Self-Assembly and Multistage Redox Chemistry of Strong Electron Acceptors on Metal Surfaces: Polynitrofluorenes on Gold and Platinum

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Nitrofluoren-9-one and nitrofluoren-9-dicyanomethylene electron acceptors **7**, **8**, and **11** functionalized with a terminal thioctic acid unit have been synthesized from 2,4,5,7-tetranitrofluorenone. The self-assembled monolayers (SAMs) of these compounds on gold, formed via gold–sulfur interaction, have been fully characterized by electrochemical, FTIR, ellipsometry, and contact angle measurements. Cyclic voltammetry of SAMs reveals two reversible single-electron reduction waves for fluorenone derivatives **7a**,**b** and **11**, and three single-electron reductions for the dicyanomethylene–fluorene **8b**, providing the first observation of a radical trianion species in SAMs. The tendency of the thioctic anchor to form multilayers via disulfide links is noted.

Introduction

Covalent binding of π-functional organic molecules to metal surfaces resulting in the formation of self-assembled monolayers (SAMs) has been a major focus of recent research in connection with molecular electronic devices (molecular diodes, switches, wires, memories, etc.),[1–3] electrochemical sensors,[4,5] electrode modification for OLEDs,[6] and photovoltaics.[7–9]

A number of moderate and strong electron donor molecules, including ferrocene,[10–12] tetrathiafulvalene[4b–d,13–17] (TTF, **1**) and its π-extended analogue,[18] oligothiophenes,[19–22] *N*-alkylcarbazole,[23] pyrene,[24] tetraalkylphenylene-*p*-diamine,[25] and porphyrin[24,26–28] de-

rivatives have been attached to gold surfaces. The ability of these monolayers to release electrons forming stable cationic states is detrimental for such applications as photocurrent generation, memory devices, switches, cation sensors, etc. (as all these processes include formation of ion radicals in the device operation process).

Significantly less is known about complimentary SAMs consisting of electron acceptor molecules. Most of the reported self-assembled π-electron acceptors possess only moderate electron affinity (E_{red} < −0.6 V vs Fc/Fc$^+$) viz. fullerene,[20,29–33] *p*-benzoquinone,[34,35] imide of naphthalene-1,4,5,8-tetracarbonic acid,[36] phthalocyanine,[37] and violo-

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Table 1. Redox Potentials[a] (vs Fc/Fc+) of Studied Electron Acceptors in Solution and SAMs

compound	media	E_{1red}	E_{2red}	E_{3red}	E_{4red}	E_{1ox}
			Solution			
2[25]	MeCN	−0.23	−0.75			
DTeF	MeCN	−0.19	−0.81	−1.47	−2.09	
TCNQ	MeCN	−0.19	−0.75			
4	MeCN	−0.57	−0.83	−1.73		
5b	MeCN	−0.84	−1.11			
6b	MeCN	−0.75	−1.06	−1.94		
6b	THF	−0.71	−1.12	−2.03		
7b	MeCN	−0.64	−0.95	−1.79		+0.69
8a	MeCN	−0.26	−0.84	−1.51	−2.09	∼+0.8 p.a.
8a	CH₂Cl₂	−0.27	−0.88	−1.53	−2.11 p.c.	+0.65
8b	MeCN	−0.29	−0.83	−1.53		+0.66
11	MeCN	−0.72	−1.11			+0.78 p.a.
13	CH₂Cl₂	−0.70	−0.97			+0.76 p.a
			Self-assembled monolayer			
2[25]	MeCN	−0.35	−0.74p.c.			
7a	THF	−0.69	−1.05			
7b	THF	−0.65	−0.98			
8a	THF	−0.30	−0.95			
8b	THF	−0.27	−0.94	−1.61		
11	THF	−0.74	−1.15			

[a] Standard potentials [$E = (E$p.a. $+ E$p.c.$)/2$] (p.a. = peak anodic, p.c. = peak cathodic) are given, unless otherwise stated.

gen derivatives.[1b,38,39] The only example of a strong electron acceptor used in the preparation of SAMs is tetracyanoquinodimethane (TCNQ) derivative **2**, reported by Frisbie et al.[25] This monolayer has been used for direct determination of charge-transfer complexation (using a tetraalkylphenylenediamine-covered AFM tip)[40] and for the construction of a molecular junction of **2** sandwiched between Ag and alkylthiol-covered Hg drop electrodes, which showed asymmetric current−voltage characteristics.[41] Although the mechanism for current rectification in this system is controversial,[42] molecular layers with such a low LUMO energy are certainly of interest for a number of applications in molecular electronics and surface science. One can also envisage the SAM-forming **2** as an intermediate toward analogues of the original Aviram−Ratner molecular rectifier TTF-TCNQ **3**. However, the relatively low stability of **2** and no easy way for further synthetic modification has prevented its widespread use in molecular electronics and related applications.

We have previously demonstrated that the polynitrofluorene electron acceptor moiety, by virtue of its very high electron affinity (cf. DTeF and TCNQ, Table 1) and

synthetic versatility, is a convenient building block for the construction of donor−acceptor diads with extremely low HOMO−LUMO gaps.[43] Molecular rectification has been recently established in Langmuir−Blodgett monolayers of nitrofluorene−TTF diad.[44] In the present paper, we report the immobilization of nitrofluorene electron acceptors on gold and platinum electrodes, their functionalization and characterization of the corresponding SAMs. We also address a problem of polymerization and multilayer formation in thioctic esters, which are reagents widely used for self-assembly on gold.
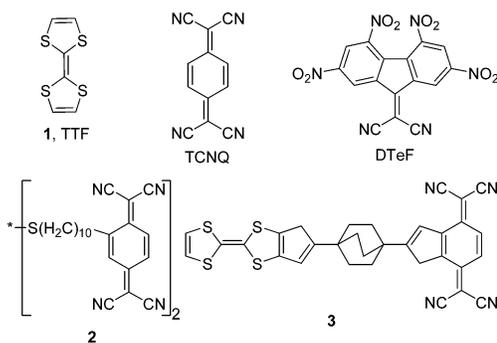
Results and Discussion

Synthesis. The synthesis of electron acceptor nitrofluorene synthons was achieved by regioselective nucleophilic substitution of a nitro group with alkanethiol reagents[45] (Scheme 1). The readily available tetranitrofluorenone **4** reacted smoothly with 2-mercaptoethanol or 3-mercaptopropanol in the presence of NaHCO₃, affording sulfides **5a** and **5b**. The electron-donating influence of the alkylthio substituent in **5** (which reduces the electron affinity of the molecule) can be eliminated by converting it into an electron-withdrawing sulfonic group via oxidation with hydrogen peroxide (compounds **6a** and **6b**). The anchoring disulfide moiety was attached to **6** by dicyclohexylcarbodiimide (DCC) promoted esterification with thioctic acid, giving compounds **7**. A unique feature of fluorene acceptors is the possibility of converting chemically stable fluorene-9-one derivatives into the stronger electron-accepting fluorene-9-dicyanomethylene derivatives under very mild conditions. Thus, treating a solution of **7** in DMF with malononitrile gave acceptors **8** in good yield.

A second functionality, which could conceivably be used for coupling the fluorene acceptors with other electronically active moieties (such as TTF), was introduced into **6a** by selective substitution of a second nitro group in position 7 to yield sulfide−sulfone **9**. The subsequent sequence of H₂O₂ oxidation and esterification with thioctic acid resulted in the formation of sulfone **10** and, finally, the thiotic ester **11** (Scheme 1). The terminal *tert*-C₄H₉ ester functionality was hydrolyzed selectively with a catalytic amount of CF₃CO₂H, affording the acid **12**. Although the

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(42) The rectification in this molecule, lacking an obvious D−A structure, was attributed to the asymmetric position of the redox center in the metal/insulator/metal junction. However, assembly of the junction under a solution of alkylthiol could result in substitution of a cyano group in the TCNQ with a donor alkylsulfide group, affording a covalent D−π−A structure. Furthermore, using a disulfide binding on one electrode and a thiol binding on the other can also result in asymmetric conductance.[46]
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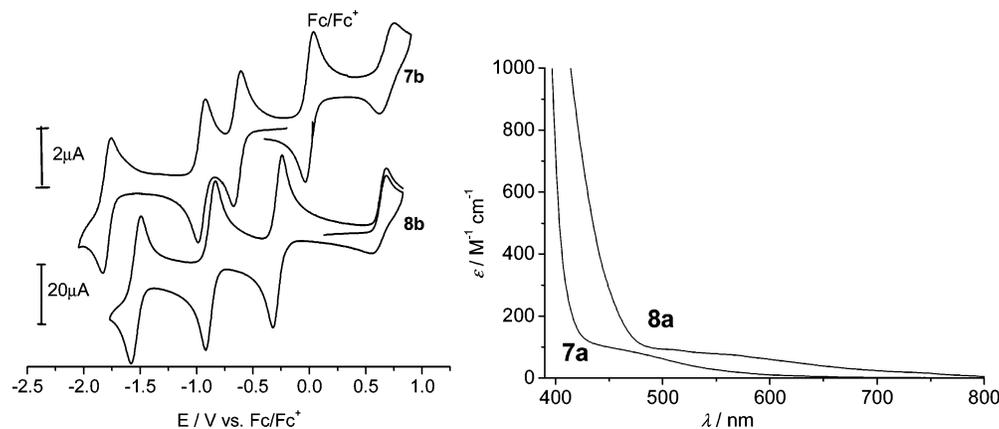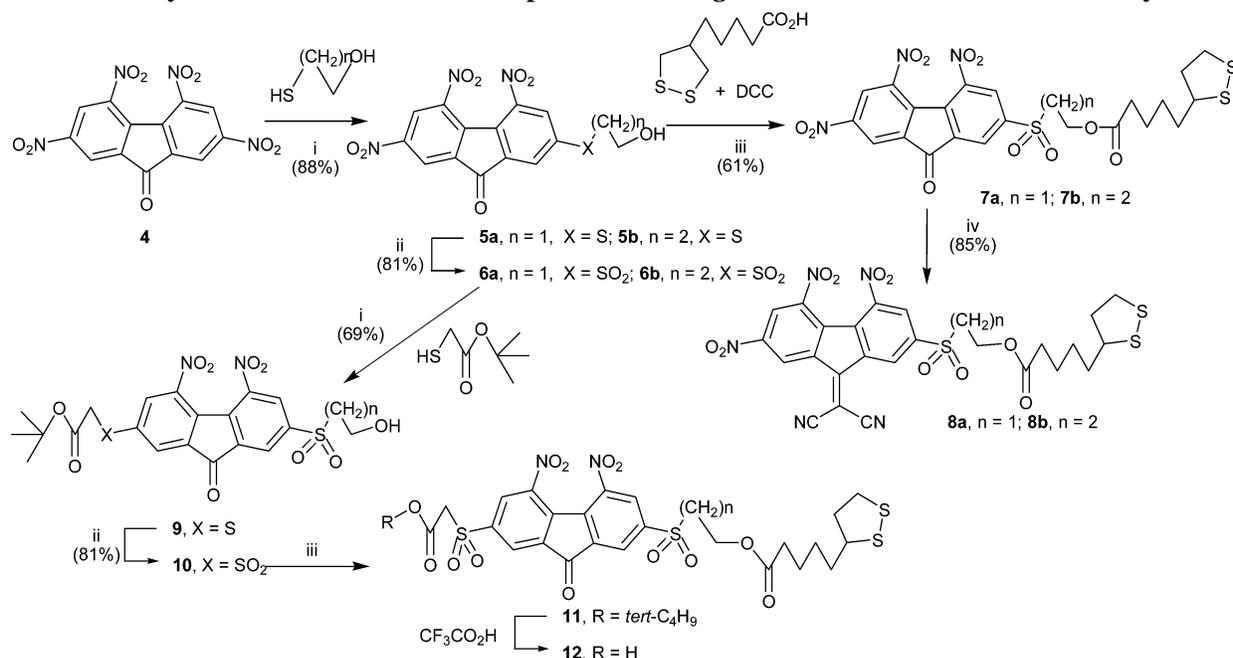
Figure 1. Cyclic voltammograms of **7b** in 0.1 M Bu$_4$PF$_6$/MeCN and **8b** in 0.1 M Bu$_4$PF$_6$/CH$_2$Cl$_2$ (left). Electronic absorption spectra of compounds **7a** and **8a** in acetone solution (right).

Scheme 1.   Synthesis of Nitrofluorene Acceptors Containing Disulfide Anchors for Self-Assembly on Au

acid **12** appeared to be metastable in the bulk, presumably due to acid-promoted polymerization of the dithiolidene cycle of the thioctic group, this approach can be used for post-functionalization of the SAM of **11**.[46]

Formation of SAMs. The disulfide functionality in fluorenes **7**, **8**, and **11** enables their covalent attachment to gold and platinum metal surfaces. Two types of metal substrates were used in these studies; polished polycrystalline Au (or Pt) disk electrodes (precleaned by immersing into hot 1:2 H$_2$O$_2$/H$_2$SO$_4$) were used for electrochemical studies, and large-area Au substrates (freshly prepared by thermal vacuum evaporation of gold onto microscope slides covered with a Cr adlayer) were used for spectroscopy, ellipsometry, and contact angle studies. Self-assembled monolayers (SAMs) have been fabricated by immersing the above substrates into ca. 10^{-3} M MeCN solutions of acceptors **7**, **8**, or **11** (in the dark) for 1−3 days. After this period, the metal substrates were thoroughly washed by rinsing with CH$_2$Cl$_2$ and soaking (followed by sonication for a few seconds) in MeCN and CH$_2$Cl$_2$ solvents (HPLC grade), dried in vacuo, and stored under Ar. It should be noted that formation of SAMs by

these fluorene acceptors is more hindered in comparison with other thioctic esters containing a tetrathiafulvalene redox unit (as determined by competitive absorption; see Supporting Information). On the other hand, prolonged exposure, particularly when combined with increased solution concentration (due to evaporation), results in the formation of multilayers of the corresponding compounds, which is manifested in increased film thicknesses and very strong electrochemical reduction signals (see below). In the case of self-assembly of **8a** on a polycrystalline gold substrate for 4 weeks (in saturated concentration and with partial light exposure), the formation of a visible film of the material, whose electrochemical properties resembled that of electropolymerized **8a**, was observed. The SAM of **11** could be hydrolyzed into acid **12** by overnight exposure to saturated vapor of trifluoroacetic acid.

Electrochemical and Spectral Studies in Solution. The electrochemical behavior of new nitrofluorene derivatives **5**−**8**, **11**, and **12** has been studied in solution by cyclic voltammetry (CV). Depending on the substituents present, the CVs reveal from two (for **5**) to four (for **8**) reversible single-electron reduction waves (Figure 1, Table 1). Comparing the reduction potentials of TCNQ and the strongest acceptor of the fluorene series (DTeF) reveals

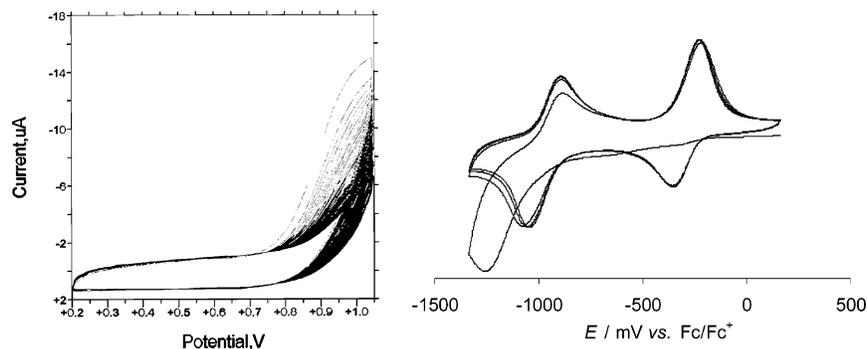(46) Kondratenko, M.; Perepichka, D. F. unpublished.

Figure 2. Electrochemical polymerization of **8a** on GCE electrode in 0.2 M Bu_4NPF_6/CH_2Cl_2 (left) and the CV of the film of poly-**8a** in fresh electrolyte solution (right).
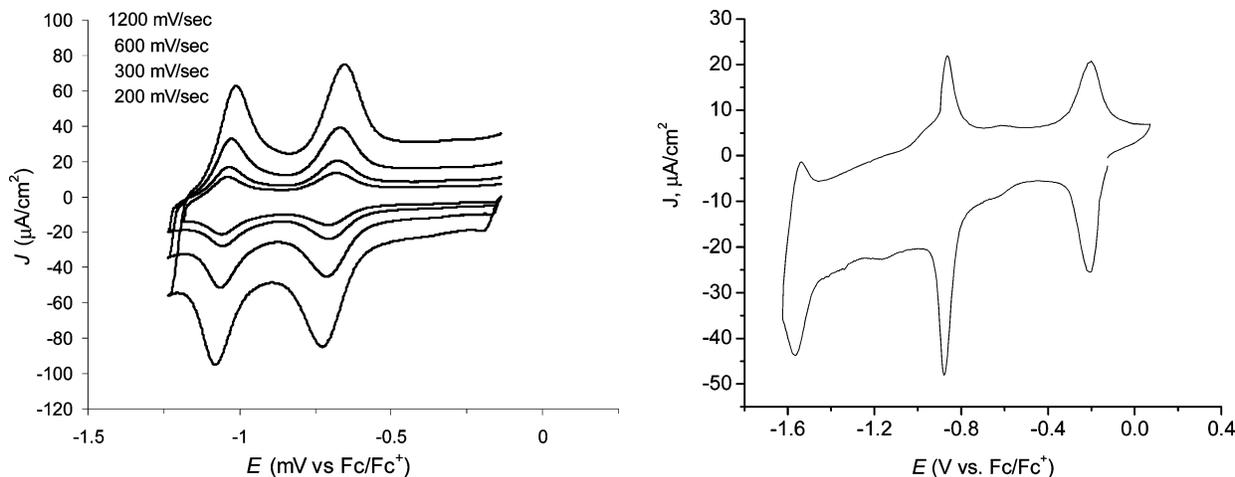

Figure 3. Cyclic voltammograms of a SAM of **7a** at different scan rates (left) and of a SAMs of **8b** (right); electrolyte 0.2 M Bu_4NPF_6 in THF.

that both compounds are equally strong electron acceptors. As seen from Table 1, substitution of a nitro group in fluorene **4** with an alkylsulfanyl moiety results in a significant decrease of the electron affinity by >250 mV (cf. E_{1red} for **4** and **5b**). A further oxidation of **5** into the sulfonyl derivatives **6** partially restores the electron acceptor properties, so the net effect of replacing a nitro group with an alkylsulfonyl group is a decrease in the electron affinity of about 70−180 mV with each group replaced (cf. **4** → **7** → **11**). The introduction of a dicyanomethylene fragment shifts the first reduction wave to less negative potentials by >400 mV, rendering **8** as strong an electron acceptor as TCNQ derivative **2** (with similar disulfide functionality).

In the positive direction, one partially reversible single-electron oxidation process was observed for compounds **7**, **8**, **11**, and **13**, revealing the electron donor properties of the dithiolane moiety.[18] Accordingly, a donor−acceptor interaction between the 1,2-dithiolane and nitrofluorene moieties (presumably through-space) is manifested in a weak charge-transfer band in the UV−vis absorption spectra.[47] The significant bathochromic shift of this band for compound **8** (∼550 nm) compared to that for **7** (∼450 nm) is in agreement with the stronger acceptor properties of the fluorene nucleus in the former.

Notably, multiple scanning of solutions of **8a** to positive potentials beyond the oxidation potential (at a scan rate of 20 mV/s) resulted in deposition of an insoluble white-creamy film on the glassy carbon electrode (GCE) surface. The CV of the film, carefully washed with the solvent, in

pure electrolyte, retains the well-defined reduction waves of the fluorene−dicyanomethylene moiety of **8a** (Figure 2). The significant potential shift during the first CV scan can be attributed to penetration of ions into a relatively thick film, and highly reproducible electrochemical behavior was observed during the subsequent scans. Although no definitive evidence of the structure of this product was obtained, we speculate that oxidation of the dithiolane fragment results in ring-opening polymerization, giving the insoluble poly(propylenedisulfide) derivative of **8a**. Indeed, ring-opening polymerization of the dithiolane fragment seems to be a common feature of the thioctic anchor;[48] the signs of such polymerization were observed occasionally during the self-assembly process (see below). Furthermore, a thioctic ester of fluorenone-9-oxime (**13**), initially prepared by us for self-assembly, had to be abandoned due to spontaneous polymerization occurring in $CDCl_3$ solution. The additional instability of **13** could be due to intermolecular reactions between the oxime ester and dithiolane functionalities in electrophile−nucleophile or radical processes.

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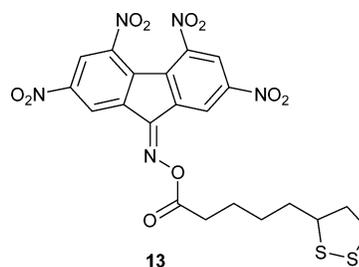
(47) The intramolecular character of this band was corroborated by its linear concentration dependence.
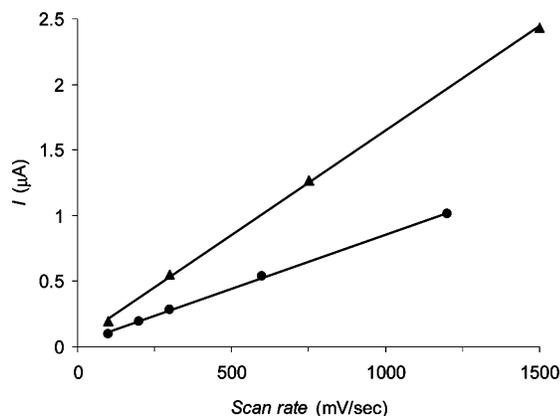
Figure 4. Dependence of the first reduction peak current on the scan rate for SAM of **7a** (circles) and **8a** (triangles).

Electrochemistry of SAMs. Multi-redox behavior has been also observed in the SAMs of the fluorenones; two reversible single-electron reduction waves have been detected for derivatives (**7a,b** and **11**), and even three single-electron reductions were observed for the di-cyanomethylene−fluorene (**8b**) (Table 1, Figure 3). It should be noted that the formation of multianionic redox species should be hindered in monolayers, as compared to solution, due to higher Coulombic repulsion energy. The high negative potentials required for multielectron reduction may result in reductive desorption of the molecule (as RS⁻).[49] Thus, for SAMs of TCNQ derivative **2**, only the first reduction wave was reversible.[25] Therefore, the sequential and reversible accepting of three electrons by a monolayer of **8b** within a readily achievable potential window is remarkable. To the best of our knowledge, it presents the first observation of a radical trianion species in SAMs.[50] The reduction potentials of the SAMs and their dependence on structural variations are very similar to those obtained in solution (Table 1). The anodic-to-cathodic peak separation in the CVs of the SAMs at lower scan rates ($\leq$ 100 mV/s) were less than 10 mV, and the peak current increased linearly with the scan rate, thus revealing the surface-confined nature of the process (Figure 4).

The surface coverage (Γ), calculated from the CV peak area (and geometrical area of the electrode), varied significantly from sample to sample, with no clear dependence on the exposure time. The highest Γ, obtained after 1−2 days of self-assembly, was $\sim$3.5 $\times$ 10⁻¹⁰ mol/cm², with typical values being in the range of (1−2) $\times$ 10⁻¹⁰ mol/cm², which correspond to molecular areas of $\sim$0.5 nm² and 0.8−1.5 nm², respectively. These values are comparable to those obtained for SAMs from other electrochemically active molecules (e.g., 3−3.5 $\times$ 10⁻¹⁰ mol/cm² for TCNQ **2**, 2.1 $\times$ 10⁻¹⁰ mol/cm² for TTF−thioctic ester [4c]). A molecular area of $\sim$0.5 nm² should be expected for dense-packed "stand-up" monolayers of molecules of this size. Generally, it was more difficult to form dense monolayers with dicyanomethylene derivatives **8** than with fluorenones **7** and **11**. Self-assembly was also observed on Pt electrodes, although the typical surface coverage was several times lower on Pt (see Supporting

Information). Prolonged exposure (for a week or more) often (but not always) resulted in significantly increased coverage of $\sim$5 $\times$ 10⁻¹⁰ to 5 $\times$ 10⁻⁹ mol/cm². This coverage is not compatible with a monolayer model considering the size of the molecule, and a multilayer structure with disulfide bridges was assumed (see also Ellipsometry section).

The SAMs possess good electrochemical stability; as judged by a gradual decrease in the current, less than 10% desorption (decomposition) was observed during 100 scans over the range of 0 and −0.75 V (formation of the radical anion; see Supporting Information). Predictably, cycling to more negative potentials (formation of the dianion, and even more, the trianion species) resulted in more rapid desorption/decomposition of the SAMs ($\sim$8% for 20 cycles between 0 and −1.1 V at 600 mV/s for **7a**; $\sim$24% for 30 cycles between +0.2 and −1.05 V at 200 mV/s for **8a**; $\sim$32% for 50 cycles between −0.2 and −1.1 V at 200 mV/s for **11**).

Reflectance−Absorbance Infrared Spectroscopy (RAIRS) of SAMs. The strong infrared absorption features of the compounds have allowed facile analysis of their SAMs even at low coverage. Grazing angle FTIR spectroscopy of the monolayers on gold confirmed the preservation of their molecular structures during the self-assembly process (Figure 5). The characteristic C=O vibration was observed in all the SAMs as a strong band near 1740 cm⁻¹ (Table 2). This band includes vibrations of the carboxylic (ester) group and, for compounds **7a,b** and **11**, also fluorenone C=O vibrations. The carbonyl peak in **11**, having two ester groups, is stronger in comparison to that of **7** and **8**, which have only one ester carbonyl. The ester C−O single bond vibration is found around 1100 cm⁻¹. The fluorene moiety is evidenced by the strong nitro group features around 1552 (asymmetric) and 1344 (symmetric) cm⁻¹, as well as by the characteristic sulfone group vibrations at 1363 (asymmetric) and 1166 cm⁻¹ (symmetric). Interestingly, the vibrations of the cyano groups, typically at $\sim$2200 cm⁻¹, are not seen in the spectra of SAMs of **8a** and **8b**, although their presence in the structure is clearly supported by the electrochemical data. This vibration is revealed as a very weak band at 2234 cm⁻¹ in powder samples of these compounds (Figure 5, left) and is not observable in solution. The C−H vibrations in all of the studied SAMs are quite weak. The observed peaks at ca. 3080 cm⁻¹ are attributed to aromatic C−H vibrations, whereas the peaks at 2850−2937 cm⁻¹ are symmetric/asymmetric vibrations within the methylene groups. A vibration at 2980 cm⁻¹ observed only for **11** is characteristic of the CH₃ group (of the *tert*-butyl ester).

The latter peak vanishes during hydrolysis of SAM-**11** (affording the acid **12**). Due to the presence of several C=O bonds in the structure and the resulting large bandwidth, the shift of the carbonyl vibration during the hydrolysis (COO-*tert*-C₄H₉ → COOH) is not obvious. However, the transformation is also evidenced by a significant change in the ratio of the intensity of the sulfo/nitro group peaks at 1364 and 1339 cm⁻¹ (from 0.51 $\pm$ 0.17 for **11** to 1.5 $\pm$ 0.5 for **12**; see Supporting Information). This can be rationalized by an expected intramolecular hydrogen bonding between the carboxylic acid proton and the oxygen of the sulfonyl group (in a six-membered ring).

Ellipsometry and Contact Angle Measurements. To shed light on the structure of monolayers, we undertook ellipsometry studies and contact angle measurements. After 24 h soaking of evaporated gold substrates in solutions of **7b**, **8b**, and **11** in MeCN, their reflectivity suggested an overlayer of organic molecules with thick-

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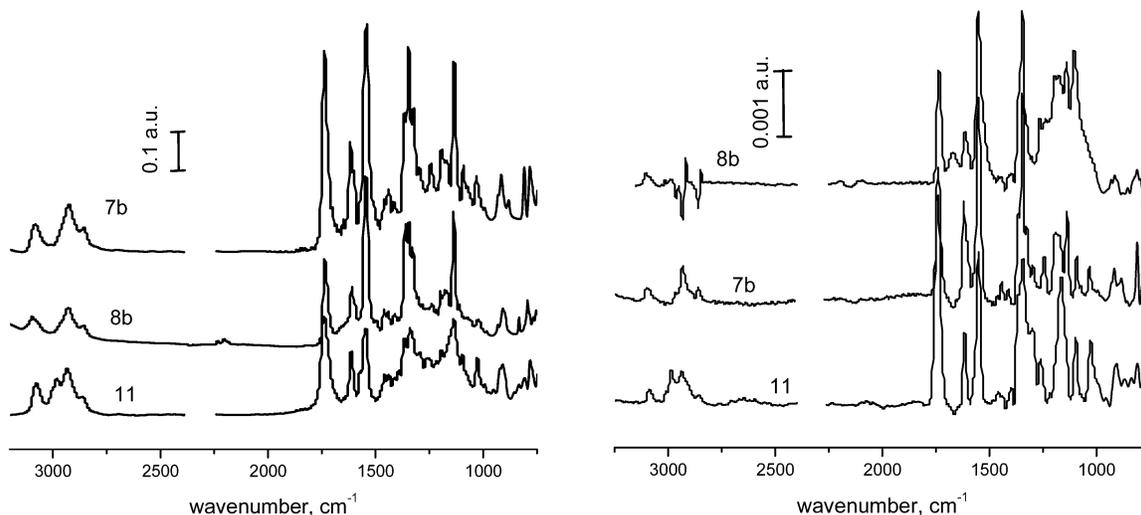
Figure 5. FTIR spectra of compounds **7b**, **8b**, and **11** in bulk (in KBr, left) and in SAMs on gold (grazing angle spectra, right).

Table 2. Assignment of the Major IR Absorption Peaks of Compounds 7b, 8b, and 11 in SAMs

peak assignment	7a (cm^{-1})	7b (cm^{-1})	8a (cm^{-1})	8b (cm^{-1})	11 (cm^{-1})
CH aromatic		3079	3077	3078	3088
CH$_3$					2980
ν_{as}/ν_{sym} (CH$_2$)	2929/2849	2922/2851	2930/2859	2926/2856	2937/2857
ν(C=O)	1742	1740	1741	1738	1742
aromatic ν(C=C)	1615	1618	1612	1617	1617
ν_{as}/ν_{sym} (NO$_2$)	1539/1346	1552/1344	1553/1346	1552/1344	1552/1344
ν_{as}/ν_{sym} (S=O)	1363/1134	1364/1161	1362/1143	1362/1166	1363/1166
ν(C−O)	1034	1092	1110	1105	1102

nesses of 1.3 ± 0.2, 1.3 ± 0.1, and 1.1 ± 0.3 nm, respectively. This thickness is significantly lower than the molecular length (2.3 nm for **7b/8b** and 2.6 nm for **11**, in fully extended conformations, Figure 6) and suggests a highly tilted and, likely, quite disordered orientation of the molecules. The static contact angle measurements indicate relatively hydrophobic surfaces for all the monolayers (see Supporting Information). The most hydrophobic of these derivatives was **11**, terminated with a *tert*-butoxycarbonyl group (monolayer static contact angle of $76 \pm 3°$), and somewhat lower contact angles were revealed by SAMs of **7b** ($67 \pm 1°$) and **8b** ($70 \pm 2°$). As expected, hydrolysis of the *tert*-butoxycarbonyl group by exposure of the SAM of **11** to triflic acid vapor for 12 h overnight decreased the contact angle by ca. 15°.

As we have already mentioned, prolonged self-assembly of fluorene−thioctic esters on gold results in the formation of multilayers; the film thickness of 3.9 ± 0.1 nm for **7b** and **8b** and 3.6 ± 0.2 nm for **11**, which is ca. twice the value expected for a monolayer, was found by ellipsometry after 1 week of self-assembly. The increased film thickness is accompanied by an increase of the contact angle (by approximately 10°). Most likely, the molecules are bound in the multilayer by a polymeric disulfide bond.
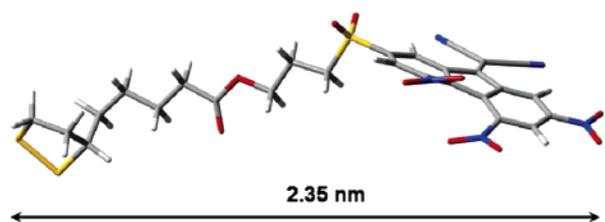

Figure 6. Molecular model of **8b**, calculated at the B3LYP/3-21G* level.

Conclusions

Nitrofluorene derivatives have been successfully employed for the preparation of SAMs for the first time. By exploiting the synthetic versatility of tetranitrofluorenone, a series of derivatives has been obtained, which retain strong electron acceptor ability and can be covalently attached to a gold electrode. The resulting SAMs possess unique electrochemical characteristics. The radical anion, dianion, and radical trianion redox states can be reversibly formed in these monolayers. The good electrochemical stability of the SAMs, especially to repeated cycling in the potential range between 0 and −0.75 V, augurs well for more advanced applications of nitrofluorene-derived acceptors. At the same time, the observed tendency of the thioctic anchor to form multilayers via disulfide links could limit the development of these specific compounds (as well as other previously reported molecules with thioctic functionality) in molecular electronics.

Experimental Section

Cyclic Voltammetry. CV experiments were performed on a Princeton EG&G PAR273A potentiostat under nitrogen, with a three-electrode cell in CH$_2$Cl$_2$, MeCN, or THF as solvent using 0.2 M Bu$_4$NPF$_6$ as an electrolyte, at different scan rates (20−1500 mV/s). Platinum wire and Ag/Ag$^+$ electrodes were used as the counter and reference electrodes, respectively. The oxidation of ferrocene under our conditions occurs at $E^{1/2}_{ox} = +0.20$ V vs Ag/Ag$^+$ (in CH$_2$Cl$_2$), $E^{1/2}_{ox} = +0.135$ V vs Ag/Ag$^+$ (in THF), and $E^{1/2}_{ox} = +0.08$ V vs Ag/Ag$^+$ (in MeCN). A glassy carbon electrode (BAS, $d = 2.5$ mm) was used as a working electrode for studying the solution electrochemistry, and gold disk electrodes (BAS, $d = 1.6$ mm and homemade, $d = 6.0$ mm) with self-assembled monolayers were used to record the CVs of SAMs. The thiol monolayer was self-assembled on gold electrodes as described above.

FTIR Spectroscopy. FTIR spectra were recorded with a Nexus 670 FTIR spectrometer (Thermo-Nicolet, Madison, WI)

equipped with a liquid-N_2-cooled MCT-II detector with spectral resolution of 4 cm^{-1}. Transmission mode was used for bulk samples (in KBr pellets), and grazing angle (80°) reflectance–absorbance mode (RAIRS), using grazing angle Smart-SAGA accessory, was employed for monolayers on gold substrates. The measurements were done in an atmosphere of dried, CO_2-free air, and an identical gold-covered slide (prepared in the same Au evaporation run, stored under methanol and dried in vacuo before use) was used to record a background spectrum.

Ellipsometry. SAM thicknesses were measured on a Sentech SE 400 ellipsometer equipped with a He–Ne laser (λ = 632.8 nm) at an incidence angle of 70° with respect to the surface normal. Optical constants of the gold-coated substrates were measured using a bare gold slide as described earlier.[21] Both reference sample and SAMs were cleaned by soaking in HPLC dichloromethane and dried immediately before the measurements. All the layer thicknesses reported were calculated after averaging over 10–20 measurements. The refractive index of the monolayer was assumed to be 1.45.

Contact Angle Measurements. The advancing, receding, and static contact angles of deionized water (>18 MΩ cm) were measured on a homemade contact angle goniometer equipped with a video camera and averaged over 3–5 spots. The advancing angles are produced as fluid is added to the drop and the receding angles as fluid is withdrawn. The "clean" Au surface produced a static contact angle of 73 ± 3°, which is believed to be due to hydrocarbon impurities absorbed from air.[51]

2-(2-Hydroxyethylsulfanyl)-4,5,7-trinitrofluorene-9-one (5a). 2-Mercaptoethanol (2.0 mL, 28 mmol) was added to a solution of fluorenone **4** (3.6 g, 10 mmol) in MeCN (400 mL) followed by addition of well-ground $NaHCO_3$ (2.78 g, 33 mmol). The resulting brown–orange reaction mixture was stirred at 20 °C for 12 h, and the inorganic salts were filtered off. The filtrate was concentrated in vacuo to 40 mL, and hot 2-propanol (120 mL) was added. The orange precipitate which formed on cooling was filtered off and washed with 2-propanol to give sulfide **5a** (3.4 g, 88%): mp 190–195 °C; ^{1}H NMR (200 MHz; acetone-d_6) δ = 8.93 (1H, br), 8.70 (1H, d, J = 2 Hz), 8.17 (1H, br), 8.11 (1H, br), 4.34 (1H, br, OH), 3.92 (2H, m), 3.47 (2H, t, J = 6 Hz); IR (KBr) ν = 1743 (C=O), 1616, 1539, 1348, 1134, 839 cm^{-1}; MS (EI) m/z 391 (M$^+$, 27%), 149 (100%). Anal. Calcd for $C_{15}H_9N_3O_8S$: C, 46.04; H, 2.32; N, 10.74. Found: C, 45.97; H, 2.25; N, 10.99.

2-(2-Hydroxypropylsulfanyl)-4,5,7-trinitrofluorene-9-one (5b). 3-Mercaptopropanol (1.5 mL, 17.5 mmol) was added to a solution of fluorenone **4** (5.0 g, 14 mmol) in MeCN (150 mL) followed by well-ground $NaHCO_3$ (3.5 g, 42 mmol), which resulted in a brown colorization. The reaction mixture was stirred at 20 °C for 12 h, and the inorganic salts were filtered off. The filtrate was concentrated in vacuo to 10 mL, and hot 2-propanol (100 mL) was added. The red precipitate which formed on cooling was filtered off and washed with 2-propanol and methanol to give sulfide **5b** (4.81 g, 86%): mp 157–159 °C; ^{1}H NMR (300 MHz; acetone-d_6) δ = 8.93 (1H, d, J = 2.1 Hz), 8.69 (1H, d, J = 2.1 Hz), 8.11 (1H, d, J = 1.86 Hz), 8.05 (1H, d, J = 1.83 Hz), 3.88 (1H, t, J = 5.5 Hz, OH), 3.74 (3H), 3.42 (3H). Anal. Calcd for $C_{16}H_{11}N_3O_8S$: C, 47.41; H, 2.74; N, 10.37. Found: C, 47.39; H, 2.70; N, 10.49.

2-(2-Hydroxyethylsulfonyl)-4,5,7-trinitrofluorene-9-one (6a). Hydrogen peroxide (7 mL, excess; 33 wt % aqueous solution) was added to a hot solution of sulfide **5a** (3.4 g, 8.8 mmol) in AcOH, and the reaction solution was stirred at 65 °C for 6 h, which resulted in a change from deep-orange to pale-yellow color. Then, hot water (120 mL) was added, and the pale-yellow precipitate which formed on cooling was filtered off and washed with water, affording sulfone **6a** (2.96 g, 81%): mp 209–213 °C; ^{1}H NMR (300 MHz; acetone-d_6) δ = 9.04 (1H, d, J = 2 Hz), 8.85 (1H, d, J = 2 Hz), 8.75 (1H, d, J = 2 Hz), 8.63 (1H, d, J = 2 Hz), 4.19 (1H, t, J = 5.5 Hz, OH), 4.06 (2H, q, J = 5.5 Hz), 3.77 (2H, t, J = 5.5 Hz); IR (KBr) ν = 1743 (C=O), 1616, 1539, 1348, 1319, 1134, 1060, 839 cm^{-1}; MS (EI) m/z 423 (M$^+$, 15%), 405 ([M – H$_2$O]$^+$, 22%), 380 (100%). Anal. Calcd for $C_{15}H_9N_3O_{10}S$: C, 42.56; H, 2.14; N, 9.93. Found: C, 42.42; H, 2.10; N, 9.91.

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2-(2-Hydroxypropylsulfonyl)-4,5,7-trinitrofluorene-9-one (6b). Hydrogen peroxide (10 mL, excess; 33 wt % aqueous solution) was added to a hot solution of sulfide **5b** (4.35 g, 10.74 mmol) in AcOH, and the reaction solution was stirred at 50–60 °C for 3 h, which resulted in a change from deep-red to yellow color. The yellow precipitate which formed on cooling was filtered off and washed with 2-propanol and methanol, affording sulfone **6b** (3 g, 70%): mp 196–199 °C; ^{1}H NMR (300 MHz; acetone-d_6) δ = 9.08 (1H, d, J = 2 Hz), 8.88 (1H, d, J = 2 Hz), 8.77 (1H, d, J = 2 Hz), 8.65 (1H, d, J = 2 Hz), 3.85 (1H, t, J = 5.5 Hz, OH), 3.6–3.7 (6H, m). Anal. Calcd for $C_{16}H_{11}N_3O_{10}S$: C, 43.94; H, 2.54; N, 9.61. Found: C, 43.98; H, 2.54; N, 9.49.

2-(2-Hydroxyethylsulfonyl)-4,5,7-trinitrofluorene-9-one thioctic ester (7a). A solution of freshly distilled DCC (126 mg, 0.61 mmol) in dry CH_2Cl_2 was added dropwise to a solution of (±)-thioctic acid (96 mg, 0.47 mmol) in CH_2Cl_2 (5 mL) at 0 °C, and the reaction mixture was stirred at 20 °C for 1 h after which period 4-(dimethylamino)pyridine (7 mg) and sulfone **6a** (170 mg, 0.41 mmol) were added in one portion. The reaction mixture was stirred for 48 h at 20 °C, then filtered from the formed dicyclohexylurea, evaporated, and chromatographed on silica (eluting with CH_2Cl_2–ethyl acetate 20:1 v/v). The brown–violet fraction was evaporated; the oily residue was triturated with MeOH, decanted, and dried in vacuo to give compound **7a** (150 mg, 61%) as a brown powder: mp 78–83 °C; ^{1}H NMR (200 MHz; CDCl$_3$) δ = 9.04 (1H, d, J = 2 Hz), 8.90 (1H, d, J = 2 Hz), 8.73 (1H, d, J = 2 Hz), 8.64 (1H, d, J = 2 Hz), 4.56 (2H, t, J = 5.5 Hz), 3.62 (2H, t, J = 5.5 Hz), 3.55–3.38 (1H, m), 3.21–2.99 (2H, m), 2.51–2.32 (1H, m), 2.15 (2H, t, J = 7.5 Hz), 1.93–1.74 (1H, m), 1.70–1.44 (4H, m), 1.44–1.24 (2H, m); IR (KBr) ν = 1739 (C=O), 1617, 1544, 1345, 1143 cm^{-1}; MS (EI) m/z 611 (88%), 123 (100%). Anal. Calcd for $C_{23}H_{21}N_3O_{11}S_3$: C, 45.17; H, 3.46; N, 6.87. Found: C, 45.29; H, 3.48; N, 6.74.

2-(2-Hydroxypropylsulfonyl)-4,5,7-trinitrofluorene-9-one thioctic ester (7b). A solution of DCC (230 mg, 1.15 mmol) in dry CH_2Cl_2 was added to a solution of thioctic acid (177 mg, 0.86 mmol) in CH_2Cl_2 (5 mL) at 0 °C, and the reaction mixture was stirred at 20 °C for 1 h after which period 4-(dimethylamino)-pyridine (4.3 mg) and sulfone **6b** (300 mg, 0.69 mmol) were added in one portion. The reaction mixture was stirred for 60 h at 20 °C, then filtered from the formed dicyclohexylurea, evaporated, and chromatographed on silica (eluting with CH_2Cl_2–ethyl acetate 5:1 v/v). The brown–violet fraction was evaporated; the oily residue was triturated with MeOH, decanted, and dried in vacuo to give compound **7b** (250 mg, 58%) as a brown powder: mp 68–71 °C; ^{1}H NMR (400 MHz; CDCl$_3$) δ = 9.05 (1H, d, J = 2 Hz), 8.86 (1H, d, J = 2 Hz), 8.75 (1H, d, J = 2 Hz), 8.63 (1H, d, J = 2 Hz), 4.18 (2H, t, J = 6.28 Hz), 3.69 (2H, t, J = 7.88 Hz), 3.57 (1H), 3.23–3.05 (2H), 2.46 (1H), 2.3 (2H, t, J = 7.34 Hz), 2.14 (2H), 1.92–1.84 (1H, m), 1.65–1.53 (4H, m); IR (KBr) ν = 1736 (C=O), 1617, 1541(NO$_2$), 1364 (S=O), 1135 cm^{-1}. Anal. Calcd for $C_{24}H_{23}N_3O_{11}S_3$: C, 46.07; H, 3.71; N, 6.72. Found: C, 46.32; H, 3.73; N, 6.52.

2-(2-Hydroxyethylsulfonyl)-4,5,7-trinitrofluorenylidene-9-dicyanomethylene thioctic ester (8a). Fluorenone **7** (115 mg, 0.188 mmol) and malononitrile (100 mg, 1.52 mmol) were stirred in DMF (0.4 mL) at 20 °C for 12 h, then diluted with MeOH (2 mL), and the resulting precipitate was filtered off and washed with MeOH. The dark-green solid was redissolved in hot acetone (1 mL), diluted with MeOH (1.5 mL), and left to crystallize at 0 °C, yielding dicyanomethylene **8a** (105 mg, 85%) as a green powder: mp 180–182 °C; ^{1}H NMR (200 MHz; acetone-d_6) δ = 9.75 (1H, br s), 9.48 (1H, br s), 9.8–8.2 (2H, br), 4.55 (2H, t, J = 5.5 Hz), 4.00 (2H, t, J = 5.5 Hz), 3.56–3.40 (1H, m), 3.23–3.00 (2H, m), 2.51–2.13 (1H, m), 2.11 (2H, t, J = 7.5 Hz), 1.91–1.72 (1H, m), 1.70–1.18 (6H, m); IR (KBr) ν = 2234w (C≡N), 1734 (C=O), 1609, 1541, 1341, 1137 cm^{-1}; MS (EI) m/z 659 (57%), 407 (100%). Anal. Calcd for $C_{26}H_{21}N_5O_{10}S_3$: C, 47.34; H, 3.21; N, 10.26. Found: C, 47.07; H, 3.13; N, 10.30.

2-(2-Hydroxypropylsulfonyl)-4,5,7-trinitrofluorenylidene-9-dicyanomethylene thioctic ester (8b). Fluorenone **7b** (50 mg, 0.08 mmol) and malononitrile (6.86 mg, 0.1 mmol) were stirred in DMF (2 mL) at 20 °C for 6 h, then the resulting precipitate was filtered off and washed with MeOH, yielding dicyanomethylene **8b** (40 mg, 80%) as a dark-green powder: mp 123–126 °C; IR (KBr) ν = 2234 (C≡N), 1736 (C=O), 1611, 1553

(NO$_2$), 1362(S=O), 1137 cm^{-1}; ^{1}H NMR (300 MHz; acetone-d_6) δ = 9.72 (1H, s), 9.44 (1H, s), 9.08 (1H, s), 8.79 (1H, s), 4.2 (2H br s), 3.68 (2H, br s), 2.84 (3H, m), 2.31 (3H, m), 1.58 (7H, m), 1.43 (3H,m).

2-(2-Hydroxyethylsulfonyl)-7-(*tert*-butyloxycarbonyl-methylsulfanyl)-4,5-dinitrofluorene-9-one (9). This was obtained similarly to **5a** from *tert*-butyl 2-mercaptoacetate (0.30 g), fluorenone **6a** (319 mg), and NaHCO$_3$ (326 mg): yield 69%, mp 195 °C (dec; phase transition at ca. 135 °C); ^{1}H NMR (300 MHz; CDCl$_3$) δ = 8.61 (1H, d, J = 2 Hz), 8.47 (1H, d, J = 2 Hz), 8.01 (1H, d, J = 2 Hz), 7.96 (1H, d, J = 2 Hz), 4.15 (2H, d, J = 5.5 Hz), 3.78 (2H, s), 3.49 (2H, t, J = 5.5 Hz), 1.48 (9H, s); MS (CI) m/z 542 (MNH$_4^+$, 7%), 524 (M$^+$, 2%), 134 (100%). Anal. Calcd for C$_{21}$H$_{20}$N$_2$O$_{10}$S$_2$: C, 48.09; H, 3.84; N, 5.34. Found: C, 47.80; H, 3.77; N, 5.32.

2-(2-Hydroxyethylsulfonyl)-7-(*tert*-butyloxycarbonyl-methylsulfonyl)-4,5-dinitrofluorene-9-one (10). This was obtained similarly to **6a** from sulfide **9** (210 mg) and H$_2$O$_2$ (2 mL): yield 81%, mp 310 °C (dec); ^{1}H NMR (300 MHz; acetone-d_6) δ = 8.75 (1H, d, J = 2 Hz), 8.74 (1H, d, J = 2 Hz), 8.62 (1H, d, J = 2 Hz), 8.61 (1H, d, J = 2 Hz), 4.69 (2H, s), 4.20 (1H, t, J = 5.5 Hz, OH), 4.06 (2H, q, J = 5.5 Hz), 3.77 (2H, t, J = 5.5 Hz), 1.48 (9H, s). Anal. Calcd for C$_{21}$H$_{20}$N$_2$O$_{12}$S$_2$: C, 45.32; H, 3.62; N, 5.03. Found: C, 44.93; H, 3.54; N, 4.95.

2-(2-Hydroxyethylsulfonyl)-7-(*tert*-butyloxycarbonyl-methylsulfonyl)-4,5-dinitrofluorene-9-one thioctic ester (11). This was obtained similarly to **7a** from sulfone **10** (82 mg), thioctic acid (31 mg), DCC (34 mg), and 4-(dimethylamino)-pyridine (3 mg): yield 61%, mp 165 °C (dec; phase transition at ca. 135−140 °C); ^{1}H NMR (300 MHz; CDCl$_3$) δ = 8.72 (1H, d, J = 2 Hz), 8.71 (1H, d, J = 2 Hz), 8.624 (1H, d, J = 2 Hz), 8.618 (1H, d, J = 2 Hz), 4.56 (2H, t, J = 5.5 Hz), 4.21 (2H, s), 3.63 (2H, t, J = 5.5 Hz), 3.55−3.38 (1H, m), 3.21−2.99 (2H, m), 2.48−2.36 (1H, m), 2.17 (2H, t, J = 7.5 Hz), 1.92−1.79 (1H, m), 1.71−1.42 (4H, m), 1.48 (9H, s), 1.42−1.23 (2H, m); MS (FAB) m/z 744 (65%). Anal. Calcd for C$_{29}$H$_{32}$N$_2$O$_{13}$S$_4$: C, 46.76; H, 4.33; N, 3.76. Found: C, 46.81; H, 4.35; N, 3.76.

2-(2-Hydroxyethylsulfonyl)-7-(carboxylmethylsulfonyl)-4,5-dinitrofluorene-9-one thioctic ester (12). Ester **11** (44 mg, 0.059 mmol) was dissolved in dry CH$_2$Cl$_2$ (0.3 mL), and trifluoroacetic acid (0.1 mL) was added at 0 °C at stirring. The reaction mixture was stirred for 1 h at 0 °C and left overnight at room temperature. The TLC analysis showed completeness of the hydrolysis, and the product was isolated by precipitation

with ether (2 mL): yield 40 mg (98%); ^{1}H NMR (300 MHz, acetone-d_6) δ = 8.78 (2H, m), 8.66 (2H, m), 4.82 (2H, s), 4.54 (2H, t), 3.99 (2H, t), 3.12 (2H, m), 2.41 (1H, m), 2.13 (2H, t), 1.92 (2H, m), 1.65−1.1 (6H, m).

***O*-Thioctyl-2,4,5,7-tetranitrofluorene-9-oneoxime (13).** Fluorenone **4** (0.34 g, 1.0 mmol) and well-powdered hydroxy-lamine hydrochloride (0.21 g, 3 mmol) were heated in DMF (3 mL) at 60 °C for 2 h. The reaction mixture was cooled, and the formed precipitate was filtered off, washed, and recrystallized from a mixture of 2-propanol and dioxane, giving tetranitrof-luorenoneoxime (0.26 g, 73%) as a yellow powder, mp >300 °C.[52] The obtained oxime (290 mg, 0.78 mmol) was esterified with thioctic acid (180 mg, 0.87 mmol) in the presence of DCC (226 mg, 1.1 mmol) and 4-(dimethylamino)pyridine (6 mg, 0.05 mmol). The reaction gave (after chromatographic purification) 135 mg (31%) of the light-violet product **13**, which slowly decomposed on storage (in solution or in solid state) into an insoluble colorless material (presumably a polymer). Monomer **13**: ^{1}H NMR (200 MHz; acetone-d_6) δ = 9.51 (1H, d, J = 2 Hz), 9.20 (1H, d, J = 2 Hz), 9.05 (1H, d, J = 2 Hz), 8.98 (1H, d, J = 2 Hz), 3.7−3.55 (1H, m), 3.3−3.05 (2H, m), 2.86 (2H, t, J = 7 Hz), 2.6−2.4 (1H, m), 2.0−1.6 (6H, m). Anal. Calcd for C$_{18}$H$_{14}$N$_2$O$_{12}$S$_2$: C, 42.03; H, 2.74; N, 5.45. Found: C, 41.78; H, 2.67; N, 5.45. CV (0.1 M Bu$_4$-NPF$_6$ in CH$_2$Cl$_2$; vs Fc/Fc$^+$): E^0_{1red} = −0.70 V, E^0_{2red} = −0.97 V, $E^{p.a.}_{1ox}$ = +0.76 (irreversible).

Supporting Information Available: Additional cyclic voltammograms of fluorene SAMs on gold and platinum electrodes. This material is available free of charge via the Internet at http://pubs.acs.org.

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