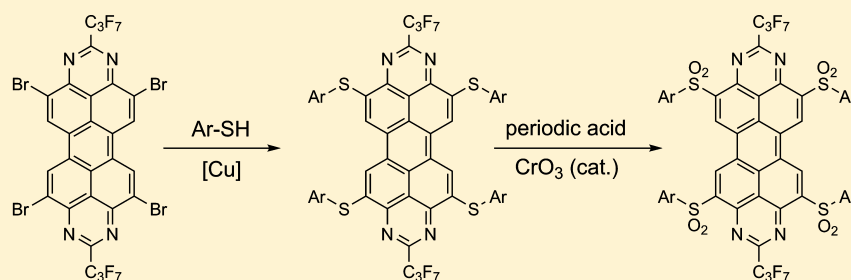


Arylmercapto Substituted Tetraazaperopyrene Derivatives and Their Oxidation to Tetrasulfones: Photophysics and Electrochemistry

Susanne Langbein, Hubert Wadepohl, and Lutz H. Gade*

Anorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany

S Supporting Information



TAPPBr₄

Ar = aromatic substituent

ABSTRACT: Fourfold arylmercapto substituted tetraazaperopyrene (TAPP) derivatives were obtained by direct nucleophilic substitution of the tetrabrominated TAPP or via Cu-catalyzed S–C coupling. These new materials display a characteristic bathochromic shift of their visible absorption and emission bands by ca. 200 nm compared to the unsubstituted parent compound. Two of the sulfide derivatives were oxidized with periodate to give their corresponding sulfones.

Polycyclic aromatic compounds have found manifold applications as functional dyes which are employed as chemical sensors and in light emitting diodes or as organic semiconductors in various electronic devices.^{1–13} Among these materials perylene-3,4,9,10-tetracarboxydiimines (PDIs) and naphthalenediimides (NDIs) have attracted particular attention.^{14–18} The development of synthetic methods for the functionalization of the polyaromatic core were at the center of this research.^{19–30} Several years ago we developed an efficient route for the synthesis of 1,3,8,10-tetraazaperopyrene (TAPP) derivatives,^{31–34} giving access to a class of organic dyes with properties which are related to those of the ubiquitous PDIs. Their electrochemical and photophysical behavior could be conveniently modified by introducing electron-withdrawing or -donating substituents at the core,^{35–37} giving rise to TAPP derivatives which have been applied inter alia as organic semiconductors in thin-film transistors^{35,37} and as biological fluorescence markers.³⁸ The fourfold core-brominated TAPP derivatives were found to be good starting materials for subsequent transformations and thus a systematic development of this class of functional organic dyes.

Herein we report the synthesis of a range of different arylmercapto substituted TAPP derivatives, and the introduction of aryl-S substituents to the polycyclic aromatic core was found to have the greatest effect on their photophysical properties observed to date. Moreover, the possibility to oxidize the thioethers subsequently and thus further modify their photo- and redox-chemical properties provided an additional incentive for this study. We note that there are only a few

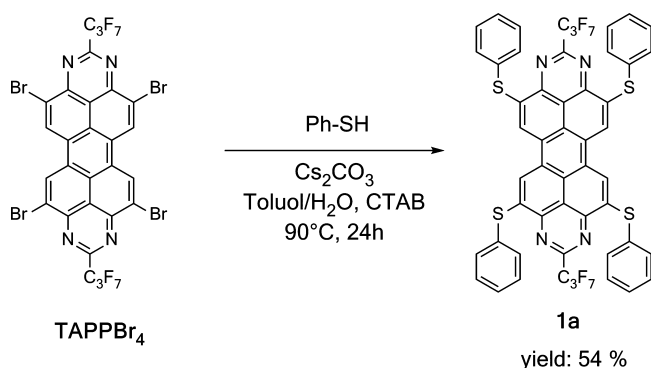
detailed investigations into the oxidation of sulfides coupled to a chromophore,^{39–42} all of which report significant changes in the photophysical behavior resulting from the oxidation. Possible applications for such sulfoxides and sulfones are visual sensors for detecting explosives such as TATP^{41,43} or nitrates.⁴⁴

The parent derivative 2,9-bis(heptafluoropropyl)-4,7,11,14-tetrakis(thiophenyl)-1,3,8,10-tetraazaperopyrene (**1a**) was synthesized via nucleophilic substitution with thiophenol of the corresponding tetrabrominated TAPP derivative (TAPPBr₄) (Scheme 1).³⁶ Since this approach proved unsuccessful for some arylthiolates we investigated alternative synthetic routes for arylmercapto substituted TAPP derivatives. Following a protocol by Guo et al.,⁴⁵ using copper iodide/L-proline as a catalyst, several different arylthiolates were coupled successfully, and this route proved to be more efficient for the preparation of most arylmercapto substituted TAPP derivatives (Scheme 2). The yield of **1c**, for example, could be more than doubled while other derivatives, which were inaccessible via the noncatalytic route, could now be successfully synthesized (**1g** and **1h**).

However, an observed limitation of the catalyzed reaction is the intolerance toward *N*-heterocycles such as pyridine, possibly due to coordination to copper. Therefore, the derivatives 2,9-bis(heptafluoropropyl)-4,7,11,14-tetrakis(4-mercaptopyridyl)-1,3,8,10-tetraazaperopyrene (**1e**) and 2,9-bis(heptafluoropropyl)-4,7,11,14-tetrakis(4-isopropylthio-

Received: August 24, 2015

Published: October 30, 2015

Scheme 1. Synthesis of the Arylmercapto Substituted TAPP Derivative **1a**³⁶

phenyl)-1,3,8,10-tetraazaperopyrene (**1f**) were synthesized via direct nucleophilic substitution. Both synthetic approaches thus complement each other in their scope. However, the shorter reaction time and yields of up to 85% generally favor the Cu-catalyzed synthesis of arylmercapto substituted TAPP derivatives.

Single crystals of a thf solvate of **1b** suitable for X-ray diffraction were grown from a saturated solution of the compound in tetrahydrofuran. The top view of the molecular structure of **1b** is depicted in Figure 1 along with a listing of selected metric parameters. The structure consists of slipped stacks of TAPP molecules (face-to-face arrangement of the molecules with an interplanar distance between the tetraazaperopyrene cores of 3.46 Å). Two of the arylmercapto substituents diagonally across the nearly planar (rmsd 0.02 Å) polycyclic aromatic core are twisted by 102° out of the plane, whereas the other two lie in the same plane, albeit with an orientation of their phenyl rings approximately orthogonal to it. The disordered thf molecules are in between the stacks, flanked

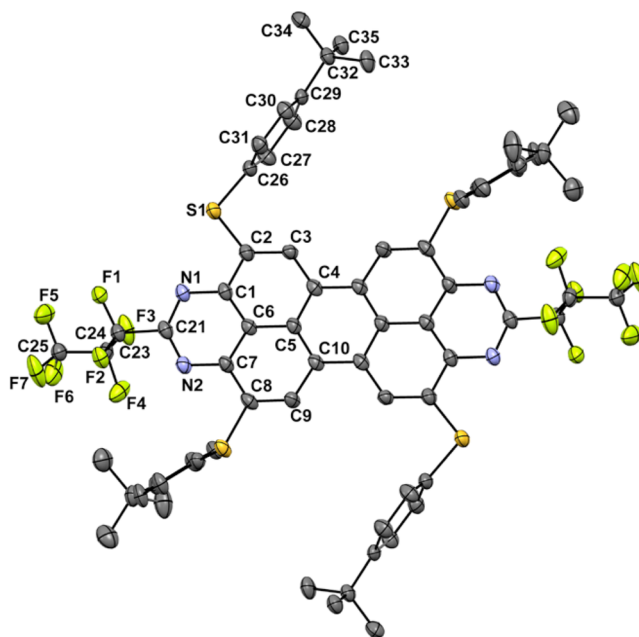
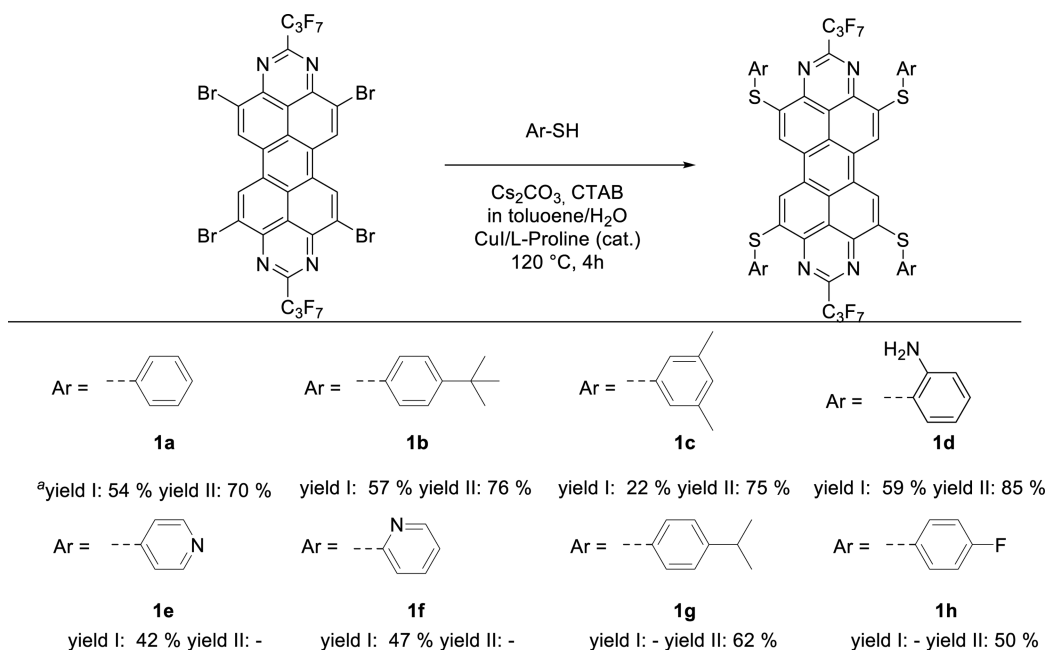


Figure 1. Top view of the molecular structure of **1b**. Hydrogen atoms and thf molecules are omitted for clarity. The ellipsoid displacement is drawn at the 50% probability level. Selected bond lengths [Å]: S1/S2–C2/C8 1.748(3)/1.773(3), S1/S2–C26/C36 1.779(3)/1.777(3), N1/N2–C21 1.334(4)/1.319(4), N1/N2–C1/C7 1.354(4)/1.350(4), C1/C7–C6 1.403(4)/1.426(4), C1/C7–C2/C8 1.450(4)/1.426(4), C2/C8–C3/C9 1.374(4)/1.359(4), C3/C9–C4/C10 1.419(4)/1.443(4), C4–C10 1.428(4), C4/C10–C5 1.428(4)/1.406(4).

by the “out of plane” S(C₆H₄tBu) substituents (Figure S1, see Supporting Information).

The photophysical properties of the arylmercapto substituted TAPP derivatives are summarized in Table 1, and exemplary absorption as well as emission spectra are shown in Figure 2.

Scheme 2. Synthesis of the Arylmercapto Substituted TAPP Derivatives **1b** to **1h**

^aYields: (I) obtained via nucleophilic substitution; (II) obtained via Cu catalysis.

Table 1. $\pi^* \leftarrow \pi$ Transition λ_{\max} [nm] and Vibrational Progression $\Delta\nu$ [cm^{-1}] in the Absorption and Emission Spectra Recorded in CH_2Cl_2

entry	Absorption λ_{\max} [nm] (log ϵ)	$\Delta\nu$ [cm^{-1}]	λ_{em} [nm] (Stokes shift, nm)	Φ
1a	568 (4.33)	1406	607 (39)	0.08
1b	559 (4.62)	1202	623 (64)	0.005
1c	568 (4.76)	1195	632 (64)	0.02
1d	561 (4.30)	1295	592 (31)	0.01
1e	547 (5.06)	871	578 (31)	0.44
1f	535 (4.18)	1280	592 (57)	0.39
1g	563 (4.50)	1142	628 (65)	0.008
1h	565 (4.56)	1349	600 (35)	0.07

All compounds $\text{TAPP}(\text{SR})_4$ absorb in a range from 535 to 568 nm ($\pi^* \leftarrow \pi$ transitions) and thus are strongly bathochromically shifted compared to the unsubstituted TAPP (436 nm) and the tetrabrominated TAPPBr_4 (475 nm) rendering their solutions red to purple. They were found to be fluorescent, again with a strong bathochromic shift [$\lambda_{\text{max}} = 578\text{--}632$ nm, compared to the unsubstituted (448 nm) and the tetrabrominated TAPPs (486 nm)] and with emission quantum yields varying widely, ranging from 0.005 to 0.44.

The strong bathochromic shift of the visible absorption and emission bands of $\text{TAPP}(\text{SR})_4$ compared to TAPP and TAPPBr_4 is reflected in the reduced HOMO–LUMO energy gap of the former [DFT, B3PW91/6-31g(d,p)]. The computed HOMO–LUMO gaps of 2.96, 2.61, and 2.34 eV for TAPP, TAPPBr_4 , and the $\text{TAPP}(\text{SR})_4$ derivative **1b** correspond the wavelengths of 419, 475, and 530 nm, respectively, indicating that the electronic transitions are dominated by the HOMO–LUMO component. As is illustrated in Figure 3, the reduced HOMO–LUMO gap for **1b** is primarily due to a significant destabilization of the HOMO upon arylmercapto substitution.

The TAPP derivatives **1c–d** and **1g–h** possess low fluorescence quantum yields ($\phi = 0.005\text{--}0.07$). On the other hand, the pyridine-thiolato substituted compounds **1e** and **1f** display drastically increased fluorescence quantum yields of 0.44 (**1e**) and 0.39 (**1f**).

All ArylS-substituted TAPP derivatives exhibit two quasi-reversible reduction waves, corresponding to the formation of the stable mono- and dianions. The cyclic voltammogram of compound **1c** is shown in Figure 4. The difference in the peak potentials was measured against the scan rate and was found to have the expected linear dependency, as well as the square-root dependency of the cathodic peak current, indicating quasi-

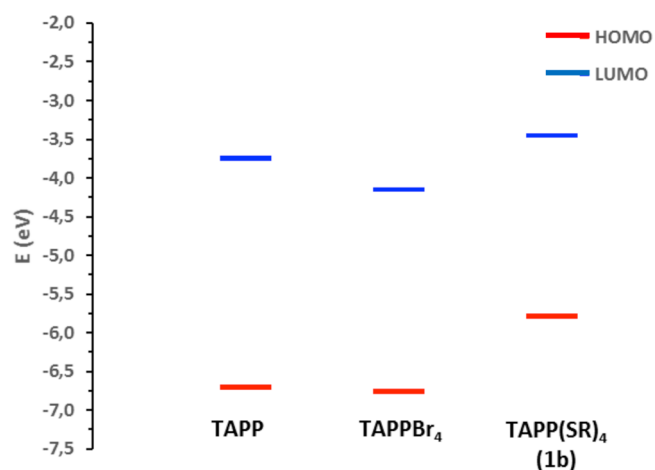


Figure 3. HOMO and LUMO energy levels of TAPP, TAPPBr_4 , and the $\text{TAPP}(\text{SR})_4$ derivative **1b**.

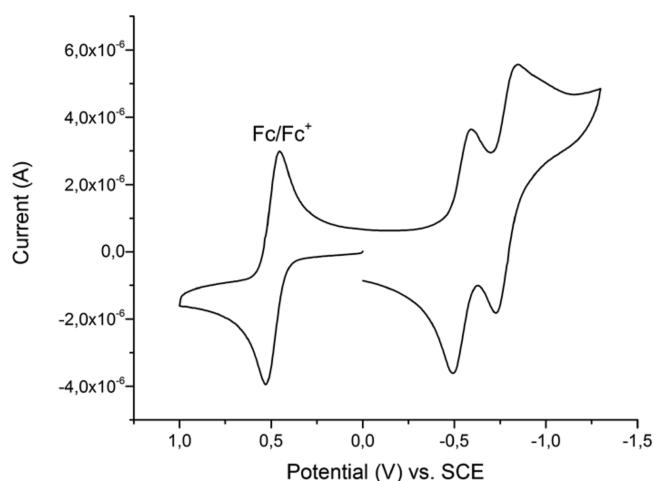


Figure 4. Cyclic voltammogram of **1c** recorded in CH_2Cl_2 (sweep rate 50 mVs^{-1} ; supporting electrolyte Bu_4NPF_6 , reference SCE).

reversibility (Figures S5 and S6; see Supporting Information). DFT modeling of the electronic properties of all the $\text{TAPP}(\text{SR})_4$ derivatives was carried out to gain additional information about the electron affinity of the compounds (Table 2).

The LUMO energy as well as the electron affinity which are indicators of electron acceptor properties of the molecular

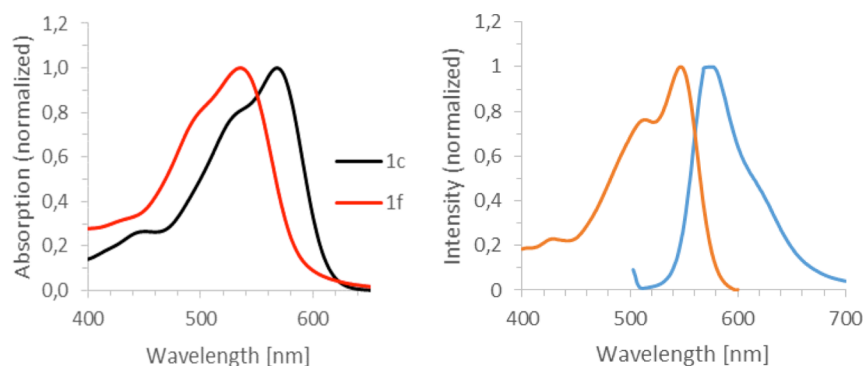


Figure 2. Normalized UV/vis absorption spectra of **1c** and **1f** in dichloromethane (left). Exemplary normalized absorption (orange) and emission (blue) spectra of **1e** in dichloromethane (right).

Table 2. Electrochemical Properties of Compounds 1b–1h

entry	$E^{1/2}_1$ (ΔE_p) [V] ^a	$E^{1/2}_2$ (ΔE_p) [V] ^a	$E_{\text{LUMO(expt)}}$ [eV] ^b	$E_{\text{LUMO(calcd)}}$ [eV] ^c	EA [eV] ^d	band gap (expt) [eV]	band gap (calcd) [eV]
1b	−0.38 (0.24)	−0.77 (0.25)	−3.77	−3.40	2.55	2.22	2.34
1c ^b	−0.57 (0.10) ^b	−0.82 (0.11) ^b	−3.77	−3.42	2.51	2.18	2.33
1d	−0.42 (0.10)	−0.70 (0.13)	−3.81	−3.45	2.76	2.21	2.24
1e ^b	−0.30 (0.08) ^b	−0.61 (0.10) ^b	−4.08	−4.18	3.28	2.27	2.40
1f	−0.33 (0.10)	−0.61 (0.11)	−3.90	−3.46	2.59	2.32	2.34
1g	−0.39 (0.22)	−0.78 (0.26)	−3.85	−3.42	2.55	2.20	2.34
1h	−0.36 (0.22)	−0.73 (0.23)	−3.88	−3.64	2.76	2.19	2.37

^aMeasured against SCE in THF or CH₂Cl₂. ^bDetermined according to literature methods using Fc/Fc⁺ as reference ($E_{\text{HOMO}}(\text{Fc}) = -4.8$ eV).⁴⁸ ^cCalculated at the B3PW91/6-31g(d,p) level of theory. ^dCalculated at the B3PW91/6-311g(2,d,2p) level of theory.

materials concerned are summarized in Table 2. The DFT calculated LUMO energies of the arylmercapto TAPPs differ slightly from the experimentally obtained data derived from cyclic voltammograms. This can be attributed inter alia to the free rotation of the substituents around the C–S bond which results in a Boltzmann weighted average of the accessible conformations, whereas the computationally derived values were based on optimized molecular structures (i.e., fixed conformations). This conformational effect is increased for bulkier substituents (and increased number of internal degrees of freedom) in the TAPP derivative which we had also found in previous studies.³⁶ We note that the LUMO energy and the electron affinity of the 4-pyridylthiolato derivative 1e lie in the range of other acceptor TAPPs such as the tetrachlorinated³⁵ and tetrabrominated³⁷ TAPP derivatives which have been used as n-channel semiconductors in organic electronic devices.

The complete S-oxidation of the arylmercapto TAPP derivatives and its effect on their photophysical properties was examined in view of previous studies of the fluorescence of sulfide and sulfoxide based polyaromatic fluorophores.^{39,40} For the full conversion to their corresponding sulfones, a strong oxidant was required. The oxidation via a protocol reported by Trudell et al.,⁴⁹ using periodic acid as the oxidant together with a catalytic amount of CrO₃, led to full oxidation of two arylmercapto TAPP derivatives to their corresponding sulfones 2a, 2b (Scheme 3), while all attempts to oxidize the compounds 1c–1h only gave product mixtures.

The oxidation is accompanied by a change of color from purple to bright orange, and the products were isolated as yellow microcrystalline solids which were found to be

(sparingly) soluble in chlorinated solvents. The absorption bands in the UV–vis spectra of the tetrasulfonyl TAPPs exhibit a hypsochromic shift of about 100 nm for 2a (452 nm) and 2b (457 nm) compared to the corresponding starting materials 1a and 1b. Their photophysical data are summarized in Table 3.

Table 3. Photophysical Data of 2a and 2b in Dichloromethane

entry	λ_{max} [nm] (log ϵ)	$\Delta\nu$ [cm ^{−1}]	λ_{em} [nm] (Stokes shift)	Φ
2a	452 (4.48)	1350	489 (37)	0.02
2b	457 (4.47)	1374	490 (33)	0.02

This hypsochromic shift of about 100 nm was also found in a time dependent DFT modeling [B3PW91/def2-TZVPP] for compounds 1a and 2a, and the computed values were found to be consistent with the experimental results (Figure S7; see Supporting Information).

Both compounds 2a and 2b are weakly fluorescent in methylene chloride with quantum yields of 0.02. The tetrasulfone substituted TAPP derivatives exhibit reversible reduction waves in the cyclic voltammograms, however as expected at more positive potentials than 1a and 1b owing to the electron-withdrawing nature of the sulfone substituents (Figure S4; see Supporting Information).

The results for the cyclic voltammetric measurements and DFT modeling are listed in Table 4. For the tetrasulfone TAPP derivatives a drastic reduction of the LUMO energies could be deduced from the electrochemical data and DFT modeling as well as an increase in the electron affinity which was found to be in the same range as for the tetrachlorinated TAPP.³⁵

In summary, we developed two alternative synthetic routes to tetra-substituted arylmercapto TAPP derivatives, via direct nucleophilic substitution or by using a copper catalyzed C–S coupling route. These new materials show interesting photophysical and electrochemical properties, in particular a bathochromic shift of their visible absorption and emission bands by ca. 200 nm compared to the unsubstituted parent compound. In favorable cases these diaryl sulfides can be further transformed by oxidation to tetrasulfones which exhibit redox-chemical properties that render them potentially interesting as n-channel semiconductors.

EXPERIMENTAL SECTION

General. Air sensitive syntheses (1e; 1f) were carried out under dried argon and handled with standard Schlenk glassware that was flame-dried prior to use. Solvents were dried over activated alumina columns using a solvent purification system (M. Braun SPS 800) and saturated with argon. 2,9-Bis-heptafluoropropyl-4,7,11,14-tetrabromo-1,3,8,10-tetraazaperopyrene³⁷ was prepared according to a literature procedure. Other materials were purchased commercially and used

Scheme 3. Synthesis of the Tetrasulfone TAPP Derivatives 2a and 2b

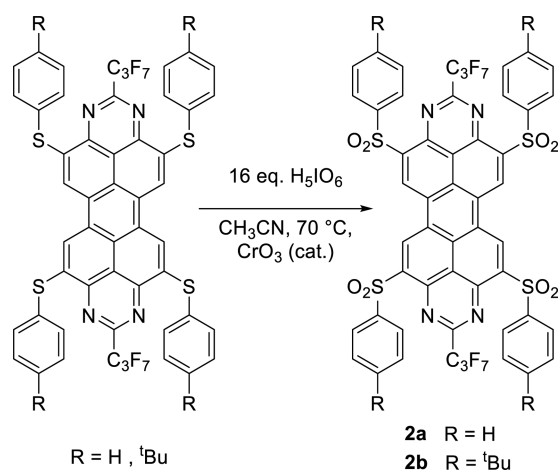


Table 4. Electrochemical Properties of 2a,b and Their Corresponding Arylmercapto TAPP Precursors

entry	$E^{1/2}_1$ (ΔE_p) [V] ^a	$E^{1/2}_2$ (ΔE_p) [V] ^a	$E_{\text{LUMO(expt)}}$ [eV] ^b	$E_{\text{LUMO(calcd)}}$ [eV] ^c	EA [eV] ^d	band gap (expt) [eV]	band gap (calcd) [eV]
1a ³⁶	-0.35	-0.67	-3.82	-3.49	2.60	2.18	2.34
1b	-0.58 (0.10)	-0.83 (0.10)	-3.77	-3.40	2.55	2.22	2.34
2a	0.10 (0.12)	-0.28 (0.13)	-4.44	-4.39	3.45	2.74	2.79
2b	0.14 (0.08)	-0.24 (0.10)	-4.44	-4.27	3.36	2.71	2.86

^aMeasured against SCE in CH₂Cl₂. ^bDetermined according to literature methods using Fc/Fc⁺ as an internal standard ($E_{\text{HOMO}}(\text{Fc}) = -4.8$ eV).

^cCalculated at the B3PW91/6-31g(d,p) level of theory. ^dCalculated at the B3PW91/6-311g(2d,2p) level of theory.

without further purification. NMR spectra were measured at 600 or 400 MHz, and the chemical shifts in the NMR spectra are expressed in ppm and calibrated according to the solvent signal, respectively. *J* values are given in Hz. Mass spectra were recorded as FAB and high resolution FAB and with an FT-ICR mass spectrometer for MALDI and ESI spectra. IR spectra were recorded on an FT-IR with an Atr unit.

General Procedure A for Preparation of Fourfold Arylmercapto Substituted Tetraazaperopyrene Derivatives. To a suspension of 2,9-bis-heptafluoropropyl-4,7,11,14-tetrabromo-1,3,8,10-tetraazaperopyrene (100 mg, 0.1 mmol) in a solvent mixture of toluene (30 mL) and water (10 mL) was added Cs₂CO₃ (8 to 16 equiv) and CTAB (36 mg, 0.1 mmol) as well as copper iodide (7.7 mg, 5 mol %) and L-proline (9.2 mg, 10 mol %). Further, the corresponding thiole was added and the reaction mixture was refluxed for 4 h at 120 °C. Then the product was extracted with chloroform, and the organic layer was washed with brine and dried over Mg₂SO₄. The solution was filtered over Celite, and the solvent was evaporated. The residue was washed with methanol, diethyl ether, and pentane. The solid product was then dried under vacuo.

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(thiophenyl)-1,3,8,10-tetraazaperopyrene (1a). Synthesized according to general procedure A with thiophenole. 76 mg, 69% yield; ¹H NMR (399.89 MHz, THF-*d*₆) δ 8.91 (s, 4H), 7.70 (d, ³*J* = 7.9 Hz, 8H), 7.60 (m, 4H), 7.52 (m, 8H). The obtained data are in accord with the literature.²¹

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(4-tert-butylthiophenyl)-1,3,8,10-tetraazaperopyrene (1b). Synthesized according to general procedure A with 4-tert-butyl-benzenethiolole. 101 mg (0.08 mmol), 76% yield; ¹H NMR (600.13 MHz, THF-*d*₆) δ 9.16 (s, 4H), 7.65 (d, ³*J* = 8.4 Hz, 8H), 7.55 (d, ³*J* = 8.4 Hz, 8H), 1.40 (s, 36H); ¹³C NMR (150.90 MHz, THF-*d*₆) δ 153.5 (C), 153.1 (C), 141.1 (C), 134.4 (CH), 130.1 (C), 129.7 (CH), 127.5 (CH), 126.4 (C), 119.6 (C), 117.6 (C), 35.3 (C), 31.4 (CH₃); ¹⁹F NMR (376.27 MHz, THF-*d*₆) δ -81.03 (m, 6F), -113.79 (m, 4F), -126.02 (m, 6F); HRMS (HR-FAB⁺) calcd for C₆₈H₅₆F₁₄N₄S₄ + H⁺ 1323.3237, found 1323.3264.

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(3,5-dimethylthiophenyl)-1,3,8,10-tetraazaperopyrene (1c). Synthesized according to general procedure A with 3,5-dimethylthiophenole. 93 mg (0.08 mmol), 77% yield; ¹H NMR (600.13 MHz, THF-*d*₆) δ 9.27 (s, 4H), 7.39 (s, 8H), 7.13 (s, 4H), 2.35 (s, 24H); ¹³C NMR (150.90 MHz, THF-*d*₆) δ 153.0 (C), 141.2 (C), 140.1 (C), 131.7 (CH), 131.6 (CH), 130.2 (C), 128.3 (CH), 126.5 (C), 119.3 (C), 117.2 (C), 21.0 (CH₃); ¹⁹F NMR (376.27 MHz, THF-*d*₆) δ -81.08 (t, ³*J*_{FF} = 10.9 Hz, 6F), -113.77 (m, 4F), -126.19 (s, 6F); HRMS (HR-FAB⁺) calcd for C₆₀H₄₀F₁₄N₄S₄ 1210.1912, found 1210.1924.

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(2-aminothiophenyl)-1,3,8,10-tetraazaperopyrene (1d). Synthesized according to general procedure A with 2-aminothiophenole. 99 mg (0.09 mmol), 85% yield; ¹H NMR (600.13 MHz, THF-*d*₆) δ [ppm] = 8.81 (s, 4H), 7.53 (d, ³*J* = 7.7 Hz, 4H), 7.37 (t, ³*J* = 7.7 Hz, 4H), 6.85 (d, ³*J* = 7.7 Hz, 4H), 7.78 (t, ³*J* = 7.7 Hz, 4H), 5.10 (s, 8H). ¹³C NMR (150.90 MHz, THF-*d*₆) δ 153.4 (C), 151.5 (C), 139.7 (C), 137.6 (CH), 132.9 (CH), 127.4 (C2), 126.7 (C), 118.9 (C), 118.6 (C11), 117.1 (C), 116.2 (CH), 111.1 (C); ¹⁹F NMR (376.27 MHz, THF-*d*₆) δ -81.09 (t, ³*J*_{FF} = 9.2 Hz, 6F), -113.41 (m, 4F), -125.82 (s, 6F); HRMS (HR-ESI⁺) calcd for C₅₂H₂₈F₁₄N₄S₄ + H⁺ 1159.1169, found 1159.1179.

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(4-mercaptopyridinyl)-1,3,8,10-tetraazaperopyrene (1e). To a suspension of 4-mercaptopyridine (100 mg, 0.80 mmol) in *N,N*-dimethylformamide (40 mL) were added 2,9-bis-heptafluoropropyl-4,7,11,14-tetrabromo-1,3,8,10-tetraazaperopyrene (100 mg, 0.1 mmol) and Cs₂CO₃ (260.7 mg, 0.8 mmol). The reaction mixture was heated up to 120 °C for 48 h. Then hypochloric acid (50 mL, 1 M) and chloroform (30 mL) was added and the precipitate filtered. The residue was washed with water, methanol and pentane. 47 mg, 43% yield; ¹H NMR (376.27 MHz, THF-*d*₆) δ [ppm] = 9.95 (s, 4H), 8.49 (d, ³*J* = 6.04 Hz, 8H), 7.40 (d, ³*J* = 6.09 Hz, 8H); ¹³C NMR (150.90 MHz, THF-*d*₆) δ 153.9 (C), 151.2 (CH), 145.4 (C), 137.1 (C), 134.6 (CH), 127.6 (C), 125.3 (CH), 119.7 (C), 118.1 (C); ¹⁹F NMR (376.27 MHz, THF-*d*₆) δ -81.19 (t, ³*J*_{FF} = 8.7 Hz, 6F), -113.96 (m, 4F), -126.38 (m, 6F); HRMS (HR-FAB⁺) calcd for C₄₈H₂₀F₁₄N₈S₄ + H⁺ 1103.0543, found 1103.0526.

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(2-mercaptopyridinyl)-1,3,8,10-tetraazaperopyrene (1f). To a suspension of 2-mercaptopyridine (100 mg, 0.80 mmol) in *N,N*-dimethylformamide (40 mL) were added 2,9-bis-heptafluoropropyl-4,7,11,14-tetrabromo-1,3,8,10-tetraazaperopyrene (100 mg, 0.1 mmol) and Cs₂CO₃ (521.4 mg, 1.6 mmol). The reaction mixture was heated up to 120 °C for 48 h. Then hypochloric acid (50 mL, 1 M) was added and the precipitate was filtered. The residue was washed with water, methanol, and pentane. 63 mg, 57% yield; ¹H NMR (376.27 MHz, THF-*d*₆) δ 10.39 (s, 4H), 8.26 (d, ³*J* = 4.7 Hz, 4H), 7.71 (t, ³*J* = 7.4 Hz, 4H), 7.64 (d, ³*J* = 7.8 Hz, 4H), 7.17 (m, 4H); ¹³C NMR (150.90 MHz, THF-*d*₆) δ 154.1 (C), 150.5 (CH), 137.6 (C), 136.6 (CH), 134.8 (CH), 130.4 (C), 127.4 (C), 125.0 (CH), 122.1 (CH), 121.1 (C4), 120.9 (C); ¹⁹F NMR (376.27 MHz, THF-*d*₆) δ -81.19 (m, 6F), -113.85 (m, 4F), -126.42 (m, 6F); HRMS (HR-FAB⁺) calcd for C₄₈H₂₀F₁₄N₈S₄ + H⁺ 1103.0543, found 1103.0526.

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(4-isopropylthiophenyl)-1,3,8,10-tetraazaperopyrene (1g). Synthesized according to general procedure A with 4-isopropylthiophenole. 79 mg (0.06 mmol), 62% yield; ¹H NMR (600.13 MHz, THF-*d*₆) δ 9.08 (s, 4H), 7.61 (d, ³*J* = 8.1 Hz, 8H), 7.36 (d, ³*J* = 8.1, 8H), 3.01 (quintet, ³*J* = 6.89, 4H), 1.32 (d, ³*J* = 6.89, 24H); ¹³C NMR (150.90 MHz, THF-*d*₆) δ 153.4 (C), 151.0 (C), 141.3 (C), 134.7 (CH), 129.8 (C), 129.6 (CH), 128.7 (C), 126.4 (C), 119.5 (C), 117.4 (C), 34.8 (CH), 24.1 (CH₃); ¹⁹F NMR (376.27 MHz, THF-*d*₆) δ -81.01 (t, ³*J*_{FF} = 8.7 Hz, 6F), -113.76 (m, 4F), -126.05 (m, 6F); HRMS (HR-MALDI pos.) calcd for C₆₄H₄₈F₁₄N₄S₄ 1266.2538, found 1266.2555.

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(4-fluorothiophenyl)-1,3,8,10-tetraazaperopyrene (1h). Synthesized according to general procedure A with 4-fluorothiophenole. 59 mg (0.05 mmol), 50% yield; ¹H NMR (376.27 MHz, THF-*d*₆) δ 8.93 (s, 4H), 7.77 (dd, ³*J*_{HHF} = 5.7 Hz, 8H), 7.38 (t, ³*J*_{HHF} = 7.7 Hz, 8H); ¹³C NMR (150.90 MHz, THF-*d*₆) δ 163.5 (C), 152.7 (C), 142.3 (C), 137.6 (CH), 128.5 (C), 126.5 (CH), 126.4 (C), 118.2 (C), 118.0 (CH); ¹⁹F NMR (376.27 MHz, THF-*d*₆) δ -81.01 (t, ³*J*_{FF} = 9.3 Hz, 6F, CF₃), -110.68 (s, 4F), -113.68 (m, 4F), -126.03 (m, 6F); HRMS (HR-FAB⁺) calcd for C₅₂H₂₀F₁₈N₄S₄ + H⁺ 1171.0356, found 1171.0334.

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(phenylsulfonyl)-1,3,8,10-tetraazaperopyrene (2a). To a freshly made solution of periodic acid (165 mg, 0.700 mmol) and chromium trioxide (0.350 mg, 8 mol %) in acetonitrile (6 mL) was added 2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(thiophenyl)-1,3,8,19-tetraazaperopyrene (1a) (50 mg, 0.045 mmol). The reaction mixture was stirred at 70 °C

for 3 h. The resultant precipitate was filtered, and the residue was washed with acetonitrile, sodium bicarbonate, water, methanol, and pentane. Due to poor solubility in organic solvents, the NMR information was gained from the deuterated species by solving **2a** in D₂SO₄. 42 mg (0.034 mmol), 75% yield; ¹H NMR (600.13 MHz, D₂SO₄) δ 11.19 (s, 4H), 8.28 (m, 8H), 7.75 (m, 4H), 7.62 (m, 8H); Poor solubility precluded the acquisition of useful ¹³C NMR data; ¹⁹F-NMR (376.27 MHz, D₂SO₄) δ -80.01 (t, ³J_{FF} = 9.7 Hz, 6F), -115.98 (m, 4F), -124.59 (m, 4F); HRMS (HR-MALDI pos.) calcd for C₅₂H₂₄F₁₄N₄O₈S₄ 1226.0253, found 1226.0279; IR 1333 (s, SO₂), 1155 (s, SO₂).

2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis((4-tert-butylphenyl)sulfonyl)-1,3,8,10-tetraazaperopyrene (2b). To a freshly made solution of periodic acid (300 mg, 1.280 mmol) and 8 mol % chromium trioxide (0.64 mg) in acetonitrile (11 mL) was added **2,9-Bis(heptafluoropropyl)-4,7,11,14-tetrakis(4-tert-butylthiophenyl)-1,3,8,19-tetraazaperopyrene (1b)** (100 mg, 0.076 mmol). The reaction mixture was stirred at 70 °C for 3 h. The resultant precipitate was filtered, and the residue was washed with acetonitrile, sodium hydro carbonate, water, methanol, and pentane. 79 mg (0.054 mmol), 72% yield; ¹H NMR (600.13 MHz, CD₂Cl₂) δ 10.99 (s, 4H), 8.35 (d, ³J = 9.1 Hz, 8H), 7.59 (d, ³J = 9.1 Hz, 8H), 1.29 (s, 36H). Poor solubility precluded the acquisition of useful ¹³C NMR data; ¹⁹F NMR (376.27 MHz, CD₂Cl₂) δ -80.41 (t, ³J_{FF} = 9.3 Hz, 6F), -114.13 (m, 4F), -125.17 (m, 6F); HRMS (HR-MALDI pos.) calcd for C₆₈H₅₆F₁₄N₄O₈S₄ 1450.2757, found 1450.2777; IR 1333 (s, SO₂), 1159 (s, SO₂).

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01969.

¹H, ¹³C, and ¹⁹F NMR spectra for all new compounds, crystal structure and data for **1b**, cyclic voltammograms, absorption and emission spectra, and computational methods (PDF)

Computational data (PDF)

Crystallographic data for **1b** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lutz.gade@uni-hd.de.

Notes

The authors declare no competing financial interest.

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