

Donor/Acceptor Interactions in Self-Assembled Monolayers and Their Consequences on Interfacial Electron Transfer

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The supramolecular association of tetrathiafulvalene (TTF) donors and bipyridinium acceptors is employed routinely to direct the formation of host/guest complexes and interlocked molecules in bulk solution. We have reproduced these donor/acceptor interactions at electrode/solution interfaces and demonstrated their pronounced influence on heterogeneous electron transfer. Specifically, we have synthesized a TTF with an oligomethylene arm terminated by a thiol group and assembled monolayers of this compound on gold. We have observed that the cyclic voltammogram of the immobilized TTF donors varies significantly upon addition of benzyl viologen, tetracyanoquinodimethane (TCNQ), or tetracyanoethylene (TCNE) acceptors to the electrolyte solution. Indeed, the supramolecular association of the complementary donors and acceptors results in a pronounced current decrease for the TTF redox waves. Consistently, the electrochemical response of the acceptors changes dramatically in the presence of TTF donors on the electrode surface. Instead, hexadecanethiolate monolayers, lacking the TTF donors at the termini of the oligomethylene chains, have a marginal influence on the voltammograms of the acceptors. Impedance measurements indicate that the charge-transfer resistance (R_{CT}) for the reduction of the acceptors increases from less than 0.3 k Ω , at bare gold, to 324, 24, and 43 k Ω for benzyl viologen, TCNQ, and TCNE, respectively, at TTF-coated electrodes. By contrast, the electrode coating has a negligible influence on the cyclic voltammogram and impedance response of ferrocene, which cannot sustain donor/acceptor interactions with the immobilized TTFs. Thus, our results demonstrate that the interfacial complexation of complementary donors and acceptors has a dramatic effect on the heterogeneous electron transfer to and from the associated components.

Introduction

The reliable electrochemical response and synthetic accessibility of tetrathiafulvalenes (TTFs) have stimulated the development of electroactive molecular and supramolecular assemblies based on these versatile building blocks.^{1–3} Indeed, TTF can be oxidized reversibly and sequentially to the corresponding mono- and dicationic forms at moderate potentials. The redox character survives the formal substitution of one or more hydrogen atoms on the TTF core with a variety of functional groups. In fact, electroactive derivatives with one or more arms appended to a TTF body can be prepared efficiently by relying on established synthetic protocols.

The electron-rich character of TTFs promotes their supramolecular association with complementary electron-deficient substrates.^{1–3} For example, the neutral form of TTF binds to bipyridinium dications in solution and solid states.^{4,5} The π -surfaces of the interacting units lie with their mean planes parallel to each other and interplanar separations of ca. 3.5 Å. The donor/acceptor interactions responsible for these supramolecular events can be exploited to template the synthesis of molecules with interlocked components.⁶ Interestingly, the relative orientations of the donors and acceptors within the resulting molecular machines⁷ can be controlled reversibly by altering the redox state of the TTF components. In fact,

molecular shuttles and switches operating in solution^{8,9} or within pairs of electrodes¹⁰ have been developed already on the basis of these fascinating principles. It is important to note, however, that no experimental information is available to assess the influence of these supramolecular interactions on the heterogeneous electron transfer to and from the associated donors and acceptors.

Monolayers of TTFs can be prepared at electrode/solution interfaces by relying on the ability of disulfides and thiols to adsorb on gold and platinum.^{11–16} The surface-confined TTFs retain their typical redox response, facilitating the electrochemical characterization of the self-assembled monolayers. Furthermore, their electroactive character can be exploited to probe supramolecular events at the electrode/solution interface. In particular, the first oxidation potential of TTF monolayers was found to increase by ca. 30 mV in the presence of a bipyridinium cyclophane in the electrolyte solution.^{15b} This change is consistent with the potential shifts observed upon association of TTF donors with bipyridinium acceptors in bulk solution. Similarly, Fourier transform reflection–absorption infrared spectroscopy and surface plasmon resonance studies indicated that tetracyanoquinodimethane (TCNQ) acceptors adsorb on monolayers of TTFs donors anchored to gold electrodes.^{11,16b,c} Thus, the supramolecular events that have been widely exploited in bulk solution to govern the association of TTFs with various acceptors can be reproduced at solid/solution interfaces. Intrigued by these observations, we realized that the interactions

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of acceptors with donors preattached to gold alter the structural and electronic properties of the electrode/solution interface. As a result, these supramolecular processes can have a significant influence on heterogeneous electron transfer and, in principle, can be used to regulate the electronic communication between the electrode and redox probes in solution. To explore these fascinating prospects, we have designed a TTF building block and studied the interactions of this compound with electroactive acceptors at gold/solution interfaces.

Experimental Procedures

General Methods. Chemicals were purchased from either Acros Organics or Aldrich and used as received. Acetonitrile (MeCN) and methanol (MeOH) were distilled over calcium hydride. Tetrahydrofuran (THF) was distilled over sodium and benzophenone. Compound **1** was synthesized adapting a literature procedure,¹⁷ and its preparation is described in the Supporting Information (Figure S1). Aluminum sheets coated with silica gel 60 F₂₅₄ were employed for thin-layer chromatography (TLC). The thioester **3** was purified by high performance liquid chromatography (HPLC) using a Varian ProStar coupled to a ProStar 330 photodiode array detector. Analytical (column dimensions = 4.6 × 250 mm, flow rate = 1.0 mL min⁻¹, injection volume = 20 μL, sample concentration = 1 × 10⁻³ M) and semipreparative (column dimensions = 21.4 × 250 mm, flow rate = 21.6 mL min⁻¹, injection volume = 1.0 mL, sample concentration = 1 × 10⁻³ M) Varian Microsorb BDS columns were employed. The mobile phase was a mixture of MeCN and H₂O (80:20). The retention time (*RT*) and the peak asymmetry (*PA*) reported were determined at a wavelength of 262.8 nm. The average purity parameter (*APP*) reported was calculated for the peak heart in the wavelength range 200–700 nm. Melting points (mp) were determined with an Electrothermal 9100 and are uncorrected. Fast atom bombardment mass spectra (FABMS) were recorded with a VG Mass Lab Trio-2 using 3-nitrobenzyl alcohol as matrix. Nuclear magnetic resonance (NMR) spectra were recorded with a Bruker DPX 300.

4-(10-Iododecylsulfanyl)-5-methylsulfanyl-tetrathiafulvalene (2). A solution of **1** (50 mg, 0.2 mmol) in degassed MeCN (50 mL) was added dropwise to a solution of CsOH·H₂O (25 mg, 0.2 mmol) in degassed MeOH (5 mL) over a period of 30 min at ambient temperature under N₂. The mixture was stirred for a further 30 min and then added dropwise to a solution of 1,10-diiododecane (293 mg, 0.8 mmol) in degassed MeCN (40 mL). The resulting mixture was stirred for 1 d at ambient temperature under N₂. After distillation of the solvent under reduced pressure, the residue was dissolved in CH₂Cl₂ (10 mL), washed with H₂O (3 × 5 mL), dried (MgSO₄), and purified by column chromatography [(SiO₂, hexane/CH₂Cl₂ (100:0 → 0:100)] to give **2** (33 mg, 53%) as a yellowish oil. FABMS: *m/z* = 548 [M]⁺. ¹H NMR [(CD₃)₂CO]: δ = 6.67 (2H, s), 3.27 (2H, t, *J* = 7 Hz), 2.88 (2H, t, *J* = 7 Hz), 2.47 (3H, s), 1.81–1.85 (2H, m), 1.59–1.68 (2H, m), 1.29–1.41 (12H, m). ¹³C NMR (CDCl₃): δ = 130.76, 126.21, 120.39, 120.35, 116.53, 105.07, 36.63, 34.46, 31.20, 30.69, 30.51, 29.77, 29.27, 29.00, 19.25, 8.08.

4-(10-Acetylsulfanyldodecylsulfanyl)-5-methylsulfanyl-tetrathiafulvalene (3). A solution of **2** (1.00 g, 2 mmol) and MeCOSK (1.03 g, 9 mmol) in MeCN (400 mL) was stirred at 40 °C for 1 d. After distillation of the solvent under reduced pressure, the residue was dissolved in CH₂Cl₂, filtered, and purified by column chromatography [(SiO₂, hexane/CH₂Cl₂ (70:30 → 0:100)] and semipreparative HPLC to give **3** (680 mg, 78%) as an orange-red oil. HPLC (analytical): *RT* = 9.5 min, *PA* =

1.3, *APP* = 262 ± 1 nm; FABMS: *m/z* = 496 [M]⁺. ¹H NMR [(CD₃)₂CO]: δ = 6.67 (2H, s), 2.82–2.88 (4H, m), 2.73 (3H, s), 2.47 (3H, s), 1.59–1.70 (2H, m), 1.53–1.58 (2H, m), 1.29–1.49 (12H, m). ¹³C NMR (CDCl₃): δ = 195.49, 130.81, 126.19, 120.41, 120.37, 116.61, 105.01, 38.46, 36.61, 30.53, 30.50, 29.78, 29.54, 29.48, 28.98, 27.61, 19.20.

4-(10-Mercaptodecylsulfanyl)-5-methylsulfanyl-tetrathiafulvalene (4). A solution of MeONa (0.5 M) in MeOH (560 μL) was added to a solution of **3** (40 mg, 0.1 mmol) in MeOH (15 mL) and THF (10 mL) maintained under N₂. The mixture was stirred for 1 d at ambient temperature under N₂, and then aqueous NH₄Cl (0.1 M, 10 mL) was added. After distillation of the solvent under reduced pressure, the residue was washed with CH₂Cl₂ (3 × 30 mL). The resulting organic solution was filtered, washed with H₂O (2 × 20 mL), and dried (MgSO₄) to afford **4** (21 mg, 58%) as a reddish brown oil. FABMS: *m/z* = 454 [M]⁺. ¹H NMR (CDCl₃): δ = 6.33 (2H, s), 2.81 (2H, t), 2.70 (2H, t), 2.65 (3H, s), 1.26–1.65 (16H, m). ¹³C NMR (CDCl₃): δ = 129.57, 126.37, 119.20, 119.11, 39.38, 36.44, 29.89, 29.61, 29.42, 29.25, 28.73, 28.62, 19.43, 1.23, 0.21.

Monolayer Preparation and Characterization. Polycrystalline gold disk electrodes (CH Instruments 101P) were polished with an Al₂O₃ slurry (0.05 μm), rinsed with H₂O and MeOH, and dried under a stream of Ar. They were then maintained in either a MeCN solution of **4** (1 × 10⁻³ M) for 3 d or an EtOH solution of hexadecanethiol (1 × 10⁻³ M) for 1 d, rinsed with the same solvent, dried under a stream of Ar, and integrated in a conventional three-electrode cell. Cyclic voltammetry and impedance measurements were run in MeCN solutions of Bu₄-NPF₆ (0.1 M) with a CH Instruments 660A, using a platinum counter electrode and a Ag/AgCl reference electrode. Prior to each experiment with the TTF monolayers, the potential of the gold working electrode was cycled between 0 and +0.7 V until a constant peak current for the TTF oxidation was obtained (Figure S2). The formation of hexadecanethiolate monolayers was confirmed by comparing the cyclic voltammograms of Ru(NH₃)₆Cl₃ (1 × 10⁻³ M) in aqueous KCl (0.1 M) recorded before (a in Figure S3) and after (b) the modification of the gold working electrode. In agreement with literature reports,¹⁸ the redox waves for the reversible reduction of Ru(NH₃)₆Cl₃ are not observed after the adsorption of a hexadecanethiolate monolayer on the electrode surface. Consistently, the impedance plots recorded before (c in Figure S3) and after (d) modification show a transition from mass-transfer to kinetic control with a charge-transfer resistance (*R*_{CT}) increase from less than 0.2 to ca. 87 kΩ (Table S1).

Results and Discussion

Design and Synthesis. The cross coupling of 1,3-dithiole-2-thiones with 1,3-dithiol-2-ones is a convenient synthetic protocol to assemble functionalized TTF cores.¹⁹ In particular, asymmetrical TTFs with 2-cyanoethylthio substituents can be prepared efficiently using this method. The subsequent removal of the 2-cyanoethyl appendages offers the opportunity to attach alkyl chains with terminal functional groups to the TTF thiolates. Following this synthetic plan and adapting a literature procedure,¹⁷ we have prepared the TTF **1** (Figures 1 and S1). The elimination of its 2-cyanoethyl group with cesium hydroxide and alkylation of the resulting thiolate with 1,10-diiododecane produced the iodide **2**. The reaction of this compound with potassium thioacetate gave the thioester **3**, after the displacement of the terminal iodide. Finally, the transesterification of the thioacetate with sodium methoxide afforded the target thiol **4**.

Monolayer Preparation and Characterization. The immersion of a polycrystalline gold disk in a MeCN solution of

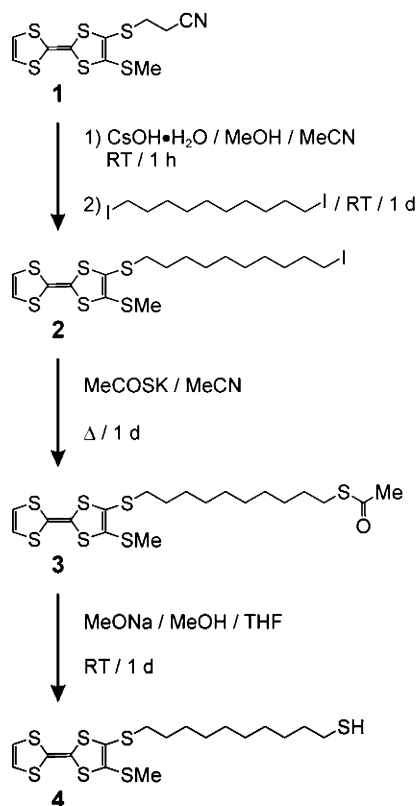


Figure 1. Synthesis of the TTF thiol 4.

the thiol 4 results in the spontaneous adsorption of this compound on the electrode surface. Consistently, cyclic voltammograms (a in Figure 2), recorded after copious rinsing of the modified electrode, reveal the characteristic oxidation of the TTFs to their radical cations. The peak current decreases to a constant value within approximately 20 potential cycles between 0 and +0.7 V.²⁰ Further cycles in this potential window have a negligible effect on the TTF response. However, significant desorption of the TTF thiolates from the electrode surface occurs, if the voltage is scanned beyond their second oxidation potential (Figure S2).

The half-wave potential ($E_{1/2}$) for the oxidation of the immobilized TTFs to the corresponding radical cations is ca. +0.58 V with a peak-to-peak separation (ΔE) of ca. 10 mV at a scan rate of 100 mV s^{-1} . The peak current of the anodic and cathodic waves increases linearly with the scan rate (b and c in Figure 2), confirming the surface confinement of the TTFs. The surface coverage (Γ) is ca. $(6 \pm 3) \times 10^{-1} \text{ nmol cm}^{-2}$. This value is the average of 10 independent measurements, includes a correction to account for surface roughness,²¹ and is close to the limiting Γ expected for TTF monolayers.¹²

Heterogeneous Electron Transfer to Redox Probes in Solution. The cyclic voltammogram (a in Figure 3) of ferrocene, recorded with a bare gold working electrode, shows waves for the characteristic and reversible oxidation to ferrocenium with a $E_{1/2}$ of ca. +0.45 V. In the presence of either a hexadecanethiolate (b in Figure 3) or a TTF monolayer (c) on the working electrode, the ferrocene response is essentially unaltered.²² Consistently, impedance plots determined at the oxidation potential of ferrocene with either hexadecanethiolate- (e in Figure 3) or TTF-coated (f) gold working electrodes are remarkably similar to that determined at bare gold (a in Figure S4). In all instances, the ferrocene response is under mass-transfer control. The corresponding charge-transfer resistance (R_{CT}) can be estimated to be less than 0.3 k Ω .

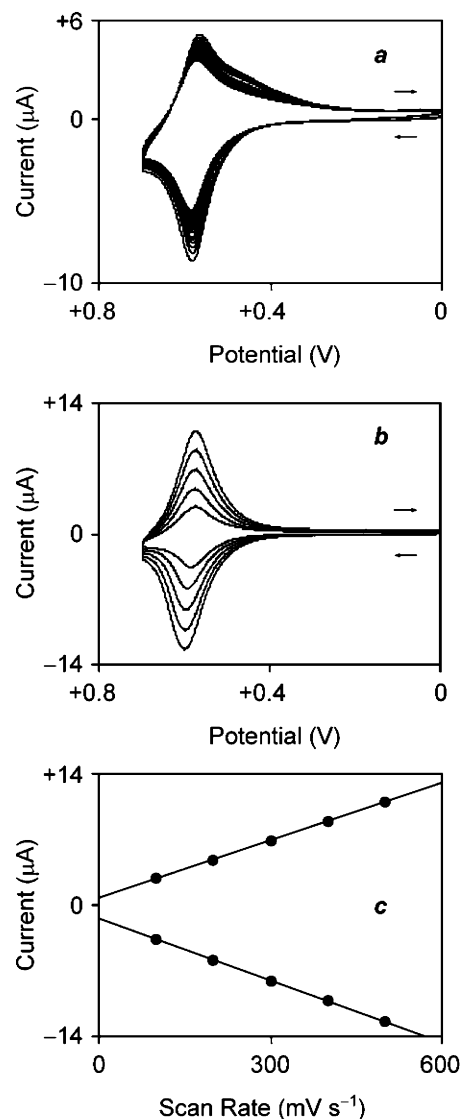


Figure 2. (a) Fifty consecutive cyclic voltammograms (0.1 M Bu_4NPF_6 , MeCN, V vs Ag/AgCl, 100 mV s^{-1}) recorded after the immersion of a gold working electrode in a MeCN solution of 4 ($1 \times 10^{-3} \text{ M}$) for 3 d and copious rinsing of the electrode surface. (b) Cyclic voltammograms of a modified electrode recorded at increasing scan rates (100–500 mV s^{-1}) after a sufficient number of potential cycles to stabilize the peak current. (c) Scan rate dependence of the peak current for the anodic and cathodic waves.

The presence of ferrocene in the electrolyte solution has a negligible influence on the voltammetric response (c and d in Figure 3) of the surface-confined TTFs. By contrast, the addition of the 1,1'-dibenzyl-4,4'-bipyridium dication (benzyl viologen) to the electrolyte solution results in a pronounced current decrease for the TTF waves (a and b in Figure 4) and a $E_{1/2}$ shift of ca. -30 mV. Thus, the transition from the electron-rich ferrocene to the electron-deficient benzyl viologen has a drastic effect on the electron-rich TTFs.

The current decrease in the presence of benzyl viologen indicates that a substantial amount (ca. 70%) of TTFs have either desorbed from the electrode surface or become electrochemically inactive within the probed potential window. The loss of a relatively large fraction of TTF thiolates from the monolayer, however, would uncover part of the underlying gold substrate, allowing benzyl viologen to access directly the electrode surface. Nonetheless, the characteristic redox waves for the two consecutive reductions of benzyl viologen at bare gold (a in Figure S5) are replaced by a single and irreversible peak (c in Figure

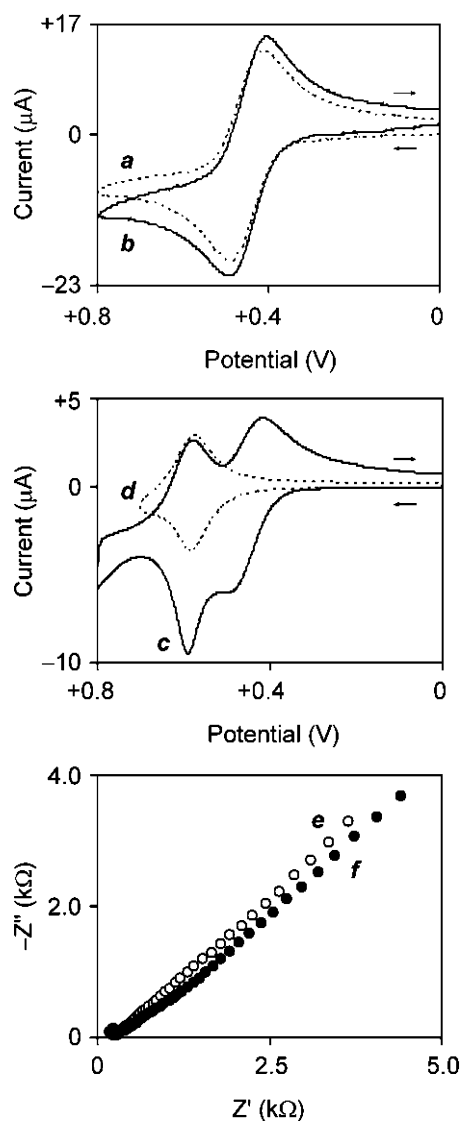


Figure 3. Cyclic voltammograms (0.1 M Bu_4NPF_6 , MeCN, V vs Ag/AgCl, 100 mV s^{-1}) of ferrocene ($1 \times 10^{-3} \text{ M}$) recorded with bare (a), hexadecanethiolate- (b), and TTF-coated (c) gold working electrodes and of the same TTF monolayer in the absence of ferrocene (d). Impedance plots (0.1 M Bu_4NPF_6 , MeCN, $+0.457 \pm 0.005 \text{ V}$ vs Ag/AgCl, 100 kHz to 0.1 Hz) of ferrocene ($1 \times 10^{-3} \text{ M}$) recorded with hexadecanethiolate- (e) and TTF-coated (f) gold working electrodes.

4) when a TTF-coated electrode is employed. These observations suggest that the TTF donors and the benzyl viologen acceptors interact at the electrode/solution interface, affecting drastically the heterogeneous electron transfer to and from both redox units. In agreement with this interpretation, the cyclic voltammogram of benzyl viologen (d in Figure 4) shows that the reduction of the bipyridinium dication to the corresponding radical cations is not completely suppressed when an alkanethiolate monolayer, lacking the terminal TTF donors, coats the gold working electrode.

Impedance measurements at the first reduction potential of benzyl viologen demonstrate that the response of the bipyridinium dication is under kinetic control in the presence of either a TTF (a in Figure 5) or a hexadecanethiolate (b) monolayer on the working electrode. However, the analysis of the frequency dependence of the real (Z') and imaginary (Z'') parts of the impedance indicates that the presence of TTF donors on the electrode surface enhances significantly the R_{CT} value. Indeed, R_{CT} is ca. 324 k Ω (Table S2), when the working electrode is

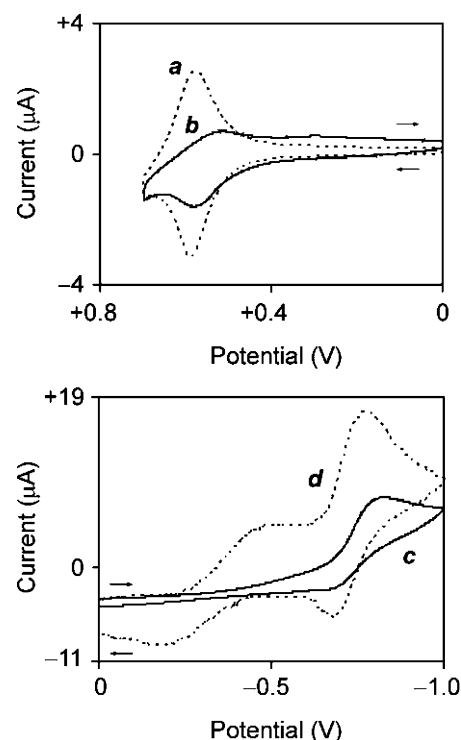


Figure 4. Cyclic voltammograms (0.1 M Bu_4NPF_6 , MeCN, V vs Ag/AgCl, 100 mV s^{-1}) of a TTF monolayer without (a) and with (b) benzyl viologen ($1 \times 10^{-3} \text{ M}$) in the electrolyte solution and of benzyl viologen recorded with TTF- (c) and hexadecanethiolate-coated (d) gold working electrodes.

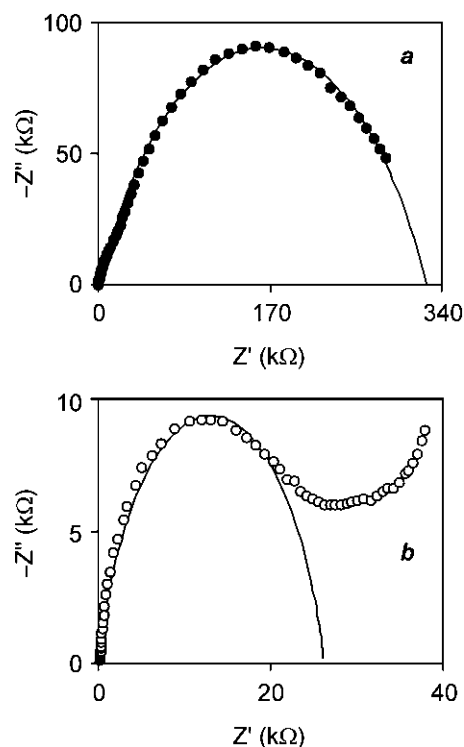


Figure 5. Impedance plots (0.1 M Bu_4NPF_6 , MeCN, $-0.316 \pm 0.005 \text{ V}$ vs Ag/AgCl, 100 kHz to 0.1 Hz) of benzyl viologen ($1 \times 10^{-3} \text{ M}$) recorded with TTF- (a) and hexadecanethiolate-coated (b) gold working electrodes.

coated by a TTF monolayer, and it is only ca. 27 k Ω (Table S1), when a hexadecanethiolate monolayer is on the electrode surface. By contrast, the reduction of benzyl viologen is under mass-transfer control (b in Figure S4) at bare gold with an R_{CT} value smaller than 0.3 k Ω .

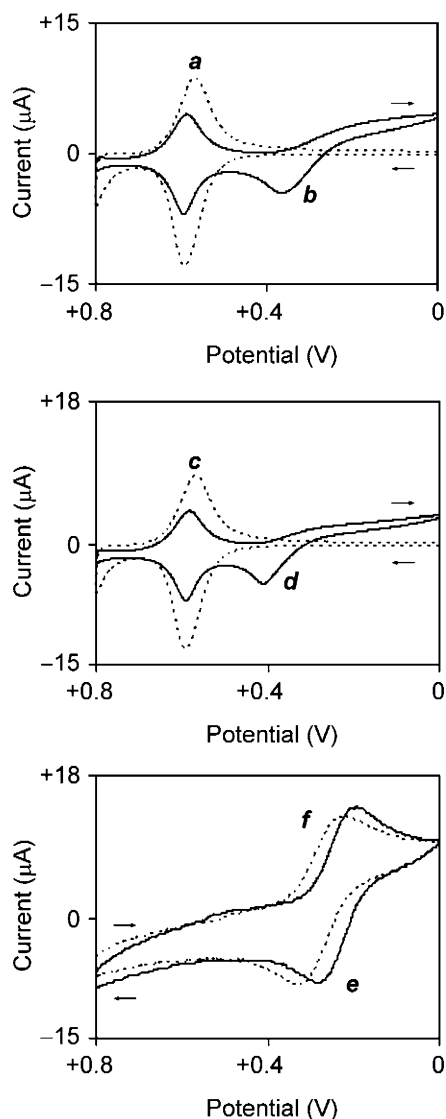


Figure 6. Cyclic voltammograms (0.1 M Bu₄NPF₆, MeCN, V vs Ag/AgCl, 100 mV s⁻¹, 1×10^{-3} M) of TTF monolayers without (a and c) and with either TCNQ (b) or TCNE (d) in the electrolyte solution and of TCNQ (e) and TCNE (f) recorded with hexadecanethiolate-coated gold working electrodes.

In analogy to bipyridinium dications, TCNQ and tetracyanoethylene (TCNE) acceptors associate with TTF donors.^{11,16b,c,23,24} In fact, the effect of benzyl viologen (a and b in Figure 4) on the voltammetric response of the TTF monolayers can be reproduced by adding either TCNQ (a and b in Figure 6) or TCNE (c and d) to the electrolyte solution. Also, these two acceptors impose a significant current decrease on the redox waves of the surface-confined TTF donors and cause a $E_{1/2}$ shift of ca. +10 mV. Once again, the current drop suggests that a large fraction (ca. 50%) of TTFs have either desorbed from the electrode surface or become electrochemically inactive within the probed potential window. However, the characteristic waves (b and c in Figure S5) of TCNQ and TCNE at bare gold turn into irreversible peaks (b and d in Figure 6) and shift by ca. +70 mV in the presence of a TTF monolayer on the working electrode. These observations demonstrate that TCNQ and TCNE do not have direct access to the gold surface and, therefore, that the TTF thiolates are not desorbing from the electrode surface. The drastic change in the voltammetric response of donors and acceptors must be a result of their interaction at the electrode/solution interface. Consistently, the

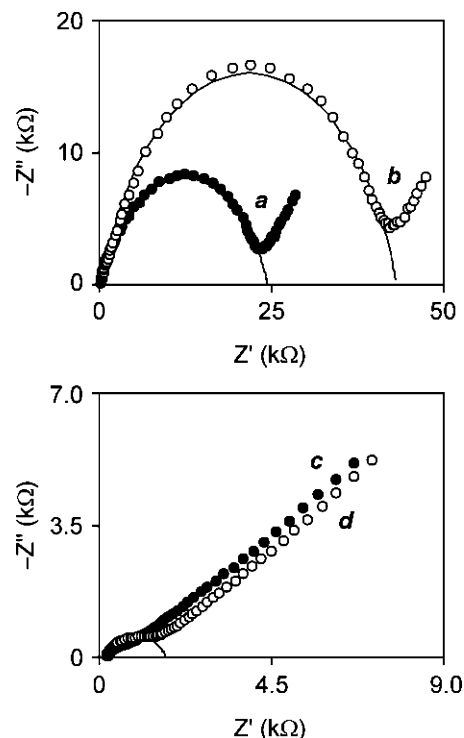


Figure 7. Impedance plots (0.1 M Bu₄NPF₆, MeCN, V vs Ag/AgCl, 100 kHz to 0.1 Hz, 1×10^{-3} M) of TCNQ (+0.249 ± 0.005 V) recorded with TTF- (a) and hexadecanethiolate-coated (c) gold working electrodes and of TCNE (+0.292 ± 0.005 V) recorded with TTF- (b) and hexadecanethiolate-coated (d) gold working electrodes.

cyclic voltammograms of TCNQ and TCNE (e and f in Figure 6) remain essentially unaltered when hexadecanethiolate monolayers, lacking the terminal TTF donors, coat the gold working electrode.

Impedance measurements (a and b in Figure 7) at the reduction potentials of TCNQ and TCNE demonstrate that their response is under kinetic control, when the working electrode is coated by TTF donors. The analysis of the frequency dependence of Z' and Z'' indicates the corresponding R_{CT} to be ca. 24 and 43 kΩ for TCNQ and TCNE, respectively (Table S2). Instead, the R_{CT} of TCNQ (c in Figure 7) is smaller than 0.3 kΩ and that of TCNE (d) drops to 2 kΩ at gold working electrodes coated by hexadecanethiolate monolayers (Table S1). Thus, the presence of TTF donors on the electrode surface is essential to slow significantly the electron transfer to both acceptors.

Conclusions

We have synthesized a TTF thiol able to adsorb on the surface of gold electrodes forming stable monolayers. The immobilized TTFs retain their characteristic redox response and tolerate tenths of potential cycles without desorbing from the electrode surface. These monolayers, however, are not sufficiently compact to prevent heterogeneous electron transfer to and from ferrocene. In fact, neither the cyclic voltammogram nor the impedance plot of ferrocene is noticeably affected by the presence of a TTF monolayer on the working electrode. On the contrary, these monolayers alter drastically the response of electroactive species known to engage in donor/acceptor interactions with TTFs. Impedance measurements reveal that the charge-transfer resistances of benzyl viologen, TCNQ, and TCNE increase from less than 0.3 to 324, 24, and 43 kΩ, respectively, in the presence of a TTF monolayer on the working electrode. Presumably, the acceptors (blue in Figure 8) are forced to associate with TTF

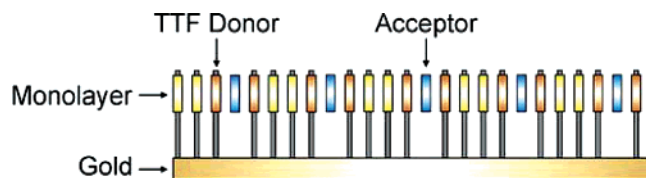


Figure 8. Supramolecular association of acceptors with TTF donors immobilized on the surface of a gold electrode.

donors (orange) when they approach the electrode surface. As a result, the heterogeneous electron transfer to the acceptors is slowed dramatically and R_{CT} increases. Concomitantly, the TTF donors associated with the acceptors lose their electroactive character and only the TTFs (yellow in Figure 8) not involved in donor/acceptor interactions produce a detectable electrochemical response. The consequence is a significant drop in current for the TTF redox waves. In agreement with this model, control experiments with hexadecanethiolate monolayers confirm that the heterogeneous electron transfer to the acceptors is slowed significantly only in the presence of TTF donors on the electrode surface. Thus, our results demonstrate that the association of TTF donors immobilized on gold electrodes with acceptors in the electrolyte solution has a drastic effect on interfacial electron transfer.

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Supporting Information Available: Experimental procedures for the synthesis of **1**; cyclic voltammograms of the TTF monolayers; cyclic voltammograms and impedance response of $\text{Ru}(\text{NH}_3)_6\text{Cl}_3$ at bare and hexadecanethiolate-coated gold; impedance response of ferrocene, benzyl viologen, TCNQ, and TCNE at bare gold; cyclic voltammograms of benzyl viologen, TCNQ, and TCNE at bare gold; determination of R_{CT} from the impedance plots. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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