3	${}^{1}B_{1}$	16.0	627	(1.24)	24.3	411	19% $1a_1(h+) \rightarrow 1b_1^*(s+); 19\% 1b_2(s-) \rightarrow 1a_2^*(l-); \dots$
$N_2$	4	${}^{1}B_{2}$	16.3	612	(0.12)	22.5	444	$88\% 1a_2 (h-) \rightarrow 1b_1^*(s+); \dots$
-	8	$^{1}A_{1}$	20.4	489	(0.15)	-	-	$85\% 1b_1 \rightarrow 1b_1^*(s+); \dots$
$\mathbf{P}_2$	21	${}^{1}B_{2}$	26.3	381	(0.22)	28.1	356	$54\% 1b_2(s-) \rightarrow 1a_1^*(l+); 31\% 3b_1^{rn} \rightarrow 1b_1^*(s+);$
-	23	'A <sub>1</sub>	26.5	378	(0.65)			$81 \% 1b_2(s-) \rightarrow 2b_1^{***}; \dots$

[a] The number of the state, which was assigned in ascending energy within the TD-DFT calculations; only states that were located below 30000 cm<sup>-1</sup> that resulted from allowed electronic transitions with an oscillator strength of greater than 0.10 are included. [b] Calculated band energies [×10<sup>3</sup> cm<sup>-1</sup>], wavelengths [nm], and oscillator strengths (*f*). [c] Observed energies [×10<sup>3</sup> cm<sup>-1</sup>] and wavelengths [nm]. [d] Wavefunctions based on the eigenvectors that were predicted by TD-DFT analysis. One-electron transitions associated with the four frontier  $\pi$ -MOs (see Figure 8) are shown in bold; "N" and "Ph" superscripts denote non-bonding  $\sigma$ -MOs and  $\pi$ -MOs that are primarily associated with the phenyl substituents, respectively. Only one-electron transitions with contributions of greater than 10% are included. Figure 8 and Figure 9 can be used as a correlation table to compare MOs with different symmetries. [e] Approximate value.



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Figure 7. MO energies of H<sub>2</sub>TPP, ZnTPP, S<sub>4</sub>TPP<sup>2+</sup> (6), and S<sub>4</sub>F<sub>20</sub>TPP (7) relative to the LUMO in TD-DFT calculations. MOs that are associated with the parent cyclic perimeter are highlighted in light gray, whilst MOs that are primarily associated with the phenyl substituents are offset to the right. The nodal patterns and MO energy values of the four frontier  $\pi$ -MOs of H<sub>2</sub>TPP, ZnTPP, and S<sub>4</sub>TPP<sup>2+</sup> (6) with  $M_L = \pm 4, \pm 5$  are tabulated in Figure 8 while those of the six frontier  $\pi$ -MOs of S<sub>4</sub>F<sub>20</sub>TPP (7) with  $M_L = \pm 4, \pm 5, \pm 6$  are tabulated in Figure 9.



Figure 8. Nodal patterns of the four frontier  $\pi$ -MOs of H2TPP, ZnTPP, and S<sub>4</sub>TPP<sup>2+</sup> (6) in the TD-DFT calculations with the B3LYP functional and 6-31G(d) basis sets at an isosurface value of 0.04.

metric C<sub>16</sub>H<sub>16</sub><sup>4-</sup> hydrocarbon parent perimeter, respectively (Figure 9 and the Supporting Information, S6). These MOs have  $M_{\rm L} = \pm 4, \pm 5, \pm 6$  nodal properties and their nodal patterns are broadly similar to those of the  $M_{\rm L} = \pm 4, \pm 5, \pm 6$ MOs of  $S_4$ TPP<sup>2+</sup> (6). In the context of his 4N-perimeter model,<sup>[33]</sup> Michl reserved the use of the term "antiaromatic" to describe even-electron cyclic  $4N-\pi$ -systems that have very strong biradical-like properties, whilst a new term, "unaromatic", was adopted to describe 4N-electron nonaromatic cyclic polyene *n*-systems in which symmetry-lowering structural perturbations remove the biradical-like character so that only the s- MO of the SOMO level is occupied. The gap that was predicted between the energies of the s- and s+ MOs in the B3LYP geometry-optimization of  $S_4F_{20}TPP$  (7; about 2 eV) is consistent with an unaromatic  $\pi$ -system (Figure 7). Michl's 4N-perimeter model predicts the presence of five major spectroscopic bands for  $\pi$ -systems of this type. The lowest-energy S band arises from the  $s \rightarrow s +$ transition (Figure 7). Although the transition is magneticdipole allowed, zero intensity is predicted in both the absorption- and MCD spectra because it is intrashell in nature.<sup>[33]</sup> This result accounts for the relative lack of intensity at the red end of the visible-light region. Two weakly-  $(N_1, N_2)$  and two electronic-dipole-alstrongly lowed bands (P1, P2) are predicted to arise from HOMO  $\rightarrow$ one-electron transitions (Figure 7). Configurational interaction between states that arise from the  $h + \rightarrow s +$  and  $s - \rightarrow l$ transitions causes a cancellation- and intensification of the transition dipole moments, thus resulting in weak and intense

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 7

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 7

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Figure 9. Nodal patterns at an isosurface value of 0.04, molecular symmetries, and MO energies of the six frontier  $\pi$ -MOs of  $C_{16}H_{16}^{4-}$  and  $S_4F_{20}TPP$  (7) that were derived from geometry-optimizations with the B3LYP functional and 6-31G(d) basis sets. The nodal patterns and MO energies for the antiaromatic  $C_{16}H_{16}^{4-}$  biradical species are derived from the  $\alpha$  electrons.

N<sub>1</sub>- and P<sub>1</sub> bands, respectively. Weak N<sub>2</sub> bands and intense  $P_2$  bands arise from the  $h \rightarrow s+$  and  $s \rightarrow l+$  transitions in a similar manner (Figure 7). The TD-DFT calculations (Table 1) appear to overestimate the energies of the major bands. The S band can be assigned to the first weaker shoulder of intensity at around 750 nm. The main absorption-band center at 411 nm and the main positively signed Faraday  $\mathbf{B}_0$  term at 356 nm are assigned as  $P_1$  and  $P_2$  bands, respectively, because these are expected to be the most-intense absorption bands in the context of Michl's 4N-perimeter model<sup>[32]</sup> and Faraday  $\mathbf{B}_0$  terms with alternating signs are anticipated in the MCD spectrum. The second shoulder of absorption intensity in the 500 nm region is assigned as the  $N_1$  band, whilst the Faraday  $B_0$  term at 444 nm is tentatively assigned as the N<sub>2</sub> band. Michl's 4N perimeter model provides a readily accessible conceptual framework for assigning what would otherwise have appeared to be a highly complex spectrum. Despite the results of the TD-DFT and ZINDO/s calculations (Figure 6 and the Supporting Information, S2), it is an S, N1, N2, P1, P2 sequence that is usually anticipated in this context.<sup>[33]</sup> The TD-DFT and ZINDO/s calculations for the B3LYP-optimized geometry are in much-closer agreement with the experimental data than those for the X-ray structure. This result suggests that  $S_4F_{20}TPP$  (7) adopts a less-severely saddled conformation in solution (Figure 10 and the Supporting Information, Table S1), owing to the absence of crystal-packing effects.

**Ring-current maps and NICS calculations**: Direct visualization of the ring-current density<sup>[34]</sup> and NICS<sup>[18,35]</sup> calculations were carried out to analyze the aromatic properties of  $S_4TPP^{2+}$  (6) and  $S_4F_{20}TPP$  (7). The SYSMO<sup>[34]</sup> package software was used to carry out ring-current calculations with the



Figure 10. B3LYP-optimized structure of  $S_4F_{20}TPP$  (7).

6-31G(d,p) basis sets, based on coupled Hartree–Fock (CHF) theory within the continuous transformation of origin of the current-density diamagnetic-zero (CTOCD-DZ) formulation,<sup>[36–38]</sup> in which the induced current density at a given point is calculated as the origin of the vector potential. The calculations were carried out for model compounds  $S_4P^{2+}$  **1**- $C_s$  and **1**- $D_{4h}$  and  $S_4P$  **12**- $C_{2v}$  (Figure 11). The



Figure 11. Molecular structures of  $S_4P^{2+}$  1- $C_s$  and  $S_4P$  12- $C_{2v}$ 

geometry-optimizations for structures  $1-C_s$  and  $1-D_{4h}$  provide model calculations for the wave- and planar conformations of  $S_4TPP^{2+}$  (6), respectively. The geometry that was predicted for the  $1-C_s$  structure showed no imaginary frequency, thus suggesting that it is not a transition-state structure but rather is one of the stable conformations of a local minimum. In contrast, the structure of the planar  $1-D_{4h}$ structure has four imaginary frequencies: 98i (doubly degenerate), 97*i*, and 69*i* cm<sup>-1</sup>, which suggests that it does not lie at a local minimum. The optimized  $1-C_s$  structure is comparable to those of the B3LYP-optimized structure of S<sub>4</sub>TPP<sup>2+</sup> (6) and the X-ray structure for  $S_4TPP^{2+}$  6b. Although the optimized  $S_4P$  **12**- $C_{2v}$  structure can be used as a model calculation for the saddle conformation of  $S_4F_{20}TPP$  (7), a ringcurrent calculation for a model compound with a planar conformation did not converge. Figure 12 contains the calculated current-density maps of  $1-C_s$  for  $\pi$ -electrons in areas



Figure 12. Current-density maps of a)  $S_4P^{2+}$  **1**- $C_s$  for  $\pi$ -electrons in areas 1–2  $a_0$  above and below the molecular mean plane and b)  $S_4P^{2+}$  **1**- $D_{4h}$  for  $\pi$ -electrons in area 1  $a_0$  above the molecular mean plane. c)  $S_4P$  **12**- $C_{2v}$  for  $\pi$ -electrons of the HOMO, HOMO–1, and HOMO–2 orbitals in the area of 1–2  $a_0$  above the molecular mean plane.

1–2  $a_0$  above- and below the molecular mean plane (Figure 12 a), **1**- $D_{4h}$  for  $\pi$ -electrons in areas 1  $a_0$  above the molecular mean plane (Figure 12 b), and **12**- $C_{2v}$  for  $\pi$ -electrons of HOMO, HOMO–1, and HOMO–2 orbitals in the area of 1–2  $a_0$  above the molecular mean plane (Figure 12 c).

Counterclockwise- and clockwise circulations are consistent with diamagnetic and paramagnetic ring currents, respectively. Although the calculations for the  $1-C_s$  and  $1-D_{4h}$ model structures predict global diamagnetic circulation of the  $\pi$ -electrons, the ring-current-circulation pathways are significantly different from that of the parent H<sub>2</sub>P porphyrin (Figure 12). The most-preferential path for the ring current of H<sub>2</sub>P is bifurcated in the pyrrole units that contain an inner hydrogen atom, whereas it is on the inside of pyrrole units that lack inner hydrogen atoms.<sup>[39]</sup> Although current flows around the outer pathway in rings B, C, D, and E in the calculation for  $1-D_{4h}$ , a bifurcated pathway is predicted in rings C and E for structure  $1-C_s$ , owing to the non-planar wave conformation. The current-density map of compound 12- $C_{2v}$  provides little evidence of diamagnetic- or paramagnetic ring currents of the HOMOs  $\pi$ -electrons. This result provides evidence for a nonaromatic  $\pi$ -system.

NICS calculations have been used as indices for evaluating the aromaticity of the porphyrin rings.<sup>[19]</sup> The NICS values were calculated at the HF/6-31+G(d) level of theory at the center of each ring. The NICS value for ring A, and also rings B–E, in the structure of S<sub>4</sub>TPP<sup>2+</sup> (**6**) are consistent with a diamagnetic ring current and an aromatic  $\pi$ -system. This result suggests that ring currents also flow around the outer perimeter of the porphyrin ring. On the other hand, although aromatic character is predicted for the A, B, and D rings of the  $D_{2h}$ -symmetric H<sub>2</sub>P porphyrin, nonaromatic values are predicted for rings C and E ( $\delta$ =-4.6 ppm). These results are consistent with a ring current that predominantly flows around the inner portion of rings C and E (Table 2). The NICS values for rings A and B/D of compound **7** (ring A: 1.2, rings B/D: -2.7 ppm), are almost non-

Table 2. NICS values [ppm] for  $S_4TPP^{2+}$  (6),  $S_4F_{20}TPP$  (7), and  $H_2P$ .

			-
Ring	S <sub>4</sub> TPP <sup>2+</sup> ( <b>6</b> )	S <sub>4</sub> F <sub>20</sub> TPP ( <b>7</b> )	$H_2P$
A	-14.1	1.2	-16.5
B/D	-17.9	-2.7	-15.3
C/E	-19.5	-11.2	-20.1

aromatic, whereas the C/E rings ( $\delta = -11.2 \text{ ppm}$ ), which are tilted out of the mean plane, are aromatic. Thus both the current density map of compound  $12-C_{2v}$  and the NICS value of  $S_4F_{20}TPP$  (7) are consistent with the nonaromatic character of  $S_4F_{20}TPP$  (7) that would be assumed based on the experimental data.

### Conclusion

The synthesis of stable fully core-modified  $S_4P$  and  $S_4P^{2+}$ structures is reported and an in-depth study of the spectroscopic properties of these species has been performed.  $S_4TPP^{2+}$  (6a) was synthesized by the reaction of tetrathiaporphyrinogen (9) with DDQ followed by treatment with HClO<sub>4</sub>. Counteranion-exchange with  $LiB(C_6F_5)_4$  afforded compound 6b. A wave conformation is observed in the Xray structure of compound 6b, which is in close agreement with the B3LYP-optimized geometry. Because pseudo- $A_1$ terms are observed in the MCD spectrum of compound 6a, which correspond to the weaker bands at 948 and 733 nm in the near-IR region of the electronic absorption spectrum and a more-intense band in the visible region at 491 nm, these bands can be readily assigned as Q<sub>00</sub>, Q<sub>01</sub>, and B<sub>00</sub> bands, respectively, by comparison with the spectra of other tetraarylporphyrins and with the results of theoretical calculations. In contrast to 21- and 21,23-core-modified porphyrinoids,<sup>[6]</sup> a marked red-shift of the Q bands into the near-IR region was observed owing to a narrowing of the HOMO-LUMO band-gap. Full core-modification results in a marked destabilization of the HOMO. The greater stability of tetraaryltetrathiaporphyrins makes these species potentially suitable for use as organic devices in practical applications. Current-density-map calculations for the model structures predict that the core-modification and non-planarity of the macrocycle results in a marked modification of the ringcurrent circulation.  $S_4F_{20}TPP$  (7) was synthesized by the condensation of hydroxymethylthiophene (11) with  $BF_3 \cdot OEt_2$  in CH<sub>2</sub>Cl<sub>2</sub> followed by treatment with FeCl<sub>3</sub>. S<sub>4</sub>F<sub>20</sub>TPP adopts a saddle conformation in the solid state. The current-density map for the HOMO  $\pi$ -electrons of model molecule 12- $C_{2v}$ and NICS calculations predict nonaromatic (rather than antiaromatic) character owing to the non-planarity of the porphyrin ring, in contrast to the tetrachalcogenisophlorins that have been reported previously. Michl's 4N-perimeter model was used to analyze the electronic structures that were predicted by DFT calculations on this basis and to fully assign the optical spectra.

### **Experimental Section**

**Tetraphenyltetrathiaporphyrinogen (9):**  $BF_3$ - $OEt_2$  (0.75 mL, 6.00 mmol) was added to a solution of 2-(1-hydroxy-1-phenylmethyl)thiophene<sup>[22]</sup> (8; 1.14 g, 6.00 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (900 mL) at RT and the mixture was stirred for 3 h. A 0.1 M aqueous solution of NaOH was added to the reaction mixture and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined CH<sub>2</sub>Cl<sub>2</sub> extracts were dried with Na<sub>2</sub>SO<sub>4</sub> and, after filtration, the filtrate

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was concentrated to dryness. The residue was purified by column chromatography on silica gel (CHCl<sub>3</sub>/n-hexane, 1:3) to provide the isomeric mixtures of compound 9 (374 mg, 36%). Further separation by column chromatography on silica gel using the same eluent resulted in the separation of one of the isomers (9a; 22 mg, 2%) as a pale-yellow solid, which was recrystallized from CHCl<sub>3</sub>/n-hexane. Isomers 9b and 9c could not be separated. 9a: M.p.>280 °C (dec.); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 5.69$  (s, 4H; CH), 6.48 (s, 8H;  $\beta$ -H), 7.26 (t, J = 7.6 Hz, 4H; ArH), 7.33 (t, *J*=7.6 Hz, 8H; ArH), 7.38 ppm (d, *J*=7.6 Hz, 8H; ArH); <sup>13</sup>C NMR (125 MHz):  $\delta = 48.3$  (CH), 124.4 (thiophene- $\beta$ ), 127.1 (*para*), 128.5 (meta), 128.6 (ortho), 142.2 (ipso), 148.8 ppm (thiophene-α); MS (FAB): m/z: 688 [M]<sup>+</sup>; HRMS (FAB, positive): m/z calcd for C<sub>44</sub>H<sub>32</sub>S<sub>4</sub>: 688.1387 [M]+; found: 688.1382. 9b: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 5.74 (s, 4H; CH), 6.47 (s, 4H; β-H), 6.59 (s, 4H; β-H), 7.24–7.39 ppm (m, 20 H; ArH). 9c: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 5.69$  (s, 1 H; CH), 5.73 (s, 2H; CH), 5.80 (s, 1H; CH), 6.44 (d, J = 3.5 Hz, 2H;  $\beta$ -H), 6.51 (d, J =3.5 Hz, 2 H;  $\beta$ -H), 6.55 (s, 4 H;  $\beta$ -H), 7.24–7.39 ppm (m, 20 H; ArH).

**S<sub>4</sub>TPP<sup>2+</sup>·2ClO<sub>4</sub><sup>−</sup> (6a)**: DDQ (20.4 mg, 0.09 mmol) was added to a solution of the isomeric mixtures of porphyrinogen **9** (20.7 mg, 0.03 mmol) in acetic acid (20 mL) at RT. After the reaction mixture was stirred for 2 h at RT, a solution of HClO<sub>4</sub> in acetic acid (1 M, 0.15 mL) was added and the mixture was stirred for a further 3 h. The solvents were removed under reduced pressure and the crude product was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to give compound **6a** (25.9 mg, 98%) as a dark-green solid. M.p. > 300 °C; <sup>1</sup>H NMR (600 MHz, CD<sub>3</sub>CN): δ=8.18–8.19 (m, 12H; ArH), 8.64–8.66 (m, 8H; ArH), 9.88 ppm (s, 8H; β-H); <sup>13</sup>C NMR (150 MHz): δ=130.9 (*para*), 133.6 (*meta*), 139.2 (*ortho*), 140.3 (*ipso*), 144.4 (thiophene-β), 151.0 (*meso*), 163.2 ppm (thiophene-α); HRMS (FAB, positive): *m/z* calcd for C<sub>44</sub>H<sub>28</sub>S<sub>4</sub>: 684.1074 [*M*–2CIO<sub>4</sub>]<sup>+</sup>; found: 684.1073.

**S<sub>4</sub>TPP<sup>2+</sup>·2B**(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub><sup>--</sup>(**6b**): LiB(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>·*n* OEt<sub>2</sub> (20 mg) was added to a solution of compound **6a** (8.80 mg, 0.01 mmol) in CH<sub>3</sub>CN (5 mL). After the reaction mixture was stirred at RT for 1.5 h, the solvent was removed under reduced pressure to afford the crude borate salt. The crude product was dissolved in CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (20:1) and the insoluble solid was removed by filtration. Recrystallization from CHCl<sub>3</sub> produced compound **6b** (20.4 mg, 100%) as dark-green needles. M.p. > 300°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.12–8.18 (m, 12 H; ArH), 8.46 (d, *J* = 7.1 Hz, 8H; ArH), 9.84 ppm (s, 8H; β-H); <sup>19</sup>F NMR (470 MHz, CDCl<sub>3</sub>):  $\delta$  = -167.3 (t, *J* = 18.9 Hz, 8F; *meta*-F), -163.0 (t, *J* = 20.2 Hz, 4F; *para*-F), -134.0 ppm (br s, 8F; *ortho*-F); HRMS (FAB, positive): *m*/z calcd for C<sub>44</sub>H<sub>28</sub>S<sub>4</sub>: 684.1074 [*M*-2B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>+</sup>; found: 678.9759 [B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>-</sup>.

2-(1-Hydroxy-1-pentafluorophenylmethyl)thiophene (11): Although the synthesis of compound 11 has recently been reported, based on the copper-bisphosphine-initiated pentafluorination of aldehydes,<sup>[40]</sup> an alternative method was developed for this study. A solution of *n*BuLi in *n*hexane (1.63 M, 9.8 mL, 16 mmol) was added to a solution of 2-bromothiophene (10; 2.44 g, 15.0 mmol) in Et<sub>2</sub>O (50 mL) at -78 °C under a nitrogen atmosphere. The reaction mixture was stirred for 30 min at -78 °C and pentafluorobenzylaldehyde (2.50 g, 12.7 mmol) was added to the reaction mixture. The reaction mixture was allowed to warm to RT over 2 h and was stirred for a further 1 h. The reaction mixture was acidified with aqueous HCl, neutralized with aqueous NaHCO3, and extracted with Et<sub>2</sub>O. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (CHCl<sub>3</sub>/n-hexane) to give compound 11 (3.13 g, 88%) as a colorless solid. Recrystallization from CHCl<sub>3</sub>/n-hexane gave colorless needles that were suitable for X-ray analysis. M.p. 58–59°C (dec.) [lit.<sup>[40]</sup> 54–56°C]; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta = 2.89$  (br s, 1H; OH), 6.38 (s, 1H; CH), 6.91 (d, J = 3.1 Hz, 1H; ArH), 6.97 (dd, *J*=5.4, 3.1 Hz, 1H; ArH), 7.32 ppm (d, *J*=5.4 Hz, 1H; ArH); <sup>19</sup>F NMR (376 MHz):  $\delta = -162.1$  (td, J = 20.6, 6.7 Hz, 2F; meta-F), -154.9 (dd, J=21.7, 20.6 Hz, 1F; para-F), -143.8 ppm (dd, J=21.7, 7.2 Hz, 2F; ortho-F); HRMS (FAB, positive): m/z calcd for  $C_{11}H_5OF_5S$ : 279.9981 [M]+; found: 279.9980.

 $S_{4}F_{20}TPP$  (7): BF<sub>3</sub>·OEt<sub>2</sub> (0.52 mL, 4.20 mmol) was added to a solution of compound 11 (1.18 g, 4.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 L) at RT under a nitrogen

atmosphere. The reaction mixture was stirred for 5 h at RT. FeCl<sub>3</sub> (about 1.5 g) was added and the solution was opened to air and stirred for an additional 24 h. The reaction mixture was filtered through Celite, the filtrate was evaporated under reduced pressure, and the residue was passed through a short column of alumina. The mixture was separated by repeated column chromatography on Sephadex (CHCl<sub>3</sub>) to give compound 7 (281 mg, 27%) as a dark-brown solid. Recrystallization from CH<sub>2</sub>Cl<sub>2</sub> gave dark-brown needles that were suitable for X-ray analysis. M.p. 265 °C (dec.); <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 6.19 ppm (s, 8H; β-H); <sup>19</sup>F NMR (470 MHz):  $\delta$  = -161.4 (td, *J*=21.6, 6.8 Hz, 8F; *meta*-F), -153.6 (dd, *J*=22.0, 21.6 Hz, 4F; *para*-F), -138.7 ppm (dd, *J*=21.6, 6.8 Hz, 8F; *ortho*-F); HRMS (FAB, positive): *m/z* calcd for C<sub>44</sub>H<sub>8</sub>F<sub>20</sub>S<sub>4</sub>: 1043.9180.

**X-ray crystallographic analysis**: Measurements were made with graphitemonochromated Mo K $\alpha$  ( $\lambda$ =0.71073 Å) radiation and a rotating-anode generator. The crystal structures were solved by direct methods using SHELXS-97<sup>[41]</sup> and refined by full-matrix least-squares procedures on  $F^2$ for all reflections with SHELXL-97.<sup>[42]</sup> Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. CCDC-806230 (**6b**) and CCDC-829927 (**7**) contain 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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## Heteroporphyrins -

M. Kon-no, J. Mack, N. Kobayashi,\* M. Suenaga, K. Yoza, T. Shinmyozu\*.....

Synthesis, Optical Properties, and Electronic Structures of Fully Core-Modified Porphyrin Dications and Isophlorins



**En-core une fois**: Fully core-modified tetrathiaporphyrin dications and tetrathiaisophlorins were synthesized (see figure). The key features of their electronic structures were elucidated by an in-depth combined analysis of experimental- and theoretical data.