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Annulation of Tetrathiafulvalene to the Bay Region of Perylenediimide

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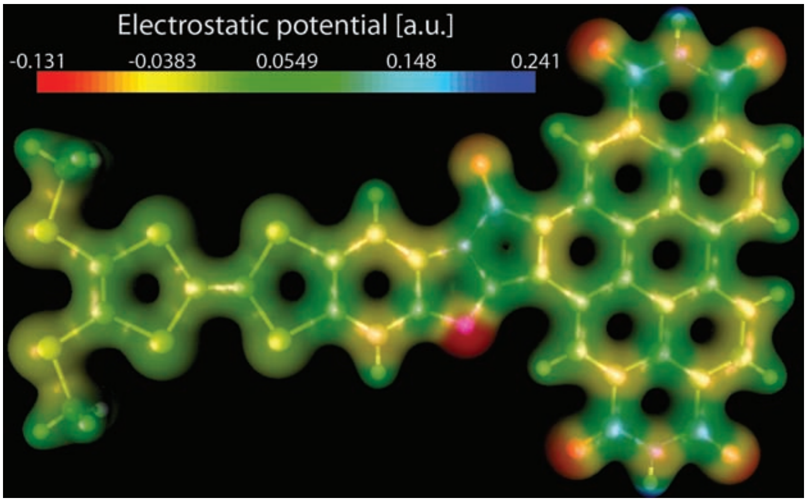
ABSTRACT



A tetrathiafulvalene donor has been annulated to the bay region of perylenediimide affording a new π-conjugated molecular dyad. Various electronic excited charge-transfer states are generated in different oxidation states, leading to almost full absorption in the visible to near-IR region with a high extinction coefficient.

This paper presents the synthesis of a compactly fused, π-conjugated donor−acceptor (D−A) dyad **1** (Scheme 1) comprising of tetrathiafulvalene (TTF) and core-extended perylenediimide (PDI) units. As the focal point of this work, we explore the electrochemical and photophysical properties, demonstrating the combination of a pronounced electrochemical amphotericity and strong photoinduced intramolecular charge-transfer (ICT) transitions within the fused dyad **1**.

Substituted PDIs have been attracting tremendous interest as n-type semiconductors and photosensitizers due to their high electron mobilities, strong fluorescence, good electron affinities, and outstanding chemical, thermal, and photochemical stability. They have thus been widely used as organic semiconducting components in devices such as solar cells, thin film transistors, and light-emitting diodes.[1]

In analogy, TTF-type compounds have been explored as p-type semiconductors and also as electron-donor units in D−A ensembles,[2] which are of prime interest in molecular (opto)electronics. In most reported systems, TTF and ac-

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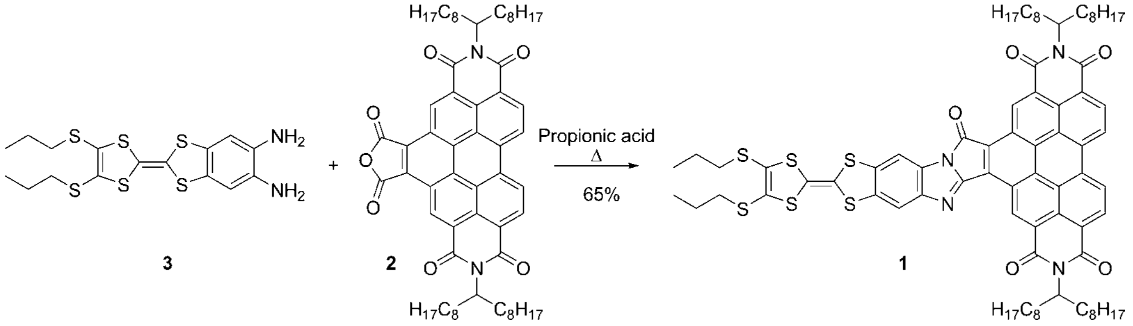
Scheme 1. Synthetic Route to **1**



ceptor components were linked via flexible or rigid σ-spacers. The same holds for D−A ensembles consisting of TTF and PDI[3a−f] or perylene.[3g] Quite often, such D−σ−A ensembles show redox and physical properties that are just given by the sum of the properties of the corresponding building blocks due to the lack of strong electronic interactions between D and A moieties. In contrast, sterically controlled and compactly fused D−π−A systems exhibit significant intramolecular interactions potentially giving rise to pronounced photoinduced charge-transfer (CT) processes. Moreover, such π-bridged systems allow the combination of a high-lying HOMO localized on D with a low-lying LUMO on A, resulting in conjugated systems bearing small HOMO−LUMO gaps. Recent examples of such systems incorporating TTFs include TTF−coronene,[4a] TTF−bithienoquinoxaline,[4b] TTF−*N*,*N*′-phenylenebis(salicylideneimine),[4c] TTF−dipyrido[3,2-*a*:2′,3′-*c*]phenazine,[4d] TTF−hexaazatriphenylene,[4e] TTF−phthalocyanine[4f] and TTF−PDI.[4g] In the last case, one TTF moiety was fused to the imide site of a PDI unit resulting in a planar D−π−A system exhibiting ICT processes and a HOMO−LUMO gap of about 1 eV. On the contrary, the herein reported TTF−PDI dyad **1** (Scheme 1) results from the annulation of the TTF unit to the bay region of PDI using a π-bridging spacer similar to the former system.[4g] Compared to a fusion to the imide site, direct annulation of a donor to the extended perylene core suggests a strong interaction between D and A moieties due to increased electronic coupling with the perylene core.[5]

Core-extended PDIs have been sought with the aim of creating various novel chromophores that function as dyes to improve their performance in molecular (opto)electronic devices.[6a−e] A popular pathway to core extension is the Diels−Alder−Clar protocol, according to which the key precursor **2** was prepared (Scheme 1).[6e]

Compound **1** was synthesized via a Schiff-base condensation of *N*,*N*′-bis(1-octylnonyl)benzoperylene-1′,2′:3,4:9,10-hexacarboxylic-1′,2′-anhydride-3,4:9,10-bis(imide) **2**[6e] with 5,6-diamino-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole **3**[4d] (Scheme 1) in reasonable yield (65%) and fully characterized (NMR, MS, elemental analysis, IR, see the Supporting Information).

The electrochemical properties of **1** were investigated by cyclic voltammetry in CH_2Cl_2 together with reference compounds **2** and **3** for comparison (Figure 1 and Table S1, Supporting Information). Compound **1** shows two reversible one-electron oxidation waves and three reversible reduction waves corresponding to the successive oxidations of the TTF moiety to the radical cation and dication species and the consecutive reductions of the PDI constituent, respectively.

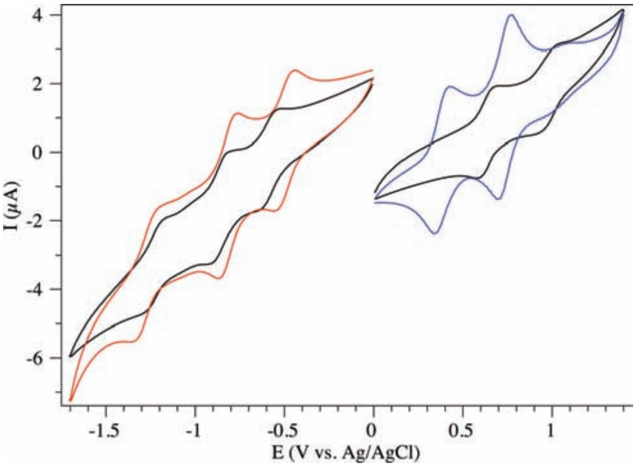


Figure 1. Cyclic voltammograms of **1** (1.5×10^{-5} M, black), **2** (0.9×10^{-5} M, red), and **3** (0.9×10^{-5} M, blue) in CH_2Cl_2 (0.1 M $TBAPF_6$ (TBA = tetrabutylammonium); platinum working electrode; scan rate 200 mV s^{-1}).

By comparison with **3**, the oxidation potentials of dyad **1** are significantly positive-shifted whereas the first reduction potential of **1** shows a small negative shift with regard to **2**. The second and third reduction processes are similar for both **1** and **2**. These results can be rationalized in terms of the electronic interaction between the donor and acceptor moieties within the fused dyad system. This chemical bonding causes the frontier orbitals in **1** to be energetically slightly more separated than the corresponding orbitals in the isolated precursors. Moreover, the electrochemical HOMO−LUMO gap for **1** of 1.23 eV (9 900 cm^{-1}) is in good agreement with the onset of the lowest energy electronic absorption in the UV−vis−NIR spectrum (1.30 eV, 10 500 cm^{-1}, vide infra).

The green compound **1** shows intense absorptions in the UV−vis−NIR spectral region (Figure 2). A strong broadband appears between 11500 cm^{-1} (870 nm) and 19000 cm^{-1} (530 nm), followed by a series of absorptions that peak at 21480 cm^{-1} (465 nm), 23000 cm^{-1} (435 nm), and 24660 cm^{-1} (405 nm). By comparison with the spectra of compounds **2** and **3**, the new electronic transitions which can only be observed in the fused molecule **1** are attributed to intramolecular $\pi-\pi^*$ CT transitions. Clearly, the typical PDI absorption pattern with its vibrational progression of about 1500 cm^{-1} is still observed within the dyad. Its lowest energy peak exhibits almost no shift compared to **2**; obviously, the effects of the fusion to the bay region (hypsochromic shift) and the incorporation of the TTF donor (bathochromic shift) nearly cancel each other.

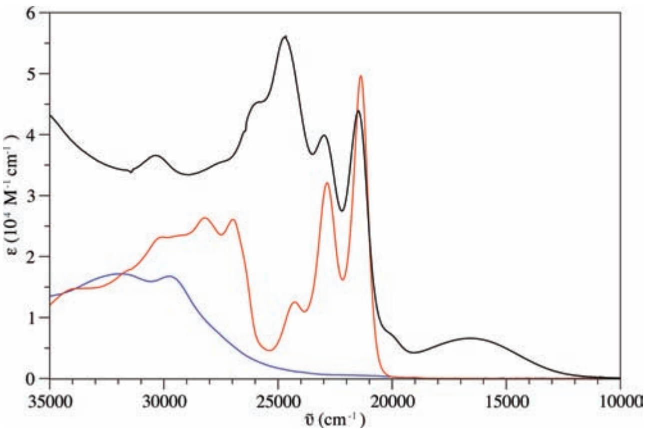


Figure 2. Electronic absorption spectra of **1** (black), **2** (red), and **3** (blue) in CH_2Cl_2 ($c = 40$ μM).

To gain insight into the ground- and excited-state electronic properties of dyad **1**, ab initio quantum chemical calculations were performed, using TURBOMOLE V5.10[7] as well as the GAMESS[8] program packages. The ground-state geometry of **1** was optimized with density functional theory (DFT) using the B3LYP functional and the valence triple-ζ plus polarization (TZVP) basis set and was constrained to C_s symmetry. The important frontier molecular orbitals are given in Figure 3. Especially interesting features are the localization and spatial separation of the HOMO and LUMO and also the extensions of the HOMO−1 and LUMO+1 into the bridging area. In particular, the latter allows for strong and low-lying charge-transfer absorptions.

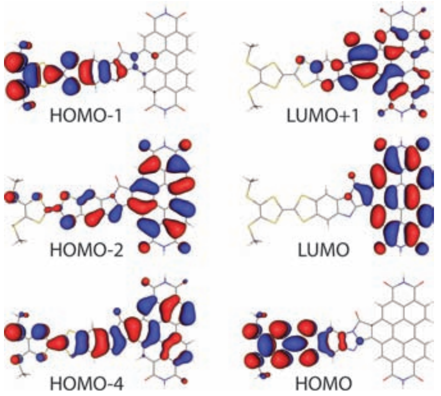


Figure 3. Frontier molecular orbitals of dyad **1** (LRC-TDBLYP/6-31G(2d), $\mu = 0.15$).

Vertical electronic transitions were calculated with the long-range corrected TDDFT (LRC-TDDFT) method applying the BLYP functional and the 6-31G(2d) basis set (see the stick spectrum in Figure 4).[9] The range separation parameter μ was set to 0.15, which has proven to be the best choice for TTF-based dyads.[4] The $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic excitations are calculated to be close-lying in-plane $\pi-\pi^*$ transitions at 15641 and 17330 cm^{-1} with oscillator strengths $f_{calc} = 0.13$ and 0.09. They are polarized along the TTF long axis and dominated by the HOMO → LUMO+1 and HOMO → LUMO one-electron contributions. Both transitions agree very well with the broad absorption band centered at 16650 cm^{-1} (600 nm). These low-energy electronic excitations clearly reflect the π-electron flow from the TTF donor to the fused PDI acceptor.

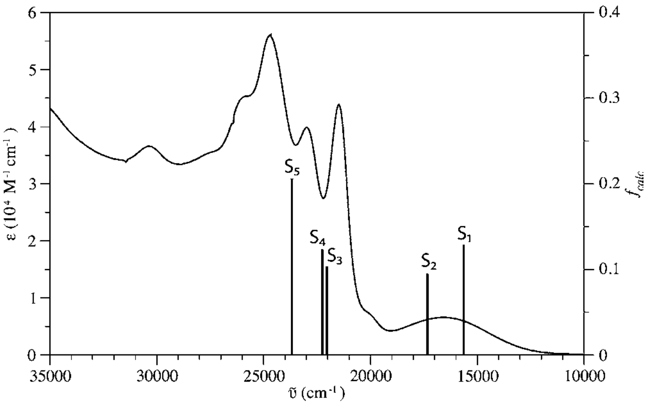


Figure 4. Electronic absorption spectrum of dyad **1** together with the vertical LRC-TDBLYP/6-31G(2d) ($\mu = 0.15$) calculated $S_0 \rightarrow S_n$ transitions.

The small shoulder at 20000 cm^{-1} (500 nm) can be rationalized by the $S_0 \rightarrow S_3$ electronic transition, predicted

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at 22056 cm^{-1} with $f_{\mathrm{calc}} = 0.10$, whereas the intense absorptions above 21000 cm^{-1} correspond to the $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$ electronic excitations with calculated energies of 22254 and 23682 cm^{-1} and oscillator strengths of 0.12 and 0.21, respectively. All three are polarized along the PDI long axis and consist of linear combinations of several one-electron transitions from the group of frontier orbitals HOMO-4, ..., HOMO to LUMO and LUMO+1, albeit with different admixtures (see Table S2, Supporting Information). Therefore, both transitions bear ICT as well as PDI localized $\pi-\pi^*$ characteristics, the latter in analogy to the HOMO to LUMO transition in isolated PDI.

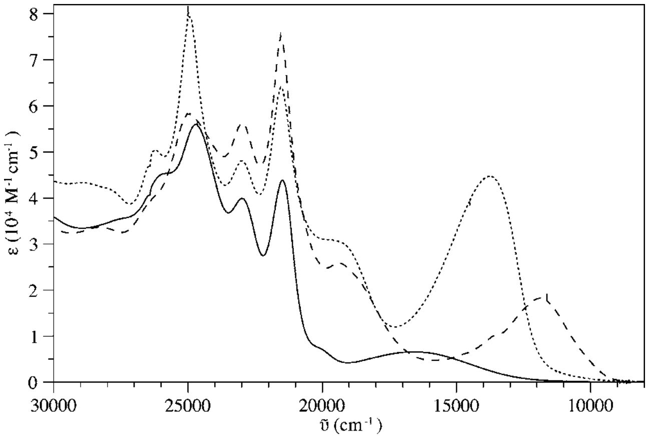

Figure 5. Electronic absorption spectra of **1** (solid), $\mathbf{1}^{\bullet+}$ (dashed), and $\mathbf{1}^{2+}$ (dotted) in CH_2Cl_2 (oxidizing agent: $[Fe(bpy)_3](PF_6)_3$ in acetonitrile).

Upon oxidation in the presence of $[Fe(bpy)_3]^{3+}$ (Figure 5), the lowest energy ICT band disappears simultaneously with the occurrence of a new intense band centered at 11900 cm^{-1} (840 nm), which can be attributed to an in-plane $\pi-\pi^*$ transition corresponding to the back electron transfer (PDI→TTF$^{\bullet+}$) combined with some TTF$^{\bullet+}$ localized contributions, as demonstrated by a LRC-TDDFT caculation (Figures S3 and S4, Supporting Information). Upon further oxidation of $\mathbf{1}^{\bullet+}$ to $\mathbf{1}^{2+}$ a pronounced band at 13700 cm^{-1} (730 nm) occurs while the low energy band of $\mathbf{1}^{\bullet+}$ disappears.[10]

In conclusion, a first example of the annulation of TTF to the bay region of PDI has been reported. Such a redox-active D−A dyad exhibits various excited charge-transfer states in different oxidation states leading to intense optical absorbances over a wide spectral range. In particular, in the search for high-performance organic semiconductors for molecular devices, fused and π-extended heteroarenes prove to be the most promising molecular scaffolds. As a consequence, TTF-fused dyads are currently explored as active materials in organic field effect transistors and photovoltaic devices.

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Supporting Information Available: Experimental procedure and characterization data for compound **1**, copy of ^{1}H NMR spectrum of **1**, redox potentials of compounds **1**−**3**, as well as additional calculations of **1** and its radical cation $\mathbf{1}^{\bullet+}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) TDDFT calculations with the common B3LYP functional showed spurious charge-transfer transitions, which were shifted to the red by more than 9 000 cm^{-1} (see Figure S1, Supporting Information). To qualitatively verify the LRC-TDBLYP/6-31G(2d) result, we performed a calculation with the second-order approximate coupled cluster singles and doubles method, employing the resolution of the identity approximation (RICC2) and the SVP basis set (see Figure S2, Supporting Information). Both methods are in good agreement. However, the $S_0 \rightarrow S_3$, S_4, and S_5 transitions calculated with RICC2 are slightly blue-shifted compared to LRC-TDDFT.

(10) In contrast to the previously reported TTF-PDI systems, no restitution of the PDI-centered luminescence upon oxidation of **1** to $\mathbf{1}^{2+}$ was observed, which might result from the photoinduced energy-transfer process.