Modified Carbon Surfaces as "Organic Electrodes" That Exhibit Conductance Switching

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Glassy carbon (GC) surfaces modified with monolayers of biphenyl and nitrobiphenyl molecules were examined as voltammetric electrodes for ferrocene, benzoquinone, and tetracyanoquinodimethane electrochemistry in acetonitrile. The modified electrodes exhibited slower electron transfer than unmodified GC, by factors that varied with the monolayer and redox system. However, after a negative potential excursion to ∼−2.0 V versus Ag⁺/Ag, the modified electrodes exhibited much faster electron-transfer kinetics, approaching those observed on unmodified GC. The effect is attributed to an apparently irreversible structural change in the biphenyl or nitrobiphenyl monolayer, which increases the rate of electron tunneling. The transition to the "ON" state is associated with electron injection into the monolayer similar to that observed in previous spectroscopic investigations and causes a significant decrease in the calculated HOMO−LUMO gap for the monolayer molecule. Once the monolayer is switched ON, it supports rapid electron exchange with outer-sphere redox systems, but not with dopamine, which requires adsorption to the GC surface. The increase in electron-transfer rate with electron injection is consistent with an increase in electron tunneling rate through the monolayer, caused by a significant decrease in tunneling barrier height. The ON electrode can reduce biphenyl- or nitro-biphenyldiazonium reagent in solution to permit formation of a second modification layer of biphenyl or nitrobiphenyl molecules. This "double derivatization" procedure was used to prepare tetraphenyl- and nitrotetraphenyl-modified electrodes, which exhibit significantly slower electron transfer than their biphenyl and nitrobiphenyl counterparts. A "switching" electrode may have useful properties for electroanalytical applications and possibly in electrocatalysis. In addition, the ON state represents an "organic electrode" in which electron transfer occurs at an interface between an organic conductor and a solution rather than an interface between a solution and a metal or carbon electrode.

Surface modification of voltammetric electrodes has been directed toward several goals, often involving electrode kinetics and chemical selectivity. In many cases, a surface-bound functional group can effect selectivity by electrostatic repulsion or attraction, by providing a binding site for particular species, or by serving as a catalyst for certain electrochemical reactions. Of direct relevance to the current report are redox polymer modifications in which electrons (or holes) are transported in a surface film by electron hopping among polymer-bound redox centers.[1−6] Electron hopping in such systems usually requires accompanying motion of counterions and is subject to a reorganization energy barrier.[3] Such electrodes "wired" by redox polymers have been applied in electroanalysis and molecular electronic devices.[6−13] There is a large literature on electrochemical formation of conducting polymers but only a few reports of conducting polymers as electrodes for redox processes in solution.[14−20] Conducting polymers differ fundamentally from redox polymers in that electron conduction does not depend on redox centers or counterion motion. The electrons are delocalized in the bands inherent in a doped conducting polymer, yielding electronic properties similar to those of a metal. Mark et al. have shown that conducting polymer surfaces can act as electrodes for

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biological molecules such as catechols and can exhibit electro-catalytic properties depending on the presence of heteroatoms and metals.[15,18,21,22]

We reported recently the conductance-switching behavior of several organic monolayers on carbon surfaces.[23,24] In the presence of a negative voltage applied between a graphitic conductor and a metallic top contact, a monolayer of nitroazobenzene, nitrobiphenyl, or biphenyl "switched" from a high-resistance state to one with a factor of 10 or more lower resistance. Switching was repeatable many times and exhibited a hysteresis of $1-2$ V. Early indications are that the conducting state is nearly metallic, with small or negligible injection barrier between the carbon and conducting monolayer. Although the monolayer has some similarities to a conducting polymer, it is oriented, very thin (~ 15 Å), and strongly bonded to the graphitic substrate by a conjugated, covalent bond.

The current work investigates conductance switching in an electrochemical context, in which a modified electrode is immersed in 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 organic monolayer thus replaces the carbon substrate to form an "organic electrode". This approach was undertaken not only to investigate the properties of a "switching" organic electrode but also to provide insight into the switching mechanism itself.

EXPERIMENTAL SECTION

Diazonium reduction is a very effective means to modify carbon surfaces,[25-30] but care is required to successfully synthesize the reagents and modify the surface without multilayer formation. Problems occur when "old" diazonium reagent, high reagent concentrations (>1 mM), and long deposition times at excessive negative potentials are used.[31,32] The following procedure is described in detail to avoid these difficulties.

Polishing and Cleaning of Glassy Carbon Electrodes. Commercial glassy carbon (GC) electrodes (Bioanalytical Systems, 0.070 cm² area) were polished successively in 1-, 0.3-, and 0.05-μm alumina slurries made from dry Buehler alumina and Barnstead Nanopure water (18 M$\Omega\cdot$cm) on Buehler polishing microcloth. Polished GC electrodes were sonicated in Nanopure

water and then in a mixture of 50:50 (v/v) 2-propanol (IPA) (Mallinckrodt AR)/acetonitrile (Aldrich 99.5+%) combined with an equal volume of Norit A activated carbon, in both cases for 10 min.[33] Pure 2-propanol containing an equal volume of activated carbon was used for cleaning in some cases and produced results similar to the IPA/MeCN mixture. Samples were rinsed with acetonitrile, which had been purified with activated carbon, and then with Nanopure water, dried with an argon gas stream, and derivatized immediately. In the procedures described below AC/MeCN, AC/IPA, and AC/IPA/MeCN refer to acetonitrile, 2-propanol, and 50/50 2-propanol/acetonitrile purified with an equal volume of Norit A activated carbon and filtered through Whatman filter paper No. 1. Derivatized electrodes were not sonicated, to reduce the possibility of damage to the monolayer.

Derivatization of GC with Diazonium Tetrafluoroborate Salt. The electrochemical derivatization procedure was adapted from published procedures.[25-29] Surface derivatization of GC was performed using 1 mM solutions of the corresponding diazonium salt in 0.1 M n-tetrabutylammonium tetrafluoroborate (TBABF$_4$, Aldrich) in acetonitrile. The diazonium salt solutions were deaerated with argon for at least 15 min before derivatization. Derivatization of the surfaces was performed using cyclic voltammetry with a scan rate of 200 mV/s for one cycle between $+0.4$ and -0.8 V versus Ag$^+$/Ag. Warning! Certain diazonium reagents are prone to multilayer formation due to electron transfer through the monolayer to additional reagent in solution.[24,32,34] Unless stated otherwise, nitrobiphenyl (NBP) and biphenyl (BP) monolayers were formed with one derivatization scan. It will become apparent later why it is important to distinguish between a "1-scan" and "10-scan" layer, the latter involving 10 complete cycles between $+0.4$ and -0.8 V.

For derivatization of GC electrodes with tetraphenyl (TeP) and nitrotetraphenyl (NTeP) layers, GC was derivatized first using biphenyldiazonium salt (1 scan) as described above. Following the derivatization with BP, the electrode was cleaned in stirred AC/IPA for 15 min; then it was placed in acetonitrile containing 0.1 M TBABF$_4$ and scanned from -1.8 to -2.0 V at a scan rate of 20 mV/s for 10 cycles. This process will be referred to as turning the electrode "ON". The ON electrode was derivatized again with BP diazonium ion or NBP diazonium ion to obtain TeP- and NTeP-derivatized surfaces, respectively.

Electrochemical Measurements. All electrochemical measurements were performed with a BAS 100-W potentiostat (Bioanalytical Systems, West Lafayette, IN), Ag/Ag$^+$ reference electrode (BAS). AgNO$_3$ (10 mM) was dissolved in 0.1 M TBABF$_4$ in acetonitrile for the reference electrode, and the Ag$^+$/Ag electrode was calibrated with ferrocene (EE = 0.307 V vs SCE) to have a potential of 0.113 V versus SCE. Unless stated otherwise, all potentials cited herein use this Ag$^+$/Ag potential as a reference. Unless indicated otherwise, an ON electrode had been scanned for 10 cycles between -1.8 and -2.0 V versus Ag$^+$/Ag at 20 mV/s.

Synthesis of 4-Biphenyl- and 4-Nitrobiphenyldiazonium Tetrafluoroborate. Approximately 0.5 g of amino precursor (4-aminobiphenyl (Aldrich) or 4-amino-4′-nitrobiphenyl (Aldrich)

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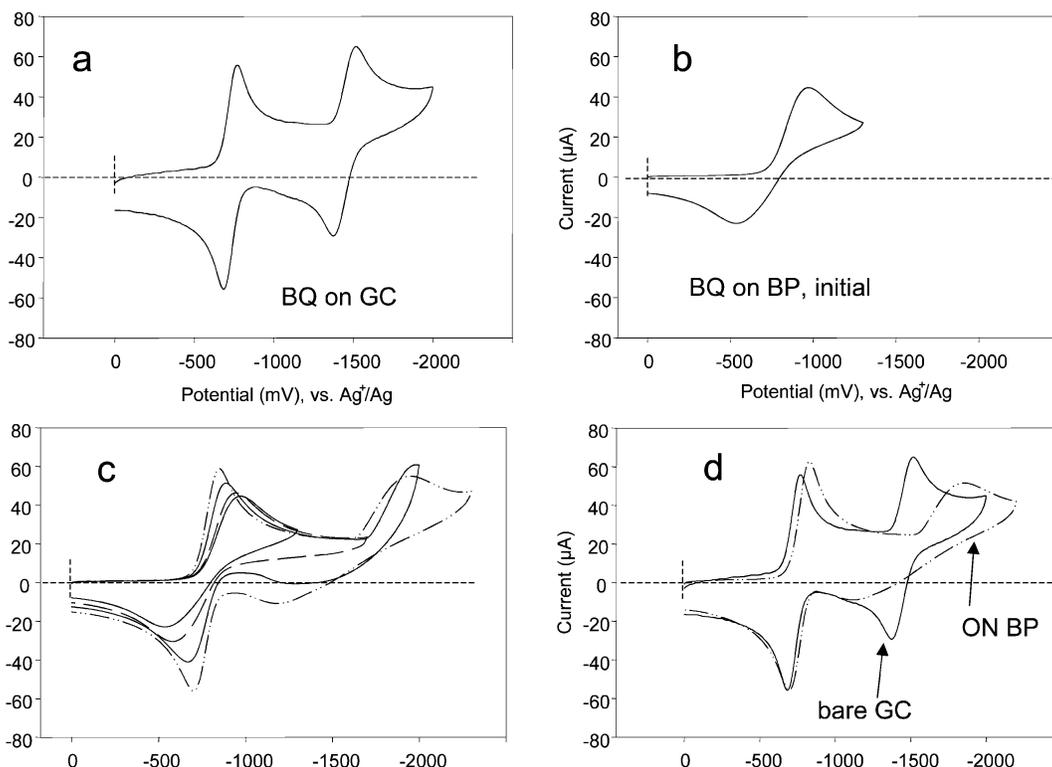
Figure 1. Voltammograms of 1 mM benzoquinone in 0.1 M TBABF$_4$ in acetonitrile, 0.5 V/s scan rate. (a) unmodified GC electrode; (b) first scan on biphenyl-modified GC; (c) four scans with progressively more negative potential limits (−1.3, −1.7, −2.0, and −2.2 V vs Ag$^+$/Ag) on BP modified GC; (d) comparison of unmodified GC (solid) with BP-modified electrode which had been cycled 10 times between −1.8 and −2.0 V at 20 mV/s (dashed).

was weighed into a three-necked 50-mL round-bottom flask; then 10 mL of 50% fluoroboric acid (Fisher "purified" HBF$_4$) was added and the resultant mixture stirred with a magnetic stirring bar. A 3:1 molar ratio of NaNO$_2$ (relative to amino precursor) was weighed into a separate container, just enough water was added to dissolve the NaNO$_2$ at room temperature, and the solution was cooled to 0 °C. A thermometer was inserted in the three-necked flask, and the precursor solution was cooled to 0 °C in the ice bath. The cold NaNO$_2$ solution was added dropwise, and the temperature was always kept below 4 °C during the reaction. Following the complete addition of NaNO$_2$, the mixture was stirred ∼30 min in the ice bath. The insoluble diazonium salt was filtered in a Buchner funnel, and anhydrous ether (Fisher) was used to remove the remaining sediments from the round-bottom flask. The product was recrystallized by dissolving in cold (0 °C) acetonitrile followed by slow addition of cold anhydrous ether to recover the diazonium tetrafluoroborate salt. NMR and mass spectrometry were used to verify the product structure. Diazonium salts should be stored in a freezer and generally should be used within 1 month of synthesis. Older diazonium salts may be recrystallized before use. Diazonium salt solutions should be used within several hours of preparation and are quite sensitive to heat.

Calculations. Molecular orbitals and geometries were calculated with density functional theory B3LYP) using Gaussian 98 with a 6-31G(d) basis set. Anion radicals used the restricted, open-shell method, and the HOMO−LUMO gap was taken as the difference between the half-occupied orbital and the highest filled orbital. Predictions of tunneling rates with the Simmons model used only the first term, which is linear in applied voltage.

RESULTS

The phenomenon of conductance switching in an electrochemical cell is illustrated in Figure 1 for the case of benzoquinone (BQ) on a biphenyl-modified GC electrode in acetonitrile. Curve 1a is a voltammogram of 1 mM BQ on an unmodified GC electrode that had been pretreated with filtered AC/IPA, showing two 1-e$^-$ reductions at about −0.7 and −1.5 V versus Ag$^+$/Ag. Panel 1b shows a voltammogram from the same electrode after modification with one scan in biphenyldiazonium tetrafluoroborate solution and cleaning with filtered AC/IPA. The quasireversible voltammetric wave on the modified surface has a significantly larger ΔE_p than that on the unmodified GC surface (399 mV compared to 96 mV). Figure 1c shows a progression of voltammograms with increasingly negative potential limits to −1.3, −1.7, −2.0, and −2.2 V. As the scan proceeds to more negative potentials, the ΔE_p for the first reduction peak decreases. Figure 1d shows an overlay of the BQ voltammogram obtained on unmodified GC and that from the biphenyl-modified electrode after extensive negative scanning (10 cycles between −1.8 and −2.0 at 20 mV/s). Notice that the BP-modified surface now exhibits a ΔE_p for the first reduction which is much closer to that on unmodified GC (135 compared to 96 mV), while the second reduction wave is qualitatively different from that on bare GC. Figure 2 shows similar experiments for the ferrocene (Fc) and TCNQ redox systems on a BP-modified GC electrode. In each case, the response on unmodified GC is overlaid with the first scan on BP-modified GC and that obtained after several potential excursions to −2.0 V. All three redox systems exhibit slow electron transfer for the initial BP surface, and all three exhibit a major decrease in ΔE_p following negative

Table 1. Electrode Kinetic Data for Modified GC

monolayer	redox system[a]	initial ΔE_p,[b] mV	ON[c] ΔE_p,[b] mV	initial $k°$, cm/s[d]	ON $k°$, cm/s[d]	$k°_{ON}/k°_{initial}$
unmodified GC	Fc	91				
	Fc (0.1 mM)	72				
	Fc (0.0 mM)[e]	68		>0.3		
	TCNQ[f]	89				
	BQ[f]	96				
BP (1 scan)	Fc	458	113	0.00065	0.029	45
	TCNQ	157	117	0.014	0.042	3.0
	BQ, 0.0 mM	377	99	0.0014	0.040	18.6
	BQ, 0.1 mM	373	105			
	BQ, 0.5 mM	407	121			
	BQ, 1.0 mM	399	135			
NBP (1 scan)	Fc	136	100	0.019	0.039	2.1
	TCNQ	225	113	0.0064	0.029	4.5
	TCNQ, 0.1 mM	172	79	0.012	0.079	6.6
	BQ	178	118	0.011	0.031	2.8
BP+ BP	Fc	613	139	1.5×10^{-4}	0.018	120
	TCNQ	323	150	2.2×10^{-4}	0.015	6.8
	BQ	877	340	1.2×10^{-5}	0.002	166
BP+ NBP	Fc	939	110	5.8×10^{-6}	0.031	5340
	TCNQ	905	120	8.5×10^{-6}	0.024	2820
	BQ	915	177	7.5×10^{-6}	0.011	1470
BP (10 scan)	Fc	246	103	5.1×10^{-3}	0.033	6.5
	TCNQ	790	152	2.5×10^{-5}	0.015	600
	BQ	973	403	4.5×10^{-6}	0.0011	244
NBP (10 scan)	Fc	986	111	3.6×10^{-6}	.030	8300
	TCNQ	867	119	1.3×10^{-5}	0.024	1850
	BQ	503	136	4.3×10^{-4}	0.019	44

[a] Solution 1 mM in 0.1 M TBABF$_4$, unless indicated otherwise. [b] At 0.5 V/s unless indicated otherwise. [c] After 0 cycles between -1.8 and -2.0 V vs Ag$^+$/Ag, 20 mV/s. [d] Determined from ΔE_p using Butler–Volmer kinetics with $\alpha = 0.5$ and D = 2.4×10^{-5} cm^2/s, using Digisim simulation software from Bioanalytical Systems. [e] Zero concentration indicates the ΔE_p is the intercept of a plot of ΔE_p vs peak current. [f] Entries are for the first reduction wave for BQ and TCNQ.

potential excursions. The three redox systems were also examined on nitrobiphenyl-modified GC with a protocol similar to that in Figure 1. The kinetic effects were similar to those observed for a biphenyl-modified GC electrode, with the results summarized in Table 1. For both the BP and NBP monolayers, the relatively small ΔE_p values (e.g., Figure 1d) persisted for at least several hours in solution or gaseous N$_2$.

A working hypothesis that will be substantiated below is that extreme negative potentials (<-1.5 V) "switch" the BP or NBP monolayer into a state that supports faster electron transfer. We will refer to this new state as an ON surface, to distinguish it from the "initial" modified surface. Note that the BP or NBP layer acts as the electrode in either the initial or ON state, but electron transfer is relatively rapid with the Fc, BQ, and TCNQ couples in the ON state. The ON state is persistent for at least several hours, and the observed ΔE_p values are close to those for the unmodified GC surface for the outer-sphere redox systems considered here.

The process of switching a BP GC electrode ON depends on the extent of the negative potential scans, as shown in Figure 3. For BP, the ΔE_p decreases gradually after potential scans to potentials between about -0.6 and -2.0 V versus Ag$^+$/Ag. Extensive scanning to -2.0 V further reduced ΔE_p, implying that the switching process is fairly slow, but becomes more rapid at progressively negative potentials. NO$_2$ group reduction has been reported for nitrophenyl and nitroazobenzene monolayers in the region of -1.4 V versus Ag$^+$/Ag.[25,26,28] The Fc response of an NBP GC electrode begins to change when the negative scan progresses to values negative of -0.6 V, while the BP surface shows changes at somewhat more negative potentials. For the NBP surface, the decrease in ΔE_p correlates approximately with the reduction of
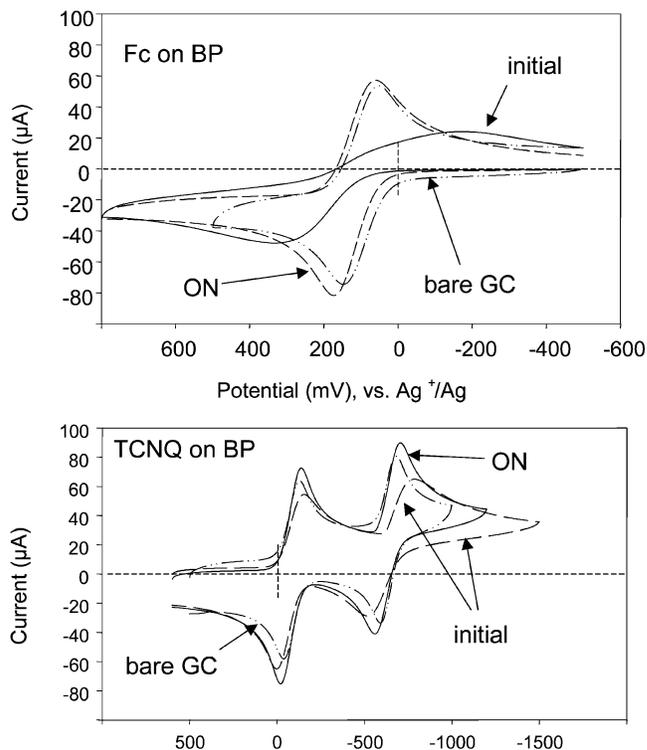

Figure 2. Voltammetry of ferrocene (upper panel) and TCNQ (lower) on a BP-modified GC electrode, 0.5 V/s scan rate. Responses on unmodified GC, initial biphenyl-modified GC, and biphenyl-modified GC after switching ON are identified in each panel.

the NO$_2$ group, but a similar surface reduction wave was not observed for the BP surface. The curve for BP is compared to
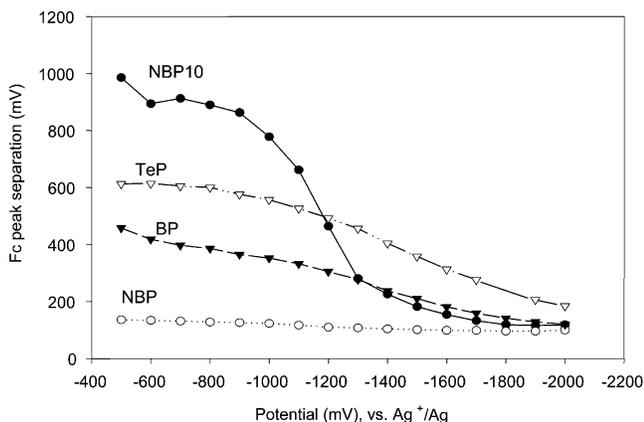
Figure 3. Peak separation for 1 mM ferrocene (0.5 V/s) on various modified electrodes following potential excursions to the values indicated on the abscissa. For each data point, the modified electrode was scanned to the negative potential indicated at 0.5 V/s and then returned to 0 V vs Ag$^+$/Ag.

two multilayer cases in Figure 3, which are discussed further below. In all cases, the transition of ΔE_p with negative potential is quite broad compared to that expected for a Nernstian process.

The results so far indicate that the BP- and NBP-modified electrodes in their ON states can transfer electrons to outer-sphere redox reactions at apparent rates approaching those of unmodified GC. A further test of electron-transfer activity is provided by an attempt to further modify the ON surface. If a biphenyl electrode is able to support electron transfer after it is turned ON, then it should also be able to reduce a diazonium ion to a radical and N$_2$. This radical might attack the previously modified surface to yield a second layer of surface modification. This process is illustrated by Figure 4, for the case of a two-step biphenyl modification. The solid curve shows two voltammetric scans of a bare GC surface in 1 mM biphenyldiazonium tetrafluoroborate solution. The second scan shows severe inhibition of the diazonium ion reduction by the initial layer of biphenyl. The electrode was then removed, placed in blank 0.1 M TBABF$_4$ solution, and turned ON by 10 scans between −1.8 and −2.0 V, as was done

for the electrodes used to make Figures 1−3. The ON electrode was then replaced in biphenyldiazonium ion solution, and the dashed curve in Figure 4 was recorded. Although the cathodic peak shape is different, the dashed curve shows restoration of the diazonium ion reduction wave, at least for one scan. The doubly modified electrode prepared in this fashion will tentatively be designated a TeP-modified GC electrode. With AFM observations to be reported separately, the modification layer thickness was determined by observing the depth of an intentional rectangular scratch made in the monolayer with the AFM tip. A line profile through such a scratch revealed a TeP layer thickness of 22−24 Å, in reasonable agreement with the length of a tetraphenyl molecule oriented perpendicular to the GC surface, 19.5 Å.

Voltammetry on the TeP-modified electrode is shown in Figure 5 for Fc and TCNQ. The initial ΔE_p for Fc (613 mV) on the TeP electrode is larger than that on the "singly" modified BP surface (458 mV). TCNQ and BQ show similar behavior, and their ΔE_p values are listed in Table 1. When the TeP electrode is turned ON, the ΔE_p decreases significantly for all three redox couples examined. For example, the ΔE_p for 1 mM Fc at 0.5V/s decreases from 613 mV for the doubly modified BP surface to 139 mV when turned ON, compared to 113 mV for the ON singly modified BP surface and 91 mV for unmodified GC. Table 1 also includes voltammetric results for a doubly modified electrode composed of biphenyl for the first step and nitrobiphenyl for the second, to tentatively yield a nitrotetraphenyl monolayer.

The results for doubly modified GC presented in Figures 4 and 5 raise a potentially serious problem with the diazonium modification of carbon surfaces. If a second modification layer can be added to an ON surface by diazonium reduction and subsequent radical attack, is it possible that a multilayer could form during the "first" derivatization if the first monolayer is switched ON during modification? In other words, could a conducting monolayer lead to uncontrolled reduction of diazonium reagent, leading to a multilayer of unknown thickness? Evidence for this behavior is shown in Figure 6(upper panel), for the case of a GC surface modified by 10 voltammetric scans to −0.8 V in nitrobiphenyldiazonium ion solution. The voltammetry of Fc on
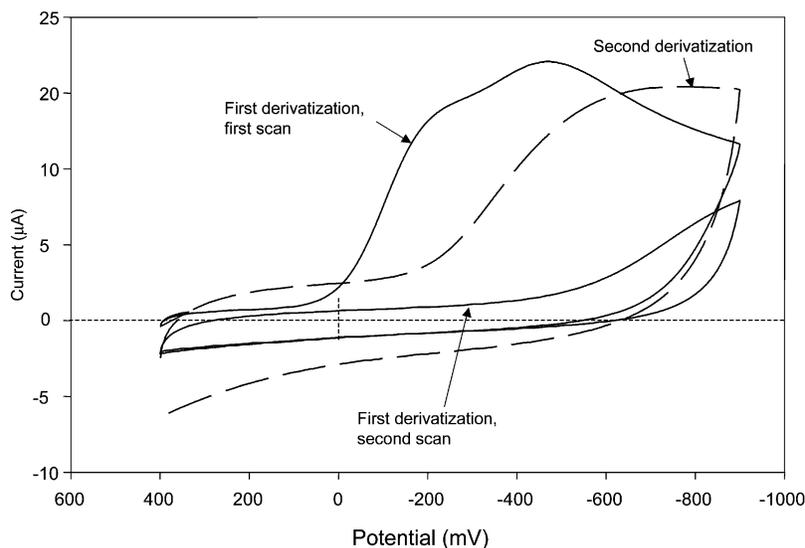

Figure 4. Voltammetry of 1 mM biphenyldiazonium ion in 0.1 M TBABF$_4$ in acetonitrile, 0.2 V/s scan rate. Two scans are shown (out of 10) for the initially bare GC electrode. Following these 10 scans, the electrode was removed, rinsed, and cycled in blank electrolyte solution 10 times between −1.8 and −2.0 V at 20 mV/s. The electrode was then returned to the BP diazonium solution for a second derivatization scan.
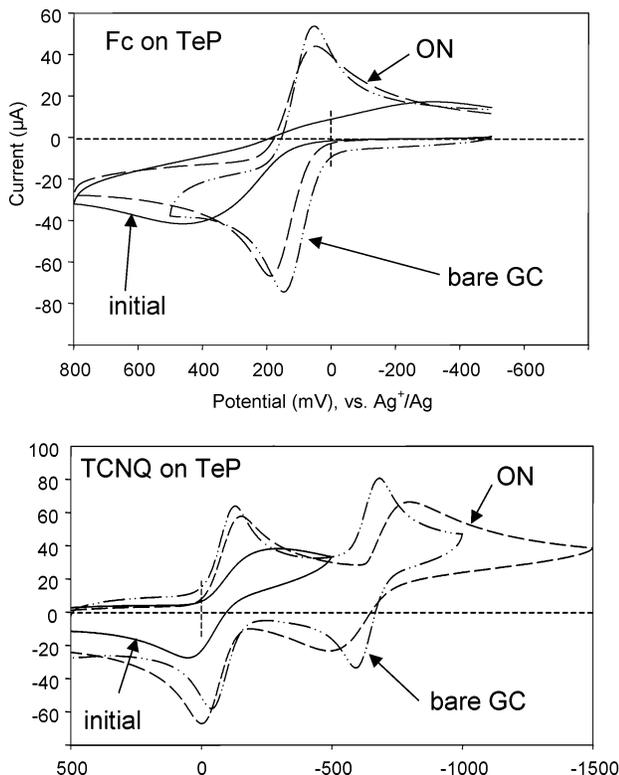
Figure 5. Voltammetry of Fc (upper panel) and TCNQ (lower panel) on GC that had been doubly derivatized by the procedure outlined in Figure 4. 0.5 V/s, 1 mM solutions in both cases. The ON electrode was prepared by cycling between −1.8 and −2.0 V.

Figure 6. Voltammetry of TCNQ in 0.1 M TBABF$_4$, 0.5 V/s, on GC that had been modified with 1 or 10 scans in 1 mM nitrobiphenyldiazonium ion solution. Upper panel is from electrodes immediately after derivatization; lower panel is for the ON state prepared as in Figure 2.

this surface shows a significantly larger ΔE_p than on a surface derivatized with a single scan, and the voltammetric wave is misshapen. The thickness of the NBP layer formed by 10 scans is 30−32 Å from AFM (to be reported separately), corresponding to approximately three NBP layers. After turning the 10-scan electrode ON with potential excursions to −2.0 V, the ΔE_p for Fc decreases from ~980 to 111 mV, only slightly larger than that for the single-scan NBP surface, 113 mV.

Dopamine (DA) oxidation in water provides a useful test of pinholes, should they be present in the initial modified electrodes or after switching ON. DA requires an adsorption site for rapid oxidation and is electroinactive on GC surfaces completely covered by nitrophenyl or trifluoromethyl monolayers.[35,36] Therefore, DA response is an indication of the presence of bare GC, as might occur from pinhole formation. Figure 7, upper panel, shows voltammograms for DA in 0.1 M H$_2$SO$_4$/H$_2$O for bare GC and for a tetraphenyl surface after turning ON. No observable DA response is visible for the TeP surface, indicating that bare GC is not exposed to the solution. The lower panel of Figure 7 shows a biphenyl-modified electrode in the initial and ON states, again in 1 mM DA solution. The initial surface shows no DA response in the potential range examined, and the ON surface shows a small oxidation current above 0.6 V. Potential scans over a wider potential range on the ON surface show a very broad DA couple with $\Delta E_p > 1200$ mV and similar to that observed on the basal plane of highly ordered pyrolytic graphite.[37,38] None of the initial or ON electrodes modified with single or multiple layers of
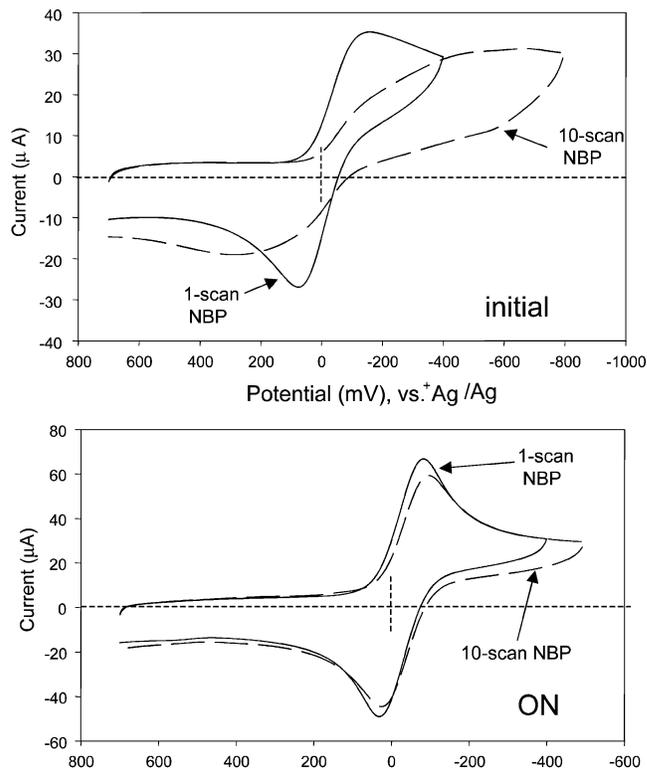
biphenyl or nitrobiphenyl exhibited a DA response similar to that shown in Figure 7 (upper panel) for the bare GC surface.

Finally, the contribution of cell or monolayer resistance to the observed ΔE_p results was evaluated by varying the concentration of the electroactive species. Results for three concentrations of BQ and two each of Fc and TCNQ are listed in Table 1 for unmodified GC and BP (1 scan) and NBP(1 scan) modifications. At a given scan rate, the increase in peak separation with higher concentration (and peak current) should be caused by uncompensated resistance, since the peak separation due to electron-transfer kinetics should be constant with concentration. The iR corrected ΔE_p is related to the peak current (i_p) and uncompensated resistance (R_u) by eq 1:

$$\Delta E_p \text{ (observed)} = \Delta E_p \text{ (corr)} + 2 i_p R_u \qquad (1)$$

A plot of ΔE_p (observed) versus i_p has a slope of $2R_u$ and intercept of ΔE_p (corr). For Fc on unmodified GC, ΔE_p (corr) is 68 mV and R_u is 186 Ω. For BQ on the singly modified BP surface, similar plots yielded R_u of 312 Ω for the initial surface and 296 Ω for the ON surface. Two ΔE_p (corr) values are included in Table 1, corresponding to zero concentration of electroactive species.

DISCUSSION

The primary hypothesis noted above stated that negative potential excursions caused a change in the monolayer that

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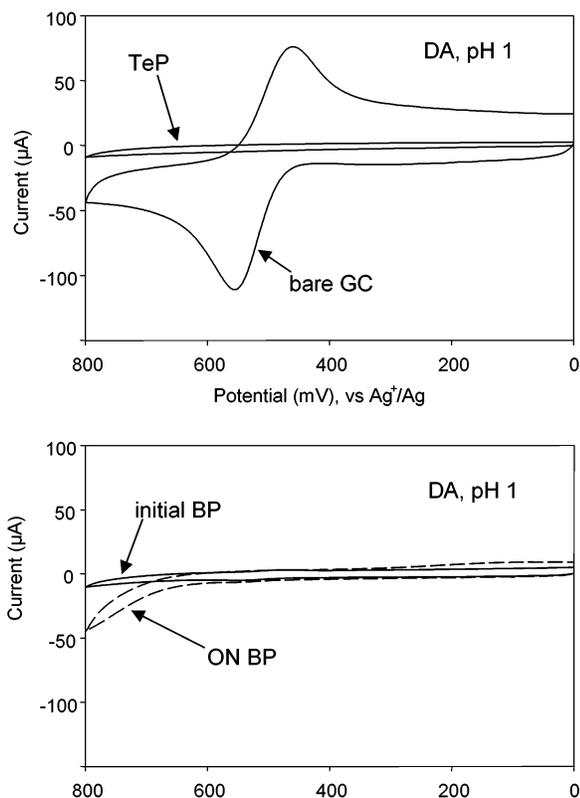
Figure 7. Voltammetry of 1 mM dopamine in 0.1 M H$_2$SO$_4$, 0.5 V/s. Upper panel shows response on an unmodified GC electrode and on a tetraphenyl electrode prepared by double derivatization with biphenyl. Lower panel shows a biphenyl (1 scan)-modified GC electrode after derivatization (solid) and after turning ON (dashed).

promoted faster electron transfer. The observed effect occurred for three redox systems on two monolayer structures singly or in combination. The initial BP or NBP monolayer significantly decelerates the electron-transfer (ET) rate for all three outer-sphere redox systems. For example, the change in ΔE_p for BQ from the *iR*-corrected value of 377 to 99 mV when a BP monolayer is turned ON corresponds to an ET rate increase from 0.0014 to 0.040 cm/s, or a factor of 29. Although the rate constants were not determined rigorously as functions of scan rate and concentration, Table 1 includes a column listing approximate rate constants and ratios of the ON to initial $k°$ values. The apparent ET rates on the NBP surface are faster than those on BP for Fc and BQ but slower for TCNQ. In addition, the thicker modification layers show a larger kinetic contrast between the initial and ON states, largely because the longer molecule decelerates the initial rate to a significantly greater degree. It should be emphasized that the electron-transfer reaction on the modified electrodes occurs at the interface between a phenyl ring or nitro group and the solution, hence the term "organic electrode". Although the current results purposely examined outer-sphere redox systems, we might expect many redox reactions to behave fundamentally differently on an organic surface than on a metal or GC.

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 GC 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 Figure 7. Although the aqueous, multistep dopamine oxidation is quite different mechanistically from the redox systems studied in acetonitrile, the lack of dopamine response rules out significant regions of uncovered GC. Furthermore, the second reduction waves for BQ and TCNQ are perturbed significantly for the ON surface compared to bare GC, indicating that the electrode surface is quite different from bare GC. In addition, the ΔE_p for the ON surface is often within 10 mV of that for the unmodified electrode (e.g., 105 mV for BQ on BP compared to 96 mV on bare GC). For the apparent rate to be this close to the bare GC value due to desorption, the surface would need to have significant bare regions and would be able to oxidize DA. Finally, if the negative potential excursion were merely creating pinholes, the second derivatization step shown in Figure 4 would patch the holes and not add a second layer of biphenyl. The AFM results and the slower kinetics of the doubly modified BP surface strongly support the conclusion that a second BP layer has resulted from the procedure illustrated in Figure 4. A second 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 in monolayer resistance upon switching ON would cause a decrease in ΔE_p. However, the weak dependence of ΔE_p on redox system concentration rules out a significant contribution of monolayer resistance to ohmic potential error. For example, a decrease in peak current of a factor of 7.5 when the BQ concentration is decreased from 1.0 to 0.1 mM on a BP surface caused a decrease in ΔE_p of only 26 mV. This is not possible if the contribution of the monolayer to ΔE_p were solely ohmic. The slopes of plots of peak potential versus peak current yield the uncompensated resistance, and these values ranged from 185 Ω for unmodified GC to 312 Ω for the initial biphenyl surface. Thus, the monolayer contributes at most 150 Ω to the uncompensated resistance and only ~14 mV to a typical ΔE_p for a 1 mM solution.

Kinetic effects that may be responsible for the observed changes in ET rate include electron tunneling through the monolayer and activation effects associated with reorganization of the redox system during ET at the solution/monolayer interface. Both tunneling and reorganization may be modified by changes in monolayer structure or orientation that accompany switching, although the latter is less likely since the initial and switched monolayers have geometrically similar surfaces. Electron tunneling through structurally similar poly(phenylethynyl) mono-layers has been studied using the Au/thiol self-assembled mono-layer system, and the ET rate decreases exponentially with monolayer thickness.[39,40] Reported exponential β factors of 0.4−0.6 Å^{-1} for electron tunneling in such monolayers lead to a predicted decrease in tunneling rate by factors of 70−700 for this range of β values and a 10.9-Å-thick biphenyl monolayer, compared to an unmodified electrode. Tunneling factors for $\beta = 0.4$ Å^{-1} are listed in Table 2 to serve as an indication of the magnitude of the effect. Previous results from our laboratory in aqueous

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Table 2. Calculated Parameters for Monolayer Molecules

molecule	dihedral angle,[a] deg	(HOMO−LUMO),[b] eV	length,[c] Å	Simmons ratio[d]	tunnel factor[e] for $\beta = 0.4$
biphenyl	38.3	5.371	10.90		0.01278
biphenyl anion radical	7.0	2.405	11.02	2850	0.01218
biphenyl monomethide anion	16.6	2.938	10.90	622	0.01278
4-nitrobiphenyl	37.0	4.256	12.08		0.00797
4-nitrobiphenyl anion radical	21.0	2.073	12.15	1400	0.00775
4-nitrobiphenyl 4′ methide anion	1.1	1.960	12.07	1400	0.00800
tetraphenyl	36.0	4.426	19.47		0.00041
tetraphenyl anion radical	16−21	1.555	19.69	1.1×10^7	0.00038
tetraphenyl monomethide anion	12−30	1.476	19.61	2.1×10^7	0.00039
4-Nitrotetraphenyl	35.7	3.512	20.72		0.00025
4-Nitrotetraphenyl anion radical	19−30	0.836	20.81	3.1×10^8	0.00024
4-Nitrotetraphenyl methide anion	12−23	0.730	20.75	1.1×10^9	0.00025

[a] From Gaussian 98, B3LYP with 6-31G(d) basis set, angle between phenyl rings. [b] From Gaussian 98, B3LYP with 6-31G(d) basis set. [c] From carbon surface to van der Waal radius of terminal atom, using Gaussian geometry. [d] Predicted ratio of tunneling rates calculated from a linear Simmons equation. Cited number is the ratio of the tunneling rate for the indicated molecule to that for the parent molecule and is controlled mainly by the difference in HOMO−LUMO gap. [e] $\exp(-\beta d)$, where d is the molecule length. Units of β are Å^{-1}.

solution revealed a β of 0.21 Å^{-1}, which yields a tunneling factor of 9.9 for a 10.9-Å monolayer thickness. Reported values for Fc$^+$/Fc exceed 1 cm/s, on unmodified carbon and Au,[41,42] so a lower limit for the decrease in Fc rate by an initial BP monolayer is a factor of ∼50. Although this factor is only an estimate of the lower limit, it is on the same order of magnitude as the rate changes associated with electron tunneling. The electronic structure and thickness of the monolayer should both affect the tunneling rate, and the dependence of electron transport on molecular structure is currently an active area of research.[3,39,43−48]

Previous experiments on molecular junctions[23] demonstrated conductance changes in NBP and BP monolayers suspended between two metallic conductors. In the initial states for both molecules, the phenyl rings are expected to be twisted relative to each another, reducing electronic coupling between rings and resulting in relatively slow ET and high resistance. It was proposed that electron injection into the monolayer from the GC substrate results in a reduced HOMO−LUMO gap and a higher electronic conductance. Figure 8 shows possible structures for the BP and NBP monolayers before and after injection of an electron. Electron injection into structurally similar nitroazobenzene monolayers on GC in acetonitrile has been monitored spectroscopically and results in a significant structural rearrangement in the monolayer.[49] Table 2 lists the HOMO−LUMO gap for the monolayers studied here, calculated with Gaussian 98, along with the molec-

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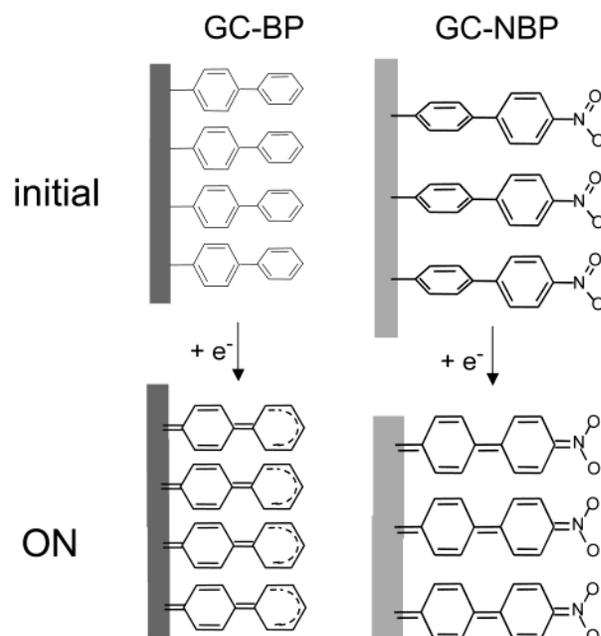
GC-BP   GC-NBP

Figure 8. Possible structures illustrating the effect of electron injection into biphenyl (left) and nitrobiphenyl (right) monolayers. Lower structures represent two of many possible resonance forms for the ON molecules.

ular length. The product of electron injection can be considered an anion radical or a "methide", depending on the nature of the monolayer−GC bond following injection. For either case, however, a significant decrease in HOMO−LUMO gap is predicted. 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 should be exponential in the product of the thickness and the square root of the barrier height.[50,51] If we consider the barrier height to equal the HOMO−LUMO gap as a first approximation, the predicted effect of electron injection on Simmons tunneling can be estimated. Table 2 includes a column listing the ratio of the Simmons tunneling rate for the

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anion radical or methide structures to that for the initial molecule. As expected qualitatively, the significant change in HOMO−LUMO gap causes a large change in Simmons tunneling rate, a factor of ∼1000 for the BP and NBP cases. Both the Simmons model and Gaussian 98 results are approximations of the real phenomena and structures, but these estimates do indicate that changes in the electronic structure of the monolayer upon electron injection can result in large changes in the rate of electron tunneling. The effects of thickness and HOMO−LUMO gap listed in Table 2 show the same trends as the observed rate constants from Table 1, with slower rates observed for longer molecules and larger HOMO−LUMO gaps.

There are some similarities between the proposed electron injection mechanism and the effect of "doping" on much thicker films of conducting polymers, with both processes resulting in a smaller HOMO−LUMO gap and higher conductivity.[21,52,53] In fact, it is possible that the injected electron is delocalized over many molecules by possibly strong lateral interactions between close-packed monolayer molecules. Spectroscopic examination of switched monolayers is currently underway in order to more precisely define the structural changes associated with the change in conductivity. The present electrochemical results indicate that facile electron transfer with the Fc^+/Fc, BQ/BQ^-, and $TCNQ/TCNQ^-$ redox systems is possible at the biphenyl/solution interface and nitrobiphenyl/solution interface for the ON state. In effect, the initially insulating biphenyl monolayer becomes the active electrode surface when switched to its conductive state. A similar mechanism applies to nitrobiphenyl, with electron injection likely to produce a quinoid structure in both BP and NBP. Figure 8 presents only one of several possible structures and resonance forms for the ON state of each molecule, but the experimental data justify the conclusion that the ON state differs significantly from the initial monolayer, in ways that support faster electron tunneling.

With the exception of dopamine, the redox systems studied here were chosen to be outer sphere and do not involve known adsorption or specific chemical interactions with the electrode surface. However, the electronic states present in the monolayer molecule may very well affect the electron-transfer rate, by analogy to semiconductor electrodes. The three redox systems cover a range of $E°$ values (+0.31 V vs SCE for Fc, +0.13 V for TCNQ, and −0.54 V for BQ)[54] and may be affected differently depending upon the energy match between their $E°$'s and the energy levels in the monolayer. The current results are insufficient to identify an effect of this energy match on the electron-transfer rate, but such a prospect may have useful consequences. If the monolayer exhibits enhanced electron transfer at certain energies by a process analogous to resonance tunneling, it may impart some selectivity of the modified electrode for certain systems with certain $E°$ values. A different effect of the monolayer on hetero-geneous kinetics is revealed by the distortion of the second reduction waves for BQ and TCNQ, even in the ON state. Either these electron transfers involve an adsorption step that is

prevented or weakened by the monolayer, or they are inherently slower than the first reductions and the monolayer effects are more evident.

There is a precedent for multilayer formation by diazonium reduction, on both ordered graphite[31] and GC[32] surfaces. Kariuki and McDermott observed formation of 200−250-Å films of nitrophenyl and diethylaminophenyl on GC following extensive diazonium reduction in acetonitrile, and they also reported that these multilayer films supported electron transfer to outer-sphere redox systems. Although they attributed their findings to defects rather than conductance switching, it is possible that electron transfer though a 250-Å film is possible due to a mechanism similar to that described here. Speaking more generally, there is likely to be a variety of diazonium reagents that can form multilayers due to conductance switching during derivatization. Multilayer formation also provides additional evidence that pinholes are not required for electron transfer through a growing film. If electrons could transfer only through pinholes, they would be rapidly "patched" and multilayer formation would be severely inhibited.

The prospect of control of electron transfer by the monolayer structure and electronic state raises many intriguing questions for further investigation, but there is an apparent inconsistency in the current results that deserves comment. Why is the transition from initial to ON state apparently irreversible? If the transition is caused by electron injection, then it should be easily reversed by the corresponding oxidation of the monolayer. One reason might be an irreversible rearrangement in the monolayer ac-companying electron injection, such as stacking of the more planar methide products into quasicrystalline domains, or cross-linking, which "locks in" the structural changes responsible for the higher tunneling rate. Another possibility is the small electric field across the monolayer once the electrode is switched ON. Electron injection is presumably driven by the electric field across the initial monolayer created between the GC and the solution. A relatively conductive monolayer cannot support an electric field once the monolayer switches to the ON state, so the driving force for reoxidation may be much smaller. For the molecular junctions composed of a biphenyl or nitrobiphenyl monolayer between two conductors, quite high fields are required for conductance switching (∼10^7 V/cm), and switching exhibits significant hys-teresis.[23] In the electrochemical analogue presented here, it may not be possible to achieve the large field required to return the monolayer to its less conductive state.

The ability to switch an electrode to a state that supports faster electron transfer may have some important consequences in electroanalysis and molecular electronics, but the current results also raise interesting possibilities in some related areas. For the ON state of a biphenyl monolayer, solution species interact with a conducting organic surface rather than a graphitic or metallic surface. For the case of outer-sphere redox systems such as ferrocene, there may be little difference between a metal surface and an "organic electrode", resulting in the similarity of the "bare" and ON voltammograms of Figures 1 and 2. However, for any electrocatalytic process involving adsorption or interaction with surface sites, the organic monolayer may behave very differently from GC or a metal. This expectation has been realized for the case of conducting polymer electrodes, for which the voltammetric

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response of several electrocatalytic systems is strongly dependent on the conducting polymer composition.[15] The solution species in the current work is interacting with a surface consisting of the edges of phenyl rings, and such a surface may have an electrocatalytic behavior profoundly different from a metal or glassy carbon. Furthermore, it is possible to introduce various functional groups (such as the nitro group of NBP) that may alter catalytic activity while still permitting electron transfer.

A different ramification of "switchable" organic electrodes is related to the electronic changes proposed to be responsible for the ON state. As noted earlier, a molecule with a small HOMO−LUMO gap promotes tunneling, and the relatively small ΔE_p values observed for long molecules such as tetraphenyl and nitrotetraphenyl in their ON states indicate that enhanced tunneling is effective over long distances (19−21 Å). It remains to be seen if an isolated organic molecule can exhibit conduction similar to that observed for the large collection of molecules studied here. However, if only a few molecules in a collection were turned ON, or if conductive molecules were isolated by dilution in a sea of insulating molecules, it may be possible for the isolated conductive molecules to exhibit behavior approximating a "molecular wire". The result may be an ultramicroelectrode array with the diameter of each ultramicroelectrode equal to the width of a phenyl ring or nitro group, ~4 Å. If individual monolayer molecules can be made to function as independent microelectrodes, very unusual double-layer, mass transport, and kinetic effects are expected.