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Cyclic voltammetric and computational study of a 4-bromophenyl monolayer on a glassy carbon electrode

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Abstract A glassy carbon (GC) surface modified with monolayer of 4-bromophenyl was examined as voltammetric electrode for some redox systems. The modified electrode exhibited very slow electron transfer in comparison to the unmodified surface by factors which varied with the redox systems. However, after scanning the modified electrode in 0.1 *M* tetrabutylammonium tetrafluoroborate (*TBA*BF_4) in acetonitrile from 0.4 to -1.1 V *vs.* Ag/AgCl for 20–25 cycles, the modified electrode showed much faster electron transfer kinetics, *e.g.*, the results for $Fe(CN)_6^{3-/4-}$ were approaching those observed with unmodified surfaces. The effect is attributed to an apparently irreversible structural change in the 4-bromophenyl monolayer, which increases the rate of electron tunneling. The transition to the conducting state is associated with electron injection into the monolayer and causes a significant decrease in the calculated HOMO-LUMO gap for the monolayer molecule. Once the monolayer is switched to the conducting state, it supports rapid electron exchange with the redox system, but not with dopamine, which requires adsorption to the electrode surface. A conductive surface modified electrode may have useful properties for electroanalytical applications and possibly in electrocatalysis.

Keywords Cyclic voltammetry; Computational study; 4-Bromophenyl; Glassy carbon.

Introduction

Chemically modified electrodes have been the subject of numerous studies in the last 2 decades since they may find applications in electrocatalysis, corrosion protection, thin film optical devices, integrated circuits, information storage, and sensing [1–6]. A recent approach for electrode modification involves the spontaneous adsorption of thiols on gold electrode surfaces to form the so-called self-assembled monolayers, SAMs [7, 8].

The adsorption of thiol results in the formation of a gold-sulfur bond that is characterized by a partial covalent character [7, 9]. However, recent studies have shown that these monolayers are not totally stable and that they can be oxidatively or reductively desorbed [10]. SAMs are interesting on their own because of their easy preparation and also because this first layer can be further modified to build up more complex chemical structure.

On the other hand, carbon electrodes are usually modified by an oxidative procedure that generates oxygen functionalities which can be used to do further chemistries [1, 11]. Since electrochemical or chemical oxidation may damage the carbon surface, a new method involving the electrochemical reduction of a phenyldiazonium derivative was developed [12].

According to Scheme 1, this surface modification procedure involves the formation of a diazonium radical followed by the formation of a covalent bond to the glassy carbon electrode.

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$$R\text{-}C_6H_4N_2^{+} + e^{-} \longrightarrow N_2 + R\text{-}C_6H_4^{\bullet}$$

$$GC + R\text{-}C_6H_4^{\bullet} \longrightarrow GC + C_6H_4R$$

Scheme 1

In Scheme 1 R is a *para*-substituent such as bromo, nitro, carboxy, *etc*. Layers close to monolayer coverage can be achieved by this procedure [12–14]. These modified electrodes have been subsequently used to immobilize glucose oxidase [13] and to control protein adsorption by appropriate selection of the R group [14]. More recently, chemical modification of polyaniline films has been performed by nucleophilic substitution reactions with substituted phenyldiazonium ions [15]. The blocking behavior of the 4-bromophenyl group has also been reported recently [16]. In addition, a large number of substituted phenyldiazonium salts has been prepared from the corresponding aniline and characterized electrochemically in the last decades [17, 18].

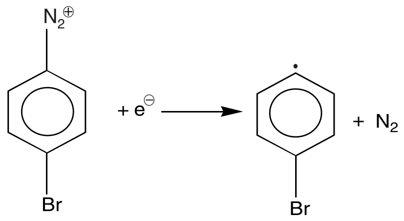
Since we are interested in applications of such modified carbon electrodes in electrocatalysis and electroanalysis, it is relevant to investigate in detail their blocking behavior [16, 19, 20].

Recently, *McCreery* and coworkers have reported the conductance switching behavior of several organic monolayers on carbon surfaces [21, 26]. In the presence of a negative voltage applied between a graphitic conductor and metallic top contact a monolayer of bromophenyl "switched" from a high resistance state to one with a resistance lower by a factor of ten or more. Early indications are that the conducting state is nearly metallic with small or negligible injection barrier between the carbon and conducting monolayer.

Results and disscusion

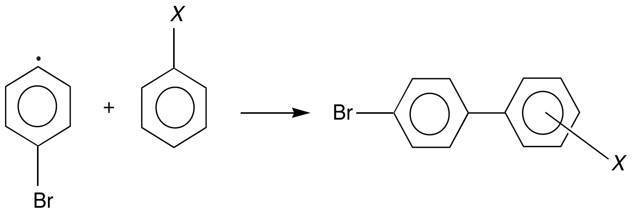
In this paper, we report conductance switching in an electrochemical context in which an electrode modified with 4-bromophenyl is immersed in an electrolyte solution containing a redox active analyte. With the monolayer in its initial state, the carbon substrate is isolated from the solution and redox reactions in solution require tunneling through the monolayer. With the monolayer "switched" to a high conductance state, electron transfer may proceed through the monolayer, but the electrode/solution interface is defined by the monolayer rather than the substrate. The conducting 4-bromophenyl monolayer thus replaces the carbon substrate to form modified conducting surfaces. The transition to the conducting state is associated with electron injection into the monolayer and causes a significant decrease in the calculated HOMO-LUMO gap for the monolayer molecule.

The cyclic voltammogram of 1 mM (4-bromophenyl)diazonium tetrafluoroborate, in 0.1 M *TBA*BF_4/ acetonitrile solution at a glassy carbon electrode is shown in Fig. 1. It is obvious from Fig. 1 that an irreversible reduction wave occurred at -0.01 V, which can be attributed to the formation of a 4-bromophenyl radical from the diazonium derivative [12, 19]. The electrochemical behavior of aryldiazonium cations has been studied in great detail by *Elofson* and coworkers, who have observed aryl radical formation and release of nitrogen upon reduction in Scheme 2 [18].



Scheme 2

Elofson et al. [27] have also shown that aromatic compounds are arylated by the electrochemically generated radical according to Scheme 3.



Scheme 3

Since carbon electrodes also have an aromatic character [11], a similar reaction can consequently occur and lead to the formation of a covalent bond between the carbon electrode and the 4-bromophenyl group. The first wave at -0.01 V disappeared completely in the second scan (see Fig. 1). This observation indicates an inhibition of the electron transfer by the bromophenyl group grafted at the carbon surface.

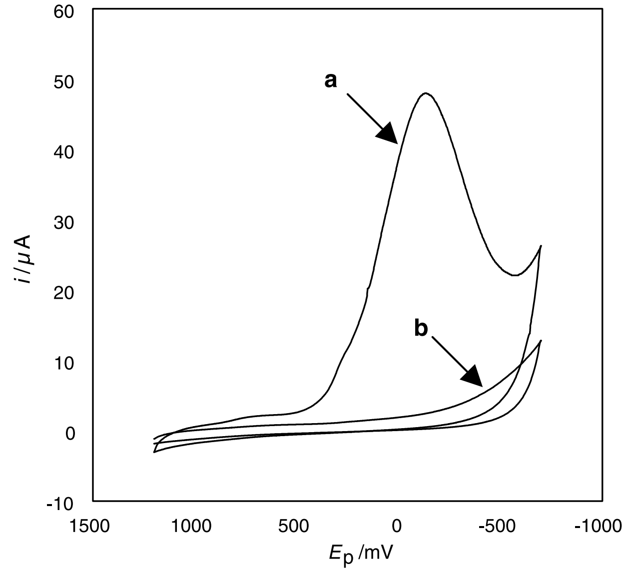


Fig. 1 Cyclic voltammograms of $1\,M$ 4-bromophenyl in $0.1\,M$ *TBA*BF_4 in acetonitrile on GC electrode, $100\,mV/s$ scan rate. a) First scan and b) second scan

The attachment of a 4-bromophenyl film on GC surfaces was also proven by the irreversible wave observed in the cyclic voltammogram of the modified electrode in a dopamine solution. As dopamine (*DA*) oxidation provides a useful test for pinholes [28, 29], *DA* requires an adsorption site for rapid oxidation and becomes electro-inactive on electrode surfaces modified by 4-bromophenyl monolayer completely.

Therefore, *DA* response is an indication of the presence of bare electrode area or might occur from pinhole formation. Figure 2 shows voltammograms of $1\,mM$ *DA* in $0.1\,M$ H_2SO_4 for GC electrode, unmodified, initial 4-bromophenyl-modified, and 4-bromophenyl-modified after placing it in acetonitrile containing $0.1\,M$ *TBA*BF_4 and scanned from 0.4 to $-1.1\,V$ *vs.* Ag/AgCl for 25 cycles at a scan rate of $100\,mV/s$. The last process will be referred to as turning the electrode to the conducting state (ON). Figure 2 shows that no observable *DA* response is visible for GC modified with 4-bromophenyl radical and there is no *DA* response on GC-4-bromophenyl electrode after scanning the modified electrode to -1.1 for 25 cycles at scan rate of $100\,mV/s$.

The cyclic voltammogram of *DA* indicated that scanning GC-4-bromophenyl in blank electrolyte at a potential of less than $-1.1\,V$ damaged the surface of the modified GC electrode. The phenomenon of conducting state of modified electrode in an electrochemical cell was examined by some redox systems. At typical voltammogram of $1\,mM$ $Fe(CN)_6^{3-/4-}$ in $0.1\,M$ KCl at scan rate of $100\,mV/s$ on unmodified, initial 4-bromophenyl-modified, and 4-bromophenyl-modified GC electrode after scanning for 25 cycles is shown in Fig. 3.

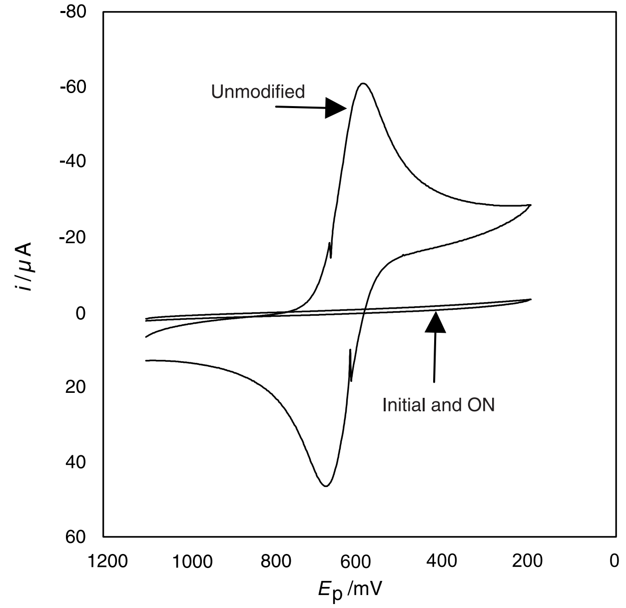


Fig. 2 Cyclic voltammogram of $1\,mM$ dopamine + $1\,mM$ H_2SO_4, $100\,mV/s$ scan rate. Responses on GC, unmodified, initial 4-bromophenyl-modified, ON

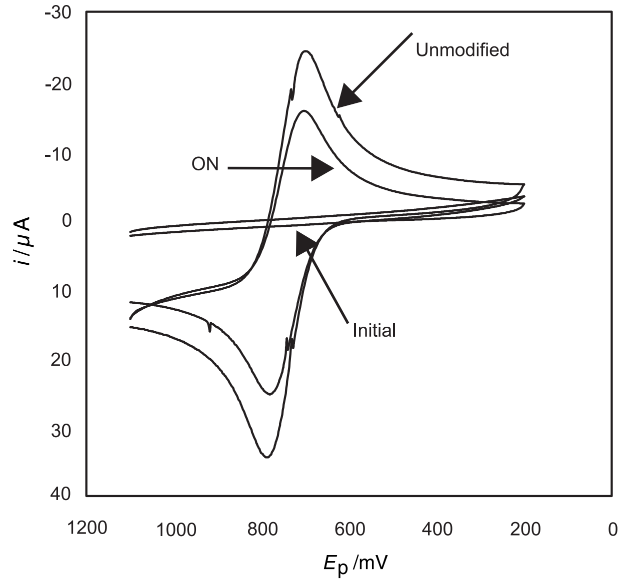


Fig. 3 Cyclic voltammogram of $1\,mM$ $Fe(CN)_6^{3-/4-}$ + $1\,M$ KCl, $100\,mV/s$ scan rate. Responses on GC, unmodified, initial 4-bromophenyl-modified, ON

Figure 3 indicates that ΔE_P for $Fe(CN)_6{}^{3-/4-}$ on the bare electrode is much smaller than that on the initial modified 4-bromophenyl surface. When 4-bromophenyl-GC electrode is placed in acetonitrile containing $0.1\,M$ $TBABF_4$ and scanned by 25 cycles at the scan rate of $100\,mV/s$, the ΔE_P decreases significantly approaching that observed on the unmodified surface.

The cyclic voltammogram of the examined redox system clearly shows that electrochemical reaction of this redox system is completely blocked when a carbon electrode is initially modified with 4-bromophenyl. As it is shown in the CV voltammograms, the peak current of $Fe(CN)_6{}^{3-/4-}$ is linear with $v^{1/2}$ and the ratio of the cathodic to anodic peak current is ≈ 1 for all concentration changes used.

In addition, the observed ΔE_P increases with concentration. The increase in peak separation with concentration should be caused by uncompensated resistance since the peak separation is related to electron transfer kinetics and should be constant with concentration. The *iR*-corrected ΔE_p is attributed to the peak current (i_p) and uncompensated resistance (R_u) as reported by *Ranganathan* [31], who detailed the properties of pyrolyzed photoresist film (PPF) electrodes and noted that the effect of film resistance on the observed ΔE_p can be corrected by applying Eq. (1).

$$\Delta E_{p,corr} = \Delta E_{p,obs} - 2|i|R_u \qquad (1)$$

where $\Delta E_{p,corr}$ is the corrected ΔE_p, i is the voltammetric peak current, and R_u is the uncompensated cell resistance. R_u can be determined from the slope of a plot of $\Delta E_{p,obs}$ *vs.* i obtained from voltammograms at a common scan rate for solution of varying concentration. Data from cyclic voltammetry on glassy carbon electrode in solution of $Fe(CN)_6{}^{3-/4-}$ with concentrations between 2 and $10\,mM$ are plotted in Fig. 4. Analysis of a number of these plots on glassy carbon electrode yields an R_u value of $23 \pm 2\ \Omega$ for $Fe(CN)_6{}^{3-/4-}$ on unmodified and $27 \pm 2\ \Omega$ for $Fe(CN)_6{}^{3-/4-}$ on 4-bromophenyl-modified GC electrode after scanning for 25 cycles.

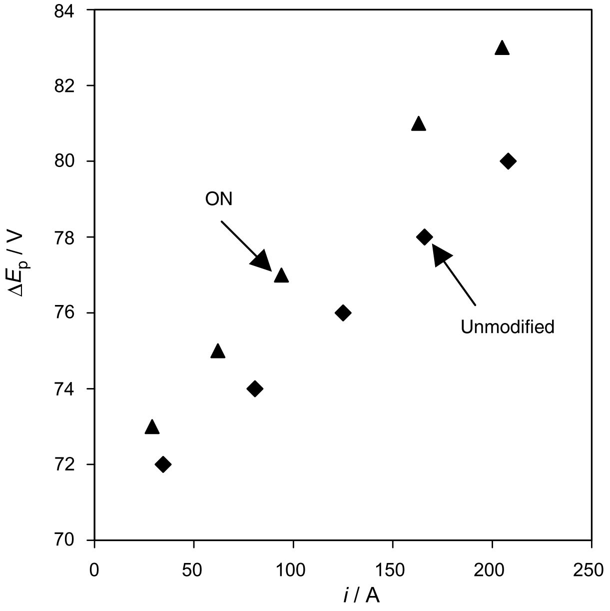


Fig. 4 Plot of ΔE_p V *vs.* i A for cyclic voltammetry data

The observed heterogenous electron transfer rate constants, k^0_{obs} were also determined from ΔE_p values by the method of *Nicholson* [30]. A summary of kinetic data for the 4-bromophenyl-modified electrode is listed in Table 1.

The primary hypothesis noted above stated that negative potential excursion caused a change in the monolayer that promoted faster electron transfer. The initial 4-bromophenyl monolayer significantly

Table 1 Kinetic data for modified electrode

Redox system	$\Delta E_{p,obs}/V$ unmodified	$k^0_{obs}/cm\,s^{-1}$ unmodified	$\Delta E_{p,corr}/V$ unmodified	$k^0_{corr}/cm\,s^{-1}$ unmodified	$\Delta E_{p,obs}/V$ modified	$k^0_{obs}/cm\,s^{-1}$ modified	$\Delta E_{p,obs}/V$ ON	$k^0_{obs}/cm\,s^{-1}$ ON
$Fe(CN)_6{}^{3-/4-}$ (2 m*M*)	72	1.76×10^{-2}	70	2.1×10^{-2}	non-determinable	non-determinable	73	1.60×10^{-2}
$Fe(CN)_6{}^{3-/4-}$ (4 m*M*)	74	1.58×10^{-2}	70	2.1×10^{-2}	non-determinable	non-determinable	75	1.51×10^{-2}
$Fe(CN)_6{}^{3-/4-}$ (6 m*M*)	76	1.48×10^{-2}	70	2.1×10^{-2}	non-determinable	non-determinable	77	1.43×10^{-2}
$Fe(CN)_6{}^{3-/4-}$ (8 m*M*)	78	1.32×10^{-2}	70	2.1×10^{-2}	non-determinable	non-determinable	81	1.10×10^{-2}
$Fe(CN)_6{}^{3-/4-}$ (10 m*M*)	80	1.14×10^{-2}	70	2.1×10^{-2}	non-determinable	non-determinable	83	1.07×10^{-2}

decelerates the electron – transfer (ET) rate for $\mathrm{Fe(CN)_6}^{3-/4-}$. When a 4-bromopheyl monolayer is turned to conducting state, the *iR*-corrected value of ΔE_p changed from zero to 70 mV, which corresponds to an ET rate increase from zero to 0.021 cm/s.

Although the rate constants were not determined rigorously as function of scan rate, Table 1 includes a column listing approximate rate constants. There are several possibilities for the mechanism of rate enhancement associated with negative potential excursions, and they will be considered in turn.

First the monolayer might be reductively desorbed to create pinholes or bare electrode areas, which exhibit faster kinetics than the intact monolayer. However such pinholes should be electroactive toward dopamine, and should not yield the flat response of Fig. 2. The lack of dopamine response rules out significant regions of uncovered GC.

Second, a possible explanation for the apparent change in ET kinetics is the contribution of monolayer resistance to the uncompensated resistance. The monolayer acts as a resistor in series with the cell, and a significant decrease upon conducting state would cause a decrease in ΔE_p. However, the weak dependence of ΔE_p on redox system concentrations rules out a significant contribution of monolayer resistance to ohmic potential error. Kinetic effects that may be responsible for the observed change in ET rate involve electron tunneling through the monolayer. The tunneling may be modified by a change in monolayer structure that accompanies conducting state.

Electron tunneling through structurally similar phenylethynyl monolayers has been studied using the Au/thiol self-assembled monolayer system, for which the ET rate decreases exponentially with monolayer thickness [32, 33]. The rate of tunneling decreases exponentially with the thickness of the barrier and is given in its simplest form by the *Simmons* relation, Eq. (2) [34, 35], where $J =$ current density ($\mathrm{A/cm^2}$), $q =$ electron charge, $V =$ applied voltage, $h =$ *Planck*'s constant, $m =$ electron mass, $\Phi =$ barrier height, and $d =$ barrier thickness.

$$J = \frac{q^2 V}{h^2 d}(2m\Phi)^{1/2}\exp\left[\frac{-4\Pi d}{h}(2m\Phi)^{1/2}\right] \qquad (2)$$

Equation (2) shows only the linear term for a rectangular tunneling barrier, but it does show the exponential dependence on *d*. This equation is often simplified to a form useful for comparison to experiment, Eq. (3), where *B* is a constant and β has units of inverse Å or inverse nanometers. By comparison to Eq. (2), we note that β is proportional to the square root of the barrier height.

$$J = Be^{-\beta d} \qquad (3)$$

The observed tunneling rates in molecular junction often depend exponentially on the junction thickness. Reported exponential β factors of 0.4–0.6 $\mathrm{Å^{-1}}$ for electron tunneling in such a monolayer lead to a predicted decrease in tunneling rate by factors 70–700 for this range of β values, compared to an unmodified electrode [36].

The calculated HOMO-LUMO gap and the tunneling which corresponds to the distance of the carbon surface to the *van der Waals* radius of the terminal atom (bromine) are shown in Table 2. Tunneling factors for $\beta = 0.4\ \mathrm{Å^{-1}}$ are listed in Table 2 to serve as an indication of the magnitude of the effect.

The electronic structure and thickness of the monolayer should both affect the tunneling rate. The dependence of electron transport on molecular structure is currently an active area of research [37–42]. It was proposed that the electron injection into the monolayer from the GC substrate results in a reduced HOMO-LUMO gap and a higher electronic conductance. The product of electron injection can be considered an anion radical and, depending on the

Table 2 Calculated parameters for monolayer molecule

Molecule	HOMO-LUMO[a] E/eV	Length[b] / Å	*Simmons*[c] ratio	Tunneling factor[d] for $\beta = 0.4\ \mathrm{Å^{-1}}$
4-Bromophenyl	0.13	6.360	–	0.0785
4-Bromophenyl anion radical	0.07	6.371	1.4069	0.0694

[a] From *Gauss*ian 98, *B3LYP* with 6-31G** basis set. [b] From carbon surface to *van der Waals* radius of terminal Br atom, using *Gauss*ian geometry. [c] Predicted ratio of tunneling rates calculated from a linear *Simmons* equation. Cited number is the ratio of the tunneling rate for the radical molecule to that for the parent molecule and is controlled mainly by the difference in HOMO-LUMO gap. [d] $\exp(-\beta d)$, where d is the molecule length

nature of the monolayer-GC bond, a significant decrease in the HOMO-LUMO gap was observed due to the electron injection. The *Simmons* model has often been used to estimate the effect of tunneling barrier height and thickness on the electron tunneling rate and predicts that the rate is exponential in the product of the thickness and the square of the barrier height [43–45].

Both the *Simmons* model and theoretical calculation results are approximations of the real phenomena and structures, but these estimates do indicate that the changes in the electronic structure of the monolayer upon electron injection can result in large changes in the rate of electron tunneling. In Table 2, the length of molecule and anion radical are not so different. However, it seems that the rate of tunneling is determined mostly by the HOMO-LUMO gap.

The effects of the thickness and HOMO-LUMO gap listed in Table 2 showed the same trends as the observed rate constants from Table 1, with slower rates observed for longer molecules and larger HOMO-LUMO gaps.

In conclusion, we have shown that a GC electrode modified with a 4-bromophenyl monolayer exhibited very slow electron transfer in comparison to the unmodified surface by factors which varied with the redox systems. However, after scanning the modified electrode in 0.1 *M* *TBA*BF_4 in acetonitrile electron transfer kinetics were improved again. This effect is attributed to an apparently irreversible structural change in the 4-bromophenylmonolayer, which increases the rate of electron tunneling. The transition to the conducting state is associated with electron injection into the monolayer and causes a significant decrease in the calculated HOMO-LUMO gap for the monolayer molecule. Once the monolayer is switched to conducting state, it supports rapid electron exchange with the redox system, but not with dopamine, which requires adsorption to the electrode surface.

Exprimental

Reagents

Acetonitrile, tetrabutylammonium tetrafluoroborate (*TBA*BF_4), potassium ferricyanide, sulfuric acid, potassium chloride, and 4-bromophenyldiazonium tetrafluoroborate were reagent grade (Fluka) and were used as received. Solutions were prepared fresh daily and degassed with ultra pure (99.99%) nitrogen gas for 10 min before use.

Electrode preparation and procedure

Glassy carbon electrodes were used as working electrodes. A platinum wire and an Ag/AgCl (3 *M* KCl) electrode were used as counter and reference electrodes. All potentials were reported *versus* the Ag/AgCl reference electrode. The glassy carbon electrode surface was cleaned by polishing with 0.05 μm alumina slurry. After polishing, the electrode was washed with water and dried with nitrogen gas. Electrochemical modification of the glassy carbon electrode was carried out in acetonitrile containing the diazonium salt and 0.1 *M* *TBA*BF_4 using cyclic voltammetry for one cycle between −0.7 and 1.1 V *vs.* Ag/AgCl. After the modification, the electrode was washed by rinsing with acetonitrile, then it was placed in acetonitrile containing 0.1 *M* *TBA*BF_4, and finally scanned from 0.4 to −1.1 V for 25 cycles. This process will be referred to as turning the electrode on conducting state.

Instrumentation and procedure

Electrochemical measurements were performed in a one-compartment cell using the three-electrode configuration. Cyclic voltammetry was performed using a potentiostat/galvanostat Model 263 A (EG & G Princeton Applied Research) interfaced with a PC and the electrochemical set-up was controlled with Model *M* 270 software.

Theoretical calculations

Molecular orbitals and geometries were calculated with density functional theory (DFT) *B3LYP* using the Gaussian 98 programs package with a 6–31G** basis set [46]. For anion radicals the unrestricted, open-shell method was used, and the HOMO-LUMO gap was taken as the difference between the half-occupied orbital and the highest filled orbital. Also the anion radical's ground state wave functions were checked for stability. The nature of optimized geometry was characterized using the *Hess*ian matrix.

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