Trialkyltetrathiafulvalene−σ−Tetracyanoanthraquinodimethane (R_3TTF−σ−TCNAQ) Diads: Synthesis, Intramolecular Charge-Transfer Properties, and X-ray Crystal Structure

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We report the use of the electron-donating 4,5-dipentyl-4′-methyl-TTF (TTF = tetrathiafulvalene) moiety in combination with the electron acceptor 11,11,12,12-tetracyanoanthraquinodimethane (TCNAQ) unit in the novel D−σ−A diad molecules **11**, **17**, and **18**. These compounds display a weak, broad, low-energy intramolecular charge-transfer (ICT) band in the UV−vis spectra (λ_{max} 430−450 nm). Cyclic voltammetric studies show two reversible one-electron oxidation processes for the R_3TTF moiety, and a reversible two-electron reduction process for the TCNAQ moiety. The electron affinity of TCNAQ is significantly enhanced by the electron-withdrawing sulfonamide and sulfonic ester groups (compounds **17** and **18**, respectively). Simultaneous electrochemistry and EPR (SEEPR) experiments show no significant intramolecular interaction between the R_3TTF and TCNAQ moieties in compounds **11** and **18**. X-ray crystallographic data are presented for **5**, **11**, and **20**. The structure of **5** reveals hydrogen-bonded dimers. In molecule **11** the bond lengths and conformations of both donor and acceptor moieties are typical for neutral species. Compound **20** is an unusual calcium complex of TCNAQ derivative obtained by dicyanomethylation of anthraquinone-2-carboxylic acid.

Introduction

The covalent linkage of tetrathiafulvalene (TTF) to a π-acceptor moiety through a π- or σ-bonded bridge[1] offers considerable potential for the study of intramolecular charge transfer (ICT) processes in D−A molecules. Several acceptor groups, such as quinones,[2] C_{60},[3] and pyridinium[4] or bipyridinium cations[5] have been studied recently in this context. Systems of this general type are central to studies on chromophores for dyes, nonlinear optics, synthetic light-harvesting systems, and theoretical aspects of charge transport at the molecular level.[6] The covalent linkage of TTF and TCNQ (7,7,8,8-tetracyanoquinodimethane) moieties has received special attention since Aviram and Ratner's theoretical proposal in 1974 that molecular rectification might be observed in assemblies of the hypothetical TTF−σ−TCNQ molecule **1** sandwiched between two metal electrodes M_1 and M_2 in the architecture M_1/D−σ−A/M_2.[7] Synthetic routes are limited by the fact that a TTF nucleus appeared to be incompatible with the standard Lehnert conditions ($TiCl_4$, malononitrile)[8] for converting a quinone into a TCNQ derivative, so preformed TTF−quinone diads[2] are not suitable as precursors. When a TCNQ component is used, a major problem can be the irreversible formation of an *inter*molecular TTF·TCNQ CT complex (which is usually insoluble), instead of the desired covalent coupling reaction.

Compound **2** was the first TTF−TCNQ diad to be synthesized,[9] but the difficult synthetic route and problems with purification precluded detailed characterization, although EPR and IR data suggested an ionic ground state. In contrast to this, compound **3** recently proved to be straightforward to synthesize and to purify.[10]

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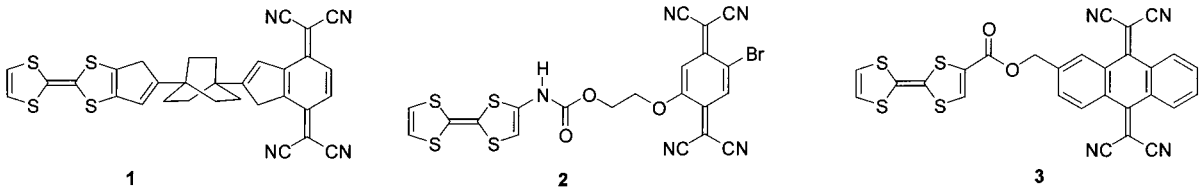
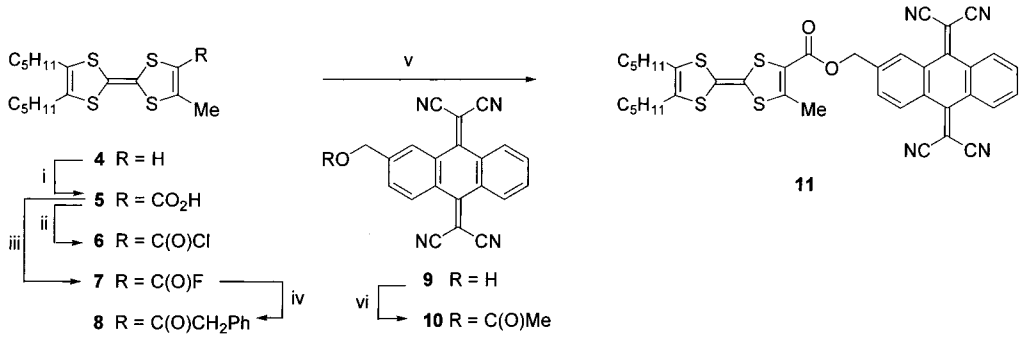
Chart 1



1 **2** **3**

Scheme 1[a]



[a] Reagents and conditions: (i) THF, LDA, −78 °C, 1.5 h, then CO_2, −78 °C, 1.5 h; (ii) toluene/MeCN, oxalyl chloride, DMF, 20 °C, 2 h; (iii) CH_2Cl_2, pyridine, then cyanuric fluoride, 20 °C, 1 h; (iv) CH_2Cl_2, $PhCH_2OH$, pyridine, 20 °C, 1.5 h; (v) CH_2Cl_2, compound **9**, Pyridine, 20 °C, 4 h; (vi) CH_2Cl_2, MeCOCl, Et_3N, 20 °C, 2 h.

The TCNQ component in this molecule (TCNAQ: 11,-11,12,12-tetracyanoanthraquinodimethane) is a weaker acceptor than TCNQ [TCNAQ, $E^{1/2} = -0.285$ V (a two-electron wave) cf. TCNQ, $E_1^{1/2} = +0.130$ and $E_2^{1/2} = -0.290$ V, in MeCN vs SCE]; and in contrast to TCNQ (which is essentially planar) TCNAQ adopts a "butterfly" conformation (according to X-ray analysis and theoretical calculations[11]) which will have the advantage of suppressing intermolecular CT complex formation. Compound **3** has an essentially neutral ground state, although simultaneous electrochemistry and EPR (SEEPR) experiments suggested intramolecular interaction of the TCNAQ fragment with TTF moiety in the radical cation state. These initial studies on molecule **3** prompted us to explore new TTF−σ−TCNAQ diads, and these results are reported herein.

Results and Discussion

Synthesis. Our targets were analogues of the prototype molecule **3** for which intramolecular charge-transfer (ICT) could be enhanced by lowering the oxidation potential of the TTF moiety and/or raising the electron affinity of the TCNAQ moiety. We, therefore, considered 4,5-dipentyl-4′-methyl-TTF **4** to be an appropriate TTF building block as alkyl substitution is known to lower significantly the oxidation potential of TTF.[12] Moreover, the pentyl chains would enhance solubility in organic solvents. Compound **4** was obtained by direct analogy with the synthesis of trimethyl-TTF.[12b] Lithiation of **4** (LDA in THF at −78 °C) followed by reaction with carbon dioxide gave the carboxylic acid derivative **5** in 61% yield. Conversion to the carbonyl chloride **6** and carbonyl fluoride **7** was readily achieved by reaction with oxalyl chloride and with cyanuric fluoride−pyridine,[13] respectively. Reaction of **6** with TCNAQ derivative **9**[11c] afforded the target molecule **11** as a brown crystalline solid in 50% yield (Scheme 1).

To enhance the acceptor properties of the TCNAQ moiety, we prepared the sulfonamide and sulfonic ester derivatives **15** and **16**, respectively, starting from readily available anthraquinone-2-sulfonyl chloride **12** (Scheme 2) and hence the molecules **17** and **18**. The low yield, observed for the acylation of compound **15** by **6** (13%) has been overcome by the use of reagent **7** (74%) instead.

Attempts to prepare TCNAQ-2-carboxylic acid were unsuccessful: reaction of anthraquinone-2-carboxylic acid with Lehnert's reagent under standard conditions[8] resulted in dicyanomethylation of the carboxy group (Scheme 3). The product was isolated as the calcium complex, the possible source of calcium being the distillation of dichloromethene (used in the synthesis) over CaH_2, when some inorganic materials were transferred into the receiving flask. The presence of calcium in the product was confirmed by atomic emission spectroscopy and crystals of the interesting bis(TCNAQ) complex **20** were grown. Its structure was proved by X-ray crystallographic analysis (see below). Related dicyanomethylations of carboxylic acid chlorides have been reported.[14]

Attempts to synthesize TCNAQ-2-carboxylic acid using the *tert*-butyl and methyl esters of anthraquinone-2-carboxylic acid were also unsuccessful: the *tert*-butyl protected group was not stable toward Lehnert's reagent, whereas the methyl group in methyl TCNAQ-2-carboxylate could not be selectively removed, neither by acidic hydrolysis (CF_3COOH/H_2O) nor by cyanide cleavage (NaCN/HMPA).

X-ray Molecular Structures of 5, 11, and 20. Molecules **5** in the crystal are linked into centrosymmet-

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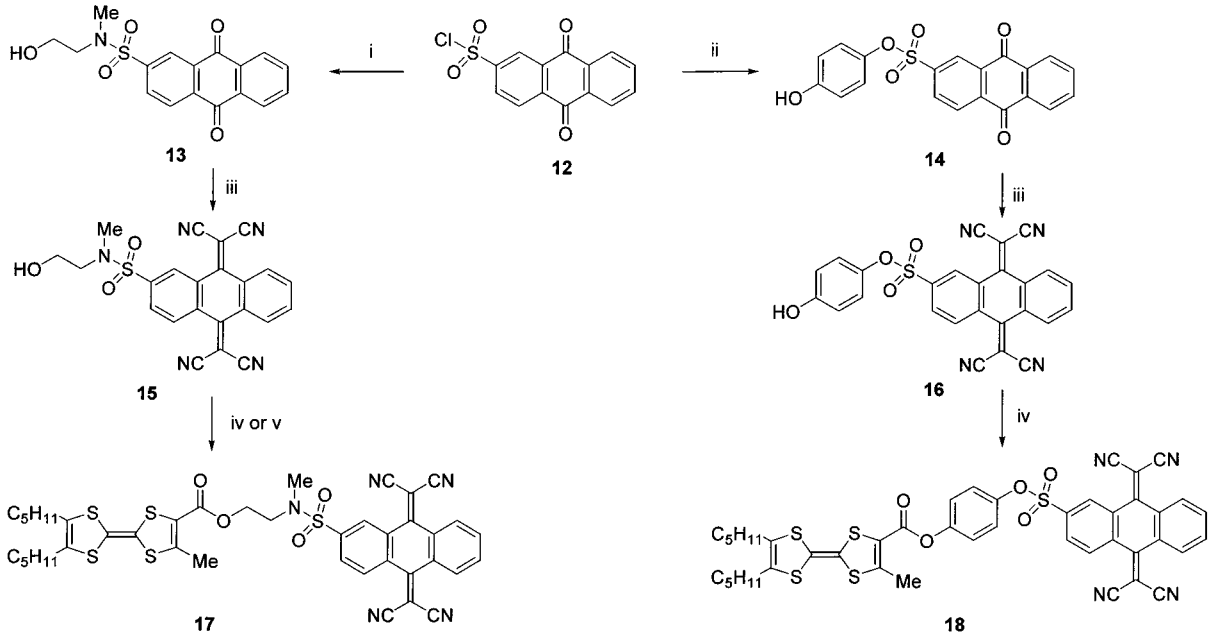
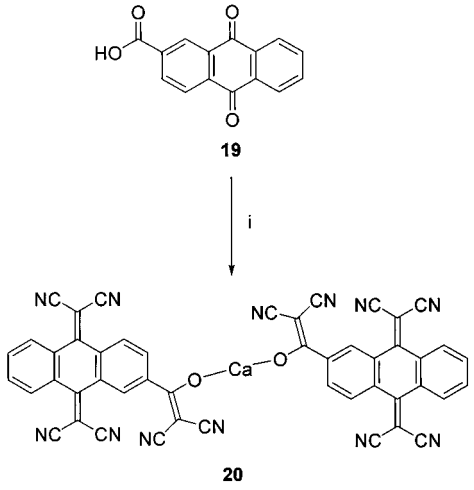
Scheme 2[a]



[a] Reagents and conditions: (i) MeCN, *N*-methylethanolamine, 20 °C, 2 h, then 60 °C, 10 min; (ii) MeCN, hydroquinone, pyridine, 20 °C, 12 h; (iii) CH_2Cl_2, $TiCl_4$, pyridine, β-alanine, reflux, 15 h; (iv) CH_2Cl_2, compound **6**, pyridine, 20 °C, 4 h; (v) CH_2Cl_2, compound **7**, *p*-(dimethylamino)pyridine, 20 °C, 24 h.

Scheme 3. Reagents and conditions: (i) CH_2Cl_2 (dried over CaH_2), $TiCl_4$, pyridine, β-alanine, reflux, 15 h.



ric dimers by strong [O−H···O 2.612(6) Å] hydrogen bonds. As in **11** (see below), the carboxy group is essentially coplanar with the TTF moiety, while the *n*-pentyl substituents adopt a distinctly out-of-plane conformation. The TTF moiety shows small boatlike folding along the S···S vectors (by 5° and 10°) and a 4° twist around the central C=C bond.

In molecule **11** (Figure 1) the TTF moiety is folded along the S(1)···S(2) and S(3)···S(4) vectors by 22° and 11° in a boat manner. The tetracyanoanthraquinone moiety adopts a usual[11] saddle-like conformation; the anthraquinone moiety is folded along the C(9)···C(10) vector by an angle $\varphi = 37°$, while the two $C(CN)_2$ moieties are tilted in the opposite direction and form a dihedral angle $\theta = 101°$. Bond distances and conformations in both the donor and the acceptor moieties are typical for neutral species, as exemplified by **5**, and TCNAQ.[11a] In the crystal, the nonplanar conformation of the TCNAQ

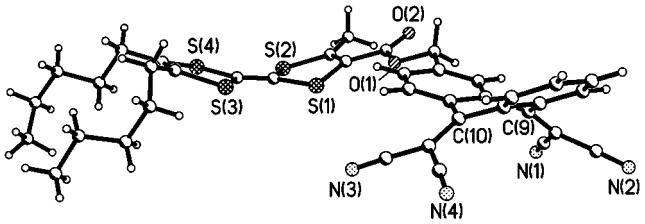


Figure 1. Molecular structure of **11**.

moiety prevents the formation of segregated stacks. The donor and acceptor fragments of **11** form an ADDA motif, with no significant $\pi-\pi$ interactions between them.

In complex **20** the Ca atom is located at an inversion center and is coordinated octahedrally by two TCNAQ anions (through their oxygen atoms), two acetonitrile and two aqua ligands, with two more acetonitrile molecules linked to the latter by hydrogen bonds. The tetracyanoanthraquinone moiety has the same conformation as in **11** ($\varphi = 37°$, $\theta = 102°$). The dicyanooxyetheno moiety is planar with strong π-delocalization, but is not conjugated with the benzene ring, with which it forms a dihedral angle of 48°.

Electrochemical and Spectroscopic Studies. The electrochemical reduction/oxidation potentials of the new diads and related compounds, obtained from cyclic voltammetry experiments are presented in Table 1. TTF-TCNAQ hybrids **3**, **11**, **17**, and **18** show electrochemically amphoteric behavior. A reversible two-electron reduction wave yields the dianion, and two single-electron oxidation waves, give, sequentially, the radical cation and dication species (Figure 2).

Judging from the reduction/oxidation potentials, the acceptor ability of TCNAQ fragment is unaffected by the presence of the TTF moiety in the same molecule, and only minor variation in the oxidation potential of the TTF fragment with different acceptor moieties has been observed. The chemical modifications to both the donor

Table 1. Oxidation and Reduction Potentials of the TTF and TCNAQ Derivatives and Their Hybrids, V vs SCE

compound	$E^{1/2}_{1ox}$	$E^{1/2}_{2ox}$	$E^{1/2}_{red}$
3	0.44	0.79	−0.36
4	0.24	0.64	−
5[a]	0.36	0.76	−
9	−	−	−0.38
11	0.36	0.71	−0.36
15	−	−	−0.28
16	−	−	−0.25
17	0.37	0.75	−0.28
18	0.38	0.76	−0.24

[a] Chemical stability of radical cation and dication species derived from compound **5** is much lower than that for the other TTF derivatives due to the presence of the carboxy group; a reversible well-defined voltammogram was obtained only at a scan rate of 5000 mV/s.

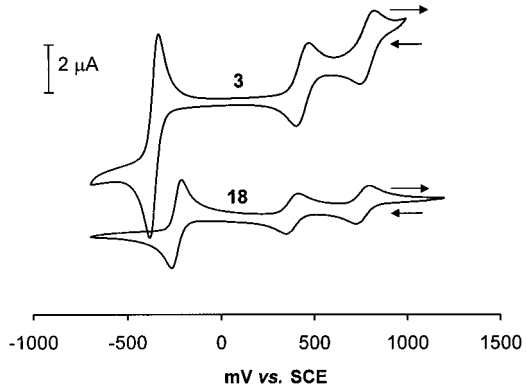


Figure 2. Cyclic voltammetry of compounds **3** and **18** in MeCN solution, scan rate 100 mV/s.

and the acceptor moieties (as compared with prototype molecule **3**) increased the electron affinity and lowered the oxidation potential, respectively: incorporation of three alkyl substituents on the TTF nucleus lowered its oxidation potential by 60−80 mV, and replacement of the oxymethyl substituent in TCNAQ by a sulfoxy substituent increased the reduction potential by 110−120 mV (Table 1, Figure 2). A smaller effect (80 mV) is seen for the dialkylsulfamido group, in agreement with the weaker electron-withdrawing ability of this substituent.

A charge-transfer interaction between donor and acceptor moieties of compounds **3**, **11**, **17**, and **18** is manifested by the appearance of weak broad absorption band in the 400−550 nm region of their electronic spectra. This absorption is not observed in solutions obtained by mixing the corresponding TTF and TCNAQ derivatives, and its intensity shows a linear dependence on concentration, as expected for an intramolecular charge-transfer (ICT) band. The maximum of the ICT band for these compounds varies only slightly with the change of substituents and σ-linkage between the donor and the acceptor (Figure 3). The lowest energy ICT band (λ_{max} = 445 nm in MeCN, 456 nm in dichloromethane, 455 nm in benzene) belongs to compound **18**, the TTF and TCNAQ moieties of which possess the strongest donor and acceptor abilities, respectively. No fluorescence from the ICT band has been found.

Simultaneous Electrochemistry and EPR (SEEPR) Studies. SEEPR spectra of $\mathbf{8}^{+\bullet}$ and $\mathbf{11}^{+\bullet}$ (Figure 4), and $\mathbf{18}^{+\bullet}$ are quite similar. Curve fitting of the experimental spectra to extract the hyperfine coupling constants (Table 2) provided results that were similar for all three compounds within the experimental error.[15] We attribute

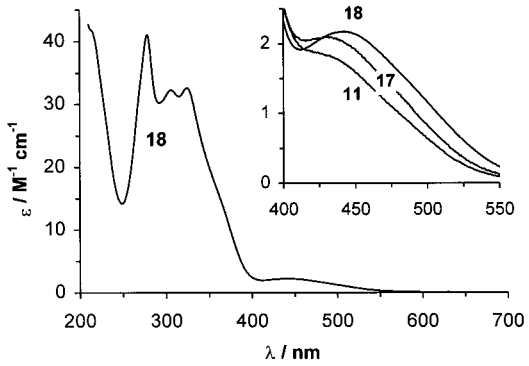


Figure 3. Electronic absorption spectra of compounds **11**, **17**, **18** in MeCN.

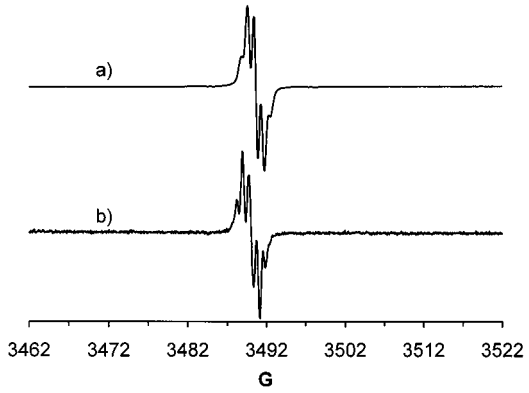


Figure 4. SEEPR spectra of (a) $\mathbf{8}^{+\bullet}$, at +0.47 V, g = 2.006; (b) $\mathbf{11}^{+\bullet}$, at +0.55 V, g = 2.006.

Table 2. Experimental Hyperfine Coupling Constants (hfc, in G) for $8^{+\bullet}$, $11^{+\bullet}$, and $18^{+\bullet}$ (r^2 for spectral curve fitting >0.98)[a]

hydrogen	number of hydrogens	hfc $8^{+\bullet}$	hfc $11^{+\bullet}$	hfc $18^{+\bullet}$
Ha	1	0.02	0.02	0.05
Hb	1	0.02	0.02	0.06
Hc	1	0.02	0.02	0.07
Hd	2	0.03	0.02	0.02
He	2	*b*	0.02	0.06
Hf	2	*b*	0.02	0.09
Hg	2	0.79	0.87	0.80
Hh	2	0.79	0.71	0.80
Hi	3	0.20	0.28	0.28

[a] For **8**, **11**, and **18**, g factor of radical cations is 2.006. [b] These hydrogens are not present in this molecular structure.

this similarity in hyperfine couplings between these radical cations to a very small or insignificant electronic communication between the TTF moiety and the rest of the molecule.

It is noteworthy that a strong EPR signal was also observed upon the reduction of compounds **8**, **11**, **16**, despite the two-electron nature of this process. As was earlier suggested by Kini,[16] we hypothesize that this signal originates from the radical anion of the TCNAQ moiety, which is in equilibrium with the dianion species:

$$\mathrm{TCNAQ} + \mathrm{TCNAQ}^{2-} \rightleftharpoons 2\ \mathrm{TCNAQ}^{-\bullet}$$

(15) This could also be influenced by the fact that EPR spectra are poorly resolved. However, this limitation is inherent to the compounds involved. Attempts to obtain better resolved spectra by changing instrumental variables and experimental conditions were unsuccessful.

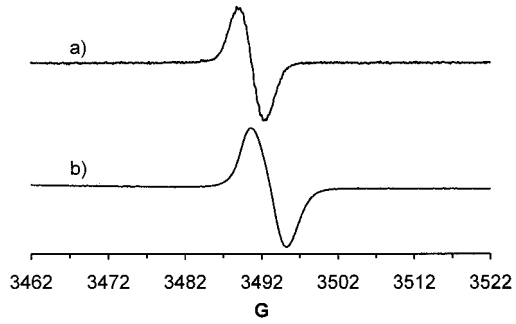


Figure 5. SEEPR spectra of (a) $\mathbf{10}^{-\bullet}$, at −0.87 V, $g = 2.006$; (b) $\mathbf{11}^{-\bullet}$, at −0.50 V, $g = 2.005$.

SEEPR spectra of $\mathbf{10}^{-\bullet}$ and $\mathbf{11}^{-\bullet}$ (Figure 5), and $\mathbf{16}^{-\bullet}$ and $\mathbf{18}^{-\bullet}$,[17] where compounds **10** and **16** lack the TTF substructure, are essentially identical, showing a broad, unresolved singlet.[18] Once again, the analysis of these spectra shows no significant electronic interaction between the TTF moiety and the acceptor part of the molecule.

Conclusions

Novel $D-\sigma-A$ diads **11**, **18**, and **19**, where D and A are TTF and TCNAQ nuclei, respectively, substituted with electron-releasing and electron-withdrawing substituents have been synthesized. ICT in these diads is manifested in a weak broad absorption band in the 400−550 nm region of their electronic spectra. In CV experiments they show a clear amphoteric behavior consisting of two single-electron oxidation waves and one two-electron reduction wave. The position of these waves is almost unaffected by the counterpart D (A) moiety. The incorporation of electron-releasing and electron-withdrawing substituents in D and A fragments, respectively, enhances the redox properties of these fragments and decrease the HOMO−LUMO gap of the molecule. The first crystal structure of a TTF−TCNQ hybrid **11** has been reported. It shows that D and A fragments of the molecule are essentially neutral, and also there are no significant $\pi-\pi$ interactions between donor and acceptor moieties in the solid state. Future work will be directed at enhancing the ICT properties of TTF−TCNQ hybrids by chemical modification of D and A moieties.

Experimental Section

General methods are the same as those described previously.[10]

Cyclic voltammetry experiments were performed using $Ag/AgNO_3$ (in MeCN) reference electrodes; the potentials were corrected using ferrocene/ferrocenium (Fc/Fc^+) couple (which was used as internal standard except when it overlapped with the oxidation peaks of the sample) and then recalculated to the SCE scale. The Fc/Fc^+ couple showed 0.37 V (vs SCE), 0.07 V (vs $Ag/AgNO_3$) and 0.45 V (vs Ag/AgCl). 0.1 M Tetrabutylammonium hexafluorophosphate in MeCN was used as the electrolyte.

SEEPR experiments were carried out in a flat quartz cell. The Pt gauze was inserted into the flat portion of the cell. The Ag wire pseudoreference electrode was positioned directly above the working electrode to reduce the iR-drop and the auxiliary electrode, a Pt wire spiral of large surface area, occupied the solvent reservoir above the flat section. EPR spectra were recorded on an IBM ESP-300 X-band spectrometer equipped with a TE_{104} single cavity. Solutions of the investigated compounds (10^{-3} M in CH_2Cl_2, 0.1 M $Bu_4N^+ClO_4^-$) were degassed by bubbling argon through them for 5 min and then injected into the SEEPR cell, which was previously flushed with argon. Bulk electrolysis was then carried out simultaneously with signal acquisition (100 kHz field modulation, modulation amplitude 0.4 G, 60 G sweep width). Experimental hyperfine coupling constants were obtained through spectral simulation and iterative curve fitting.[19] The g factors given are within the error of 0.25%.

X-ray Crystallography. X-ray diffraction experiments were carried out on a SMART 3-circle diffractometer with a 1K CCD area detector, using graphite-monochromated Mo−Kα radiation ($\bar{\lambda} = 0.71073$ Å) and a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. A combination of 4 sets of ω scans; each set at different φ and/or 2θ angles, nominally covered over a hemisphere of reciprocal space (for, **20** full sphere was covered by five sets). Reflection intensities were integrated using SAINT program (Version 6.01, Bruker Analytical X-ray Systems, Madison, WI, 1999) and corrected for absorption by numerical method based on crystal face indexing (**5**, **11**) or by semiempirical method based on the intensities of Laue equivalents (**20**), using SADABS software (G. M. Sheldrick, University of Göttingen, 1998). The structures were solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software (Version 5.1, Bruker AXS, Madison, WI, 1998). Full structural information has been deposited with the Cambridge Crystallographic Data Centre.[20]

4-Methyl-4′,5′-dipentyltetrathiafulvalene 4. Trimethyl phosphite (3.3 mL, 28 mmol) was added dropwise to 4-methyl-1,3-dithiolium iodide[21] (6.2 g, 25.5 mmol) suspended in dry MeCN (150 mL) at 0−5 °C, and the reaction mixture was stirred for 40 min at 20 °C, resulting in full dissolution of the dithiolium salt. The solvent was then removed in vacuo, the residue was dissolved in dry THF (120 mL), and potassium *tert*-butoxide (2.99 g, 26.7 mmol) was added at −78 °C. The reaction mixture was stirred at −78 °C for 1 h, and then *N*-(4,5-dipentyl-1,3-dithiol-2-ylidene)piperidinium hexafluorophosphate[22] (8.9 g, 20 mmol) was gradually added. The reaction mixture was allowed to reach 20 °C overnight, it was diluted with ether (100 mL), stirred for 1 h, and filtered through Celite, affording a clear dark-brown solution, which was reduced to ca. 15 mL, and toluene (100 mL) and acetic acid (10 mL) were added. The solution was stirred for 1.5 h, washed with ice-cold water, and dried over $MgSO_4$, and the solvent was removed in vacuo. The resulting brown oil was chromatographed on silica gel, eluting with ethyl acetate/petroleum ether (1:3 v/v), giving pure **4** (5.95 g, 65%) as an orange oil. ^1H NMR (300 MHz, acetone-d_6) δ 6.17 (1H, q, $J =$ 1.5 Hz), 2.42 (4H, t, $J = 7.5$ Hz), 2.07 (3H, d, $J = 1.5$ Hz), 1.52 (4H, m), 1.26−1.40 (8H, m), 0.90 (6H, t, $J = 6.9$ Hz); ^{13}C NMR (75 MHz, acetone-d_6) δ 132.3, 129.7, 129.6, 114.4, 110.2, 108.3, 31.9 (2C), 30.17, 30.16, 29.18, 29.16, 23.1 (2C), 16.2, 14.3 (2C); IR (neat) ν/cm^{-1} 1463, 1110, 779; MS (EI) m/z 358 (M^+, 100%). Anal. Calcd for $C_{17}H_{26}S_4$: C, 56.93, H, 7.31. Found: C, 57.31, H, 7.44.

(16) Kini, A. M.; Cowan, D. O.; Gerson, F.; Mockel, R. *J. Am. Chem. Soc.* **1985**, *107*, 556

(17) The SEEPR spectrum of $\mathbf{18}^{-\cdot}$ changes over time, due to decomposition of the radical anion into unidentified species. Its conversion over time is shown in the supplementary data, along with SEEPR of compound **16**.

(18) Spectral curve fitting was not performed on $\mathbf{10}^{-\bullet}$, $\mathbf{11}^{-\bullet}$, or $\mathbf{16}^{-\bullet}$ SEEPRs, since no meaningful values will be obtained due to the low resolution of the spectra and the large number of variables to adjust.

(19) NIEHS WinSym EPR, version 0.95, D. Duling, 1994, Laboratory of Molecular Biophysics, NIEHS, NIH, DHHS.

(20) Supplementary publication number CCDC-142177 (**5**), -142176 (**11**), and -142178 (**20**) can be obtained on request from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB12 1E2, U.K.

(21) Bryce, M. R.; Finn, T.; Moore, A. J.; Batsanov, A. S.; Howard, J. A. K. *Eur. J. Org. Chem.* **2000**, 51.

(22) This was prepared by analogy with 4,5-dimethyl-1,3-dithiol-2-ylidene piperidinium hexafluorophosphate from 7-chloro-6-dodecanone: Mora, H.; Fabre, J.-M.; Giral, L.; Montginoul, C. *Bull. Soc. Chim. Belg.* **1992**, *101*, 137.

4-Carboxy-5-methyl-4′,5′-dipentyltetrathiafulvalene 5. To a solution of **4** (0.67 g, 1.86 mmol) in anhydrous ether (80 mL) was added LDA (1.5 M in hexane; 1.8 mL, 2.7 mmol) at −78 °C, and the solution was stirred at this temperature for 1.5 h (a light-yellow precipitate formed after 0.5 h) and a strong flow of dry CO_2 was bubbled through the reaction mixture for 1.5 h. The reaction mixture was allowed to warm to 20 °C overnight, it was diluted with aqueous HCl (0.5 M; 30 mL), and the organic layer was separated, washed with water and brine, and dried over $MgSO_4$. The solution volume was reduced to 5 mL and hot hexane (20 mL) was added, and then the solvent was distilled, until red needles of the product started to precipitate from the hot solution. After cooling, the red crystalline precipitate was filtered off and washed with hexane, yielding **5** (0.45 g, 61%), mp 132−133 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 2.46 (4H, t, J = 7.2 Hz), 2.40 (3H, s), 1.58−1.48 (4H, m), 1.37−1.30 (8H, m), 0.90 (6H, t, J = 6.9 Hz); ^{13}C NMR (75 MHz, acetone-d_6) δ 161.2, 147.5, 129.9, 129.6, 121.4, 111.1, 104.2, 31.9 (2C), 30.18, 30.17, 29.17, 29.15, 23.0 (2C), 16.0, 14.3 (2C); IR (KBr) ν/cm^{-1} 3400−3600 (OH), 1678 (C═O), 1652 (C═O), 1574, 1298, 1276; MS (EI) m/z 402 (M^+, 16%), 358 [$(M - CO_2)^+$, 33%], 83 (100%). Anal. Calcd for $C_{18}H_{26}O_2S_4$: C, 53.72, H, 6.52. Found C, 53.40, H, 6.48.

4-(Chlorocarbonyl)-5-methyl-4′,5′-dipentyltetrathiafulvalene 6. To a solution of acid **5** (86 mg, 0.213 mmol) in toluene/acetonitrile (5:1 v/v; 10 mL) were added oxalyl chloride (0.021 mL, 0.24 mmol) and DMF (1 drop of a 10% solution in toluene), and the solution was stirred at 20 °C for 2 h. The reaction mixture was filtered through a pad of dry silica gel (1 cm) and dry neutral alumina, the filter was washed with toluene, and the filtrate was evaporated in vacuo yielding **6** (80 mg, 89%) as a dark-red oil, which was used without further purification.

4-(Fluorocarbonyl)-5-methyl-4′,5′-dipentyltetrathiafulvalene 7. To a solution of acid **5** (101 mg, 0.25 mmol) and pyridine (0.04 mL, 0.25 mmol) in dry dichloromethane (3 mL) was added cyanuric fluoride (0.04 mL, 0.25 mmol) at 0 °C, and the dark-red solution was stirred at 20 °C for 1 h. Then the organic layer was washed thoroughly with water and brine and dried over $MgSO_4$, and the product was purified by flash chromatography on silica gel (eluent: dichloromethane) yielding **7** (63 mg, 62%) as a dark-red oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.41 (3H, d, J = 0.9 Hz), 2.35 (4H, d, J = 7.5 Hz), 1.56−1.44 (4H, m), 1.38−1.24 (8H, m), 0.90 (6H, t, J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.2 (d, $^3J_{CF}$ = 6 Hz), 149.9 (d, $^1J_{CF}$ = 332 Hz), 129.4, 128.8, 115.5, 114.8 (d, $^2J_{CF}$ = 70 Hz), 101.2, 31.48, 31.47, 29.67, 29.65, 29.00, 28.97, 22.6 (2C), 16.9 (d, $^4J_{CF}$ = 3 Hz), 14.2 (2C); ^{19}F NMR (188 MHz, $CDCl_3$) δ 34.6 (COF); IR (KBr) ν/cm^{-1} 1793 (C═O), 1217; MS (EI) m/z 404 (M^+, 100%). Anal. Calcd for $C_{18}H_{25}FOS_4$: C, 53.43, H, 6.23. Found C, 53.54, H, 6.27.

4-(Benzyloxycarbonyl)-5-methyl-4′,5′-dipentyltetrathiafulvalene 8. To a cold (0 °C) solution of carbonyl fluoride **7** (36 mg, 0.089 mmol) and *p*-(dimethylamino)pyridine (19 mg; 0.156 mmol) in dry dichloromethane was added benzyl alcohol (200 μL, 0.194 mmol), and the reaction mixture was stirred at 20 °C for 1.5 h. The solvent was removed, and the residue was chromatographed on silica gel [eluent: ethyl acetate/petroleum ether (1:4 v/v)] giving compound **8** (42 mg, 96%) as an oily solid. ^{1}H NMR (300 MHz, acetone-d_6) δ 7.47−7.32 (5H, m), 5.26 (2H, s), 2.42 (3H, t, J = 7.2 Hz), 2.41 (3H, s), 1.57−1.46 (4H, m), 1.38−1.26 (8H, m), 0.89 (6H, t, J = 6.6 Hz); ^{13}C NMR (75 MHz, acetone-d_6) δ 159.7, 148.0, 136.1, 129.3, 129.0, 128.8 (2C), 128.5, 128.4 (2C), 119.6, 111.0, 103.2, 67.0, 31.2 (2C), 29.54, 29.51, 28.53, 28.50, 22.4 (2C), 15.5, 13.6 (2C); IR (KBr) ν/cm^{-1} 1705 (C═O), 1249; MS (EI) m/z 492 (M^+, 28%), 129 (100%). Anal. Calcd for $C_{25}H_{32}O_2S_4$: C, 60.94, H, 6.55. Found C, 61.04, H, 6.56.

2-Acetoxymethyl-13,13,14,14-tetracyanoanthraquinodimethane 10 was prepared as described before.[10]

2-(4-Methyl-4′,5′-dipentyltetrathiafulvalenyl-5-carbonyloxymethyl)-13,13,14,14-tetracyanoanthraquinodimethane 11. To a solution of TCNAQ−CH_2OH[23] **9** (51.8 mg, 0.155 mmol) and pyridine (24 mg, 0.30 mmol) in dry dichloromethane was added compound **6** (0.17 mmol), and the reaction mixture was stirred for 4 h at 20 °C. The solvent was removed, and the residue was chromatographed on silica gel, eluting with ethyl acetate/hexane (2:3 v/v). The first red fraction on evaporation gave a red oily solid, which was assumed to be anhydride of acid **5** (18 mg). ^{1}H NMR (300 MHz, acetone-d_6) δ 2.49 (3H, s), 2.45 (4H, t, J = 7.5 Hz), 1.47−1.60 (4H, m), 1.29−1.40 (8H, m), 0.90 (6H, t, J = 6.9 Hz); IR (KBr) ν/cm^{-1} 1773 (C═O), 1684 (C═O).

Evaporation of the second yellow-brown fraction gave product **11** (68 mg, 61%). It was stirred in 2-propanol (3 mL) at 35 °C and then cooled to 20 °C, and the brown crystalline product was filtered off and washed with 2-propanol, resulting in pure **11** (56 mg, 50%), mp 200 °C (from acetone). ^{1}H NMR (300 MHz, acetone-d_6) δ 8.42−8.32 (4H, m), 7.97−7.85 (3H, m), 5.49 (2H, s), 2.43 (4H, t, J = 7.5 Hz), 2.42 (3H, s), 1.58−1.46 (4H, m), 1.39−1.27 (8H, m), 0.89 (6H, t, J = 6.9 Hz); ^{13}C NMR (75 MHz, acetone-d_6) δ 161.02, 160.98, 160.2, 149.6, 141.6, 133.1 (2C), 132.1, 132.0, 131.6 (2C), 131.3, 130.0, 129.7, 128.8, 128.51, 128.49, 127.2, 119.8, 114.6 (2C), 114.5 (2C), 111.9, 103.8, 84.7, 84.4, 66.3, 31.9 (2C), 30.18 (2C), 29.15 (2C), 23.0 (2C), 16.3, 14.2 (2C); IR (KBr) ν/cm^{-1} 2227 (C≡N), 1712 (C═O), 1560, 1229; λ/nm (ϵ/M^{-1} cm^{-1}) 283 (40500), 304 (28100), 317 (27600), 430 (2100); MS (EI) m/z 718 (M^+, 21%), 358 (100%). Anal. Calcd for $C_{39}H_{34}N_4O_2S_4$: C, 65.15; H, 4.77; N, 7.79. Found: C, 64.92; H, 4.70; N, 7.70.

***N*-Methyl-*N*-(9,12-anthraquinone-2-sulfonyl)ethanolamide 13.** To a suspension of sulfonyl chloride **12** (1.76 g, 5.74 mmol) in dry MeCN (30 mL) was added *N*-methylethanolamine (1.05 mL, 13.1 mmol), resulting in an exothermic reaction and dissolution of the sulfonyl chloride. The reaction mixture was stirred for 2 h at 20 °C, heated to 60 °C to dissolve the precipitate of the product, and cooled to 0 °C. The precipitate was filtered off and washed with cold MeCN and hot water, yielding pure **13** (1.64 g, 83%), mp 149−151 °C; ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.41 (1H, d, J = 1.2 Hz), 8.38 (1H, d, J = 8.5 Hz), 8.18−8.30 (3H, m) 7.91−8.01 (2H, m), 4.82 (1H, t, J = 5.6 Hz), 3.52 (2H, q, J = 5.6 Hz), 3.12 (2H, t, J = 5.6 Hz), 2.81 (3H, s); ^{13}C NMR (75 MHz, DMSO-d_6) δ 181.6, 181.4, 142.3, 135.4, 134.78, 134.76, 133.6, 132.9 (2C), 131.9, 128.2, 126.84, 126.80, 124.8, 58.8, 51.8, 53.4; IR (KBr) ν/cm^{-1} 1675 (C═O), 1589, 1326 (S═O), 1150 (S═O); MS (CI) m/z 363 (MNH_4^+, 49%), 346 (MH^+, 100%), 314 ($M^+ - CH_2OH$, 12%). Anal. Calcd for $C_{17}H_{15}NO_5S$: C, 59.12; H, 4.38; N, 4.06. Found: C, 58.89; H, 4.20; N, 3.99.

4-(9,12-Anthraquinone-2-sulfoxy)phenol 14. To a solution of hydroquinone (500 mg, 4.54 mmol) and pyridine (0.08 mL, 1.0 mmol) in dry MeCN (10 mL) was added dropwise a solution of sulfonyl chloride **12**[24] (300 mg, 0.907 mmol) in dry dichloromethane (10 mL). The reaction mixture was stirred overnight at 20 °C, the solvent was removed in vacuo, and the residue solid was stirred with 60% aqueous methanol (10 mL), filtered off, and washed with methanol, yielding crude ester **14** (310 mg). It was dissolved in refluxing acetic acid (8 mL), cooled, and filtered from the minor precipitate which formed immediately on cooling and left to crystallize overnight to give pure **14** (235 mg, 64%), mp 230−232 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.77 (1H, s), 8.45−8.39 (2H, m), 8.34−8.20 (3H, m) 8.03−7.96 (2H, m), 6.86 (2H, d, J = 9 Hz), 6.69 (2H, d, J = 9 Hz); ^{13}C NMR (100 MHz, acetone-d_6) δ 182.3, 181.8, 157.2, 142.7, 140.9, 137.7, 135.6 (2C), 134.9, 134.1, 134.0, 133.8, 129.1, 127.85, 127.83, 127.5, 124.0 (2C), 116.7 (2C); IR (KBr) ν/cm^{-1} 1673 (C═O), 1590, 1503, 1353 (S═O), 1293, 1195 (S═O), 869 (S−O), 849 (S−O); MS (EI) m/z 380 (M^+, 33%), 208 (100%). Anal. Calcd for $C_{20}H_{12}O_6S$: C, 63.15; H, 3.18. Found: C, 62.66; H, 3.24.

2-[(2-Hydroxyethyl)methylamidosulfonyl)-13,13,14,14-tetracyanoanthraquinodimethane 15. This was synthesized using anthraquinone **13** (1.43 g, 4.14 mmol), malononitrile (4.04 g, 61.8 mmol), pyridine (4.05 mL, 50 mmol), and titanium tetrachloride (1 M solution in dichloromethane, 21 mL, 21 mmol) and β-alanine[25] (1.6 g, 18 mmol) as described

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(24) Armitage, B.; Changjun Yu; Devadoss, C.; Schuster, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9847.

for **9**. After removal of dichloromethane, the residue was vigorously stirred with a mixture of ethyl acetate (100 mL) and 5% aqueous HCl (100 mL), and the precipitate was filtered off, washed with the same solvent mixture, with water and MeOH, yielding crude **15** (1.28 g, 69%). The mother liquor was combined with washing ethyl acetate, the organic layer was separated, washed with water, and dried over $MgSO_4$, and its volume was reduced to 30 mL, resulting in precipitation of an additional portion of **15** (0.16 g, 10%). Both portions were recrystallized from MeCN (50 mL; filtering from insoluble impurities while hot), yielding pure **15** (1.37 g, 74%), mp > 300 °C (dec). ^{1}H NMR (200 MHz, DMSO-d_6) δ 8.59 (1H, d, J = 1.4 Hz), 8.46 (1H, d, J = 8.2 Hz), 8.35−8.18 (3H, m) 7.98−7.83 (2H, m), 4.86 (1H, d, J = 5.4 Hz), 3.54 (2H, d, J = 5.4 Hz), 3.15 (2H, t, J = 5.6 Hz), 2.88 (3H, s); ^{13}C NMR (50 MHz, acetone-d_6) δ 158.5 (2C), 140.3, 133.7, 132.5 (2C), 131.3, 130.1, 129.9, 129.8, 128.5, 127.6, 127.5, 125.6, 113.8 (4C, br), 84.5 (2C, br), 59.1, 52.1, 35.6; IR (KBr) ν/cm^{-1} 2231 MS (CI) m/z 459 (MNH_4^+, 100%), 442 (MH^+, 18%), 410 ($M^+ - CH_2OH$, 17%). Anal. Calcd for $C_{23}H_{15}N_5SO_3$: C, 62.57, H, 3.43, N, 15.87. Found: C, 62.60; H, 3.34; N, 15.66.

2-(4-Hydroxyphenyloxysulfonyl)-13,13,14,14-tetracyanoanthraquinodimethane 16. Anthraquinone **14** (190 mg, 0.500 mmol), β-alanine (200 mg, 2.25 mmol), and malononitrile (500 mg, 7.58 mmol) were suspended in dry dichloromethane (12 mL) and titanium tetrachloride (1 M in dichloromethane; 2.5 mL, 2.5 mmol) was added dropwise, keeping the temperature at 0 °C. Then pyridine (0.46 mL, 6.0 mmol) was added, and the reaction mixture was refluxed for 15 h. After removing the solvent, the residue was dissolved in a mixture of ethyl acetate (30 mL) and 5% aqueous HCl (20 mL), and the organic layer was washed with 5% HCl and then brine and dried over $MgSO_4$. The solvent was removed, and the residue was chromatographed on silica gel, eluting initially with dichloromethane (to remove an excess of malononitrile) and then with dichloromethane/ethyl acetate (5:1 v/v) to elute a product which was dissolved in hot methanol (5 mL). Evaporation of methanol (1−2 mL) in vacuo resulted in the precipitation of a yellow solid which could not be redissolved in methanol, even at reflux. It was filtered off, washed with MeOH, yielding pure **16** (165 mg, 69%) as a yellow solid, mp 260 °C (dec) (phase transition at ca. 150 °C). ^{1}H NMR (300 MHz, acetone-d_6) δ 8.85 (1H, dd, J = 1.8 and 0.3 Hz), 8.67 (1H, s), 8.56 (1H, dt, J = 8.1 and 0.3 Hz), 8.41−8.35 (2H, m), 8.24 (1H, dd, J = 8.1 and 1.8 Hz), 7.98−7.92 (2H, m), 6.94 (2H, d, J = 9 Hz), 6.76 (2H, d, J = 9 Hz); ^{13}C NMR (75 MHz, acetone-d_6) δ 159.0, 158.9, 156.9, 142.1, 138.4, 136.1, 132.9, 132.8, 132.4, 131.7, 130.6, 130.5, 128.9, 128.1, 128.0, 127.2, 123.3 (2C), 116.4 (2C), 113.7, 113.5 (2C), 113.4, 85.8, 85.4; IR (KBr) ν/cm^{-1} 2231 (C≡N), 1503, 1380 (S═O), 1198 (S═O), 869 (S−O), 848 (S−O); (MS (EI) m/z 476 (M^+, 29%), 304 (100%). Anal. Calcd for $C_{26}H_{12}N_4O_4S$: C, 65.54; H, 2.54; N, 11.76. Found: C, 65.64; H, 2.60; N, 11.51.

***N*-Methyl-*N*-[2-(4-methyl-4′,5′-dipentyltetrathiafulvalenyl-5-carbonyloxy)ethyl]-13,13,14,14-tetracyanoanthraquinodimethane-2-sulfonylamide 17.** This was obtained using TCNAQ **15** (110 mg, 0.25 mmol) and carbonyl chloride **6** [from acid **5** (101 mg, 0.25 mmol)] under the same conditions as described for **11**. After chromatography, the product was stirred in warm methanol (2 mL) and cooled, and the precipitate was filtered, yielding **17** (26 mg, 13%) as a brown solid, mp 193−196 °C.

***N*-Methyl-*N*-[2-(4-methyl-4′,5′-dipentyltetrathiafulvalenyl-5-carbonyloxy)ethyl]-13,13,14,14-tetracyanoanthraquinodimethane-2-sulfonylamide 17 (alternative synthesis).** To a cold (0 °C) solution of carbonyl fluoride **7** (62 mg, 0.153 mmol) and *p*-(dimethylamino)pyridine (19 mg, 0.156 mmol) in dry dichloromethane was added TCNAQ derivative **15** (67 mg, 0.153 mmol), and the reaction mixture was stirred at 20 °C for 24 h, resulting in full dissolution of starting materials. The solvent was removed, and the residue was chromatographed on silica gel [eluent: ethyl acetate/petroleum ether (1:3 v/v)]. The fraction containing product was collected and evaporated in vacuo, and the residue (102 mg) was stirred in methanol, filtered off, and washed with methanol, giving compound **17** (93 mg, 74%), mp 196−198 °C. ^{1}H NMR (200 MHz, acetone-d_6) δ 8.73 (1H, d, J = 1.6 Hz), 8.56 (1H, d, J = 8.2 Hz), 8.44−8.26 (3H, m), 7.99−7.88 (2H, m), 4.42 (2H, t, J = 5.0 Hz), 3.60 (2H, t, J = 5.0 Hz), 3.03 (3H, s), 2.44 (2H, t, J = 6.0 Hz), 2.40 (2H, t, J = 6.0 Hz), 2.35 (3H, s), 1.60−1.42 (4H, m), 1.41−1.25 (8H, m), 0.90 (6H, t, J = 6.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 158.4, 142.5, 133.4, 133.0, 132.9, 131.3, 130.5, 129.8, 129.6, 128.5, 127.9, 127.8, 126.0, 112.78, 112.61, 112.55, 112.45, 84.7, 84.6, 62.8, 49.0, 36.2, 31.2 (2C), 29 (4C, br), 22.4 (2C), 16 (br), 13.98, 13.97; λ/nm (ϵ/M^{-1} cm^{-1}) 283 (40200), 307 (30000), 327 (30800), 425sh (1900); IR (KBr) ν/cm^{-1} 2229 (C≡N), 1717 (C═O), 1560, 1458, 1340 (S═O), 1156 (S═O), 1236; MS (EI) m/z 825 (M^+, 100%). Anal. Calcd for $C_{41}H_{39}N_5O_4S_5$: C, 59.61, H, 4.76, N, 8.48. Found: C, 59.95, H, 4.77, N, 8.48.

1-(4-Methyl-4′,5′-dipentyltetrathiafulvalenyl-5-carbonyloxy)-4-(13,13,14,14-tetracyanoanthraquinodimethane-2-sulfonyloxy)benzene 18. This was obtained using **16** (65 mg, 0.137 mmol) and carbonyl chloride **6** [from acid **5** (67 mg, 0.166 mmol)] as described for **11**. After chromatography crude **18** (45 mg, 38%) was stirred in warm methanol (2 mL) and cooled, and the precipitate was filtered, yielding pure **18** (28 mg, 24%) as a brown solid, mp 120−125 °C. ^{1}H NMR (300 MHz, acetone-d_6) δ 8.86 (1H, d, J = 1.2 Hz), 8.59 (1H, d, J = 8.1 Hz), 8.40−8.30 (3H, m), 7.98−7.90 (2H, m), 7.29−7.20 (4H, m), 2.45 (3H, s), 2.44 (4H, t, J = 7.5 Hz), 1.58−1.46 (4H, m), 1.39−1.25 (8H, m), 0.89 (6H, t, J = 6.3 Hz); ^{13}C NMR (125 MHz, acetone-d_6) δ 159.5, 159.4, 158.6, 151.5, 150.0, 147.7, 138.7, 137.0, 133.5, 133.4, 133.1, 132.2, 131.2, 131.1, 130.0, 129.7 (2C), 128.7, 128.6, 127.9, 124.3, 124.1, 119.1, 114.3, 114.14, 114.10, 114.0, 112.6, 103.2, 86.5, 86.1, 31.8 (2C), 30.1 (2C), 29.10, 29.09, 23.0 (2C), 16.4, 14.2 (2C); IR (KBr) ν/cm^{-1} 2228 (C≡N), 1718 (C═O), 1495, 1384 (S═O), 1208, 1147 (S═O), 873 (S−O); UV (MeCN) λ/nm (ϵ/M^{-1} cm^{-1}) 279 (41000), 306 (32200), 325 (32600), 445 (2150); MS (EI) m/z 860 (M^+, 9%), 109 (100%). Anal. Calcd for $C_{44}H_{36}N_4O_5S_5$: C, 61.37; H, 4.21; N, 6.51. Found: C, 61.75; H, 4.54; N, 6.12.

Compound 20. The reaction was carried out similarly to the synthesis of **16**, from the acid **19** (0.25 g, 1.0 mmol), malononitrile (1.0 g, 15 mmol), titanium tetrachloride (1 M solution in dichloromethane; 5 mL, 5 mmol), and pyridine (0.95 mL, 12.3 mmol). After workup, the orange solution in ethyl acetate was concentrated and chromatographed on silica gel, eluting with ethyl acetate/acetone (starting with 4:1 v/v, gradually changing to 1:4 v/v). The first orange fraction was evaporated in vacuo, and the residue was redissolved in ethyl acetate (5 mL); the orange powder **20** as a mixture of Ca and Na salts (100 mg, ca. 10%) precipitates out of this solution on storage, mp > 300 °C (dec). ^{1}H NMR (300 MHz, acetone-d_6) δ 8.53 (1H, d, J = 1.2 Hz), 8.42−8.32 (2H, m), 8.29 (1H, d, J = 8.1 Hz), 8.11 (1H, dd, J = 8.1 and 1.5 Hz), 7.91−7.84 (2H, m); ^{13}C NMR (75 MHz, acetone-d_6) δ 187.8, 161.1, 160.8, 144.1, 133.0 (2C), 132.1, 131.7, 131.53, 131.48, 131.36, 128.6, 128.5, 128.0, 127.3, 121.3, 120.0, 114.61, 114.57, 114.54, 114.43, 84.5, 84.4, 52.1; IR (KBr) ν/cm^{-1} 2224 (C≡N), 2205 (C≡N), 2183 (C≡N), 1560, 1542, 1361, 1341, 1325, 1279, 849, 770, 695; CV $E_{1red}^{1/2}$ −0.37 (2e), $E_{1ox}^{p.a.}$ 1.29 V (irreversible). A sample for X-ray analysis was grown from MeCN solution, concentrated by slow evaporation of the solvent at 20 °C.

The second yellow fraction which immediately followed the first one was evaporated, and the residue was refluxed in ethyl acetate (5 mL), filtered off, and washed with acetone, giving another product (110 mg), mp > 300 °C (dec), which was not identified.

(25) β-Alanine was used by analogy with the synthesis of 2-hydroxymethyl-11,11,12,12-tetracyanoanthraquinodimethane,[23] where the authors noted that its presence is essential if the hydroxyl group is present; however, the role of β-alanine was not explained.

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Supporting Information Available: Table of crystal data and details of X-ray experiments; molecular structures of acid **5** and complex **20**·2H_2O·4MeCN; crystal packing pattern of TTF−TCNAQ diad **11**; SEEPR spectra of $\mathbf{16}^{-\bullet}$, $\mathbf{18}^{-\bullet}$, $\mathbf{18}^{+\bullet}$; ^{1}H NMR and ^{13}C NMR spectra of **20**. This information is available free of charge via the Internet at http://pubs.acs.org.

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