JOC Note

Star-Shaped Tetrathiafulvalene-Fused Coronene with Large π-Extended Conjugation
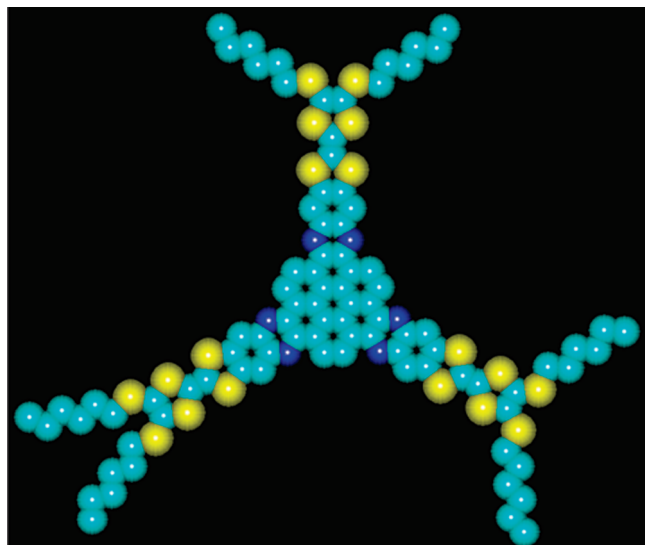
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Received May 20, 2009

A tristar shaped, planar TTF-fused coronene **1** was synthesized. Its electronic properties have been studied experimentally by the combination of electrochemistry and UV−vis−NIR spectroscopy. Thereby, a nano-sized graphite fragment is largely extended in its size, supplemented with a multielectron donor functionality, and shaped to a strongly chromophoric species absorbing intensely in the visible part of the optical spectrum.

Polycyclic aromatic hydrocarbons are of immense importance due to their unique electronic properties and propensity to form self-assembled graphitic nanostructures or columnar assemblies, thereby leading to potential applications in a variety of (opto)electronic devices such as field effect transistors, photovoltaic cells, and electroluminescent

displays as well as in chirotechnology.[1] In this context, the coronene molecule represents a flat nanosized graphite fragment of D_{6h} symmetry. With the appropriate functionalization, the coronene derivatives are particularly good candidates for obtaining discotic liquid−crystalline phases over a wide temperature range and with high charge carrier mobilities.[2] However, owing to the limited preparative accessibility and the lack of an efficient and convenient synthetic methodology, there have been only a few functionalized coronene derivatives reported in the literature.[3] We present here the 3-fold tetrathiafulvalene (TTF) fused coronene **1** (Scheme 1), which as a combination of TTFs and coronene represents a novel redox-active, star-shaped and to a large extent π-conjugated system, displaying a defined D_{3h} symmetry. By that, the annulated compound **1** exceeds with its large planar π-conjugated skeleton the size of the hexaperihexabenzocoronene (HBC) moiety, which is regarded as the smallest highly symmetric graphene fragment.[1e] Advantageously, the herein reported synthetic concept easily allows for additional peripheral solubilizing substituents which circumvent the dramatic solubility problems occurring with the increased size of nanographenes. Most importantly, however, the actual annulation process renders the new compound simultaneously a good multielectron donor and a strong chromophore.

As is well-known, both components of this merged molecule **1** are widely seen in several functional molecular materials. The TTFs, as strong π-donors, are main components in the field of organic conductors and superconductors.[4] Moreover, they have frequently been used in the construction of a large variety of donor−acceptor (D−A) systems showing photoinduced electron or energy transfer processes, further leading to long-lived charge-separated states.[5]

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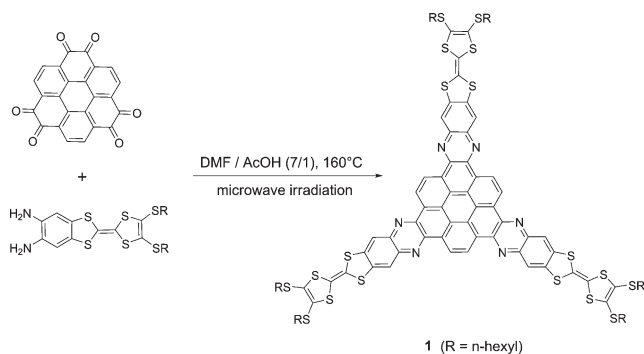
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SCHEME 1. **Synthesis of the TTF-Fused Coronene System 1**

1 (R = n-hexyl)

FIGURE 1. Evolution of the absorption spectra of **1** (2×10^{-4} M; 1 mm path length) in CH_2Cl_2/THF (1:1) with increasing amounts of $NOSbF_6$.

It is noteworthy that TTF-fused D−A systems are not yet fully explored.[6] Significantly, the annulation of donors and acceptors into a planar configuration facilitates and rules by symmetry arguments the occurrence of photoinduced intramolecular charge-transfer (CT) processes. As a consequence, we have investigated the electrochemical and spectroscopic properties of the TTF-annulated coronene derivative **1**, aiming at assessing the effects of their mutual electronic interactions.

The fused target compound **1** was obtained in reasonable yield via the direct condensation reaction of 1,2,5,6,9,10-coronene−hexaone with 5,6-diamino-2-[4,5-bis(hexylthio)-1,3-dithio-2-ylidene]benzo[d]-1,3-dithiole (TTF−diamine) in DMF in the presence of glacial acetic acid under microwave irradiation (Scheme 1). TTF−diamine was prepared by a phosphite-mediated cross-coupling reaction of 4,5-bis-(hexylthio)-1,3-dithiole-2-one with 5,6-diaminobenzene-1,3-dithiole-2-thione while the synthesis of coronene−hexaone based on the reported procedure[3c] revealed some drawbacks. Much effort has been devoted to modify reaction conditions and also simplify the purification procedures (Supporting Information). In particular, during the conversion of 2,3-dimethoxyterephthalicdialdehyde to 3,6-di(triphenylposphoniumbromide)methylveratrol, bromination with PBr_3 instead of hydrobromic acid turns out to be more efficient due to the elimination of side reactions. Also the high-dilution condition is critical to obtain [2.2.2]paracyclophane via a McMurry reaction, using titanium tetrachloride and zinc.[7] Thus, it turns out to be advantageous to add a solution of the corresponding dialdehyde in THF over a long period of 12 h. Importantly, to quench the reaction with a 10% K_2CO_3 aqueous solution at 0 °C, rather than using 1 M hydrochloric acid at rt, has been proven to give a much cleaner reaction. All precursors to coronene−hexaone have been fully characterized, giving the same analytical data as reported in the literature.[3c]

The UV−vis−NIR spectrum of the neutral, deeply purple-colored compound **1** shows as a main characteristic feature an intense broad absorption band centered at 580 nm ($\varepsilon \approx 6 \times 10^4$ L·mol^{-1}·cm^{-1}) and additional intense absorptions in the UV region below 400 nm (Figure 1 and Supporting Information). It is well established that both coronene and TTF absorb strongly and exclusively in the UV region below 400 nm.[3c,6e] Thus, this new absorption band of the fused molecule **1**, which covers the visible spectral part from 450 to 750 nm, renders this compound highly chromophoric. It can be attributed to an intramolecular electronic π−π* charge-transfer transition (ICT) from the TTF donors to the quinoxaline annulated coronene acceptor core, in analogy to related D−A systems.[6c,6e] The spectral region below 400 nm is assigned to the π−π* transitions of the quinoxaline annulated TTF moieties and the coronene center. Not surprisingly, the new ICT excited state of **1** quenches the fluorescence emission, which is known to occur from plain coronene molecules. The very distinct changes of the optical spectrum of **1** upon oxidation of its donor moieties will be discussed below in relation to its electrochemical characteristics.

The electrochemical properties of **1** were investigated by cyclic voltammetry. At fairly low negative potentials (Supporting Information), two reduction waves were observed at −1.77 and −1.93 V, respectively. They could be attributed to the consecutive reduction steps of the pyrazine moieties by comparison with the reduction of the related fused TTF−HAT (HAT = hexaazatriphenylene) system[6c] as well as with that of coronene derivatives.[8]

At positive potentials (Figure 2), two reversible multielectron oxidation processes occur. The first oxidation wave[9] is rather broad (in a range from 0.07 to 0.31 V), suggesting that the three TTF moieties of **1** can be oxidized successively

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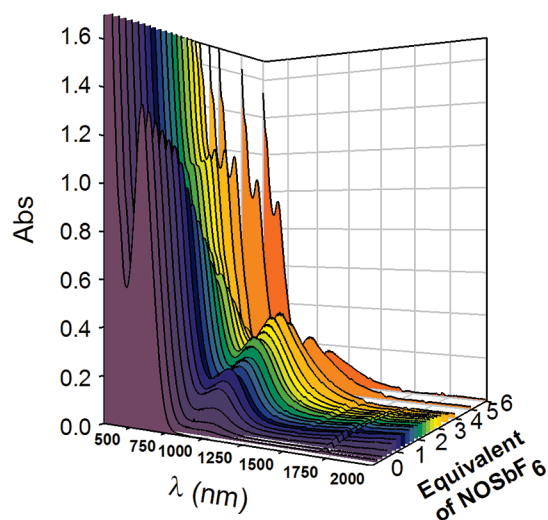(7) Tanner, D.; Wennerström, O.; Norinder, U. *Tetrahredron* **1986**, *42*, 4499.

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(9) It should be noted that the first broad oxidation process could not be clearly deconvoluted in three one-electron processes as in the TTF−HAT molecule, because an adsorption phenomenon occurs at the end of the oxidation process. Many attempts to circumvent this adsorption (probably due to **1**$^{3+}$) by changing the solvent conditions were not successful.
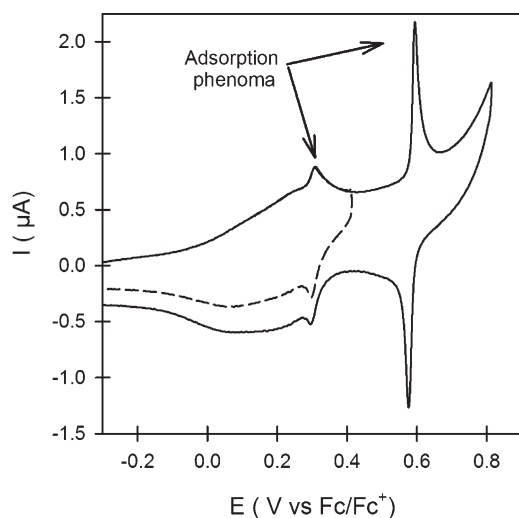
FIGURE 2. Cyclic voltammograms of **1** (2.7×10^{-5} M) in CH$_2$Cl$_2$/THF (1:1), 0.05 M TBAPF$_6$ (TBA = tetrabutylammonium), on platinum electrode; scan rate 0.5 V s^{-1}.

to their TTF$^{\bullet+}$ cation-radical states. This splitting also indicates possible intramolecular electronic interactions among the TTF moieties, as previously observed in the related fused TTF−HAT molecule, for which intramolecular through-bond interactions among the three TTF units were electrochemically detected.[6c] Next, the very narrow peak of the second oxidation wave at 0.58 V suggests that all three TTF$^{\bullet+}$ cation radicals can simultaneously be oxidized to their TTF^{2+} states, leading to the cation **1**$^{6+}$. It can therefore be deduced that the three TTF units now behave like isolated molecules as a result of the Coulombic repulsion among the positively charged species. Such a phenomenon also occurs in other TTF-fused D−A systems.[6c,6d]

Intramolecular electronic interactions among the TTF moieties have been confirmed by the UV−vis−NIR investigation carried out after the chemical oxidation of **1** by a successive aliquot addition of NOSbF$_6$ (Figure 1). Chemical oxidation initially leads to the gradual disappearance of the ICT band at 580 nm and the concomitant emergence of a new absorption band around 900 nm, corresponding to the formation of the cation radical species TTF$^{\bullet+}$. Further addition of NOSbF$_6$ leads to a decrease of the intensity of the radical absorption band and a new absorption band around 420 nm concomitantly emerges, characteristic for the formation of TTF^{2+} dications, taken all together, indicating the presence of two species (**1**$^{3+}$ and **1**$^{6+}$) in chemical equilibrium. Notably, a quite broad absorption band around 2000 nm (Supporting Information) occurs additionally and specifically for the generated **1**$^{2+}$ mixed-valence state. Again, this observation is analogous to the fused HAT−TTF system.[6c]

A ^{1}H NMR study of **1** in toluene shows that all the resonances from the protons of the aromatic rings are almost invisible, while those from the protons of the hexyl groups are quite broad. Temperature-dependent ^{1}H NMR experiments were also performed; however, the aggregation still remains even at high temperatures (up to 100 °C). In contrast, this aggregation could not be clearly evidenced by the concentration-dependent UV−vis spectra, very

probably because of the presence of the strong and broad ICT band.

In summary, a tristar shaped, planar, and widely extended π-conjugated molecule **1** bearing redox-active donor functionalities fused onto a coronene core is accessible via a Schiff-base reaction. Thereby, a nanosized graphite fragment is largely extended in its size, supplemented with a multielectron donor functionality, and shaped to a strongly chromophoric species absorbing intensely in the visible part of the optical spectrum. Since coronene derivatives tend to form columnar and nanotubular assemblies important for electronic and optoelectronic application, the optimization of self-assembling conditions in solution and at a solid−liquid interface for compound **1** and its derivatives with various alkyl chains of different lengths and functional groups is currently under investigation.

Experimental Section

5,6-Diamino-2-(4,5-bis(hexylthio)-1,3-dithio-2-ylidene)benzo-[d]-1,3-dithiole. Triethylphosphite (30 mL) was added slowly to a solution of 4,5-bis(hexylthio)-1,3-dithiole-2-one (1.64 g, 4.68 mmol) and 5,6-diaminobenzene-1,3-dithiole-2-thione (500 mg, 2.34 mmol) in toluene (20 mL) under N$_2$. The resulting solution was heated at 120 °C and stirred for 3 h. The solution was then cooled to room temperature and all solvents were evaporated in vacuum affording an oily red residue, which was subjected to chromatography on silica gel with CH$_2$Cl$_2$/EtOAc (1/3, v/v) as eluant. The crude product was further purified by recrystallization from CH$_2$Cl$_2$/hexane to give a pure compound as a yellow solid. Yield: 42%. Mp 105−106 °C. IR (KBr) (cm^{-1}) 3382, 2949, 2924, 2853, 1615, 1482, 1289, 848, 773. ^{1}H NMR (300 MHz, DMSO-d_6) δ 0.83 (t, 6H), 1.23 (m, 8H), 1.34 (m, 4H), 1.50 (m, 4H), 2.82 (t, 4H), 4.70 (s, 4H), 6.54 (s, 2H). ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 13.8, 21.9, 27.3, 29.2, 30.6, 35.3, 105.2, 107.4, 114.5, 120.9, 126.9, 134.9. EI-MS m/z (I%) 516 (M$^+$, 65). Anal. Calcd for C$_{22}$H$_{32}$N$_2$S$_6$: C, 51.12; H, 6.24; N, 5.42. Found: C, 51.47; H, 6.19; N, 5.21.

TTF-Fused Coronene (1). 1,2,5,6,9,10-Coronene−hexaone was synthesized according to the modified procedure[3c] (Supporting Information). To a 10 mL tube were added 1,2,5,6,9,10-coronene−hexaone (5 mg, 12.81 μmol), 5,6-diamino-2-(4,5-bis (hexylthio)-1,3-dithio-2-ylidene)benzo[d]-1,3-dithiole (20 mg, 38.75 μmol), DMF (3.5 mL), and glacial acetic acid (0.5 mL). The mixture was purged with argon for 10 min and then treated under microwave irradiation (160 °C, 40 min). The resulting precipitate was collected by centrifuge and washed with DMF and ethanol. The residue was further purified by column chromatography on silica gel with EtOAc/CH$_2$Cl$_2$ (1/10, v/v) as eluant to give **1** (6 mg, 25%) as a deep-purple solid. IR (KBr) (cm^{-1}) 3429, 2920, 2851, 1721, 1633, 1428, 1343, 1197, 1099, 854, 824, 775, 609. MALDI-TOF m/z calcd for C$_{90}$H$_{90}$N$_6$S$_{18}$ 1830.22, found 1830.22. Anal. Calcd for C$_{90}$H$_{90}$N$_6$S$_{18}$: C, 58.98; H, 4.95; N, 4.59. Found: C, 60.47; H, 5.44; N, 4.25.

Supporting Information Available: General experimental methods, detailed experimental procedures for the precursor 1,2,5,6,9,10-coronene−hexaone, ^{1}H and ^{13}C NMR spectra of TTF−diamine, UV−vis spectrum and cyclic voltammograms of compound **1**, as well as evolution of the absorption spectra of **1** with increasing amount of NOSbF$_6$. This material is available free of charge via the Internet at http://pubs.acs.org.