A Compactly Fused π-Conjugated Tetrathiafulvalene−Perylenediimide Donor−Acceptor Dyad
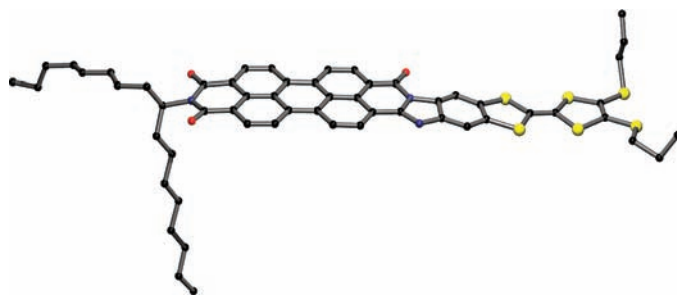
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ABSTRACT

The synthesis and structural characterization of a tetrathiafulvalene-fused perylenediimide molecular dyad is presented. Its largely extended π-conjugation provides intense optical absorption bands over a wide spectral range. The planar functional molecule exhibits a short-lived nonluminescent excited state attributed to intramolecular charge separation.

This paper puts forward a study of a, to a large extent, π-conjugated molecule, which results from fusing tetrathiafulvalene (TTF) and perylenediimide (PDI) into a single planar molecular structure. Both components of this fused molecule possess their distinct and characteristic properties: the objective of this study is to assess the effects of their mutual electronic interactions.

TTF and its derivatives are used as strong π-donors in the field of organic conductors and superconductors[1] and as electron donor units in donor−acceptor (D−A) ensembles, which are of interest due to their potential applications in molecular electronics and optoelectronics.[2] In such molecular ensembles, donors and acceptors are often covalently linked by flexible or rigid σ-spacers (D−σ−A) which keep the moieties apart from each other. Only few examples of fused D−A systems have been reported in the literature,[3] for instance the TTF donor with TCNQ-type bithienoquinoxaline,[3b] hexaazatriphenylene,[3c] or phthalocyanine[3d] acceptors. The first case is a striking example of a fused π-conjugated molecule that exhibits electrochemically amphoteric properties due to a combination of a high-lying HOMO located on D with a low-lying LUMO confined on


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Scheme 1. Synthetic Route to **1**
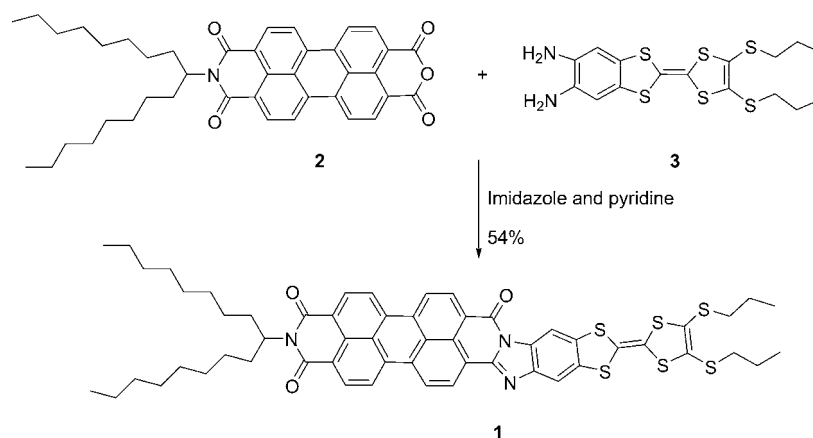
A ($E_{ox} - E_{red} = 0.52$ V). The annulation of donors and acceptors into a planar configuration facilitates photoinduced intramolecular charge-transfer (CT) processes, a topic that is in the focus of the present study. For more information, especially on conjugated TTF−acceptor systems, the reader may consult a recent review by Wudl et al.[2a]

The interest in perylenediimide (PDI) compounds is due to the unique combination of good electron accepting ability, high absorption in the visible, and outstanding chemical, thermal, and photochemical stability.[4] They have thus been used in a variety of D−A systems showing photoinduced electron or energy transfer processes, potentially leading to long-lived charge separated states. Their extended aromaticity together with the possibilities for functionalization render them good candidates for potential applications in electronic materials, sensors, and photovoltaics.[4−6] Examples abound

of the different PDI-containing molecular ensembles, including combinations with [60]fullerenes,[5a,b] phthalocyanines,[5c−e] porphyrins,[5f,g] corroles,[5h] and TTFs.[6] As mentioned above, in most cases, these donors and the PDI acceptor units are linked through flexible spacers. Especially for all reported TTF−PDI dyads,[6] the moieties were connected by σ-linkers either to the "imide" region or to the "bay" region of PDI, thus giving rise to only weak electronic interactions between the two components. In contrast, the herein reported TTF−PDI compound **1** (Scheme 1), which results from the annulation of sulfur- and nitrogen-containing polycycles, allows an experimental study of intense optical CT absorptions and photoinduced CT processes between the fused fragments of the π-extended polycyclic system as a result of significant intramolecular electronic interactions.

Direct condensation of N-(1-octylnonyl)perylene-3,4,9,10-tetracarboxylic acid 3,4-anhydride-9,10-imide (**2**)[7] with 5,6-diamino-2-(4,5-bis(propylthio)-1,3-dithio-2-ylidene)benzo[d]-1,3-dithiole (**3**)[3e] afforded **1** in 54% yield. Its molecular structure was confirmed by spectroscopic data (NMR, MS, IR), and for the first time, a TTF−PDI dyad was elucidated by X-ray structure analysis.

Dyad **1** crystallizes as solvate-free purple plates in the triclinic space group $P\bar{1}$. Its molecular structure is shown in Figure 1. The skeleton of the π-conjugated molecule is nearly planar and exhibits only a slight undulation along its long molecular axis. The rms deviation from a least-squares plane through all atoms, excluding the alkyl and thioalkyl groups, is 0.1596 Å, and for the TTF core alone it amounts to 0.1001 Å, which reflects its slight boat conformation as observed in other related D−A systems.[8] Due to crystal packing effects, the alkyl substituents on PDI are arranged distinctly

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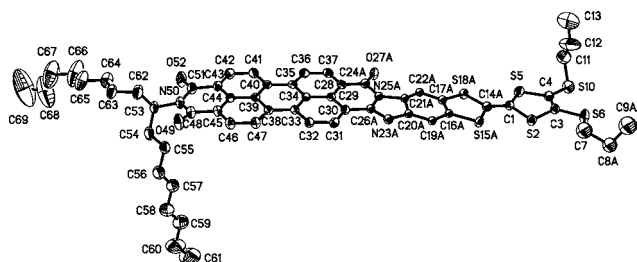(7) Wescott, L. D.; Mattern, D. L. *J. Org. Chem.* **2003**, *68*, 10058.

Figure 1. ORTEP (30% probability ellipsoids) structure of **1** (one of the two positionally disordered molecules). Hydrogen atoms and disordered parts of the terminal alkyl groups are omitted for clarity.

in an out-of-plane conformation. The bond lengths within the TTF and PDI units are in good agreement with those of their corresponding neutral species.[9]

In the crystal lattice, the molecules are stacked in a head-to-tail manner, thus forming a *trans*-cofacial mode of association (see Supporting Information). This parallel alignment is mainly caused by $\pi\cdots\pi$ interactions: the two inter-planar separations between the least-squares planes amount to 3.565 and 3.679 Å, and the shortest contact amounts to 3.480(5) Å between S18B and C31. There is no short S$\cdots$S contact less than 4 Å. Some unconventional intermolecular hydrogen bonds C$-$H$\cdots$O show up at 3.221(6) and 3.277(8) Å. Due to the asymmetry of the single molecular dyad with respect to its short molecular axis, a positional disorder (1:1) occurs in the crystal lattice.

The electrochemical properties of the molecular dyad **1** and of the reference compounds **2** and **3** in CH_2Cl_2 were investigated by cyclic voltammetry (CV). As shown in Figure 2, compound **1** undergoes two reversible one-electron
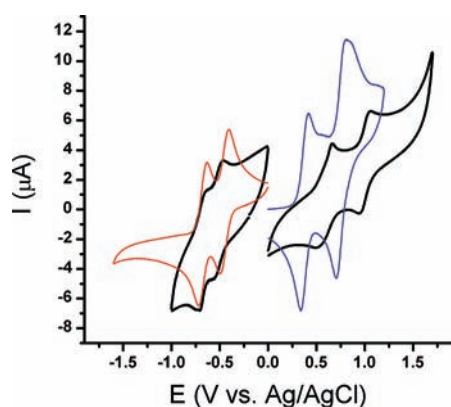

Figure 2. Cyclic voltammograms of **1** (black line), **2** (red line), and **3** (blue line) in CH_2Cl_2 (0.1 M TBAPF$_6$ (TBA = tetrabuty-lammonium); on platinum electrode; scan rate 0.1 V·s^{-1} for the reference compounds **2** and **3**, 0.5 V·s^{-1} for **1**).

oxidations for the successive generation of the TTF$^+$ radical cation and the TTF^{2+} dication, as well as two reversible one-electron reductions corresponding to the consecutive reduc-

tion processes of the PDI moiety. Compared to the corresponding reference compounds **2** and **3**, the oxidation waves are substantially positive-shifted (**1**: $E_{1/2}^{ox1}$ = 0.58 V, $E_{1/2}^{ox2}$ = 1.00 V; **3**: $E_{1/2}^{ox1}$ = 0.38 V, $E_{1/2}^{ox2}$ = 0.76 V), while only the first reduction wave is slightly negative-shifted (**1**: $E_{1/2}^{red1}$ = −0.52 V, $E_{1/2}^{red2}$ = −0.67 V; **2**: $E_{1/2}^{red1}$ = −0.45 V, $E_{1/2}^{red2}$ = −0.68 V). This observation reflects the electronic interaction between D and A within the fused system: the HOMO of **1** is energetically lowered, and its LUMO is energetically raised through chemically bonding **2** to **3**.[v]
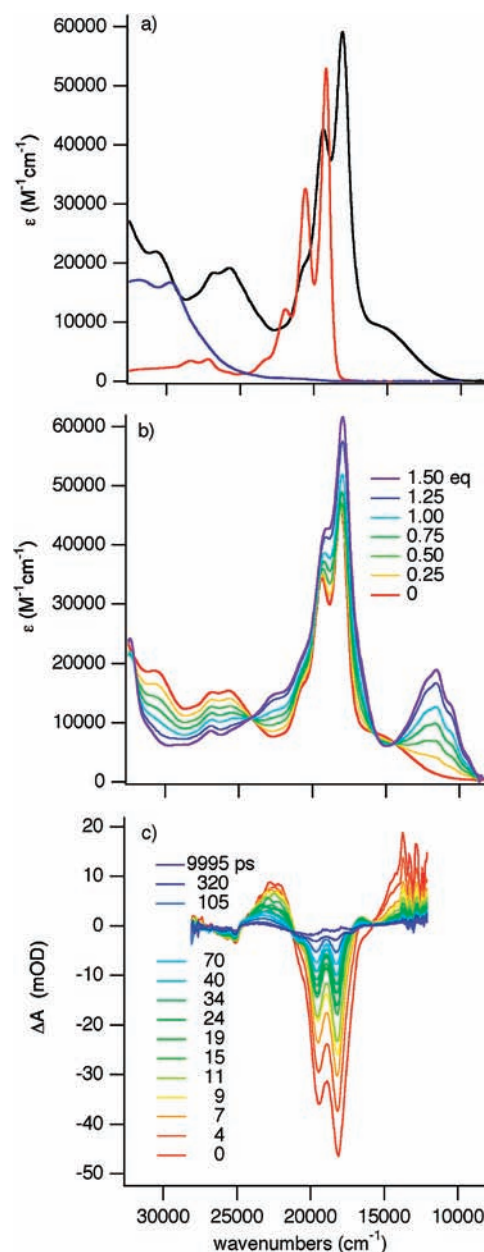

Figure 3. (a) Electronic absorption spectrum of **1** (black line) together with those of the reference compounds **2** (red line) and **3** (blue line), in CH_2Cl_2 ($c = 2 \times 10^{-5}$ M) at room temperature. (b) Electronic absorption spectra of **1** upon oxidation with different equivalents of [Fe(bpy)$_3$]$^{3+}$, corrected for the absorption of [Fe(bpy)$_3$]$^{2+}$. (c) Transient absorption spectrum of **1** upon pulsed excitation at 400 nm.

The molecular dyad **1** strongly absorbs in the green spectral region as evidenced by its deep purple color. The UV−vis−NIR spectrum of **1** (Figure 3a) recorded in CH_2Cl_2 shows a strong and broad absorption band from 11 000 cm^{-1} (910 nm) up to 17 000 cm^{-1} (590 nm), followed by a very intense and structured band that peaks at 18 030 cm^{-1} (555 nm), with a clear progression in a 1250 cm^{-1} vibrational mode. Further strong absorptions appear above 23 000 cm^{-1} (435 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 $\pi\pi*$ charge-transfer (ICT) transitions from the TTF unit (HOMO and HOMO-1) to the PDI core (LUMO and LUMO+1) (for the relevant orbitals, see Supporting Information). The intense absorption band of **1** at 18 030 cm^{-1} (555 nm) reflects the $\pi\pi*$ orbital excitation corresponding to a PDI-localized transition. Compared to the unsubstituted PDI **2**, which peaks at 19 340 cm^{-1} (517 nm) and exhibits also the vibrational progression, the red-shift of 1310 cm^{-1} is due to the extension of the π-conjugation of the PDI unit in **1**. The electrochemical HOMO−LUMO gap (1.1 eV, 8900 cm^{-1}) is in fairly good agreement with the energy (11 000 cm^{-1}) deduced from the onset of the lowest ICT absorption band.

The absorption spectrum of **1** depends on the oxidation state. Figure 3b shows its evolution upon chemical oxidation using $[Fe(bpy)_3]^{3+}$ as the oxidizing agent. The TTF unit can be oxidized to the $TTF^{\bullet+}$ radical as borne out by the isosbestic points at 15 000 cm^{-1} (667 nm) and 24 800 cm^{-1} (403 nm) and the similarity to the final spectrum obtained upon electrochemical oxidation (see Supporting Information). Whereas the PDI centered $\pi\pi*$ transition is not much affected by the oxidation, the ICT band at 15 000 cm^{-1} (667 nm) of the neutral form of **1** decreases in intensity and is replaced by a new band centered at 12 000 cm^{-1} (830 nm) for **1**$^{+}$. On the basis of the previous observations,[3c,e] this new transition can be ascribed either to an ICT, however, now in the opposite direction to that of the neutral compound **1**, that is, PDI→TTF^+, or to an alkylthio−TTF^+ transition.[10]

In contrast to the TTF-fused dppz molecule,[3e] TTF−PDI in its neutral form does not show any luminescence, neither from the $\pi\pi*$ transition on PDI, known to fluoresce strongly in the absence of quenchers, nor from the ICT transition itself. The former is reductively quenched by the TTF unit. The latter would appear strongly Stokes shifted in the near-infrared. The transient absorption spectra obtained upon pulsed laser excitation at 400 (Figure 3c) and 650 nm show

that the excited state returns to the ground state within approximately 10 ps (see Supporting Information). With a radiative lifetime of the lowest energy ICT state of ∼5 ns estimated from the oscillator strength of the corresponding transition, a maximum luminescence quantum yield of <0.2% would result. This is too weak for reliable detection in the near-infrared. The transient absorption shows bleaching of the $\pi\pi*$ transition on the PDI as well as of the ICT transitions and a transient absorption around 13 000 cm^{-1} (770 nm). The former indicates that in the excited state the PDI unit is strongly perturbed, and the latter is characteristic for the presence of a $TTF^{\bullet+}$ radical. Finally, chemical oxidation of **1** does not restore the PDI centered luminescence. This is in contrast to TTF-fused phthalocyanine,[3d] for which the phthalocyanine-based fluorescence could be restored upon oxidation of the TTF. The key difference is that for PDI the $\pi\pi*$ transition is at higher energy, and thus its luminescence is quenched by either oxidative electron transfer or energy transfer.

In conclusion, we have demonstrated that a redox-active TTF unit can be annulated to a PDI core, giving rise to a large extended π-conjugation. Therefore, this new dyad **1** shows intense optical absorbances over a wide spectral range. In particular, the new molecule also combines in a complementary manner the functional properties of PDI with the strong electron-donating properties of TTF.

Supporting Information Available: Experimental procedure and characterization data for compound **1**, copy of ^{1}H NMR spectrum of **1**, CIF file for **1** (CCDC 727690), the crystal packing of **1**, as well as some additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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