In Search of Molecular Rectifiers. The Donor−σ−Acceptor System Derived from Triptycenequinone and Tetrathiafulvalene

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Several donor−σ−acceptor compounds (**8**, **9**, **13**, and **14**) have been synthesized that contain a sterically hindered quinone tethered by a tetramethylene chain to a substituted tetrathiafulvalene. Compounds **13** and **14** show a dramatic increase (≈450 mV) in the oxidation potential of the dipyrrolo-TTF unit, suggestive of considerable electron withdrawal through the σ-bridge. Monolayers of **9** and **14** are metastable at the air−water interface.

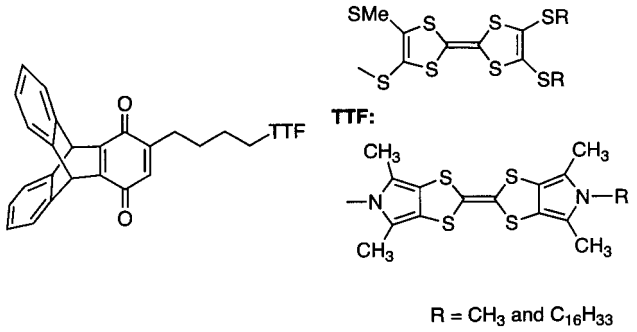
Introduction

The research area of molecular electronics was initiated in 1974 with a proposal by Aviram and Ratner.[1] They proposed a so-called "Gedankenmolekül" D−σ−A that consists of a donor (D) and an acceptor (A) connected via a saturated σ-bond system. As the donor, they suggested a TTF (tetrathiafulvalene) derivative, with the acceptor being a TCNQ (tetracyanoquinodimethane) unit, and the σ-spacer being a bicyclooctane. It was proposed that alignment of that molecule between two appropriate metal electrodes and application of a suitable potential should lead to an electron flow through that molecule, resulting in a "molecular rectifier". The "Gedankenmolekül" has not been synthesized, and only a few examples of true σ-bond connected donor−acceptor systems are known.[2] Unimolecular rectification in such a system has not yet been observed.

In this study, we were interested in devising a σ-bond-linked donor−acceptor systems (D−σ−A) that could be suitable for the formation of Langmuir−Blodgett (LB) films. Therefore, long aliphatic chains should be present at one end. These films could then be used for the investigation of their potential rectifying properties. Since the presence of a donor and an acceptor could lead to the formation of a charge-transfer complex, which would probably surpress the proper alignment of the molecules in an LB film, the presence of bulky groups close to the acceptor or the donor could sterically hinder the formation of charge-transfer complexes. Theoretical estimations proposed that the difference between the redox potentials of donor and acceptor should be smaller than $\Delta E \approx 0.6$ V and the length of the connecting chain should be between two and seven atoms.[2c]

With these requirements in mind, we embarked upon the synthesis of a system in which a quinone acceptor is incorporated in a bulky triptycene unit and connected via a σ-butylene chain to a TTF-derivative donor. The quinone moiety could then be converted into a DCNQI (dicyanoquinodiimine) derivative, to increase the acceptor strength. Two different kinds of TTF derivative were chosen, to vary the donor strength. (Scheme 1)

Scheme 1



In this paper we now report the synthesis of several σ-bond-linked quinone-TTF derivatives, as well as their electrochemical and spectroscopic properties and their film-forming behavior.

Results and Discussion

Synthesis. Since many synthetic operations are not compatible with the simultaneous presence of a quinone and a TTF moiety, we chose to connect the TTF unit to a quinone precursor, which could later be converted into a quinone. The bromo-functionalized MOM-protected hydroquinone **3** was prepared in the following way. MOM-triptycene **2** was prepared in 67% yield by deprotonation of the known hydroquinone **1**[33] with sodium hydride in THF, followed by reaction of the phenolate with chloromethyl methyl ether (Scheme 2).

Lithiation of **2** with *n*-butyllithium in THF,[4] followed by reaction of the carbanion with excess 1,4-dibromobutane, gave the bromobutyl-substituted MOM-triptycene **3** in 40% yield.

With compound **3** as a building block in hand, coupling reactions with several TTF derivatives were performed. In the series of the tetra-*S*-alkyl TTF derivatives, a method developed by Becher and co-workers[5] led to good results. Reaction of the monocyanoethyl-protected TTF

(1) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277−283.
(2) (a) Segura, J. L.; Martîn, N.; Seoane, C.; Hanack, M. *Tetrahedron Lett.* **1996**, *37*, 2503−2506. (b) Metzger, R. M.; Panetta, C. A. *New J. Chem.* **1991**, *15*, 209−221. (c) Metzger, R. M. In *Molecular and Biomolecular Electronics;* Birge, R. R. Ed., Am. Chem. Soc. Adv. Chem. Ser.; American Chemical Society: Washington, DC, 1994; Vol. 240, pp 81−129. (d) Metzger, R. M. *Mater. Sci. Eng.*. **1995**, *C3*, 277−285.
(3) Bartlett, P. D.; Ryan, M. J.; Cohen. S. G. *J. Am. Chem. Soc.* **1942**, *64*, 2649−2653.
(4) (a) Stern, R.; English, J.; Cassidy, H. G. *J. Am. Chem. Soc.* **1957**, *79*, 5792−5797. (b) Townsend, C. A.; Bloom, L. M. *Tetrahedron Lett.* **1981**, *22*, 3923−3924. (c) Schill, G.; Logemann, E. *Chem. Ber.* **1973**, *106*, 2910−2917.
(5) Svenstrup, N.; Rasmussen, K. M.; Hansen, T. K.; Becher, J. *Synthesis* **1994**, 809−812.

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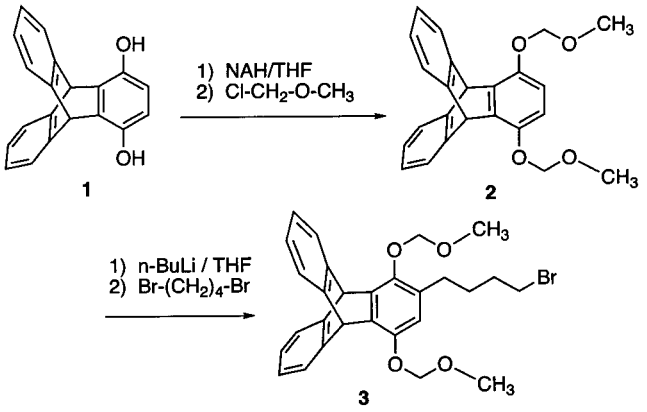
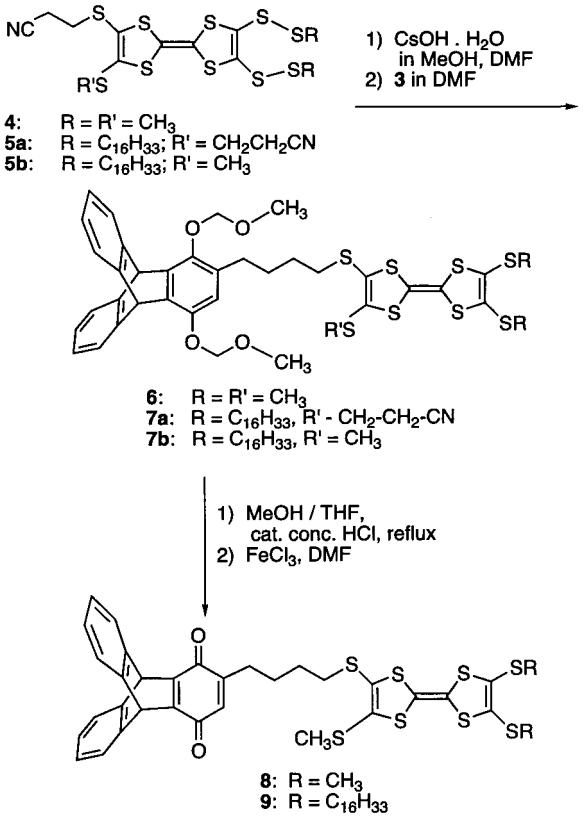
Scheme 2



Scheme 3

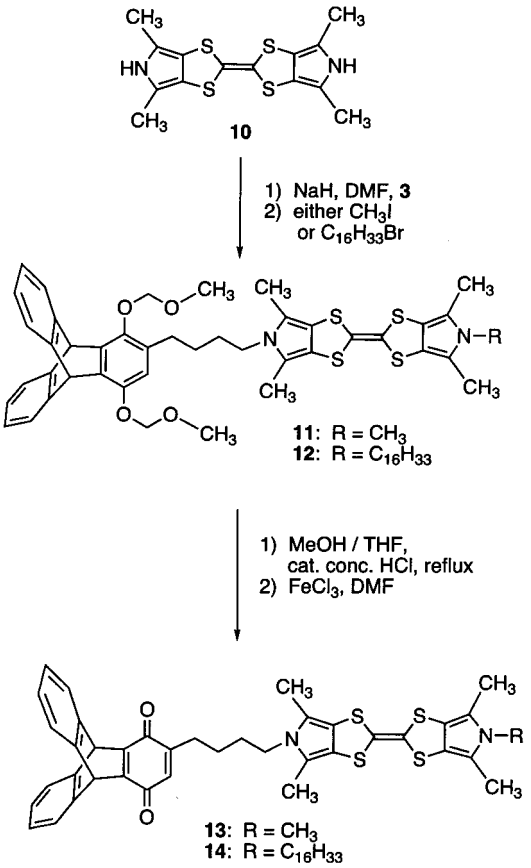


4[5] with cesium hydroxide/methanol in DMF led to the deprotected thiolate, which was alkylated by the bromo compound **3**, giving the MOM-TTF **6** in 89% yield (Scheme 3).

Reaction of the hexadecyl-substituted TTF derivative **5a** with cesium hydroxide/methanol in DMF and attempted coupling with compound **3** did not lead to the expected product **7a**, probably due to the low solubility of the TTF derivative **5a** in DMF. On the other hand, deprotection of the dicyanoethyl-protected TTF derivative **5a** with one equivalent cesium hydroxide/methanol in DMF, followed by reaction of the thiolate of **5a** with the bromide **3** led, in 82% yield, to compound **7a**, was then deprotected and methylated, to give the desired MOM-TTF **7b** in 71% yield.

The MOM protecting group could be removed quantitatively by refluxing compound **6** or **7b** for 1−3 h in a mixture of methanol/THF containing several drops of concentrated hydrochloric acid. The hydroquinones were

Scheme 4



then oxidized with anhydrous ferric chloride in DMF[6] to yield the TTF-quinones **8** and **9** in 54% and 43% yields, respectively.

The preparation of the pyrrolo-TTF derivatives **13** and **14** was accomplished in a similar way. Reaction of the pyrrolo-TTF **10**[7] with sodium hydride in DMF, followed by 1 equiv of **3** and 1 equiv of methyl iodide or hexadecylbromide, led to the MOM-protected derivatives **11** and **12** in 46% and 42% yields, respectively (Scheme 4). The compounds could be separated from the symmetrically substituted byproducts by chromatography on basic alumina. Contrary to the situation for the deprotection of the tetra-*S*-alkyl derivatives **6** and **7b**, the deprotection of the pyrrolo-TTF derivatives **11** and **12** to the corresponding hydroquinones could not be performed with hydrochloric acid in methanol/THF. Addition of one drop of concentrated hydrochloric acid to a solution of **12** in methanol/THF led immediatiely to a dark green/black solution, from which no definite product could be isolated.

The deprotection was finally realized by refluxing the MOM derivatives **11** or **12** for 5 d in a mixture of 4 N acetic acid/*n*-butanol. The corresponding hydroquinones could then be oxidized with anhydrous ferric chloride in DMF, to give the pyrrolo-TTF-quinones **13** and **14** in 36% and 9% yields, respectively.

An attempt was made to convert the TTF-quinone **8** into a DCNQI derivative by reaction with $TiCl_4$/bistrimethylsilylcarbodiimide, a procedure developed by Hünig.[8]

(6) Tobinaga, S.; Kotani, E. *J. Am. Chem. Soc.* **1972**, *94*, 309−310.
(7) Zong, K.; Chen. W.; Cava, M. P.; Rogers, R. D. *J. Org. Chem.* **1996**, *61*, 8117−8124.
(8) (a) Aumüller, A.; Hünig, S. *Angew. Chem., Intl. Ed. Engl.* **1984**, *23*, 447−448. (b) Aumüller, A.; Hünig, S. *Liebigs Ann. Chem.* **1986**, 142−163.

Scheme 5

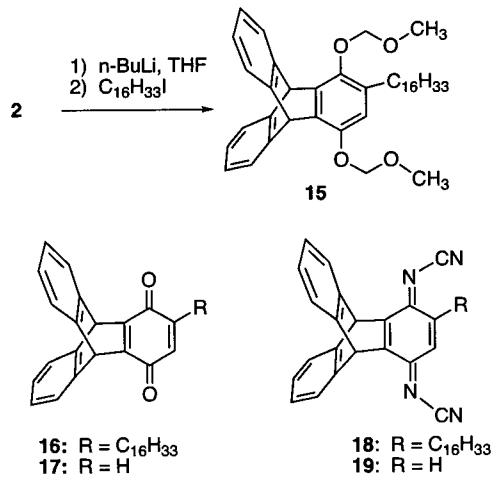


Table 1. Redox Potentials of Compounds 6 through 19[a]

compd	$E^{\circ red}$ (V)	$E^{\circ ox1}$ (V)	$E^{\circ ox2}$ (V)	$E^{ox\ irr}$ (V)
6		0.50	0.85	1.51
7b		0.48	0.83	1.50
8	−0.59	0.50	0.84	
9	−0.60	0.51	0.85	
11		0.27	0.79	1.54
12		0.27	0.79	1.55
13	−0.55	0.70	1.27	
14	−0.56	0.69	1.23	
15				1.52
16	−0.61			
17	−0.51			
18	0.09/−0.52			
19	0.19/−0.44			

[a] Concentration of the compounds: 1 mM; electrolyte: 0.1 M CH_2Cl_2/Bu_4NPF_6; scan rate: 100 mV/s. All potentials are in volts vs SCE.

During the addition of the $TiCl_4$ solution, a black-blue precipitate was formed immediately. Addition of the carbodiimide and subsequent workup afforded a complex mixture which was not further investigated.

Two DCNQI derivatives were prepared from triptycenequinones **16** and **17** as model compounds. The preparation of the quinones **16** and **17** was conducted as follows. The MOM-protected triptycene **2** was lithiated with *n*-butyllithium in THF, followed by reaction with hexadecyl iodide (Scheme 5). The resulting hexadecyl-substituted triptycene derivative **15** could be isolated in 74% yield. The MOM protecting groups were removed by hydrochloric acid in methanol/THF, and the resulting hydroquinone was oxidized to the quinone **16** with ferric chloride in DMF in 82% yield. Triptycenequinone **17** was prepared from the hydroquinone **1** through oxidation with potassium bromate.[3]

The conversion of the quinones **16** and **17** to the dicyanoquinodiimines **18** and **19** could be performed by Hünig's method as described above. DCNQI **18** could be isolated as an intensely red, oily solid but could not be purified satisfactorily, due to its instability on both silica and alumina. DCNQI **19** could be isolated as a red microcrystalline powder.

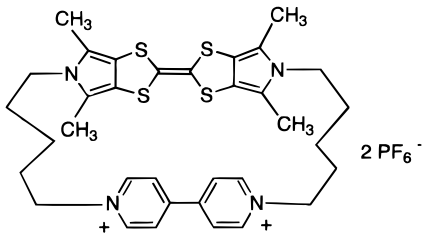
Electrochemistry and Electronic Spectra. The MOM-protected TTF derivatives **6**, **7b**, **11,** and **12** all show the expected redox potentials for the TTF unit (Table 1); these are seen at $E^{\circ 1} = 0.48-0.50$ V vs SCE and $E^{\circ 2} = 0.83-0.85$ V for the tetra-*S*-alkyl derivatives **6** and **7b**, and $E^{\circ 1} = 0.27-0.28$ V and $E^{\circ 2} = 0.79-0.81$ V for the pyrrolo-TTF derivatives **11** and **12**. The same redox potentials are observed with tetra-*S*-methyl-TTF ($E^{\circ 1} = 0.47$ V and $E^{\circ 2} = 0.82$ V) and with di-hexadecyl-pyrrolo-TTF ($E^{\circ 1} = 0.25$ V and $E^{\circ 2} = 0.78$ V). An additional irreversible oxidation is observed with a potential of $E^{ox} = 1.50-1.53$ V in all four compounds **6**, **7b**, **11,** and **12**, due to the oxidation of the MOM-protected hydroquinone unit. The same potential of $E^{ox} = 1.52$ V is seen in the cyclic voltammetry of the simple MOM-protected hexadecyl-substituted hydroquinone **15**.

The cyclic voltammograms of the tetra-*S*-alkyl-TTF quinones **8** and **9** show about the same oxidation potentials for the TTF unit as in the MOM-protected compounds **6** and **7b** and a new reduction wave at $E_{red} = -0.59$ to -0.60 V, due to the redox-active quinone unit. The hexadecyl-substituted triptycene quinone **16** also shows a redox potential of $E_{red} = -0.61$ V, while the unsubstituted triptycene quinone **17** shows a value of $E_{red} = -0.51$ V.

The triptycenequinonepyrrolo-TTF derivatives **13** and **14** show oxidation potentials for the pyrrolo-TTF unit of $E^{\circ 1} = 0.69-0.70$ V and $E^{\circ 2} = 1.23-1.27$. These potentials are shifted by $\Delta E^{\circ 1} = 0.45$ V and $\Delta E^{\circ 2} = 0.49$ V, compared to the MOM-protected derivatives **11** or **12**.

The remarkably large shift in oxidation potentials in **13** and **14** is indicative of considerable electron withdrawal from the TTF unit. The cause of this effect may be attributed to one of three possible phenomena: (1) the close proximity of the TTF unit to the quinone moiety by twisting of the σ-bridge; (2) appreciable concentration of a bimolecular charge-transfer (CT) complex in solution, in which the TTF donor of each molecule is situated over the quinone acceptor of the second molecule; or (3) an inductive electron withdrawal from donor to acceptor taking place *through the* σ*-chain*. It should be noted that the poorer TTF electron donor units of **8** and **9** show no shifts in their oxidation potentials.

A comparison of the properties of **13** with those of the recently reported D−A sandwich **13a**[9] is of interest. Both contain moderate acceptors and the same strong donor, but the rigid sandwich structure of **13a** effects direct π-overlap between donor and acceptor, as evidenced by a strong ($\epsilon = 403$) CT band.[9] In contrast, no CT band is discernible in the UV−vis spectrum of **13** between 500 and 820 nm, even though the E^{ox} for **13** is shifted by 450 mV, compared to only 160 mV for the rigidly held **13a**.[9] Furthermore, models of **13** show that modest D−A overlap is possible only in a conformation in which the hydrogens of the σ-bridge are held in a highly staggered configuration. The E^{red} of the quinone acceptor of **13** is shifted by only about 50 mV, a situation similar to that observed in **13a**.[9]



13a

(9) Simonsen, K. B.; Zong, K.; Rogers, R. D.; Cava, M. P.; Becher, J. *J. Org. Chem.* **1997**, *62*, 679−686.

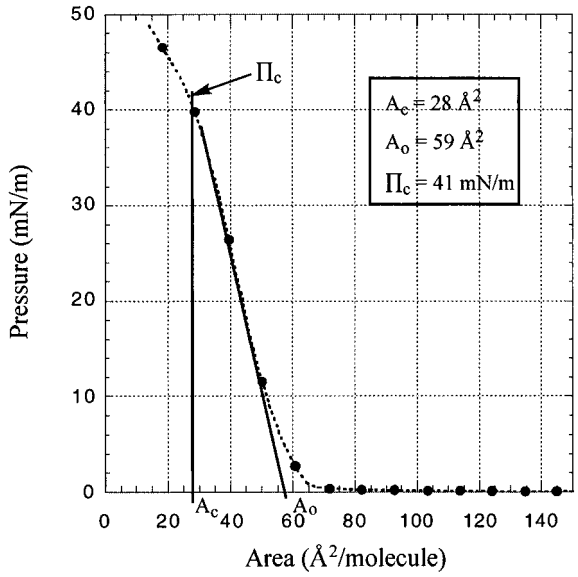


Figure 1. Pressure−area isotherm of **9** at rt.

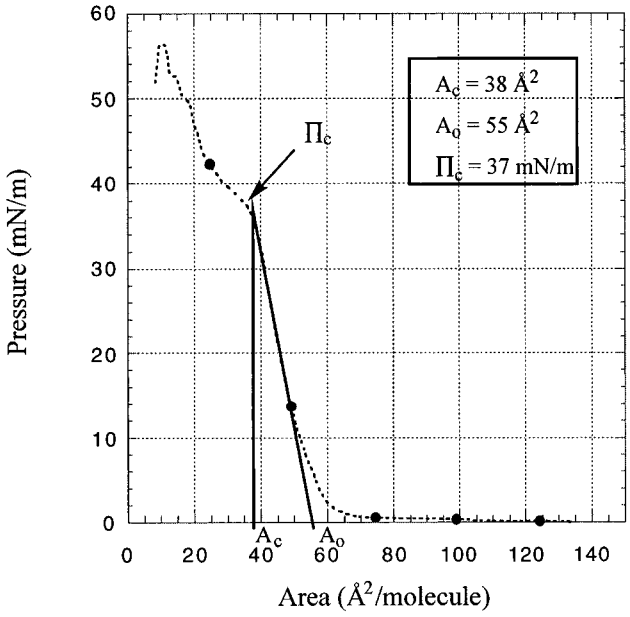


Figure 2. Pressure−area isotherm of **14** at rt.

Equimolar mixtures of dihexadecylpyrroloTTF or dimethylpyrroloTTF with triptycenequinone or hexadecyltriptycenequinone showed only the individual redox waves in cyclic voltammetric experiments (concentration of each compound, 1 mmol, the same conditions as described for the other electrochemical experiments). This rules out a bimolecular CT complex in the case of **13**.

Possibilities 1 and 2 having been eliminated; explanation 3 remains: an inductive effect through the σ-bridge must have considerably shifted the oxidation potential of a very strong donor, though the reduction potential of the weak quinone acceptor was only slightly shifted.

Pockels−Langmuir and Langmuir−Blodgett Films. Both molecules **9** and **14** make Pockels−Langmuir monolayers at the air−water interface. Molecule **9** has an extrapolated area at zero pressure (A_o) of 59 Å^2 molecule^{-1} (Figure 1), while molecule **14** has A_o = 55 Å^2 molecule^{-1} (Figure 2). The collapse pressure Π_c for **9** is 41 mN m^{-1}, and that for **14** is 37 mN m^{-1}. However, the

Figure 3. Brewster angle micrograph (area 6.4 mm × 4.8 mm) of **9**, after letting the Pockels−Langmuir film equilibrate over the water subphase for 15 min at 20 °C.

Figure 4. Brewster angle micrograph (area 6.4 mm × 4.8 mm) of **9**, after letting the Pockels−Langmuir film equilibrate over the water subphase for 1 s at 10 °C.

Pockels−Langmuir film is not steady, i.e., the monolayer area is not constant with time: when the film balance pressure was held at 20 mN/m, the area decreases steadily (10−20% area loss/h for **9**). A Brewster angle micrograph (MiniBAM, Nanofilm Technologie, Göttingen, Germany) of **9** taken after waiting for 15 min produces a very inhomogeneous layer (Figure 3), while a micrograph taken immediately after film compression (Figure 4) shows a much smoother film surface.

Molecules **9** and **14** differ in their LB transfer ratios. Multilayers of molecule **9** (10−20 layers) were transferred to HOPG (highly oriented pyrolytic graphite), mica, and quartz. For molecule **9,** the best transfers were to quartz. Molecule **9** transfers as a modified Z-type multilayer: the first film is transferred to the slide on the down stroke, and the successive layers are all transferred on the up stroke. Compound **14** transferred as a Y-type multilayer to a quartz substrate.

The absorbances of the yellow LB films of **9** and **14** on quartz were measured on a UV−vis spectrophotometer (200−1000 nm), but no charge-transfer band was found.

Work on monolayer and LB film formation and the electrical properties of each is in progress and will be reported at a later date.

Conclusion

The intent of preventing intermolecular association by LB-film-forming D−σ−A molecules **9** and **14** was accomplished. The conversion of **14** into a D−σ−A system with A = strong acceptor along with D = strong donor failed. The quinone is a weak acceptor and is too protected by the triptycene moiety to make **9** or **14** truly amphiphilic. The electron depletion of the donor unit of **14** is probably due to a direct withdrawal through the σ-bridge. Molecules **9** and **14** make Pockels−Langmuir monolayers, but these are somewhat unstable.

Experimental Section

Electrochemistry. Cyclic voltammograms were acquired in a single compartment cell with a platinum disk working electrode (1 mm diameter), a platinum wire auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. For each measurement, a 0.1 M solution of tetrabutylammonium hexafluorophosphate (TBAHFP) in dry dichloromethane was employed with ca. 1 mM of the substrate. The potentials are given at a scan rate of 100 mV/s. A computer-controlled EG&G potentiostat (PAR263) was used for all the measurements.

MOM-Protected Triptycene Hydroquinone 2. Under a N_2 atmosphere in oven-dried glassware, 10.0 g (34.9 mmol) of triptycene hydroquinone **1**[3] was dissolved in 250 mL of dry THF. Then 5.68 g (148 mmol) of a NaH suspension in mineral oil (60%) was added slowly. After 1 h of stirring at rt, a solution of 10 mL (10.6 g, 132 mmol) of chloromethyl methyl ether in 10 mL of THF was added slowly and the mixture stirred for another hour. Then 70 mL of 5% NaOH solution was added slowly. The reaction mixture was extracted with $CHCl_3$, and the organic phase was washed with bicarbonate and dried over Na_2SO_4. The solvent was evaporated and the resulting solid recrystallized from toluene−hexane, yielding 8.8 g (23.5 mmol, 67%) of slightly yellowish crystals: mp 129−130 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.42−7.40 (m, 4 H), 7.01−6.99 (m, 4H), 6.70 (s, 2H), 5.90 (s, 2H), 5.18 (s, 4 H), 3.52 (s, 6H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 147.29, 145.47, 136.25, 125.05, 123.73, 113.32, 95.69, 56.07, 47.58. Anal. Calcd for $C_{24}H_{22}O_2$: C, 76.99; H, 5.92. Found: C, 76.85; H, 5.92.

ω-Bromobutyl MOM Ether 3. Under a N_2 atmosphere in oven-dried glassware, 13.6 g (36.4 mmol) of the MOM-triptycene **2** was dissolved in 200 mL of dry THF. Then 32 mL (49.9 mmol) of *n*-butyllithium in hexane was added via a dropping funnel, and the solution stirred at rt for 10 h. It was then added slowly to a solution of 17 mL (30.7 g, 142 mmol) of 1,4-dibromobutane in 200 mL of THF, and the solution refluxed for 10 h. The reaction mixture was poured into water and the THF evaporated under reduced pressure. The product was extracted into $CHCl_3$, and the organic phase was washed with water and bicarbonate and dried over Na_2SO_4. After evaporation of the solvent, the brown oil was chromatographed twice on silica gel (CH_2Cl_2−hexane 8:2), yielding 7.37 g (14.5 mmol, 40%) of compound **3** as a viscous oil which solidified in a refrigerator after about 2−3 weeks to give slightly yellow crystals: mp 79−81 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.39−7.36 (m, 4 H), 7.00−6.97 (m, 4 H), 6.57 (s, 1 H), 5.84 (s, 1 H), 5.76 (s, 1 H), 5.17 (s, 2 H), 5.01 (s, 2 H), 3.69 (s, 3 H), 3.51 (s, 3 H), 3.39 (t, 2 H, J = 6.76), 2.55 (t, 2 H, J = 7.75), 1.90−1.82 (m, 2 H), 1.70−1.62 (m, 2 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 148.46, 146.12, 145.53, 145.23, 139.55, 133.85, 132.73, 125.12, 125.06, 123.71, 123.65, 113.57, 100.46, 95.41, 57.43, 56.13, 48.88, 47.31, 33.61, 32.52, 29.53, 29.14, 28.91. Anal. Calcd for $C_{28}H_{29}BrO_4$: C, 66.02; H, 5.74; Br, 15.68. Found: C, 66.27; H, 5.79; Br, 15.46.

TTF Derivative 5a. A mixture of 1.00 g (3.47 mmol) of 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one[5] and 4,5-bis(hexadecylthio)-1,3-dithiol-2-one[10] (2.25 g, 3.48 mmol) in freshly distilled triethyl phosphite (12 mL) was heated at 110 ° for 3.5 h. After cooling, excess MeOH was added and the red-orange product was filtered off and washed with MeOH. Filtration through silica and crystallization from $CHCl_3$−hexane afforded 1.75 g (57%) of **5a**: mp 114−115 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 3.09 (m, 4H), 2.82 (m, 4H), 2.77 (m, 4H), 1.60 (m, 4H), 1.39 (m, 4H), 1.26 (m, 4H), 0.88 (m, 6H); HRMS (m/z) calcd for $C_{44}H_{74}N_2S_8$ 887.61, found 886.95.

Compound 5b. The TTF derivative **5a** (1.20 g, 1.35 mmol) was dissolved in DMF (200 mL) at 80 °C (N_2) and then cooled to precipitate **5a** as fine needles. A solution of $CsOH\cdot H_20$ (0.250 g) in MeOH (13 mL) was added over 25 min. After stirring for 45 min, MeI (1 mL) was added dropwise, and stirring continued at rt overnight. Water was then added, and the orange solid was filtered off and crystallized from $CHCl_3$−MeOH to afford **5b** (1.07 g, 93%): mp 94−95 °C; ^{1}H NMR (360 MHz, $CDCl_3$) 83.09 (m, 4H), 2.82 (m, 4H), 2.77 (m, 4H), 2.47 (s, 3H), 1.60 (m, 4H), 1.39 (m, 4H), 1.26 (m, 4H), 0.88 (m, 6H); HRMS (m/z) calcd for C_{42} $H_{73}NS_8$ 848.57, found 848.34.

MOM-triptycene TTF Derivative 6. TTF-derivative **4**[5] (1.01 g, 2.36 mmol) was dissolved in 45 mL of dry DMF, which was degassed with nitrogen for 30 min. Then, 490 mg (2.92 mmol) of cesium hydroxide in 7 mL of methanol was added and the solution stirred rt for 45 min. After that time, a solution of 1.20 g (2.36 mmol) of bromide **3** in 10 mL of DMF was added via a syringe and the mixture stirred at rt for 14 h. The solvent was evaporated, and the remaining red oil was dissolved in CH_2Cl_2, washed with water and bicarbonate, and dried over Na_2SO_4. Filtration through silica gel yielded 1.68 g (2.09 mmol, 89%) of an intensely red-orange amorphous solid. An analytical sample of **6** was obtained after chromatography on basic alumina with chloroform−hexane 1:2: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.40−7.36 (m, 4 H), 7.01−6.97 (m, 4 H), 6.57 (s, 1 H), 5.83 (s, 1 H), 5.76 (s, 1 H), 5.17 (s, 2 H), 5.01 (s, 2 H), 3.70 (s, 3 H), 3.51 (s, 3 H), 2.80 (t, 2 H, J = 6.55, 2.54 (t, 2 H, J = 7.19), 2.43 (s, 3 H), 2.41 (s, 3 H), 2.34 (s, 3 H), 1.66−1.64 (m, 4 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 148.47, 146.09, 145.55, 145.26, 139.54, 133.78, 132.94, 125.12, 125.07, 123.73, 123.66, 113.59, 100.48, 95.43, 57.48, 56.16, 48.90, 47.32, 29.97, 29.65, 29.55, 19.15. Anal. Calcd for $C_{37}H_{38}O_4S_8$: C, 55.33; H, 4.77; S, 31.93. Found: C, 55.14; H, 4.86; S, 31.76.

TTF-quinone 8. A quantity of 1.2 g (1.49 mmol) of the MOM-triptycene-TTF **6** was dissolved in 125 mL of a THF−methanol (1:5) mixture, and a few drops of concentrated HCl were added. The solution was heated under reflux for 3 h, the solvent was evaporated, and the remaining solid was dissolved in CH_2Cl_2, washed with water and bicarbonate, and dried over $NaSO_4$. Evaporation of the solvent yielded 1.02 g (1.43 mmol, 96%) of a brown solid. A portion of 770 mg (1.08 mmol) of the hydroquinone was dissolved in 15 mL of DMF and 2.2 g (13.7 mmol) of anhydrous $FeCl_3$ in 20 mL of DMF was added. After stirring at rt for 18 h, another 0.50 g (3.1 mmol) of $FeCl_3$ in 3 mL of DMF was added. After 5 h the reaction mixture was poured into water and extracted with $CHCl_3$. The organic phase was washed with water and bicarbonate and dried over Na_2SO_4. The solvent was evaporated and the black brown oil was chromatographed on basic alumina (CH_2Cl_2−hexane 1:1), yielding 410 mg (0.58 mmol, 54%) of the TTF-quinone **8** as a green-brown glass: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.43−7.41 (m, 4 H), 7.05−7.02 (m, 4 H), 6.38 (s, 1 H), 5.80 (s, 1 H), 5.77 (s, 1 H), 2.79 (t, 2 H, J = 6.8), 2.43 (s, 3 H), 2.42 (s, 3 H), 2.38 (s, 3 H), 1.66−1.64 (m, 4H); ^{13}C NMR: (93 MHz, $CDCl_3$) δ 183.60, 151.93, 151.71, 147.79, 143.73, 143.67, 131.71, 130.41, 127.52, 127.30, 125.47, 125.44, 124.77, 124.35, 124.31, 110.85, 110.62, 47.48, 47.20, 35.72, 29.15, 28.49, 26.74, 22.60, 19.13; MS (EI) m/z 711.9.

TTF Derivative 7a. The TTF derivative **5a** (0.46 mg, 0.52 mmol) was suspended in 100 mL of DMF and the solvent degassed with N_2 for 20 min. To the suspension was added a solution of 100 mg (0.596 mmol) of cesium hydroxide in 10 mL of CH_3OH and the mixture stirred for 1 h. To the then clear solution was added 270 mg (0.53 mmol) of bromide **3** in 5 mL of DMF and the solution stirred for 15 h. The solvent was

(10) Tormos, G. V.; Cava, M. P.; Wu, X.-L.; McKinley, A. J.; Metzger, R. M. *Synth. Met.* **1992**, *52*, 131−146.

evaporated, the resulting red-brown solid was dissolved in $CHCl_3$, and the organic phase was washed with water and bicarbonate and dried over Na_2SO_4. Evaporation of the solvent yielded 0.54 g (0.43 mmol 82%) of **7a**: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.40−7.36 (m, 4 H), 6.98 (m, 4 H), 6.57 (s, 1 H), 5.84 (s, 1 H), 5.76 (s, 1 H), 5.18 (s, 2 H), 5.01 (s, 2 H), 3.69 (s, 3 H), 3.52 (s, 3 H), 2.88−2.79 (m, 8 H), 2.59−2.55 (m, 4 H), 1.62 (m, 4 H), 1.40 (m, 4H), 1.26 (m, 48 H), 0.88 (m, 6 H).

Compound 7b. An amount of 480 mg of the MOM-TTF **7a** was dissolved in 50 mL of DMF, which was degassed with N_2 for 1 h. Then 80 mg (0.48 mmol) of cesium hydroxide in 7 mL of CH_3OH was added and the mixture stirred for 30 min. Then 0.5 mL of CH_3I was added and the mixture stirred for 1.5 h. The solvent was evaporated, and the remaining red solid was dissolved in CH_2Cl_2, washed with water and bicarbonate, and dried over Na_2SO_4. The solvent was removed and the remaining solid chromatographed on silica CH_2Cl_2 (6:4), yielding 330 mg (0.27 mmol, 71%) of **7b** as a red solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.39−7.37 (m, 4 H), 7.00−6.97 (m, 4 H), 6.57 (s, 1 H), 5.83 (s, 1 H), 5.76 (s, 1 H), 5.17 (s, 2 H), 5.01 (s, 2 H), 3.70 (s, 3 H), 3.51 (s, 3 H), 2.83−2.78 (m, 6 H), 2.59−2.55 (m, 2 H), 2.34 (s, 3 H), 1.66−1.62 (m, 4 H), 1.40 (m, 4 H), 1.m, 48 H), 0.88 (m, 6H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 148.47, 146.11, 145.56, 145.27, 139.53, 133.78, 132.94, 129.71, 127.78, 125.62, 125.11, 125.06, 123.73, 123.65, 113.60, 100.48, 95, 43, 57.47, 56.15, 53.40, 48.91, 47.33, 36.29, 36.03, 31.92, 29.98, 29.70, 29.60, 29.53, 29.36, 29.13, 28.52, 22.68, 19.05; PDMS *m*/*z* 1222.4 calcd for $C_{63}H_{90}S_8O_2$, 1224.0.

Compound 9. The MOM-protected TTF derivative **7b** (300 mg, 0.25 mmol) was dissolved by heating in 20 mL of a mixture of CH_3OH/THF (1:1), 2 drops of concentrated HCl were added, and the mixture was heated under reflux for 1 h. The solvents were evaporated, and the remaining oil was dissolved in CH_2Cl_2, washed with water and bicarbonate, and dried over Na_2SO_4. Evaporation of the solvent yields 270 mg (0.244 mmol, 98%) of a dark solid. The crude hydroquinone (180 mg, 0.163 mmol) was dissolved in 25 mL of DMF. Then 150 mg (0.93 mmol) of anhydrous $FeCl_3$ in 4 mL of DMF was added and the mixture stirred at rt. After both 1.5 and 3 h, another 150 mg of $FeCl_3$ was added. After stirring at rt for another 15 h, the mixture was poured into water and extracted with $CHCl_3$. The organic phase was washed with water and bicarbonate and dried over Na_2SO_4. The solvent was evaporated and the remaining solid chromatographed on a silica chromatron with CH_2Cl_2−hexane 1:1, yielding 80 mg (7.06 10^{-5} mol, 43%) of compound **9** as a brown-red solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.43−7.41 (m, 4 H), 7.04−7.02 (m, 4 H), 6.39 (s, 1 H), 5.80 (s, 1 H), 5.78 (s, 1 H), 2.83−2.78 (m, 6 H), 2.38 (s, 3 H), 2.37−2.34 (m, 2 H), 1.67−1.59 (m, 6H), 1.39 (s, broad, 4 H), 1.25 (s, 52 H), 0.90−0.86 (m, 4H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 183.65, 152.00, 151.78, 147.86, 143.79, 143.73, 131.25, 130.45, 127.83, 127.74, 125.49, 124.78, 124.36, 110.97, 109.47, 47.55, 47.26, 36.43, 36.30, 35.73, 35.52, 33.46, 31.92, 30.22, 29.70, 29.52, 29.35, 29.18, 29.13, 28.81, 28.53, 26.82, 22.68, 19.09; PDMS *m*/*z* 1132.4 calcd for $C_{63}H_{90}S_8O_2$, 1132.5.

Compound 11. Under a N_2 atmosphere in oven-dried glassware, 200 mg (0.59 mmol) of the pyrrolo-TTF **10**[7] was dissolved in 25 mL of DMF. To the yellow solution was added 80 mg (3.33 mmol) of NaH (paraffin free, washed with hexane) in one portion. After another 15 min, a solution of 310 mg (0.61 mmol) of the triptycene bromide **3** in 25 mL of DMF was added slowly. The reaction mixture was stirred for 1 h at rt, and then 0.5 mL (1.14 g, 8.03 mmol) of CH_3I was added in one portion. After 15 min, the mixture was poured on water and extracted with $CHCl_3$. The organic phase was washed with water and bicarbonate and dried over Na_2SO_4. The solvent was evaporated and the remaining solid chromatographed on alumina ($CHCl_3$−hexane 2:1) and twice again on a silica plate (chromatron) with CH_2Cl_2−hexane 4:1 and 2:3, yielding 210 mg (0.27 mmol, 46%) of compound **11** as a yellow foam: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.39−7.38 (m, 4 H), 7.00−6.98 (m, 4 H), 6.55 (s, 1 H), 5.84 (s, 1 H), 5.75 (s, 1 H), 5.17 (s, 2 H), 5.00 (s, 2 H), 3.66 (s, 3 H), 3.62 (s, broad, 2 H), 3.51 (s, 3 H), 3.34 (s, 3 H), 2.54 (t, 2 H), 2.14 (s, 3 H), 2.12 (s, 3 H), 2.04 (s, 3 H), 2.03 (s, 3 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 148.50, 146.12, 145.52, 145.21, 139.57, 133.88, 132.55, 126.08, 125.14, 125.09, 123.91, 123.71, 123.67, 123.33, 120.01, 118.59, 118.08, 114.64, 114.38, 113.45, 110.50, 100.49, 95.37, 57.42, 56.15, 48.91, 47.31, 44.61, 44.39, 31.14, 30.99, 30.77, 30.49, 29.94, 27.69, 12.00, 11.91. Anal. Calcd for $C_{43}H_{44}N_2O_4S_4$: C, 66.12; H, 5.68; N, 3.59; S, 16.42. Found: C, 65.85; H, 5.81; N, 3.54; S, 16.31.

Compound 12. Under a N_2 atmosphere in oven-dried glassware, 400 mg (1.18 mmol) of the pyrrolo-TTF **10** was dissolved in 50 mL of DMF. To the yellow solution was added 200 mg (8.33 mmol) of NaH in one portion. After stirring for 30 min at rt, a solution of 630 mg (1.24 mmol) of triptycene bromide **3** in 35 mL of DMF was added slowly and the mixture stirred for another 75 min. Then, 0.9 mL (0.9 g, 2.95 mmol) of hexadecyl bromide was added neat and the solution stirred for 15 h at rt. Water was added and the mixture was extracted with $CHCl_3$. The organic phase was washed with water and bicarbonate and dried over Na_2SO_4. The solvent was evaporated and the remaining solid chromatographed on alumina with CH_2Cl_2−hexane 2:3, yielding 490 mg (0.49 mmol, 42%) of compound **12** as a yellow foam: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.40−7.39 (m, 4 H), 7.02−6.99 (m, 4 H), 6.56 (s, 1 H), 5.85 (s, 1 H), 5.76 (s, 1 H), 5.17 (s, 2 H), 5.00 (s, 2 H), 3.67−3.62 (m, 4 H), 3.67 (s, 3 H), 3.51 (s, 3 H), 2.54 (t, 2 H), 2.14 (s, 6 H), 2.05 (s, 6 H), 1.27 (m, 2H), 0.88 (t, 3 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 148.49, 146.12, 145.51, 145.21, 139.55, 133.85, 132.61, 125.12, 125.07, 123.70, 123.65, 120.12, 119.97, 118.04, 114.64, 114.61, 113.44, 100.47, 95.36, 57.40, 56.12, 48.90, 47.30, 44.59, 44.36, 31.90, 31.10, 30.75, 29.94, 29.64, 29.59, 29.53, 29.48, 29.34, 29.29, 27.65, 26.76, 22.67. Anal. Calcd for $C_{58}H_{74}N_2O_4S_4$: C, 70.62; H, 7.52; N, 2.83; S, 12.93. Found: C, 70.33; H, 7.62; N, 2.74; S, 13.02.

Compound 13. A 160 mg (0.16 mmol) portion of the MOM-derivative **11** was suspended in a mixture of 250 mL of 4 N acetic acid and 80 mL of *n*-butanol and heated under reflux for 72 h. Then another 100 mL of 4 N acetic acid and 50 mL of *n*-butanol were added, and the solution was heated under reflux for a further 24 h. The two phases which formed were separated, and the aqueous phase was extracted twice with $CHCl_3$. The combined organic phases were washed with bicarbonate and dried over Na_2SO_4. The solvents were evaporated, the remaining pale yellow solid was dissolved in 15 mL of DMF, a solution of 380 mg (2.35 mmol) of anhydrous $FeCl_3$ in 10 mL of DMF was added, and the solution was stirred at rt for 30 h. Then another 350 mg of $FeCl_3$ in 10 mL of DMF was added. After 12 h, the mixture was poured into water, the aqueous phase was extracted three times with $CHCl_3$, and the organic phase was washed with bicarbonate. After evaporation of the solvent, the remaining solid was chromatographed on alumina (CH_2Cl_2−hexane 2:1), yielding ca. 40 mg of a brown solid which was mainly the desired product. Purification by chromatron (CH_2Cl_2−hexane 1:1) yielded 40 mg (0.058 mmol, 36%) of **13** as an amorphous brown solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.44−7.42 (m, 4 H), 7.06−6.99 (m, 4 H), 6.35 (s, 1 H), 5.81 (s, 1 H), 5.78 (s, 1 H), 3.66 (t, 2H, J = 7.25 Hz), 3.34 (s, 3 H), 2.12 (s, 6 H), 2.09 (s, 6 H), 1.61−1.54 (m, 2 H), 1.49−1.41 (m, 2 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 183.61, 183.54, 151.96, 151.82, 147.54, 143.78, 143.73, 143.67, 136.65, 134.96, 134.34, 131.35, 126.06, 125.51, 125.49, 124.40, 124.35, 123.92, 123.71, 123.24, 115.89, 110.84, 110.41, 47.51, 47.23, 44.31, 31.71, 31.56, 31.13, 30.54, 29.67, 28.76, 28.25, 25.45, 11.21; HRMS (*m*/*z*) calcd for $C_{39}H_{34}N_2O_2S_4$ 690.1503, found 690.1486.

Compound 14. A 500 mg (0.50 mmol) portion of the MOM-derivative **12** was dissolved in a mixture of 120 mL of 4 N acetic acid, 120 mL of butyl acetate, and 20 mL of *n*-butanol. Then, 600 mg (5.45 mmol) of hydroquinone and 3 drops of concentrated HCl were added, and the mixture was heated to reflux for 24 h. Several drops of concentrated HCl were added, and the mixture was refluxed for a further 24 h. More HCl (10 drops) was then added and the mixture heated under reflux for another 96 h. The phases were separated, and the aqueous phase was extracted with $CHCl_3$. The organic phase was washed with bicarbonate and dried over Na_2SO_4. Evaporation of the solvents and filtration through alumina yielded 340 mg of a black solid, which was dissolved in 15 mL of DMF. A

solution of 1 g (6.17 mmol) of $FeCl_3$ in 5 mL of DMF was added. After 24 h, another 400 mg (2.47 mmol) of $FeCl_3$ was added and the mixture stirred for 15 h. The solution was poured into water and extracted with $CHCl_3$. The organic phase was washed with bicarbonate and dried over Na_2SO_4. The solvent was evaporated, and the remaining solid was filtered through alumina and then chromatographed three times on silica (chromatron) with CH_2Cl_2−hexane (1:1), yielding 40 mg (0.044 mmol, 9%) of the TTF-quinone **14** as a brown amorphous solid: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.44−7.41 (m, 4 H), 7.05−7.02 (m, 4 H), 6.36 (s, 1 H), 5.80 (s, 1 H), 5.77 (s, 1 H), 3.66−3.63 (m, 4H), 2.37−2.31 (m, 2 H), 2.12 (s, 6 H), 2.09 (s, 6 H), 1.61−1.54 (m, 2 H), 1.49−1.41 (m, 2 H), 1.26 (m, 28 H), 0.88 (t, 3 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 183.57, 151.99, 151.85, 147.55, 143.74, 143.68, 131.39, 126.00, 125.51, 124.41, 124.37, 123.35, 123.26, 110.94, 110.54, 47.53, 47.25, 44.84, 44.33, 31.91, 30.85, 30.56, 29.67, 29.55, 29.48, 29.35, 29.28, 28.79, 26.81, 25.49, 22.68; HRMS (*m*/*z*) calcd for $C_{54}H_{64}N_2O_2S_4$ 900.3851, found 900.3871.

Compound 15. Under a N_2 atmosphere in oven-dried glassware, 1.61 g (4.3 mmol) of the MOM-protected hydroquinone **1** was dissolved in 15 mL of dry THF, and the solution was cooled in an ice bath. Then 3 mL (5.1 mmol; 1.7 M in hexane) of *n*-butyllithium was added dropwise via a syringe and the red solution stirred at rt for 2 h. Then 2.0 mL (2.24 g, 6.36 mmol) of hexadecyl iodide was added. After 14 h of stirring at rt, the reaction mixture was poured into water and extracted with $CHCl_3$. The organic phase was washed with water and bicarbonate and dried over Na_2SO_4. After evaporating the solvent, the resulting brown oil was chromatographed on silica (CH_2Cl_2−hexane 1:1) to yield 1.91 g (3.19 mmol, 74%) of **15** as a pale green oil which solidifies after some weeks: mp 42−44 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.40−7.37 (m, 4 H), 7.01−6.96 (m, 4 H), 6.58 (s, 1 H), 5.84 (s, 1 H), 5.78 (s, 1 H), 5.18 (s, 2 H), 5.01 (s, 2 H), 3.71 (s, 3 H), 3.52 (s, 3 H), 2.51 (t, 2 H), 1.26−1.25 (m, 28 H), 0.90 (t, 3 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 148.44, 146.00, 145.64, 145.37, 139.43, 133.87, 133.42, 125.07, 125.03, 123.73, 123.63, 113.61, 100.40, 95.43, 57.40, 56.12, 48.91, 47.34, 31.92, 30.88, 30.51, 29.83, 29.68, 29.52, 29.35, 22.69, 14.12. Anal. Calcd for $C_{40}H_{54}O_4$: C, 80.22; H, 9.09. Found: C, 79.97; H, 8.99.

Compound 16. The MOM-protected derivative **15** (1.67 mmol) was dissolved in a 1:1 mixture of CH_3OH−THF, 3 drops of concentrated HCl was added, and the solution was refluxed for 14 h. The solvents were evaporated, and the remaining oil was dissolved in CH_2Cl_2, washed with water and bicarbonate, and dried over Na_2SO_4. After evaporation of the solvent, the red oil was dissolved in 25 mL of DMF and 3.0 g (11.1 mmol) of ferric chloride in 15 mL of DMF was added in one portion. After 3 h at rt, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic phase is washed with bicarbonate and dried (Na_2SO_4). After evaporation of the solvent, the remaining oil was chromatographed into silica (CH_2Cl_2−hexane 1:1), yielding 700 mg (1.38 mmol, 83%) of the quinone **16** as a red oil: ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.43−7.41 (m, 4 H), 7.05−7.00 (m, 4 H), 6.36 (s, 1 H), 5.80 (s, 1 H), 5.77 (s, 1 H), 2.35 (t, 2 H), 1.25−1.23 (m, 28 H), 0.87 (t, 3 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 183.90, 183.83, 152.00, 151.64, 148.69, 143.86, 143.79, 130.98, 125.48, 125.46, 125.08, 125.00, 124.37, 123.68, 47.55, 47.24, 31.92, 29.68, 29.64, 29.61, 29.59, 29.46, 29.35, 29.29, 29.00, 28.01, 22.68. Anal. Calcd for $C_{36}H_{44}O_2$: C, 84.99; H, 8.72. Found: C, 84.89; H, 8.74.

Dicyanoquinodiimine 18. Under N_2 in oven-dried glassware, 0.70 g (1.38 mmol) of the quinone **16** was dissolved in 20 mL of dry CH_2Cl_2. Then 7 mL (7 mmol) of $TiCl_4$ solution (0.1 M in CH_2Cl_2) was added via a syringe. The yellow solution became dark red. After 30 min, 1.6 mL (7 mmol) of TMS-carbodiimide was added dropwise via a syringe. After addition, the mixture was stirred at rt for 23 h. The red solution was poured onto ice, extracted with CH_2Cl_2, and dried over Na_2SO_4. The red oil was dissolved in a few milliters of CH_2Cl_2, and hexane was added. The gray-brown precipitate was filtered off, the solvent was evaporated, and the remaining red oil was dissolved in hexane and filtered again, yielding 430 mg (0.77 mmol, 56%) of a deep red amorphous solid. Chromatography on silica or alumina leads to decomposition of the compound: MS (EI) *m*/*z* 558 ($M^+ + 2H$). The deep red oil turns green/black after a few weeks.

Dicyanoquinodiimine 19. Under N_2 in oven-dried glassware, 290 mg (1.02 mmol) of the triptycene quinone **17** was dissolved in 24 mL of dry CH_2Cl_2. To the solution was added 4.8 mL (4.8 mmol) of a $TiCl_4$ solution (0.1 M in CH_2Cl_2) dropwise. After addition of the $TiCl_4$, the mixture was stirred for 30 min. Then, 1.4 mL (1.15 g, 6.17 mmol) of bis(trimethylsilyl)carbodiimide was added dropwise and the mixture stirred at rt for 21 h. The red solution was poured onto ice, extracted with CH_2Cl_2, and dried over Na_2SO_4. Recrystallization from CH_2Cl_2−hexane yielded 148 mg (0.45 mmol, 44%) of an intensely red microcrystalline compound: mp >300 °C; ^{1}H NMR (360 MHz, $CDCl_3$) δ 7.47−7.45 (m, 4 H), 7.21 (s, 2 H), 7.10−7.08 (m, 4 H), 6.00 (s, 2 H); ^{13}C NMR (93 MHz, $CDCl_3$) δ 170.92, 154.64, 142.60, 126.83, 126.18, 124.57, 113.35, 48.37.

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