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A redox-active tri-star molecule: merging of TTF and HAT chemistry

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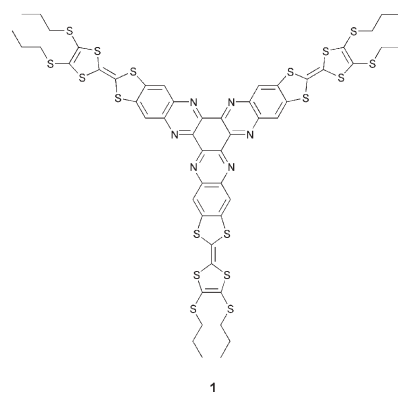
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A planar π -conjugated heteroaromatic molecule **1** has been synthesized and fully characterized; it combines two characteristics, a charge-transfer transition originating from its inherent donor–acceptor nature in its neutral state and an intervalence charge-transfer transition in its 1^{2+} mixed-valence state.

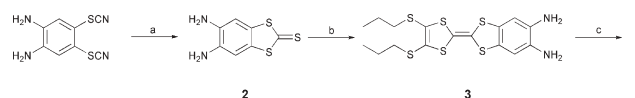
It is well known that tetrathiafulvalene (TTF) and its derivatives are strong π -donors capable of forming persistent cation radical and dication species upon oxidation, leading to the formation of mixed-valence systems.¹ As a consequence, they are frequently used as donor units in donor–acceptor (D–A) ensembles, which are of prime interest due to their potential applications in molecular electronics and optoelectronics.² A few examples of TTF-fused D–A systems were reported in the literature,³ for example, TTF-diquinone and TTF-annulated phthalocyanines. In the former case, an intramolecular electron transfer between two quinone groups mediated by a TTF bridge in a purely organic mixed-valence system has been demonstrated.⁴ In the latter case, the intramolecular through-bond electronic interactions among TTF moieties were electrochemically evidenced.⁵

The nitrogen heterocyclic molecule hexaazatriphenylene (HAT) and its derivatives were originally studied in the context of their coordination to metal ions and their photophysical properties, liquid crystalline ordering, chirality, and DNA related chemistry.^{6,7} A particularly appealing and characteristic aspect of HAT is its electron-deficient π -system which affords three reversible redox transitions as well as three chelating coordination sites for the metal ions.⁷ The topology of the coordination sites renders HAT an especially interesting building block for creating self-assembled 3D frameworks⁸ as well as for probing the spin-frustrated behavior promoted by the triangular geometry in systems where the magnetic interactions between paramagnetic metal ions are antiferromagnetic.⁹ In spite of the interest in HAT, its chemistry has not been fully explored, mainly due to synthetic difficulties. Our combined interest in conducting magnets and molecular electronics, and in discotic liquid crystals led us to the synthesis, electrochemical and spectroscopic investigations of the TTF-annulated HAT derivative **1**. Such a system is expected to exhibit unusual properties caused by facile electronic communication between the HAT core and the three appended TTF units.



The target compound **1** was obtained *via* the direct condensation reaction of hexaketocyclohexane with the diamine precursor **3** in the presence of acetic acid (Scheme 1). The latter was prepared by a phosphite-mediated cross-coupling reaction of 4,5-bis(propylthio)-1,3-dithiole-2-one with **2**, the synthesis of which was based on the known compound 1,2-diaminobenzene-4,5-bis(thiocyanate).¹⁰ The compounds synthesized were easily purified by chromatographic separation on silica gel and have been fully characterized.[†]

The thin layer cyclic voltammogram of **1** (Fig. 1) exhibits two reversible multi-electron oxidation waves for the oxidation of the three TTF fragments. The first $E_{1/2}^{ox1}$ is broad, ranging from 0.11 to 0.36 V and the second is sharp at $E_{1/2}^{ox2} = 0.65$ V. The first oxidation process can be deconvoluted into three separate one electron peaks. This splitting within the first wave indicates that the three TTF units in **1** can be oxidized successively to the cation radical states, while the very narrow peak of the second system suggests that all three TTF cation radicals can be oxidized simultaneously to the triple TTF²⁺ species, leading to the +6 charged form of **1**. The splitting, being observed under various experimental conditions, also shows clearly the existence of intramolecular through-bond interactions among the TTF moieties, as previously observed in the related TTF oligomers.¹¹ These findings are confirmed by the investigation of the UV-Vis-NIR spectroelectrochemistry. Firstly, electrochemical oxidation leads to the appearance of new absorption bands characteristic for the formation of the cation radical species (at 430 nm and 810 nm).



Scheme 1 Synthesis of the TTF-fused HAT system **1**: (a) $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (3.3 equiv.), CS_2 (2.1 equiv.), H_2O , 50 °C, 52%; (b) 4,5-bis(propylthio)-1,3-dithiole-2-one (2 equiv.), triethylphosphite-toluene, 120 °C, 37%; (c) hexaketocyclohexane octahydrate (0.3 equiv.), acetic acid, 120 °C, 60%.

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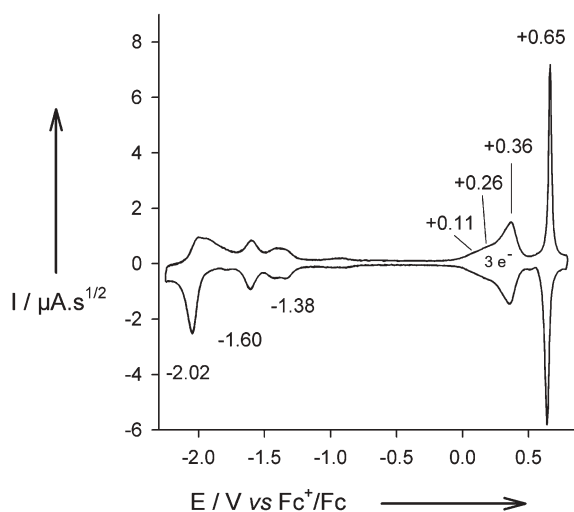


Fig. 1 Deconvoluted cyclic voltammogram of **1** in CH_2Cl_2 ; 0.2 M TBAPF₆ (TBA = tetrabutylammonium); on platinum electrode; scan rate 0.1 V s⁻¹; dichloronaphthoquinone was used as an internal reference for the number of exchanged electrons.

Secondly, an intense broad absorption band, centered at about 2150 nm, occurs additionally and specifically for the generated **1**²⁺ mixed-valence state. This intervalence charge-transfer transition is currently being further investigated.

Moreover, in the negative direction, three reversible reduction waves at $E_{1/2}^{\text{red1}} = -1.38$ V (splitting), $E_{1/2}^{\text{red2}} = -1.60$ V and $E_{1/2}^{\text{red3}} = -2.02$ V are observed, which represent the consecutive reduction steps of the three pyrazine moieties. Differential pulsed voltammetry showed that each process involves the exchange of one electron. In comparison with the reduction of hexaazatri-naphthylene (HATNA), the waves are negatively shifted by 0.07 V due to the electron-donating effect of the TTF units.

The UV-Vis-NIR spectrum of **1** (Fig. 2) shows a broad absorption band centered at 15 500 cm⁻¹ and a very strong band at 30 000 cm⁻¹. The former is attributed to an intramolecular π - π^* charge-transfer transition from the TTF units to the HAT fragment while the latter is characteristic for a π - π^* transition of the benzene annulated TTF moieties of the molecule by comparison with the spectrum of **3**. Moreover, a weaker band at 24 000 cm⁻¹ is characteristic for a π - π^* transition of the HAT unit.¹²

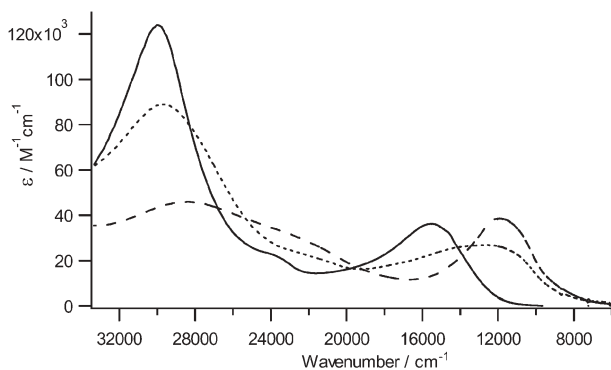


Fig. 2 Absorption spectra of **1** in CH_2Cl_2 (—); **1** with 3 equiv. of $\text{Fe}(\text{ClO}_4)_3$ added (---); **1** with 3 equiv. of FeCl_2 added (···).

Upon slow addition of FeCl_2 to a CH_2Cl_2 solution of **1**, the charge-transfer band broadens out somewhat, gradually shifts to lower energies and reaches its maximum with 3 equivalents of FeCl_2 . Further addition of FeCl_2 leaves the spectrum unchanged, indicating that Fe^{2+} coordinates to all three diimine coordination sites of the HAT moiety. The coordination of Fe^{2+} to HAT increases its acceptor properties, and therefore the charge-transfer transition shifts to lower energies. The TTF centered band at 30 000 cm⁻¹ is much less influenced by the coordination of Fe^{2+} to HAT.

Chemical oxidation with 3 equivalents of $\text{Fe}(\text{ClO}_4)_3$ leads to the appearance of new bands at 24 000 and 11 500 cm⁻¹ which are characteristic of the cation radical species **1**³⁺. The latter transition can be attributed to an alkylthio-TTF⁺ transition corresponding to the promotion of an electron from the fully occupied HOMO-1 to the SOMO.¹³

Ab initio calculations of **1** (with methyl instead of propyl groups) in the D_{3h} ground state symmetry were performed at the Hartree-Fock level with the Midi! basis set using Gaussian 03.¹⁴

The HOMO of **1** is a degenerate e'' pair of π orbitals, shown in the MO diagram of Fig. 3 as orbitals 302 and 303, and depicted in Fig. 4. Each orbital consists of nearly separated regions centered on the TTF subunits. Taken individually they correspond closely to the HOMO of isolated TTF. The HOMO-1 lies just below the HOMO and corresponds to the symmetric a_2'' combination of the HOMOs of the three TTF subunits. The small energetic splitting between the HOMOs and the HOMO-1 reflects the large spatial separation between the three TTF subunits.

To rationalize the electronic absorption spectrum, CIS/Midi! calculations were performed for the low-lying excited states of **1** in

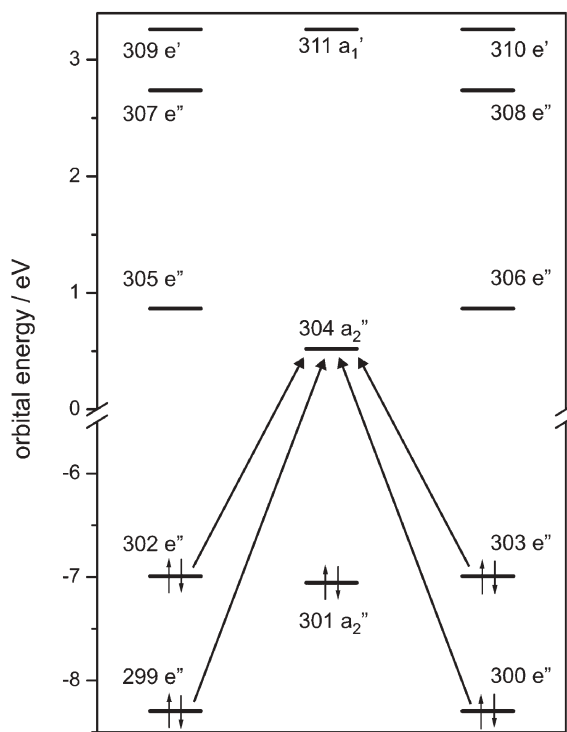


Fig. 3 Hartree-Fock/Midi! orbital energy diagram of **1**. The arrows indicate the main orbital excitations that contribute to the intramolecular charge-transfer transition, see also Fig. 4.

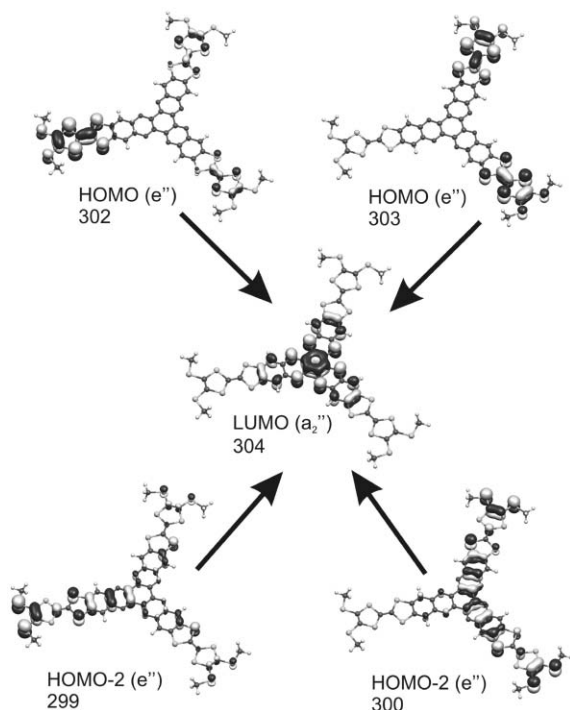


Fig. 4 Molecular orbitals of **1** that are involved in the intramolecular charge-transfer transition: excitation from the degenerate HOMO and HOMO-2 orbitals to the LUMO. Note the charge flow from the molecular periphery to the centre of **1**.

the D_{3h} ground state geometry. The lowest-energy electronic transitions consist of two essentially degenerate sub-transitions from the A_1' electronic ground state (S_0) to the A_2'' (S_1) and E' (S_2) excited states. The transitions correspond to excitations from the HOMO and HOMO-1 orbitals (302, 303 and 301) to the three orbitals 309, 310 and 311. The latter are dominated by the in-plane S atom lone-pairs of the TTF moieties. The resulting π -n/ π - σ^* transitions are extremely weak ($f_{\text{calc}} = 10^{-4}$) and polarized out-of-plane, thus they are difficult to observe experimentally. The $S_0 \rightarrow S_3$ ($A_1' \rightarrow E'$) π - π^* transition is very intense ($f_{\text{calc}} = 2.28$) and polarized within the molecular plane. The transition involves roughly equal excitations from the two pairs of degenerate π -orbitals 299/300 (HOMO-2) and 302/303 (HOMO) that are centered on the TTF moieties to the LUMO π^* -orbital (304), which is centered on the HAT moiety, as shown in Fig. 4. This transition has strong intramolecular charge-transfer character and corresponds to the 15 500 cm^{-1} band in the absorption spectrum, see Fig. 2.

In summary, the molecule **1** combines two characteristics, a charge-transfer transition originating from its inherent donor-acceptor nature in its neutral state and an intervalence charge-transfer transition in its 1^{2+} mixed-valence state. It is noteworthy that the 1^+ , 1^{2+} and 1^{3+} species are all susceptible to ground state Jahn-Teller distortions. The results reported here are parts of an initial exploratory study of the potential of HAT to generate a range of well-defined coordination networks as well as to display a thermotropic discotic liquid crystalline phase.

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Notes and references

† Selected physical data for **2**: mp 210–211 °C; IR (KBr, cm^{-1}): ν 3384, 3315, 1621, 1557, 1487, 1293, 1050, 1033, 892; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 5.07 (s, 4H), 6.76 (s, 2H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ 105.4, 127.9, 136.8, 210.1; EI-MS: m/z (%): 214 (100) [M^+]; Anal. Calcd for $\text{C}_7\text{H}_6\text{N}_2\text{S}_3$: C, 39.23; H, 2.82; N, 13.07. Found: C, 39.57; H, 2.71; N, 12.93%. for **3**: mp 127–128 °C; IR (KBr, cm^{-1}): ν 3392, 3320, 2960, 1619, 1489, 1292, 854; ^1H NMR (300 MHz, $\text{DMSO}-d_6$): δ 0.91–0.96 (t, 6H), 1.52–1.59 (m, 4H), 2.78–2.83 (t, 4H), 4.69 (s, 4H), 6.54 (s, 2H); ^{13}C NMR (75 MHz, $\text{DMSO}-d_6$): δ 12.7, 22.6, 37.3, 105.3, 107.5, 114.3, 121.0, 126.9, 134.9; EI-MS: m/z (%): 432 (45) [M^+]; Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{N}_2\text{S}_6$: C, 44.41; H, 4.66; N, 6.47. Found: C, 44.68; H, 4.67; N, 6.33%. for **1**: IR (KBr, cm^{-1}): ν 2960, 1434, 1408, 1100, 776; ^1H NMR (300 MHz, CDCl_3): δ 1.05–1.09 (t, 18H), 1.69–1.76 (m, 12H), 2.85–2.89 (t, 12H), 7.32 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.3, 23.2, 38.4, 107.1, 115.2, 119.4, 127.8, 141.2, 141.4, 144.9. Anal. Calcd for $\text{C}_{54}\text{H}_{48}\text{N}_6\text{S}_{18}$: C, 47.76; H, 3.56; N, 6.19. Found: C, 47.82; H, 3.54; N, 5.88%. MALDI-MS calcd for $\text{C}_{54}\text{H}_{48}\text{N}_6\text{S}_{18}$: 1356.90 [$\text{M} + \text{H}^+$]. Found: 1356.89.

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