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Targeting π -Conjugated Multiple Donor–Acceptor Motifs Exemplified by Tetrathiafulvalene-Linked Quinoxalines and Tetrabenz[*bc*,*ef*,*hi*,*uv*]ovalenes: Synthesis, Spectroscopic, Electrochemical, and Theoretical Characterization

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Abstract: An efficient synthetic approach to a symmetrically functionalized tetrathiafulvalene (TTF) derivative with two diamine moieties, 2-[5,6diamino-4,7-bis(4-pentylphenoxy)-1,3benzodithiol-2-vlidene]-4,7-bis(4-pentylphenoxy)-1,3-benzodithiole-5,6-diamine (2), is reported. The subsequent Schiff-base reactions of 2 afford large π -conjugated multiple donor-acceptor (D-A) arrays, for example, the triad 2-[4,9-bis(4-pentylphenoxy)-1,3-dithiolo-[4,5-g]quinoxalin-2-ylidene]-4,9-bis(4pentylphenoxy)-1,3-dithiolo[4,5-g]quinoxaline (8) and the corresponding tetrabenz[bc,ef,hi,uv]ovalene-fused pentad 1, in good yields and high purity. The novel redox-active nanographene 1 is so far the largest known TTF-functionalized polycyclic aromatic hydrocarbon (PAH) with a well-resolved ¹H NMR spectrum. The electrochemically highly amphoteric pentad 1 and triad 8 exhibit various electronically excited chargetransfer states in different oxidation states, thus leading to intense optical intramolecular charge-transfer (ICT)

Keywords: charge transfer • donoracceptor systems • nanographene • redox chemistry • tetrathiafulvalene absorbances over a wide spectral range. The chemical and electrochemical oxidations of **1** result in an unprecedented TTF⁺ radical cation dimerization, thereby leading to the formation of $[1^{++}]_2$ at room temperature in solution due to the stabilizing effect, which arises from strong π - π interactions. Moreover, ICT fluorescence is observed with large solvent-dependent Stokes shifts and quantum efficiencies of 0.05 for **1** and 0.035 for **8** in dichloromethane.

Introduction

Tetrathiafulvalene (TTF) is one of the most intensively investigated redox-active organic molecules due to its intrinsic properties, namely, two easily accessed oxidized states (TTF⁺ and TTF²⁺), which display distinctly different physical properties.^[1] A comprehensive study of TTF-based or-

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ganic (super)conductors has spurred scientists for several decades. Despite the abundance of synthetic methods involving TTF, there is an ongoing effort to explore efficient approaches to appropriately functionalize TTFs as promising building blocks within the wider context of supramolecular and materials chemistry towards molecular (opto)electronics. As a consequence, a variety of TTF-incorporated systems find applications in diverse fields, such as redox-controllable molecular machines, biological probes, switches, liquid crystals, gels, organic field-effect transistors, and solar cells.^[2]

Large π -conjugated TTF systems have rarely been reported in the literature so far, owing to the limited preparative accessibility and the lack of an efficient and convenient synthetic methodology.^[3] In response, we have introduced a concept for the annulation of TTFs to acceptor moieties by a Schiff-base reaction, and this leads to various electron donor-acceptor (D-A) ensembles, which have structurally rigid and planar configurations.^[4] In contrast to D– σ –A ensembles, sterically controlled and compactly fused D– π –A systems exhibit pronounced photoinduced charge-transfer (CT) processes, thus giving rise to interesting photophysical phenomena such as long-lived charge-separated states.^[5] Moreover, such π -bridged systems allow the combination of an energetically high-lying HOMO (highest occupied molecular orbital) localized on a D with a low-lying LUMO (lowest unoccupied molecular orbital) on an A, thereby resulting in conjugated systems with small HOMO–LUMO energy gaps,^[4b] which are of current interest in molecular (opto)electronics. It has been documented that π -conjugated multiple D–A arrays of precise length and shape are expected to show unique physical features that range, for example, from narrow HOMO–LUMO gaps to high polarizabilities,

and thus are desirable in the fields of organic conductive materials, nonlinear optical (NLO) materials, near-infrared dyes, and molecular wires.^[6] A crucial issue concerns the optimal way to interlock the various D and A components into ordered arrays that allow them to efficiently perform specific functions such as wires, motors, diodes, rectifiers, antennas, and so on.^[7] With respect to attaining a π -conjugated multi-D-A alignment, our strategy involves the judicious design and effective preparation of a requisite precursor 2 with a diamine functionality on each side of the TTF core (Figure 1), which can readily undergo a conden-

can readily undergo a condensation reaction with appropriate diketones. The incorporation of 4-pentylphenoxy groups makes the resultant compounds more soluble in a variety of solvents. This combination renders **2** a promising building block for the construction of a wide variety of π -conjugated multichromophoric D–A ensembles to study in depth photoinduced electron and energy transfer as well as the photogeneration of longlived charge-separated states.

Polycyclic aromatic hydrocarbons (PAHs) possessing a high degree of conjugation, are very important. Their unique physical properties render them promising as active components in organic electronic devices, for example, in field-effect transistors, injection layers, and solar cells.^[8] However, it is still a highly challenging task to attain large π -extended PAHs with different functional groups, tuning their electronic structures, and endowing a facile solution processing.^[9] Therefore, we set ourselves the synthetic task to fuse together two prominent moieties, namely, TTF and *tert*-butylated tetrabenz[*bc,ef,hi,uv*]ovalene units through electron-deficient N-heteroaromatic linkers, thus leading to the formation of the symmetric D'–A–D–A–D' array of compound **1** (Figure 2). As the focal point of the work presented herein, we developed an efficient synthetic approach



Figure 1. Molecular structure of the key precursor 2.



Figure 2. Molecular structure of the target compound 1.

to such a large π -extended and redox-active chromophore **1** starting from the key precursor **2**. A thorough experimental and theoretical study of photoinduced intramolecular charge-transfer (ICT) processes in the multiple D–A array **1** and the reference compound **8** (**1** without the ovalene groups) was performed. The multiple light-induced CT processes occurring between spatially separated electron-rich and electron-deficient fragments within the extended polycyclic system are illustrated in Figure 2.

Results and Discussion

The synthetic pathway to the target compound **1** is outlined in Scheme 1, and this involved the direct condensation reaction of 4,6,9,12,15,17-hexakis(1,1-dimethylethyl)tetrabenz[*bc,ef,hi,uv*]ovalene-1,2-dione with the key precursor **2**. The latter was prepared by a reductive sulfur extrusion from the corresponding 2,1,3-benzothiadiazole derivative **6** with NaBH₄ in the presence of catalytic amounts of CoCl₂·6H₂O. The synthesis of **6** is based on a phosphite-mediated selfcoupling reaction of 4,8-dibromo[1,3]dithiolo[4,5-*f*]-2,1,3benzothiadiazol-6-one (**4**), followed by substitution with 4-



Scheme 1. A synthetic route to the target compound ${\bf 1}$ and the reference compound ${\bf 8}.$

pentylphenol. The same methodology was applied to obtain the reference compound **8** in reasonable yield. Good solubilities of all compounds (except for **5**) in common organic solvents allowed easy purification by standard chromatographic techniques or crystallization, as well as full characterization. Notably, nanographene **1**, the largest TTF-conjugated PAH, shows a well-resolved ¹H NMR and a structure-rich UV/Vis spectrum; this indicates a low self-association propensity in solution.

Preparation of the important precursor 4,8-dibromo-[1,3]dithiolo[4,5-f]-2,1,3-benzothiadiazol-6-one (4) is highly challenging. Our strategy involved the treatment of 5,6-diamino-1,3-benzodithiole-2-thione with thionyl chloride in the presence of pyridine in toluene to afford 3, which subsequently reacted with bromine (added dropwise) in aqueous hydrobromic acid to produce 4. Several published protocols for bromination of deactivated aromatics were initially attempted. However, 4 was only isolated in quite poor yields. This precursor 4 is anticipated to emerge as an ideal building block for the construction of 2-D conductive polymers or metallopolymers owing to its unique structure. First, the dithiocarbonate moiety of 4 can be readily converted into dithiolate ligands by hydrolysis under basic conditions, thereby affording a metal-bis-1,2-dithiolene complex, which represents one class of the most extensively studied hybrid materials as potential organic superconductors.^[10] Second, novel benzothiadiazole-tetrathiafulvalene (BTD-TTF)- based systems can be generated through trialkyl phosphitemediated coupling reactions with a variety of 1,3-dithiole-2thione derivatives. The most prominent feature of **4** is its capability to undergo C–C bond formation by transmetalation reactions such as Heck, Stille, and Suzuki reactions,^[11] to introduce a large range of functional groups.

Furthermore, apart from being a protecting group in organic synthesis, 2,1,3-benzothiadiazole (BTD) is of prime interest because of the potential applications, for example, as a strong electron-acceptor unit in conducting materials, leading to an improved photovoltaic performance,^[12] or as BTD-incorporated polymers, resulting in luminescent components in electroluminescence devices.[13] Consequently, with the precursors 4 and 5 in hand, incorporation of BTD-TTF moieties into conjugated polymer systems through various spacers can

readily be achieved, not only yielding unique hybrid architectures, but also exhibiting some promising electro-optical properties, which are desirable for the fabrication of molecular electronics.^[14]

The electrochemical properties of the π -conjugate **1** and the reference compound **8** in dichloromethane were investigated by cyclic voltammetry (CV). Both compounds undergo two reversible single-electron oxidation $(E_{\text{ox1}}^{1/2}=0.91 \text{ V}$ and $E_{\text{ox2}}^{1/2}=1.19 \text{ V}$ for **1**; $E_{\text{ox1}}^{1/2}=1.08 \text{ V}$ and $E_{\text{ox2}}^{1/2}=1.40 \text{ V}$ for **8**) and one reversible one-electron reduction processes $(E_{\text{red}}^{1/2}=-1.14 \text{ V}$ for **1**; $E_{\text{red}}^{1/2}=-1.42 \text{ V}$ for **8**), which can be assigned to the oxidation of the TTF core and the reduction of the quinoxaline moiety, respectively (Figure 3). Upon the incor-



Figure 3. Cyclic voltammograms of $1~(1\times10^{-4}\,\text{m},$ dashed line) and the reference compound $8~(1\times10^{-4}\,\text{m},$ black line) in $CH_2Cl_2~(0.1\,\text{m}~Bu_4N(PF_6);$ Pt-disk working electrode; scan rate 100 mVs^-1).

poration of ovalene units, marked cathodic shifts in the two oxidation potentials were observed, consistent with the electron-donating effect of the ovalene units. On the other hand, the reduction potential is anodically shifted by 280 mV due to the large π -extended conjugation, substantially lowering the energy level of the LUMO.

The dark purple compound **1** shows intense optical absorption bands over an extended range within the UV/Vis spectral region (Figure 4). The electronic transitions can



Figure 4. Electronic absorption spectra of 1 (top) and 8 (bottom) in a CH_2Cl_2 solution, together with the calculated $S_0 \rightarrow S_n$ transitions at the TD-B3LYP/TZVP level of theory.

best be characterized in terms of three distinct energy ranges. Firstly, at low energy, a single strong absorption band appears at 17300 cm^{-1} (578 nm). Secondly, in the energy range beginning from the shoulder on the highenergy side of this first absorption band to about 22000 cm⁻¹ (455 nm), a series of less-intense electronic transitions appear. Finally, a structure-rich intense absorption profile covers the whole spectral range at energies higher than 22000 cm^{-1} (455 nm). As we will discuss below, the division into these three distinct parts actually reflects the electronic structure of 1, which can be represented as a D'-A–D–A–D' pentad (see Figure 2). In contrast, the orange colored reference compound 8 as the central fragment of 1, consisting of the TTF core and the two pending quinoxaline linking units, represents "only" an electronic A-D-A triad b) system. In accordance with this description, the optical spectrum of 8 (Figure 4) looks much simpler, and due to the decreased π extension of the molecule, its lowest energy absorption band appears hypsochromically shifted at 22200 cm^{-1} (450 nm). In both cases, the single low-energy absorption band can be attributed to the corresponding intramolecular TTF-quinoxaline CT transition within the common central A-D-A unit, which is corroborated by the computational results (see below). Now, in the case of spectrum 1, the additional terminal tetrabenz[bc,ef,hi,uv]ovalene moieties bound to the linking A units from opposite sides

are expected to show up with their own ICT signatures, that is, an ovalene \rightarrow quinoxaline (D' \rightarrow A) CT, which essentially makes up the less-intense absorption pattern up to 22000 cm⁻¹ (455 nm). Finally, many π - π * transitions, mainly located on the tetrabenz[*bc*,*ef*,*hi*,*uv*]ovalene moieties combined with ICT transitions from the central D unit to the molecular periphery, are expected to result in the structurerich absorption profile at higher energies.

Quantum-chemical calculations were carried out to determine energies, intensities, and the type of the electronic excitations of 1 and its reference compound 8. The important frontier molecular orbitals (MOs) together with their calculated energies are given in Figure 5a for 1 and Figure 5b for 8.

To describe and analyze the electronic transitions, it is advantageous to apply a suitable symmetry frame to the molecules, although it is well-known that such large π systems are structurally slightly corrugated.^[9] Thus, the discussion is based on the C_{2h} point group, and by that the applied molecular symmetry is not higher than necessary; the mirror plane allows for a strict σ - π separation, and the C_2 axis (or alternatively the inversion center) reflects an equivalence of the right and left parts of the molecules. In fact, the overall good agreement of the computational results with the experimental ones justifies this approach; the calculated symmetry-allowed in-plane electric dipole transitions match the



Figure 5. Frontier molecular orbitals of the π -conjugated skeleton of a) **1** and b) **8**.

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electronic spectra quite well. Basically, the MOs result from symmetry-adapted linear combinations of orbitals from the central TTF core with the plus/minus linear combinations of orbitals from the pending units, while taking into account their respective energy separations. By evaluating 1, as expected, the HOMO (a_u) shows its main electron-density localization on the central TTF, and the LUMO (bg) and LUMO+1 (a_u) largely represent the in and out-of-phase linear combinations of the orbitals located on the attached quinoxaline and the inner edge of the ovalene units. Clearly, this outcome reflects the electronic structure, as qualitatively represented in the manner A-D-A for the inner part of the molecule 1. Next, from the LUMO+2 upwards, the pairs (b_{g}, a_{u}) of orbitals from the peripheral tetrabenz[*bc,ef,hi,u*v]ovalene moieties appear predominantly, and analogously this is the case from the HOMO-1 downwards in energy. The MO scheme for 8 follows the analogous line of arguments.

The calculated vertical electronic transitions for **1** and **8** are shown by sticks in the spectra in Figure 4, and the calculated energy values and oscillator strengths of both compounds are given in Tables 1 and 2. For **1**, the TD-DFT calculation predicts the $S_0 \rightarrow S_1$ excitation to be dominated (97%) by a one-electron HOMO \rightarrow LUMO promotion and thus exhibits CT character as electron density is moved from the TTF center to the linking quinoxaline units (A \leftarrow D \rightarrow A, ICT₁). The calculated energy and oscillator strength compare fairly well with the first single absorption

Table 1. Values of energies, oscillator strengths and dominant contributions of the respective molecular orbitals for $S_0 \rightarrow S_n$ of **1**.

State	Excitation ener- gy [cm ⁻¹]	Oscillator strength	Dominant contribution [%]
S ₁	15541	0.12	H→L (97)
S ₂	19207	0.05	H-1 \rightarrow L+1 (52), H-2 \rightarrow L (43)
S_4	20467	0.11	H-2→L (54), H-1→L+1 (44)
S ₅	21197	0.10	H→L+2 (87)
S ₆	22308	0.16	$H \rightarrow L+4$ (25), $H-3 \rightarrow L+2$ (24),
			H-4→L+3 (23)
S ₇	23216	0.16	H-1 \rightarrow L+3 (52), H-2 \rightarrow L+2 (28)
S ₈	23907	0.45	$H \rightarrow L+4$ (71), $H-3 \rightarrow L+2$ (12),
			H-4→L+3 (11)
S ₉	25307	0.89	H-1→L+5 (27), H→L+6 (22),
			H-2→L+4 (13)
S ₁₁	26339	0.56	$H \rightarrow L+6$ (35), $H-1 \rightarrow L+5$ (26),
			H-4→L+3 (15)
S ₁₃	26570	0.61	H-3→L+4 (36), H-4→L+5 (35)
S ₁₅	27 522	0.10	H-2 \rightarrow L+4 (70), H-1 \rightarrow L+5 (26)

Table 2. Values of energies, oscillator strengths and dominant contributions of the respective molecular orbitals for $S_0 \rightarrow S_n$ of **8**.

State	Excitation ener- gy [cm ⁻¹]	Oscillator strength	Dominant contribution [%]
$egin{array}{c} \mathbf{S}_1 \ \mathbf{S}_4 \ \mathbf{S}_6 \ \mathbf{S}_7 \end{array}$	20374 33503 37573 39360	0.47 0.16 1.32 0.24	$H \rightarrow L$ (99) $H - 3 \rightarrow L + 1$ (82) $H \rightarrow L + 7$ (84) $H - 6 \rightarrow L$ (43), $H - 1 \rightarrow L + 3$ (33), $H - 3 \rightarrow L + 1$ (12)

band centered at 17300 cm⁻¹ (578 nm). The calculated $S_0 \rightarrow$ S_2 and $S_0 \rightarrow S_4$ excitations are mixtures of HOMO-2 \rightarrow LUMO and HOMO-1-LUMO+1 transitions, albeit with different ratios. These transitions predominantly move electron density from the peripheral tetrabenz[bc,ef,hi,uv]ovalene moieties to the linking quinoxaline units (D'-A-D- $A \leftarrow D'$, ICT₂). They are attributed to the next absorption bands following the first single absorption peak. Next, the calculated $S_0 \rightarrow S_5$ excitation is dominantly (87%) a one-electron HOMO→LUMO+2 transition, and it describes a CT from the center to the peripheral parts of the molecule $(\leftarrow \leftarrow D \rightarrow \rightarrow, ICT_3)$. The following calculated excitations, $S_0 \rightarrow S_6$ up to $S_0 \rightarrow S_{15}$, are mostly combinations of tetrabenz[bc,ef,hi,uv] ovalene localized π - π * transitions with CT transitions of the type analogous to $S_0 \rightarrow S_5$, but involving the MOs from HOMO-4 to LUMO+6. In total, these excitations are attributed to the structure-rich intense absorption profile at energies higher than $22\,000 \text{ cm}^{-1}$ (455 nm). For 8, the TD-DFT calculation predicts the $S_0 \rightarrow S_1$ excitation to be dominated (99%) by a one-electron HOMO→LUMO promotion and thus exhibits CT character as electron density is moved from the TTF center to the linking quinoxaline units $(A \leftarrow D \rightarrow A, ICT_1)$. Again, the calculated energy and oscillator strength compare fairly well with the first single absorption band centered at 22200 cm^{-1} (450 nm).

The quantum-chemical calculations for **1** and **8** led to theoretical HOMO–LUMO gaps (HLG) of $HLG_{calcd}=2.28 \text{ eV}$ (18390 cm⁻¹) and 2.91 eV (23470 cm⁻¹), respectively. These values compare favorably with the experimental CV data, $HLG_{CV}=2.05 \text{ eV}$ (16530 cm⁻¹) for **1** and 2.50 eV (20160 cm⁻¹) for **8**. Accordingly, the optical HLG values of 16670 and 19240 cm⁻¹ for **1** and **8**, respectively, determined from the intersections of their absorption and emission spectra (Figure 8 and Figure S6, see the Supporting Information) are in good agreement with the above-mentioned HLG_{CV}.

Both compounds, 1 and 8, exhibit fluorescence in solution at room temperature, which is rarely observed in D-A systems containing TTF. The quantum efficiency of the emission in dichloromethane was determined to be 0.05 for 1 and 0.035 for 8 at room temperature. Their good solubilities in a variety of organic solvents allowed the study of their solvatochromic behavior. The electronic absorption spectrum of **1** is less dependent on the polarity of the solvent, whereas a substantial hypsochromic shift of the ICT absorption band in 8 with increasing solvent polarity is observed (Figures S1 and S2, see the Supporting Information). However, in methanol this trend is reversed as the formation of intermolecular hydrogen bonds between 8 and methanol molecules leads to a significant bathochromic shift of the ICT absorption band. Figures 6 and 7 show the emission spectra of 1 and 8 in a range of solvents with varying polarities. In both cases, the red-shift of the fluorescence as a function of the solvent polarities is quite pronounced. This solvent dependence of the fluorescence indicates that the solvent rearrangement stabilizes the excited states increasingly in more polar solvents, as expected for ICT states. Table 3 summarizes the relevant spectroscopic data for both



Figure 6. Emission spectra of $\mathbf{1}$ ($c=3 \times 10^{-6}$ M) in different solvents at room temperature ($\lambda_{ex}=580$ nm).



Figure 7. Emission spectra of **8** ($c=6 \times 10^{-6}$ M) in different solvents at room temperature ($\lambda_{ex}=450$ nm).



Figure 8. Emission and excitation spectra of $\mathbf{1}$ ($c=2\times10^{-6}$ M) for different excitation and detection wavelengths, respectively, in CH₂Cl₂ solution at room temperature. The absorption spectrum of the same solution is included for direct comparison.

absorption and emission. Therein, the solvent polarity parameter Δf is calculated from Equation (1),^[15] where ε and *n*

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Solvent	Δf	$A_{ m max} [m cm^{-1}]$		$E_{\rm max} [{ m cm}^{-1}]$		$\nu_{\rm ST} [{\rm cm}^{-1}]$			
		1	8	1	8	1	8		
methanol	0.309	16978	19803	14837	17 182	2141	2621		
acetonitrile	0.305	16892	23148	14702	15 528	2190	7620		
DCM	0.219	17243	22224	15385	16393	1858	5831		
chloroform	0.218	17241	21933	15480	16779	1761	5154		
THF	0.210	17361	22673	15625	17007	1736	5666		
cyclohexane	-0.002	17454	21978	16722	19305	732	2673		
toluene	0.013	17 153	22029	15873	18116	1280	3913		

are the dielectric constant and the refractive index of the solvent, respectively.

$$\Delta f = \frac{(\varepsilon - 1)}{(2\varepsilon + 1)} - \frac{(n^2 - 1)}{(2n^2 + 1)}$$
(1)

The different Stokes shifts (v_{ST}) can be plotted as a function of the solvent polarity parameters (Δf), and from the corresponding correlation diagrams and an analysis according to Lippert and Mataga^[15b] (Figures S3 and S4, see the Supporting Information), a formal change in the dipole moments of 20 and 24 Debye for 1 and 8 can formally be derived, in accordance with expectations for CT transitions. As the molecules are symmetric, the interpretation of this change in dipole moment is not straightforward. In the ground state, the total dipole moment consisting of the sum of two opposing and comparatively small dipole moments is zero. In the optically excited state this is still the case, and even in the relaxed excited state this could still be the case, that is, the solvent molecules rearrange individually around the two opposing dipole moments of the symmetric charge redistribution according to the LUMO. However, it is more likely that the rearrangement of the solvent molecules results in spontaneous symmetry breaking with localization of the charge on one wing of the molecule.^[16]

It is important to note that the excitation spectra of 1 almost duplicate the corresponding absorption spectra for the solvents of the series, as shown for dichloromethane in Figure 8. Only in the region of low-energy absorptions, depending on the detection wavelength, the excitation spectra look slightly different; this observation is most pronounced in the case of polar solvents (Figure S5, see the Supporting Information). This could indicate that more than one luminescent state close in energy to each other are involved. Emission decay curves were measured in a solution of dichloromethane at room temperature with irradiation at $395 \text{ nm} (25320 \text{ cm}^{-1})$ and detection at different wavelengths across the emission spectrum (Figure 9). The logarithmic plot shows a double exponential behavior, with a fast component ($\tau_1 = 0.49(2)$ ns) and a slower component ($\tau_2 =$ 4.70(20) ns) as determined from a least-squares fit using the experimentally determined response function of the system for deconvolution. The corresponding relative amplitudes are $A_1 = 0.95$ and $A_2 = 0.05$, which translate into relative in-



Figure 9. Decay profile of the emission at 650 nm (15400 cm⁻¹) of **1** in CH₂Cl₂ solution (λ_{ex} =395 nm) at room temperature (c=5×10⁻⁶M), the instrumental response function and the convolution of the best fit to a biexponential function. Inset: decay curves at different wavelengths on a logarithmic scale.

tensities given by $A_1 \tau_1 / A_2 \tau_2$ of 7:3 at $\lambda_{em} = 650 \text{ nm}$ (15400 cm^{-1}) , that is, at the maximum of the emission band. The relative amplitudes of the two components vary slightly with emission wavelength. The full analysis of the decay curves (see Figures S7 and S8 and Table T1 in the Supporting Information) confirms that 30% of the observed luminescence is due to the slow component and that the emission maximum of the slow component is around 250 cm⁻¹ higher in energy. Before drawing any conclusions, it is essential to rule out impurity luminescence. From careful analysis of the NMR spectra, impurity levels in 1 are below 0.5%, and thin-layer chromatography on the sample, as used for the emission experiments, showed a single luminescent spot. However, despite the seemingly photochemical stability of 1 in dichloromethane (Figure S9, see the Supporting Information), luminescence from a photochemically formed impurity cannot be entirely ruled out. Thus, although it is tempting to ascribe the dual luminescence to a single species, we do so with caution even though emission wavelength-dependent excitation spectra (Figure S10, see the Supporting Information) do not contradict the notion of luminescence due to a single species. Indeed, the two close-lying excited states, S_1 and S₂, reveal quite different character. The first one is of the CT type $A \leftarrow D \rightarrow A$ (ICT₁), whereas the latter one shows an orthogonal CT character, namely, $D' \rightarrow A-D A \leftarrow D'$ (ICT₂). Now, because of the different localization of these two electronic CT transitions and their almost equal energy and rather large reorganization energies along different reaction coordinates, internal conversion between them could be slower than their respective lifetimes. However, this will have to be more thoroughly investigated by using ultrafast transient absorption and fluorescence up-conversion spectroscopy, which is beyond the scope of the present work.

In situ electronic absorption analysis of pentad **1** and triad **8** by applying an oxidation potential of 1.05 and 1.23 V (vs

Ag/AgCl), respectively, revealed a gradual growth of a new absorption band around 15000 cm^{-1} in the near-infrared (NIR) region (Figure 10) and a concomitant bleaching of



Figure 10. UV/Vis spectral changes obtained during the first oxidation of a) **1** at 1.05 V vs Ag/AgCl ($c=6\times10^{-5}$ M) and b) **8** at 1.23 V vs Ag/AgCl ($c=1.3\times10^{-4}$ M) in CH₂Cl₂ solution containing 0.1 M Bu₄N(PF₆) at room temperature (cell: 0.7 mm).

the ICT absorption band at 17300 cm^{-1} (for 1) or 22200 cm^{-1} (for 8). The oxidation of the TTF unit into the TTF⁺ radical in pentad 1 and triad 8 is borne out by the similarity to the final spectra obtained upon chemical oxidation (Figures S11 and S12, see the Supporting Information). On the basis of the previous observations,^[4d-f] the new transition around 15000 cm⁻¹ can be ascribed either to an ICT transition, however, now in the opposite direction to that of the neutral compound 1 or 8, that is, quinoxaline \rightarrow TTF⁺ or to a transition centered on the TTF+ radical.^[17] An additional broad absorption band at 11000 cm⁻¹, characteristic of the dimeric radical cation species of the TTF cores (π dimers) arising from the π - π interactions of the monomer singly occupied molecular orbitals (SOMOs),^[18-19] was observed in the case of 1. This finding indicates that the spontaneous self-association of 1^+ to form a diamagnetic dimer $[1^+]_2$ takes place, owing to the stabilization effect, which arises from the strong π - π interaction. It can therefore be deduced that 1^+ shows a strong tendency to undergo π dimerization, in which the long-distance attractive interaction overcomes the electrostatic repulsion. The direct observation of such intermolecular dimerizations in solution at room temperature is still quite challenging because the intermolecular interactions are usually too weak to dimerize the TTF⁺ units noncovalently. Up to now, only a few examples have been reported, in which enforced interactions are accomplished either by suitable hosts (e.g., cucurbituril, selfassembled molecular cages) or through a unique TTF⁺CB⁻ salt (CB = permethylcarboranyl) or a glycoluril-based molecular clip.^[18] Very recently, Stoddart and co-workers demonstrated that highly stable TTF radical π dimers could be generated by virtue of the mechanical bonding of two macrocyclic polyethers containing TTF residues.^[19] In the present case, an elegant approach has been developed to meet this challenge through the direct fusion of ovalene units to the TTF core.

Conclusions

We have described 1) a strategy for the efficient synthesis of the key precursor 2 with a diamine functionality on each side of the TTF core, a vital intermediate that can now be employed in the construction of large π -conjugated multiple D-A arrays, for example, triad 8 and pentad 1, and 2) an experimental and computational study on their electrochemical, optical absorption, photoinduced ICT, and fluorescence characteristics. The redox-active pentad 1 and triad 8 exhibit various electronically excited CT states in different oxidation states, thus leading to intense optical absorbances over a wide spectral range. Particularly, the chemical and electrochemical oxidation of 1 allowed us to identify an unprecedented TTF⁺ radical cation dimerization, and this led to the formation of $[1^+]_2$ at room temperature in solution. Although the π dimerizations of TTF⁺ are of paramount importance for conductor/insulator modeling of p-doped solidstate arrays, they are quite rare in the literature. Our observations reported herein provide a convenient approach to significantly enhance the intermolecular π - π interactions through the direct fusion of ovalene units to the TTF core. Moreover, the corresponding ICT fluorescence is also observed with large solvent-dependent Stokes shifts; quantum efficiencies being 0.05 for 1 and 0.035 for 8. Ultrafast transient absorption spectroscopy will be required to probe the nature of the luminescent states further.

In search of high-performance organic semiconductors for molecular devices, heterocycle-fused and π -extended TTF derivatives prove to be very promising molecular scaffolds in organic field-effect transistors (OFETs). It has been shown that the introduction of electron-accepting quinoxaline rings to the TTF skeleton was effective to enhance the intermolecular interactions, thus leading to excellent *n*-type or *p*-type FET performance with high carrier mobilities.^[20] Tests of the performance of the aforementioned π -conjugated systems **1** and **8** for charge transport in molecular electronic applications will be of particular interest. As a consequence, the TTF-containing triad **8**, chemically and structurally related to the reported systems,^[20] is currently explored as an active material for OFETs.

Experimental Section

General

Air and/or water-sensitive reactions were conducted under Ar in dry, freshly distilled solvents. Elemental analyses were performed on an EA 1110 Elemental Analyzer CHN Carlo Erba Instruments. FT-IR spectra were recorded on a Perkin–Elmer One FT-IR spectrometer. Mass Spectra were recorded with an Auto Spec Q spectrometer for EI and with an FTMS 4.7T BioAPEX II for the MALDI ionization method. Cyclic voltammetry (CV) was performed in a three-electrode cell equipped with a Pt-disk working electrode, a glassy carbon counter-electrode, and Ag/AgCl was used as the reference electrode. The electrochemical experiments were carried out under dry and an oxygen-free atmosphere in dichloromethane (DCM) with $Bu_4N(PF_6)$ (0.1M) as a support electrolyte. The voltammograms were recorded on a PGSTAT 101 potentiostat.

Materials

Unless stated otherwise, all other reagents were purchased from commercial sources and used without additional purification. 5,6-Diamino-1,3benzodithiole-2-thione,^[4d] 1,4-dioxane-2,3-diol,^[21] and 4,6,9,12,15,17-hexakis(1,1-dimethylethyl)tetrabenz[*bc,ef,hi,uv*]ovalene-1,2-dione^[9a] were prepared according to literature procedures.

Photophysical Measurements

Photophysical measurements were performed on degassed solutions of 1 and 8 dissolved in CH22Cl2 and a number of other organic solvents. Absorption spectra were recorded on a Cary 5000 UV/Vis spectrophotometer. Emission and excitation spectra were measured on a Horiba Fluorolog 3. Time-resolved fluorescence measurements were performed by using the same time-correlated single photon counting (TCSPC) setup as described in ref. [22]. Excitation was carried out with <90 ps pulses generated with a laser diode at 395 and 470 nm (PicoQuant model LDH-PC-400B) and fluorescence was detected at magic angle. The full-width-athalf-maximum (FWHM) of the instrument response function (IRF) was around 200 ps. The preparation of samples in different solvents started from an initial concentrated CH2Cl2 solution, and the volume proportion of CH₂Cl₂ was less than 5% in all of the tested solutions. Solution samples with proper concentrations were prepared by optical dilution for steady-state photoluminescence (OD < 0.1 at the excitation wavelength) and deoxygenated for 30 min by bubbling N_2 in a 1 cm path-length quartz cell prior to measurements. Precautions were taken to limit exposure of the photosensitive complexes to light in between measurements and during bubbling.

Spectroelectrochemical experiments were performed under a N₂ flow in deoxygenated CH₂Cl₂ with Bu₄N(PF₆) (0.1 m) as the supporting electrolyte. All these measurements were carried out in a three-compartment electrolytic cell equipped with a Pt-mesh working electrode, a Pt-mesh auxiliary electrode, and potentials were referenced to an Ag-wire pseudo reference electrode.

Ab initio Calculations

Density-functional-theory (DFT) and time-dependent DFT calculations of **1** and **8** were performed with the B3LYP hybrid functional and the TZVP as well as the SVP basis sets. All calculations were carried out with the TURBOMOLE V6.0 program package.^[23] The molecular ground state geometries of **1** and **8** were optimized at the B3LYP/SVP level of theory and constrained to have C_{2h} symmetry. The electronic excitation spectra were calculated with the larger TZVP basis set of triple- ζ quality.

[1,3]Dithiolo[4,5-f]-2,1,3-benzothiadiazole-6-thione (3)

Thionyl chloride (400 mg, 3.36 mmol) was added to the slurry of 5,6-diamino-1,3-benzodithiole-2-thione (214 mg, 1 mmol) in toluene (8 mL).

Several drops of pyridine were added, and the mixture was refluxed under Ar for 1 h. Then, the clear brown solution was cooled down to about 100 °C; EtOH (0.5 mL) was carefully added dropwise to quench the residual thionyl chloride. The color of the solution immediately changed to yellow, and a significant amount of precipitate was formed. This hot mixture was filtered quickly, and the precipitate was washed with hot toluene. The filtrate was concentrated under vacuum to a small volume, and EtOH (20 mL) was added to precipitate **3** as a yellow powder. Yield: 125 mg (52 %); m.p. 176–178 °C; IR (KBr): $\tilde{\nu}$ =3435, 1484, 1240, 1070, 860 cm⁻¹; ¹H NMR (300 MHz, [D₆]DMSO): δ =8.68 ppm (s, 2H); ¹³C NMR (75 MHz, [D₆]DMSO): δ =214.9, 152.5, 143.4, 114.0 ppm; MS (EI): *m/z* (%): 242 (95) [*M*⁺]; elemental analysis calcd (%) for C₇H₂N₂S₄: C 34.69, H 0.83, N 11.56; found: C 34.91, H 0.83, N 11.14.

4,8-Dibromo[1,3]dithiolo[4,5-f]-2,1,3-benzothiadiazol-6-one (4)

The solution of Br₂ (1.2 mL, 23 mmol) in 47% aqueous HBr solution (10 mL) was slowly added to the suspension of **3** (1.5 g, 6.2 mmol) in 47% aqueous HBr solution (20 mL). The resulting solution was refluxed for 8 h (TLC monitoring). If bromination is incomplete, more Br₂ (1.2 mL) should be added to this suspension. Upon completion of the reaction, the resulting solid was filtered off and washed three times with H₂O to afford **4**. Yield: 1.62 g (68%); m.p. 236–237 °C; IR (KBr): $\tilde{\nu}$ = 3436, 1742, 1675, 1446, 1203, 874 cm⁻¹; ¹³C NMR (75 MHz, CDCl₃): δ = 150.9, 138.0, 132.5, 106.6 ppm; MS (EI): *m/z* (%): 382 (31) [*M*⁺]; element al analysis calcd (%) for C₇Br₂N₂OS₃: C 21.89, N 7.29; found: C 21.82, N 7.16.

4,8-Dibromo-6-(4,8-dibromo[1,3]dithiolo[4,5-f]-2,1,3-benzothiadiazol-6-ylidene)-[1,3]dithiolo[4,5-f]-2,1,3-benzothiadiazole (5)

Triethyl phosphite (2 mL) was added to a solution of **4** (60 mg, 0.156 mmol) in toluene (2 mL) under Ar. The mixture was refluxed for 3 h. The resulting orange solid was collected and washed with EtOH to afford **5**. Yield: 50 mg (87%); m.p. > 350°C (dec.); IR (KBr): $\tilde{\nu}$ =3435, 1477, 1449, 1254, 1238, 1210, 1123, 876, 840 cm⁻¹; ¹³C NMR is unavailable due to poor solubility; MS (MALDI-TOF): *m*/*z* calcd for C₁₄Br₄N₄S₆: 731.52; found: 731.52; elemental analysis calcd (%) for C₁₄Br₄N₄S₆:0.5C₂H₅OH: C 23.73, H 0.40, N 7.38; found: C 24.11, H 0.09, N 7.60.

6-[4,8-Bis(4-pentylphenoxy)[1,3]dithiolo[4,5-f]-2,1,3-benzothiadiazol-6ylidene]-4,8-bis(4-pentylphenoxy)[1,3]dithiolo[4,5-f]-2,1,3benzothiadiazole (**6**)

A solution of **5** (20 mg, 2.72 µmol), K₂CO₃ (15 mg, 108.8 mmol), and 4pentylphenol (0.03 mL, 175 mmol) in *N*,*N*-dimethylformamide (DMF; 1.5 mL) was degassed with Ar and then kept at 150 °C under microwave irradiation for 1 h. The precipitate was collected by centrifuge and washed with H₂O and EtOH several times. The crude product was purified by silica-gel column chromatography (CH₂Cl₂/hexane 1:1) to afford pure compound **6** as an orange solid. Yield: 12 mg (41 %); m.p. 273-275 °C; IR (KBr): $\bar{\nu}$ = 3436, 2955, 2925, 2853, 1606, 1532, 1505, 1478, 1336, 1200, 1167, 830 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ = 7.11 (d, *J* = 8.7 Hz, 8H), 6.85 (d, *J* = 8.7 Hz, 8H), 2.55 (t, *J* = 7.8 Hz, 8H), 1.58 (m, 8H), 1.31 (m, 16H), 0.88 ppm (t, *J* = 6.6 Hz, 12 H); ¹³C NMR (75 MHz, CDCl₃): δ = 168.3, 154.5, 138.3, 129.6, 116.06, 35.1, 31.5, 31.1, 22.5, 14.0 ppm; MS (MALDI-TOF): *m*/z calcd for C₅₈H₆₀N₄O₄S₆·0.5C₆H₁₄: C 65.85, H 6.07, N 5.04; found: C 65.61, H 6.20, N 4.73.

2-[5,6-Diamino-4,7-bis(4-pentylphenoxy)-1,3-benzodithiol-2-ylidene]-4,7bis(4-pentylphenoxy)-1,3-benzodithiole-5,6-diamine (2)

The suspension of **6** (150 mg, 140 μ mol) in a mixture of CH₂Cl₂ (60 mL) and EtOH (50 mL) was purged with Ar for several minutes, and then NaBH₄ (280 mg, 7.4 mmol) and CoCl₂·6H₂O (125 mg, 0.53 mmol) were added sequentially. Evolution of H₂S was observed immediately, and the color of the solution slowly changed from orange to dark brown. The resulting solution was heated at 40 °C for 30 min and then was stirred for another 3 h at room temperature. A significant amount of black precipitate was formed. After filtration, the filtrate was concentrated under vacuum. The residue was redissolved in CH₂Cl₂ while the insoluble part was filtered off. The filtrate was concentrated to afford **2** as a brown solid. Yield: 110 mg (77%); m.p. >230 °C (dec.); IR (KBr): $\tilde{\nu}$ =3433, 2923, 2852, 1608, 1503, 1465, 1214, 1164, 817 cm⁻¹; 1H NMR (300 MHz, CDCl₃): δ =7.05 (d, *J*=8.7 Hz, 8H), 6.77 (d, *J*=8.4 Hz, 8H), 2.53(t, *J*=7.5 Hz, 8H), 1.54 (m, 8H), 1.28 (m, 16H), 0.88 ppm (t, *J*=6.6 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃): δ =153.9, 137.3, 129.6, 115.1, 114.8, 35.1, 31.5, 31.2, 22.5, 14.0 ppm; MS (MALDI-TOF): *m/z* calcd for C₅₈H₆₈N₄O₄S₄: 1012.41; found: 1012.66; elemental analysis calcd (%) for C₅₈H₆₈N₄O₄S₄: C 68.74, H 6.76, N 5.53; found: C 68.35, H 6.89, N 5.22.

2,5,8,11,13,23-Hexakis(1,1-dimethylethyl)-18-[2,5,8,11,13,23-hexakis(1,1dimethylethyl)-16,20-bis(4-pentylphenoxy)[1,3]dithiolo[4,5g]tetrabenz[7,8:9,10:11,12:13,14]ovaleno [3,4-b]quinoxalin-18-ylidene]-16,20-bis(4-pentylphenoxy)[1,3]dithiolo[4,5-g]tetrabenz [7,8:9,10:11,12:13,14]ovaleno[3,4-b] quinoxaline^[24] (1)

A solution of **2** (15 mg, 0.015 mmol), 4,6,9,12,15,17-hexakis(1,1-dimethylethyl)tetrabenz[*bc,ef,hi,uv*]ovalene-1,2-dione (28 mg, 0.03 mmol), and acetic acid (6 mL) was refluxed for 14 h under Ar. After cooling to room temperature, the solvent was evaporated. The residue was purified by silica-gel column chromatography (petroleum ether (b.p. 50–70°C)/ CH₂Cl₂ 1:1) to give **1** as a dark-purple emissive powder. Yield: 28 mg (67%); m.p. > 350°C (dec.); IR (KBr): $\tilde{\nu}$ = 3450, 2922, 2851, 1637, 1503, 1384, 1200, 869 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ =9.71 (s, 4H), 9.34 (s, 8H) 9.25 (s, 4H), 8.86 (s, 4H), 7.28 (d, *J*=81 Hz, 8H), 2.63 (t, *J*=7.5 Hz, 8H), 1.84 (s, 36H), 1.78 (s, 36H), 1.71 (s, 36H), 1.53 (s, 24H), 0.84 ppm (m, 12H); ¹³C NMR (75 MHz, CDCl₃): δ =157.2, 147.0, 145.6, 137.2, 136.1, 133.5, 132.6, 130.7, 130.1, 129.7, 129.2, 119.7, 116.0, 39.2, 35.9, 35.3, 34.6, 32.1, 32.0, 31.9, 29.7, 29.4, 22.7, 14.1 ppm; MS (MALDI-TOF): *m/z* calcd for C₁₉₄H₁₈₈N₄O₄S₄: 2765.35; found: 2765.44.

2-[4,9-Bis(4-pentylphenoxy)-1,3-dithiolo[4,5-g]quinoxalin-2-ylidene]-4,9bis(4-pentylphenoxy)-1,3-dithiolo[4,5-g]quinoxaline (8)

1,4-Dioxane-2,3-diol (10.4 mg, 86.5 µmol) was added to a suspension of **2** (35 mg, 34.6 µmol) in EtOH (10 mL) and acetic acid (99%, 2 mL). The mixture was refluxed for 8 h under Ar and by then a red precipitate was formed. After filtration, the red powder was purified by column chromatography (basic Al₂O₃, CH₂Cl₂) to give **8** as an orange powder. Yield: 19.2 mg (53%); m.p. > 350 °C (dec.); IR (KBr): $\bar{\nu}$ =3437, 3153, 2927, 1635, 1506, 1449, 1400, 1383, 1210, 1075, 1029 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ =8.64 (s, 4H), 7.08 (d, *J*=7.90 Hz, 8H), 6.80 (d, *J*=7.90 Hz, 8H), 2.54 (t, *J*=7.1 Hz, 8H), 1.59–1.56 (m, 8H), 1.30–1.29 (m, 16H), 0.87 ppm (t, *J*=6.6 Hz, 12H); ¹³C NMR (75 MHz, CDCl₃): δ =155.2, 144.2, 139.6, 137.5, 137.2, 134.8, 129.6, 115.4, 35.1, 31.4, 31.2, 22.5, 14.0 ppm; MS (MALDI-TOF): *m*/z calcd for C₆₂H₆₅N₄O₄S₄: 1057.39; found: 1057.14; elemental analysis calcd (%) for C₆₂H₆₅N₄O₄S₄: C 70.42, H 6.10, N 5.30; found: C 70.19, H 5.84, N 5.16.

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