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Pronounced Electrochemical Amphotericity of a Fused Donor–Acceptor Compound: A Planar Merge of TTF with a TCNQ-Type Bithienoquinoxaline

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Multistage organic redox systems,^[1] in particular, electrochemically highly amphoteric compounds with a small HOMO/LUMO gap (HLG, for example, $E_{\text{ox}} - E_{\text{red}} < 0.5$ eV), are of current interest due to their potential applications in molecular electronics and optoelectronics.^[2] Consequently, research efforts have been directed toward the design and synthesis of molecular systems composed of powerful electron donor (D) and acceptor (A) units. However, any strong electronic interaction in such molecules renders them neither strong electron donors nor acceptors. In practice, therefore, D and A components are often covalently linked by saturated flexible or rigid σ spacers (D- σ -A). Thereby, the structural D and A moieties on which the HOMO and LUMO are localized, respectively, are kept apart from each other. This hinders their strong coupling in the electronic ground state, so as to keep the HLG small.^[3] Conjugated bridges of D- π -A assemblies, although providing easier

steric control, generally favor stronger electronic coupling. Besides the amphoteric ground-state properties, photoinduced intramolecular charge-transfer (CT) processes may result in interesting photophysical phenomena such as long-lived, charge-separated states.

From a preparative point of view, the linkage of a strong donor (e.g., tetrathiafulvalene (TTF)) to a strong acceptor (e.g., 7,7',8,8'-tetracyano-*p*-quinodimethane (TCNQ)) in a D- π -A system is a synthetic challenge.^[3] In response, we recently introduced a concept for the annulation of TTF derivatives to acceptor moieties and reported synthetic routes to various fused D- π -A assemblies.^[4] All of them are tailored into rigid and planar configurations exhibiting defined symmetries, thus providing full geometric control over the relative positions and orientations of the subunits. As the focal point of the work presented herein, we explore the synthesis of a new system, in which both strong electron-donor and strong electron-acceptor properties are organized into an annulated molecular D- π -A triad for probing the resulting HLG. More specifically, the first example of the annulated assembly (**1**), incorporating TTF and TCNQ-type bithienoquinoxaline, is presented. As will be demonstrated, a pronounced electrochemical amphotericity can be achieved in a way that precludes strong electronic coupling of the energetically close-lying HOMO and LUMO within the fused D- π -A system. Essentially, this is due to the strict symmetry control of the planar conjugate. Additionally, the remarkable redox properties are combined with strong photoinduced intramolecular CT transitions.

A direct condensation reaction of 5,6-diamino-2-(4,5-bis(methylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole (**P1**),^[4c] with a TCNQ-type bithienoquinoid (**P3**)^[5] afforded **1** in 86 % yield. Similarly, the reference compound **2** was obtained in good yield (Scheme S1 in the Supporting Information). It is noteworthy that the annulation of a quinoxaline group to the TTF core could lead to a considerable increase in stability and charge mobility of the resulting D-A molecules.^[6]

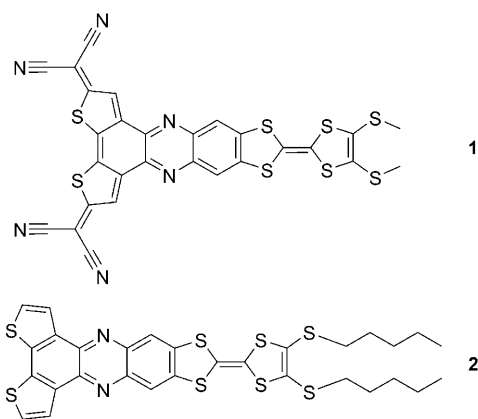
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The electrochemical properties of **1** and of the reference compounds **2**, **P1** and **P3** in DMF were investigated by cyclic voltammetry (CV). To circumvent the effects of aggregate formation in solution (see below) and adsorption on the working electrode, compound **1** was studied as a thin layer on Pt (for details, see the Supporting Information). As shown in Figure 1, compounds **2** and **P1** show two reversible

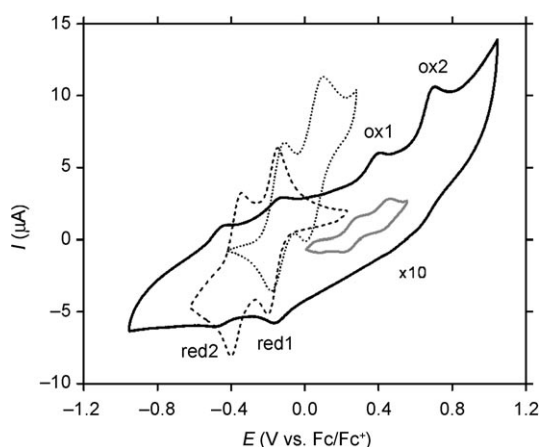


Figure 1. Cyclic voltammograms of **1** (black line, thin film on Pt electrode in benzonitrile), **2** (gray line, 0.2 mM), and of the precursors **P1** (dotted line, 1 mM) and **P3** (dashed line, 1 mM) in DMF. Supporting electrolyte: 0.1 M TBAPF₆, scan rate 50 mV s⁻¹.

single electron oxidation waves corresponding to $E_{1/2}^{\text{ox1}}$ and $E_{1/2}^{\text{ox2}}$ for the oxidation of their TTF units. As anticipated from its structure, compound **1** undergoes two one-electron reductions and two one-electron oxidations. The potential values $E = -0.14$ and 0.38 V (versus ferrocene) thus delimit the region in which compound **1** as a whole is neutral. Particularly striking is that the reduction waves, caused by the TCNQ-type subunit, occur at potentials similar to those of its precursor **P3** (**1**: $E_{1/2}^{\text{red1}} = -0.14$ V, $E_{1/2}^{\text{red2}} = -0.45$ V; **P3**: $E_{1/2}^{\text{red1}} = -0.20$ V, $E_{1/2}^{\text{red2}} = -0.40$ V), whereas the oxidation waves, due to the TTF subunit, are substantially positively shifted relative to **P1** (**1**: $E_{1/2}^{\text{ox1}} = 0.38$ V, $E_{1/2}^{\text{ox2}} = 0.69$ V; **P1**: $E_{1/2}^{\text{ox1}} = -0.15$ V, $E_{1/2}^{\text{ox2}} = 0.06$ V). This observation implies that the proximity of the TTF core has only a marginal influence

on the electron-accepting ability of the TCNQ-type bithienoquininoxaline moiety, in good agreement with the computational results presented below. Reference compound **2** demonstrates the orbital interaction of the pyrazine ring through oxidation potentials in between those of compounds **P1** and **1** (**2**: $E_{1/2}^{\text{ox1}} = 0.25$ V, $E_{1/2}^{\text{ox2}} = 0.44$ V). Finally, we notice that the potential spacing between first and second oxidation or reduction increases by about 50% on fusing **P1** and **P3** to form compound **1** (from ca. 200 mV in **P1** and **P3** to ca. 310 mV in **1**).

Compound **1** strongly absorbs in the UV-visible-NIR spectral region as evidenced by its deep-purple color. The electronic absorption spectrum of **1** recorded in DMF ($c = 2 \times 10^{-5}$ M) is presented in Figure 2. The intense absorption

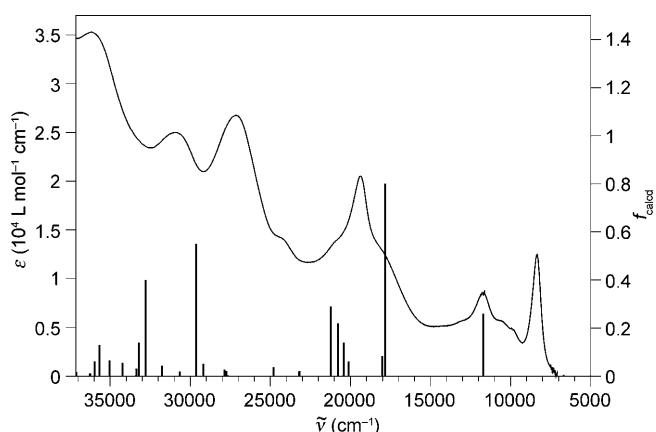


Figure 2. Electronic absorption spectrum of **1** in DMF solution at room temperature, together with the calculated oscillator strengths.

bands in the UV and blue part of the spectrum are characteristic for π - π^* transitions, specifically of the quinoxaline-annulated TTF moiety. Furthermore, the clear-cut and strong absorption band around 19200 cm^{-1} (520 nm) can be attributed to the lowest energy π - π^* transition located on the acceptor site because it is also observed for the acceptor precursor **P3**.^[5] Two specific and intense absorption bands remain at around 11800 (847 nm) and 8200 cm^{-1} (1220 nm), which are not observed in a solution of **2** (Figure S3 in the Supporting Information), nor in solutions of the donor **P1** and acceptor **P3** components. Consequently, they reflect charge-transfer-type transitions characteristic for **1**.

To rationalize the electronic absorption spectrum of **1**, a detailed computational study has been performed.^[7-8] As depicted in Figure 3, the HOMO shows large amplitudes on the TTF skeleton, and the LUMO on the TCNQ-type bithienobenzene moiety, both in good agreement with their expected electron-donor and -acceptor properties. A particularly interesting feature is the localization and spatial separation of the HOMO (b_1) and the LUMO (a_2), despite the fusion of the donor and acceptor through the π -conjugated quinoxaline bridge. Therefore, the acceptor (LUMO) part retains its low reduction potential within the D- π -A ensemble, as demonstrated with the CV data. Only the HOMO lo-

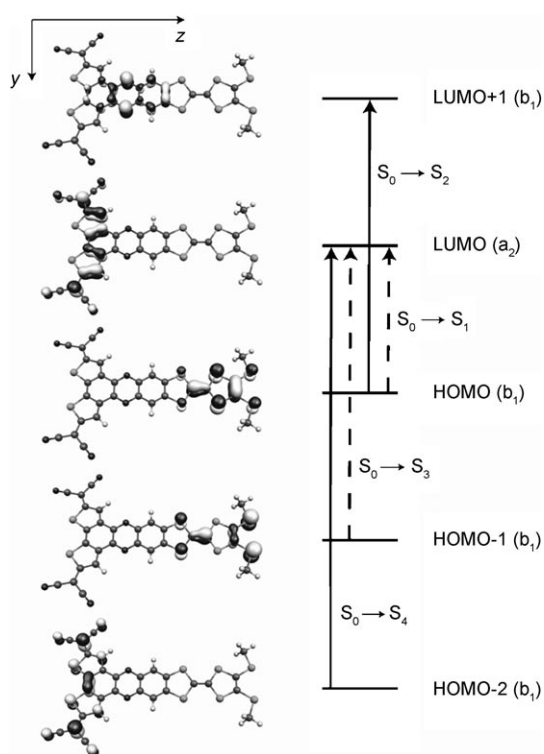


Figure 3. Selected molecular orbitals with C_{2v} symmetry labels and the indication of their major participation in some electronic transitions of **1**.

cated on the donor part interacts to some extent with energetically higher lying molecular orbitals with the same b_1 symmetry (LUMO+1, etc.), leading to a limited positive shift of the redox potentials of the donor subunit. Finally and most importantly, this results in an HLG_{calcd} of 0.69 eV, which compares quite well with the experimental CV data ($HLG = 0.52$ eV).

For **1**, the time-dependent (TD)-DFT calculations predict the S_0 (1A_1) $\rightarrow$ S_1 (1B_2) vertical electronic excitation to be a symmetry-allowed electric-dipole transition at 3480 cm^{-1} (0.43 eV; 2874 nm), but with a marginal oscillator strength $f_{\text{calcd}} = 0.0005$. This low-energy electronic excitation is fully dominated by the HOMO $\rightarrow$ LUMO contribution. However, it is polarized along the y axis, and is therefore not expected to move electronic density between the involved HOMO and LUMO. The same holds for the S_0 (1A_1) $\rightarrow$ S_3 (1B_2) transition at 12500 cm^{-1} (800 nm), characterized by HOMO-1 $\rightarrow$ LUMO (91 %) and $f_{\text{calcd}} = 0.0004$.

In striking contrast, the S_0 (1A_1) $\rightarrow$ S_2 (1A_1) electronic excitation, which is calculated to be 11720 cm^{-1} (853 nm) and is dominated by the HOMO $\rightarrow$ LUMO+1 contribution (99 %), shows a high oscillator strength of $f_{\text{calcd}} = 0.26$ and an in-plane polarization along the long molecular axis (z). This transition exhibits strong intramolecular CT character and we assign it to the intense absorption band at 11800 cm^{-1} (847 nm) in Figure 2.

This type of optical excitation recognizably conforms with the intramolecular CT transition observed at 18500 cm^{-1} (540 nm) in a fused TTF–dipyrido[3,2- a :2',3'- c]phenazine

(dppz) compound.^[4c] Upon metal-ion coordination to the dppz moiety, the above mentioned CT transition exhibits a pronounced redshift of at least 2000 cm^{-1} .^[4c] In a similar fashion, the TCNQ-type bithienobenzene moiety of **1** reduces the electron density on the adjacent quinoxaline bridge (LUMO+1) to an even larger extent, which leads to a redshift of 7600 cm^{-1} for this CT transition on going from **2** to **1**. This observation is corroborated by calculations that show a lowering of the LUMO+1 for **1** in the order of 5000 cm^{-1} relative to **2**. The calculated dipole moment for the S_2 state (32.1 Debye) is enormous compared to 11.8 Debye for the S_0 state; both dipole vectors lie along the long molecular axis and point toward the acceptor group (δ^- pole). These values lend further support to the CT character involved in this electronic excitation. In other words, the strong acceptor unit provokes, through lowering of the LUMO+1 on the quinoxaline bridge, an intense CT absorption in the red to NIR spectral region. With regard to relaxation processes, the non-negligible overlap of the coefficients from LUMO+1 and LUMO traces an exoergic pathway for moving electron density from the quinoxaline bridge fully to the acceptor site. This would result in a potentially long-lived, charge-separated state, namely, the S_1 state, which is only weakly coupled to the S_0 ground state. Clearly, this process would have to compete with the direct back transfer ($S_2 \rightarrow S_0$).

Finally, the S_0 (1A_1) $\rightarrow$ S_4 (1B_2) transition calculated at 17820 cm^{-1} (561 nm) with $f_{\text{calcd}} = 0.80$ is dominated by the HOMO-2 $\rightarrow$ LUMO contribution (76 %) and is polarized along the y axis. Here the large oscillator strength is due to the fact that both HOMO-2 and LUMO are located on the acceptor site of the molecule. This electronic excitation is, with respect to both the transition energy and intensity, in acceptable agreement with the observed intense absorption band at 19200 cm^{-1} (520 nm).

Regarding the observed absorption band at 8200 cm^{-1} (1220 nm), the extensive theoretical study (see the Supporting Information) of **1** does not reveal any electronic transition with a sizable oscillator strength within this energy range. A key characteristic of the band is the unusually narrow (full width at half maximum (fwhm): 750 cm^{-1}) and intense absorption profile, which points to aggregation effects, specifically to a redshifted J-band, derived from the $S_0 \rightarrow S_2$ transition (see the above).^[9] Similar aggregation is found for other planar π -extended systems, for example, perylene bisimides.^[9b]

The degree of polarization of the conjugated D- π -A system **1** in its electronic ground state, thus the level of charge depletion at the donor site and charge accumulation at the acceptor site as the result of the fusion of D and A, can be experimentally monitored through the stretching frequencies of the carbon–carbon double bonds, $\nu(\text{C}=\text{C})$, for the donor and of the cyano groups, $\nu(\text{C}\equiv\text{N})$, for the acceptor.^[10] Specifically, the Raman stretching frequencies $\nu(\text{C}=\text{C})$ of the TTF unit show downward shifts from 1559 to 1548 cm^{-1} and from 1497 to 1489 cm^{-1} on going from **2** to **1** (Figure S5 in the Supporting Information). Analogously, the

Raman spectrum of **1** reveals a $\nu(\text{C}\equiv\text{N})$ stretching mode at 2216 cm^{-1} , which is also lower than that of **P3** (2224 cm^{-1}). The main IR stretching frequency $\nu(\text{C}\equiv\text{N})$ of **1** at 2211 cm^{-1} is likewise shifted in comparison to **P3** (2218 cm^{-1});^[5] a weaker band appears at 2185 cm^{-1} . These data consistently point to a level of charge distribution for the ground state that, in a simplified picture disregarding the bridge, is best described by a 10–20% contribution of the “zwitterionic” form $\text{D}^+-\pi-\text{A}^-$ in the ground state of the D- π -A triad. This degree of polarization matches the calculated dipole moment of 11.8 Debye for **S**₀ well.

As has been observed for strongly electrochemically amphoteric D- π -A compounds,^[3a] the high donor and acceptor abilities of **1** facilitate a partial occurrence of electron transfer. The resulting paramagnetic contributions cause compound **1** to be silent in the ^1H NMR spectrum (in contrast to **2**). These observations are also manifested in isotropic EPR signals ($g_{\text{iso}}=2.000$) in solution and in the solid state (Figure S6 in the Supporting Information).

In conclusion, we have demonstrated the de novo design of a compactly fused π -conjugated molecule that combines a high-lying HOMO with a low-lying LUMO (electrochemical HLG=0.52 eV) and a fairly low-lying LUMO+1 on the bridging unit, whereby the latter gives rise to strong optical CT transitions. The rich variety of properties is due to the interplay between the π -electronic structure and the well-defined geometrical structure. Tests of the performance of this π -conjugated material for charge transport in molecular electronic applications will be of particular interest.

Experimental Section

Experimental procedures, characterization data for new compounds, and complete details about the synthesis of new compounds are available in the Supporting Information.

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Keywords: charge transfer • donor–acceptor systems • HOMO–LUMO gap • redox chemistry • tetrathiafulvalenes

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