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Nucleophilic and electrophilic displacements on covalently modified carbon: introducing 4,4′-bipyridinium on grafted glassy carbon electrodes

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4,4′-Bipyridinium (*i.e.*, viologen) was immobilized on 4-(chloromethyl)phenyl grafted glassy carbon electrodes by a nucleophilic substitution reaction involving 1-ethyl- or 1-benzyl-4-(4′-pyridyl)pyridinium. Reaction times of about 5 days were required for these surface-constrained processes to go to completion in aqueous solution at room temperature. The applicability of the described procedure was demonstrated by performing the equivalent modification in 2 steps by reacting first with 4,4′-bipyridine, followed by quaternization of the available nitrogen to obtain the viologen functionality, that is, the surface acts as a nucleophile in a substitution reaction. However, the quaternization step was found to be possible for introducing the benzyl group but not the ethyl group. The covalently modified electrodes were reasonably stable to repeated electrochemical sweeping in acetonitrile with a 25% decrease in the observed electroactivity after 100 sweeps at a sweep rate of 2 V s^{-1}. The coverage was determined from the electrochemical response of the viologen moiety to be approximately 3×10^{-10} mol cm^{-2}. In addition to cyclic voltammetry, the presence of viologen was demonstrated by means of X-ray photoelectron spectroscopy and time-of-flight secondary ion mass spectrometry. Scanning images (500×500 μm^2) obtained by the latter technique indicated that the molecules were distributed uniformly over the entire surface. Scanning tunnelling microscopy was used to follow the individual steps of the modification procedure on highly ordered pyrolytic graphite.

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Introduction

Covalent modification of carbon surfaces has been a subject of growing interest in recent years.[1–3] In earlier studies, the preferred approach relied on oxidative treatments to introduce an oxygen functionality on the surface (*e.g.*, carboxylic, phenolic, and quinoic), followed by formation of amide bonds between the surface carboxylic groups and pendant amine groups from target molecules. Radio-frequency O_2 plasma, heating in air, chemical oxidation, and electrochemical anodization in aqueous solution have provided routes for accomplishing the oxidative treatment.[1] Unfortunately, carbon electrodes treated by any of these methods are roughened and exhibit markedly high background currents.[4] Moreover, the resulting layer is not uniform, adding to the difficulties of using such modified electrodes for analytical purposes.

Electrochemically assisted covalent coupling of various molecular species to carbon surfaces has been accomplished by oxidative procedures involving amines,[5–8] aliphatic alcohols,[9,10] or aryl acetates[11–13] and more extensively by reductive procedures employing diazonium salts under mild conditions.[14–16] The modification procedures involve the electrogeneration of reactive radicals in the vicinity of the carbon surface, leading to the formation of covalent linkages with the surface.[2,3] With these methods, the surfaces are not roughened and sub-monolayer,[6,17] monolayer,[5,11,18] or multilayer[15,19,20] coverage can be obtained. Applications have been reported in fields as diverse as material chemistry,[5] electrocatalysis,[21,22] combinatorial chemistry,[23,24] and analytical sensors.[25,26] The further development of convenient approaches to fabricate such covalently modified surfaces is therefore important.

Herein, we wish to present our results concerning the covalent coupling of 4,4′-bipyridinium (*i.e.*, viologen) to carbon electrodes. For other kinds of electrode materials there have been several articles describing the immobilization of this redox system, utilizing different techniques such as self-assembly,[27,28] Langmuir–Blodgett assembly,[29] and electropolymerization.[30] However, to our knowledge, this is the first report on the simple fabrication of viologen-functionalized electrodes in the area of electrochemically assisted grafting of carbon surfaces.[31] We selected viologen as our target molecule due to its convenient detection in the immobilized layer by electroanalytical and spectroscopic techniques, in addition to its potential applications in surface-confined molecular shuttles or switchable nano-structures and electrocatalysis.[32] The electrodes are characterized by cyclic voltammetry (CV), X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and scanning tunnelling microscopy (STM). The results demonstrate that the modified electrodes are reasonably stable to electrochemical sweeping, that measured potentials for the immobilized species correspond to their solution analogs, and that a coverage of approximately 3×10^{-10} mol cm^{-2} can be obtained.

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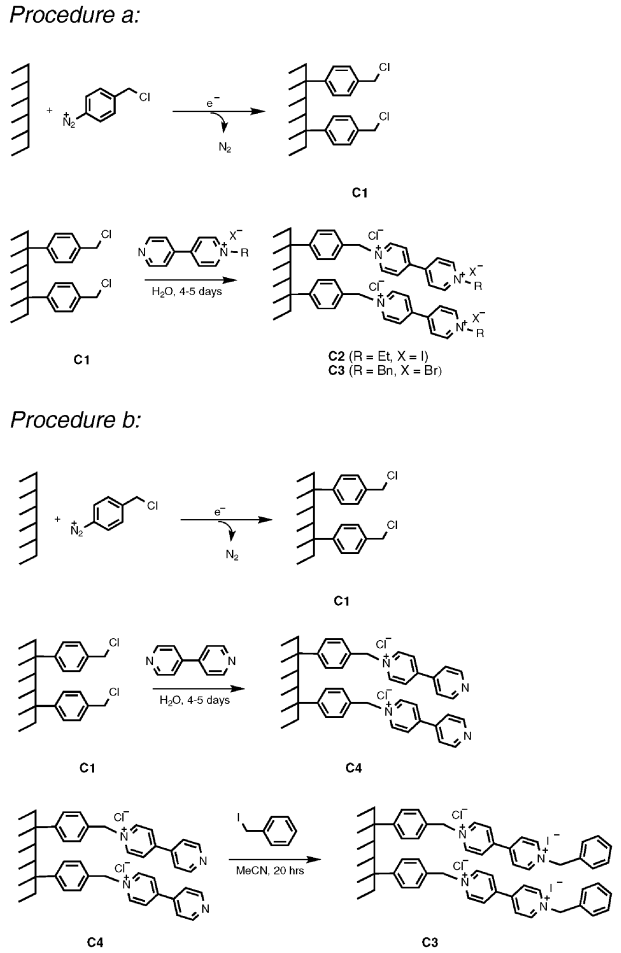
Results and discussion

Fabrication of electrodes

The fabrication of the electrodes was carried out using two different approaches outlined as procedures (a) and (b) in Scheme 1. In both approaches, a layer of 4-(chloromethyl) phenyl is initially grafted at the carbon surface (C1) by means of electrochemical reduction of 4-(chloromethyl)phenyl diazonium tetrafluoroborate.[23,24] In procedure (a) the second and final step consists of a nucleophilic attack by 1-ethyl- or 1-benzyl-4-(4′-pyridyl)pyridinium to produce the corresponding viologen-modified electrodes denoted C2 and C3, respectively. The nucleophilic displacement reaction was performed in aqueous solution for 4–5 days at room temperature as this seemed to produce the best results. It is well-known that nucleophilic reactions involving surface-constrained electrophiles are kinetically retarded,[33,34] as the backside attack has to take place in close vicinity to the surface. Accordingly, reaction rates are much slower than for analogous solution processes. There was no significant decrease in reaction times by raising the temperature, which presumably can be attributed to the complex kinetic situation, in which the conformational mobility and permeability of the modified layer, among other factors, will contribute to the overall kinetic barrier. In addition, the use of aprotic solvents such as *N*,*N*-dimethylformamide and acetonitrile did not decrease reaction times and only unsatisfactory results with lower coverages and less reproducibility were obtained.

In the alternative procedure (b) the grafted 4-(chloromethyl)phenyl carbon surface is allowed to react with 4,4′-bipyridine to afford the covalently linked monoquaternized 1-benzyl-4-(4′-pyridyl)pyridinium C4. In order to illustrate the usability of this moiety for building larger molecular structures at the surface, a subsequent quaternization of the free nitrogen is carried out using benzyl iodide, thus leading to the fabrication of C3 in an overall three-step sequence. In other words, in this approach, both the electrophilic (*i.e.*, C1) and nucleophilic (*i.e.*, C4) properties of the surface can be exploited to carry out chemical modifications.



Scheme 1 Protocols used for the fabrication of the modified electrodes.

Cyclic voltammetry

Fig. 1(A) shows cyclic voltammograms of C1 and C2 glassy carbon (GC) electrodes, that is, before and after modification of the 4-(chloromethyl)phenyl grafted surface with 1-ethyl-4-(4′-pyridyl)pyridinium, recorded in acetonitrile at a sweep rate ν of 2 V s^{-1}. While no signal is apparent for the C1 electrode in the investigated potential region, the C2 electrode displays the expected voltammetry of surface-confined viologen,[35] which demonstrates that the electroactive center is in electrical contact with the electrode.

The two one-electron electrode processes associated with the redox reactions of the dication/radical cation and the radical cation/neutral couples[34] shown in Scheme 2 are clearly identifiable by their standard potentials E°, (determined as midpoint potentials) situated at −0.39 and −0.83 V_{SCE}, respectively. These potentials are comparable to those of the solution analog, 1-benzyl-1′-ethyl-4,4′-bipyridinium, at −0.39 and −0.79 V_{SCE} , respectively [see Fig. 1(B)]. For the related C3 electrode, in which the ethyl group in C2 has been replaced by a benzyl group, the electrochemical characteristics, with E° = −0.39 and −0.87 V_{SCE}, resemble those of C2 as well as the solution analog, 1,1′-dibenzyl-4,4′-bipyridinium (E° = −0.30 and −0.70 V_{SCE}). As expected for covalently attached redox units, a plot of the logarithm of the peak currents log i_p *versus* log ν ($0.1 \leq \nu \leq 5$ V s^{-1}) exhibits a linear relationship with a

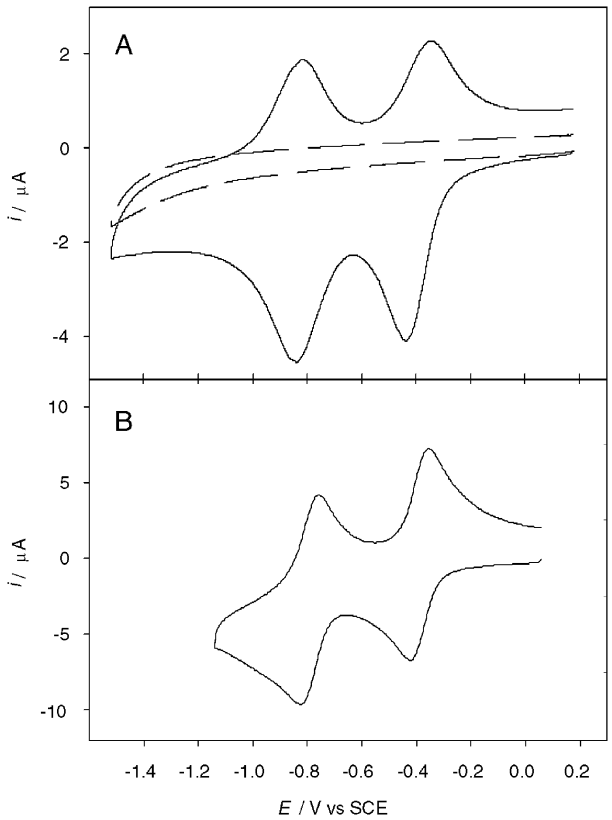
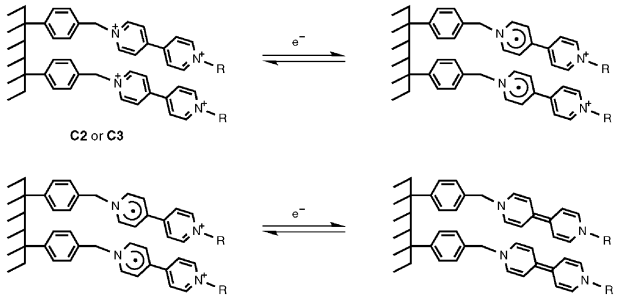


Fig. 1 Cyclic voltammograms of (A) C1 grafted GC electrode before (— —) and after (——) modification with 1-ethyl-4-(4′-pyridyl)pyridinium (C2) and (B) 0.5 mM 1-benzyl-1′-ethyl-4,4′bipyridinium dibromide in solution recorded at a GC electrode. Electrolyte: 0.1 M Bu_4NI/acetonitrile; sweep rate: 2 V s^{-1}.



Scheme 2 Electrochemical transformations of the viologen-functionalized electrodes.

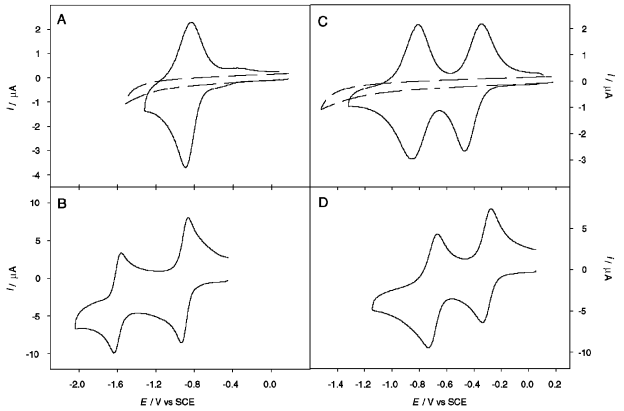


Fig. 2 Cyclic voltammograms of: (A) C1 grafted GC electrode before (— —) and after (——) modification with 4,4′-bipyridine (C4); (B) 0.5 mM 1-benzyl-4-(4′-pyridyl)pyridinium iodide in solution recorded at a GC electrode; (C) C1 grafted GC electrode before (— —) and after (——) modification with 4,4′-bipyridine and benzyl iodide (C3); (D) 0.5 mM 1,1′-dibenzyl-4,4′-bipyridinium dibromide in solution recorded at a GC electrode. Electrolyte: 0.1 M Bu_4NI/acetonitrile; sweep rate: 2 V s^{-1}.

slope close to unity (~0.95). Moreover, the peak potential separation ΔE increases as a function of ν. In absolute terms, ΔE is found to be larger for the radical cation/neutral couple (90 and 180 mV for C2 and C3, respectively) than for the dication/radical cation couple (30 and 100 mV for C2 and C3, respectively); the total width at half-height is ~180 mV for both waves at ν = 2 V s^{-1}. In comparison, ΔE for the two waves of C2 is found to be 60 and 20 mV, respectively, with total widths of ~170 mV at ν = 0.2 V s^{-1}. This non-Nernstian behavior of surface-confined viologen with a relatively low value of the standard heterogeneous rate constants stands in contrast to that observed for the solution analogs. It may be noted that the voltammetric features of viologen obtained herein for covalently modified GC surfaces are quite similar to those found for self-assembled monolayers on gold surfaces.[28]

By means of integration of the electrochemical response, the coverage Γ of electroactive centers is calculated to be 3.1 × 10^{-10} mol cm^{-2} for C2, corresponding to a molecular area of 50 $Å^2$/molecule; a similar result is obtained for C3. The coverage on carbon is comparable to that found for self-assembled monolayers on gold.[27,28,36–38] However, it should be underlined that the geometrical area is used in the calculation, and hence does not take the microscopic roughness of the GC surface into account. All relevant data are collected in Table 1.

Interestingly, if 4,4′-bipyridine is used in the surface displacement reaction [C4, procedure (b) in Scheme 1], the voltammetric behavior of the electrode changes in that only a single reduction at E° = −0.87 V_{SCE} with ΔE = 30 mV is observed [see Fig. 2(A)]. Again a linear relationship with a slope close to unity is found in a plot of log i_p *versus* log ν ($0.1 \leq \nu \leq 5$ V s^{-1}). Clearly, the molecular structure of C4 is different from that of C2 and C3, resembling now that of monoquaternized 1-benzyl-4-(4′-pyridyl)pyridinium. The solution voltammogram of the latter compound [see Fig. 2(B)] shows two waves centered at −0.90 and −1.60 V_{SCE}, corresponding to the cation/radical and the radical/anion redox couples, respectively.[35] Consequently, the single redox process observed for C4 can be assigned to the cation/radical redox couple of 1-benzyl-4-(4′-pyridyl)pyridium. At this point, the reason for the absence of the second redox process is unclear. These results demonstrate that 4,4′-bipyridine is not dialkylated at the surface; that is, upon the first substitution reaction, the free nonquaternized pyridine ring in C4 is not able to reach the right geometry for a further substitution reaction with a neighboring 4-(chloromethyl)phenyl group. Upon reacting C4 with benzyl iodide, however, the final quaternization can be accomplished and the characteristic voltammogram of C3 containing the viologen moiety emerges as shown in Fig. 2(C). The cyclic voltammogram of the solution analog 1,1′-dibenzyl-4,4′-bipyridinium is included in Fig. 2(D) for comparison purposes. These results underline that the perspectives for developing surfaces with even more complex chemical systems such as nano-switches[32,39] should be within reach, by taking advantage of the fact that both the electrophilic and nucleophilic properties of the surfaces may be exploited.

It should be noted that the quaternization and, thus, the formation of C2 from C4 was unsuccessful when the less reactive ethyl iodide was employed in place of benzyl iodide. Consequently, the only approach to form C2 is by procedure (a), in which the desired alkylation of the nitrogen atom is carried out in a solution reaction prior to the actual modification step at the surface.

In order to ascertain that viologen is indeed covalently bound to the surface through the benzyl moiety and not just immobilized directly on the surface, it was checked that GC electrodes, either unmodified or grafted with a phenyl[40] rather than a 4-(chloromethyl)phenyl group, exhibited, upon

Table 1 Standard potential E°, peak separation ΔE, and coverage Γ data obtained from modified glassy carbon electrodes and solution analogs by cyclic voltammetry[a]

	Modified GC electrodes						
	Procedure (a)		Procedure (b)		Solution analogs		
	C2	C3	C4	C3	1-bn-1′-et-bpy[b]	1,1′-dibn-bpy[c]	1-bn-bpy[d]
E_1°/V	−0.39	−0.39	−0.87	−0.42	−0.39	−0.30	−0.90
ΔE_1/mV	90	180	30	180	60	60	60
E_2°/V	−0.83	−0.87	—	−0.84	−0.79	−0.70	−1.60
ΔE_2/mV	30	100	—	70	60	60	60
Γ/mol cm^{-2}	3.1 × 10^{-10}	3.2 × 10^{-10}	3.9 × 10^{-10}	3.0 × 10^{-10}	—	—	—

[a] In 0.1 M Bu_4NI/acetonitrile at a sweep rate of 2 V s^{-1}; all potentials are given in V_{SCE}. [b] 1-Benzyl-1′-ethyl-4,4′-bipyridinium. [c] 1,1′-Dibenzyl-4,4′-bipyridinium. [d] 1-Benzyl-4-(4′-pyridyl)pyridinium.

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treatment with 4,4′-bipyridine or 1-ethyl-4-(4′-pyridyl)pyridinium, no voltammetric waves. Moreover, when C1 was treated with the diquaternized bipyridinium species 1,1′-dibenzyl-4,4′-bipyridinium, the electrochemical response still corresponded to that of untreated C1, meaning that 1,1′-dibenzyl-4,4′-bipyridinum is not adsorbed to the surface. These experiments serve to illustrate the necessity of having an unquaternized nitrogen in the bipyridine unit and a S_N2 displaceable group such as chlorine in the grafted layer.

The modified electrodes are reasonably stable to electrochemical sweeping. After 100 cycles in the potential range from 0.1 to −1.6 V_{SCE}, recorded at $\nu = 2$ V s^{-1} in 0.1 M Bu_4NI/acetonitrile, approximately 75% of the original electrochemical activity is retained. The decline in activity is presumably due to the fact that the neutral quinoic-like structure of the fully reduced viologen reacts slowly with protons and residual water.[30] If the electrode is left at a potential of −2 V_{SCE} (∼ −1.1 V below the second redox process) for 300 s, the electroactivity is lost completely. However, the electrodes are still blocked, as shown by their strong inhibition of the redox process of a ferrocene solution in cyclic voltammetry. This demonstrates the high stability of the covalently bonded chemical structures, which clearly surpasses that found for most self-assembled layers on gold.[41] Actually, the blocking property is only lost after sweeping to −2.5 V_{SCE}, probably because of changes induced in the topography of the electrode and/or destruction of the grafted layer.[42] In addition, thermal desorption experiments employing a mass spectrometer showed that the 4-(chloromethyl)phenyl layer in C1 was stable up to a temperature of 400 °C, at which point it started to decompose and fragments were detected.

X-Ray photoelectron spectroscopy

The surface elemental distribution of modified GC plates corresponding to C1 and C2 was investigated by XPS. The elemental distribution obtained after integration of the peaks with the relevant percentages is collected in Table 2.

As expected, the XPS spectrum of C1 demonstrates the presence of chlorine. Surprisingly, nitrogen is found in substantial amounts on the surface. However, for grafting procedures employing diazonium salts, this observation is not without precedent in the literature.[42] Compared to C1, the spectrum of C2 shows an increase of ∼2.6% in nitrogen content along with a concomitant ∼1.5% decrease in chlorine. This change in the distribution of the two elements is in agreement with the expected trend, even if the 2 : 1 relationship theoretically predicted in procedure (a) is not observed. The fact that a small amount of chlorine persists on C2 indicates either an incomplete substitution process with a few 4-(chloromethyl)phenyl groups being inaccessible for reaction at the surface or, alternatively, that chloride ions expelled from the nucleophilic displacement remain in the layer *via* ion-pairing with the positively charged bipyridinium layer. As a further test of the surface reactivity, samples were modified with phenyl[40] rather than 4-(chloromethyl)phenyl groups, followed by treatment with 1-ethyl-4-(4′-pyridyl)pyridinium. As expected, the nitrogen content of the resulting sample is low (see Table 2). This observation is also in line with the cyclic voltammetry analysis, which gave no indication of the presence of bipyridinium units. On the other hand, if a clean GC surface is treated with 1-ethyl-4-(4′-pyridyl)pyridinium, the result is an increase of the nitrogen content from 0.7% to 1.5% on average. This can be ascribed to the spontaneous adsorption of modest amounts of this molecule on the surface. These experiments serve to illustrate that the performed reactions are inefficient, unless the grafted surface carries a displaceable electrophilic group, that is, chlorine in 4-(chloromethyl)phenyl.

Time-of-flight secondary ion mass spectrometry

Inherently, ToF-SIMS is a more surface sensitive technique than XPS and can provide detailed information about the molecular surface composition. The analysis was performed on C1 and C2 GC plates. In addition, SIMS analysis of unmodified GC was performed in order to establish a background reference spectrum for the carbon material.

Aside from the peaks also seen for unmodified GC, in negative SIMS of C1, chloride (m/z = 34.9704 and 36.9665; [37]/[35] ∼ 37%) is the source of the most prominent peaks, this being consistent with the presence of chlorine in the 4-(chloromethyl)phenyl group. In positive SIMS of C1, peaks corresponding to those found for unmodified GC were observed in addition to an unexpected trace of ions at m/z = 242.2909 (isotopic ratio: [242]/[243] ∼ 18%), 185.2164, and 142.1650. The latter observation indicates the presence of the tetrabutylammonium ion $[(C_4H_9)_4N^+]$ accompanied by the expected fragments. Although tetrabutylammonium salts are not required as supporting electrolyte during the grafting procedure because of the presence of the diazonium salt, the GC plates may still have been exposed to them through leakage of electrolyte solution from the reference electrode. At the same time this may also provide an explanation for some of the nitrogen found in the XPS analysis of C1. No signs of the (chloromethyl)phenyl ion at m/z = 125 and 127 were detected. Likewise, there was no indication of the presence of the 4-(chloromethyl)phenyl diazonium ion (m/z = 153 and 155) employed in the grafting procedure.

The negative SIMS of C2 demonstrated the presence of chloride (m/z = 34.9704 and 36.9665; [37]/[35] ∼ 37%) and iodide (m/z = 126.9040). The finding of these two counter ions (see Scheme 1) is in agreement with the XPS data. In addition to the peaks observed for the unmodified GC and C1, the positive SIMS spectrum of C2 has important peaks at higher masses. The peak at m/z = 185.1122 (isotopic ratio: [186]/[185] ∼ 15%) is assigned to the 1-ethyl-4-(4′-pyridyl)pyridinium ion,

Table 2 XPS elemental compositions of modified glassy carbon plates

	Atomic concentration/%[a]				
	C 1s	N 1s	Cl 2p	N/C ratio	Cl/C ratio
GC[b]	96.8	0.7	—	0.007	—
C1[c]	81.2	2.1	1.9	0.026	0.023
C2[d]	78.0	4.7	0.4	0.060	0.005
GC-Ph/1-et-bpy[e]	88.8	1.8	—	0.020	—
GC/1-et-bpy[f]	88.9	1.5	—	0.017	—

[a] In addition to reported elements, the surfaces contained oxygen and minute amounts of impurities originating from the carbon material. [b] GC plate after ultrasonic cleansing. [c] GC plate electrochemically grafted with 4-(chloromethyl)phenyl groups. [d] C1 after treatment with 20 mM of 1-ethyl-4-(4′-pyridyl)pyridinium in aqueous solution for 5 days. [e] GC plate electrochemically grafted with phenyl groups and treated with 20 mM of 1-ethyl-4-(4′-pyridyl)pyridinium in aqueous solution for 5 days. [f] Clean GC plate exposed to 20 mM of 1-ethyl-4-(4′-pyridyl)pyridinium in aqueous solution for 5 days.

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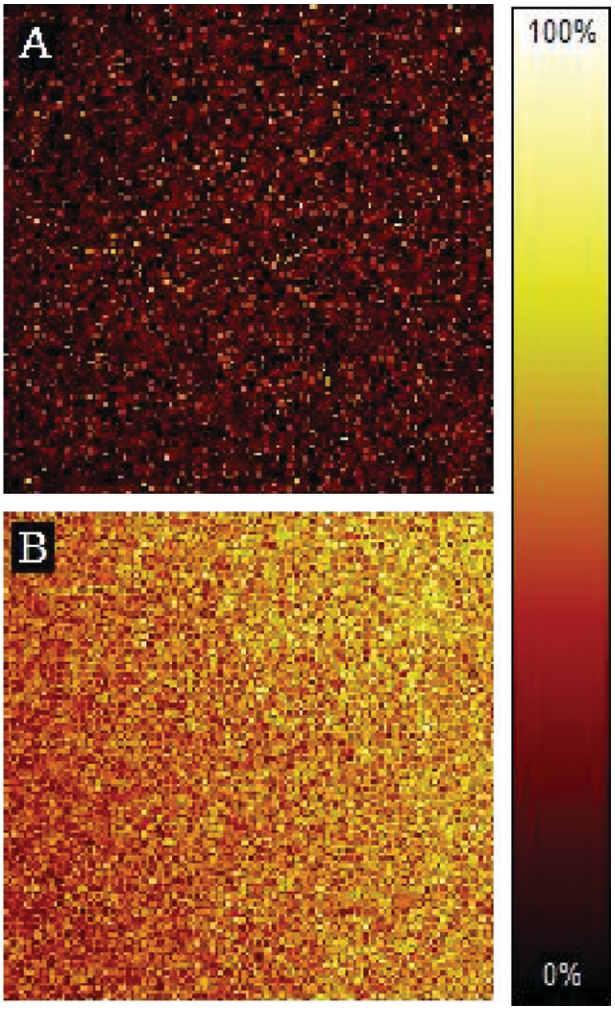

Fig. 3 SIMS imaging (500 × 500 μm^2) of C2: (A) 1-ethyl-4-(4′-pyridyl)pyridinium (m/z = 185) in positive mode SIMS; (B) iodide (m/z = 126.9) in negative mode SIMS (for details on ions and fragments, see text).

fragmenting to m/z = 170 (CH_3) and 157 (C_2H_4). The accurate mass demonstrates that this ion is different from the tributylamine ion (fragment of the tetrabutylammonium ion) observed in the positive SIMS of C1. No important fragments are observed at m/z > 200, which indicates that the complete molecular structure of C2 is not desorbed from the surface by cleavage of the covalent C–C bond between the phenyl ring and the carbon framework in the surface of the carbon material. Rather, the important fragment ions are formed by cleavage of the much weaker benzylic C–N bond between the grafted benzyl layer and 1-ethyl-4-(4′-pyridyl)pyridinium.

Imaging SIMS was performed in order to investigate the surface uniformity of C2. Figs. 3(A) and 3(B) depict 500 × 500 μm^2 images illustrating the intensities of 1-ethyl-4-(4′-pyridyl)-pyridinium in positive SIMS (m/z = 185) and iodide (m/z = 126.9) in negative SIMS, respectively. The figures indicate that the ions are uniformly distributed on this scale. Whether the individual molecules are uniformly distributed or not on a molecular scale cannot, however, be answered with this technique since the resolution is inadequate. Furthermore, GC would be a far too-rough material for such high-resolution investigations, so we decided to carry out a STM study on a related material, highly ordered pyrolytic graphite (HOPG), following an analogous modification protocol.

Scanning tunnelling microscopy

At the outset, the basal plane of freshly cleaved HOPG crystals was investigated to establish the STM micrograph of the unmodified HOPG material as shown in Fig. 4(A) and 4(B). Fig. 4(C) and 4(D) depict the corresponding STM micrographs of C1 on HOPG surfaces. In Fig. 4(C) the small white protrusions on the surface might represent islands of 4-(chloromethyl)phenyl molecules. The grafting of the 4-(chloromethyl)-phenyl diazonium salt on HOPG compared with GC is obviously quite inefficient. The reason is that edge plane defects are much more reactive towards molecular anchoring than basal plane carbon. Moreover, for the STM investigation on HOPG we decided to terminate the grafting before completeness, since our aim was not to optimize the coverage but rather to obtain information on the individual steps of the modification process.

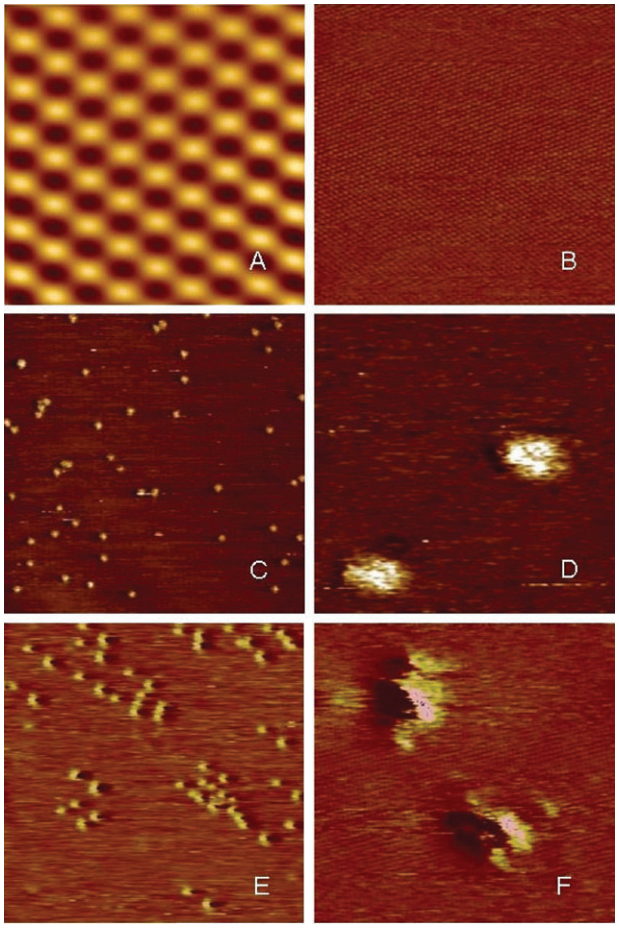

Fig. 4 STM micrographs of (A) HOPG, scale: 2 × 2 nm^2; (B) HOPG, scale: 15 × 15 nm^2; (C) C1 on HOPG, scale: 100 × 100 nm^2; (D) C1 on HOPG, scale: 15 × 15 nm^2; (E) C2 on HOPG, scale: 100 × 100 nm^2; (F) C2 on HOPG, scale: 15 × 15 nm^2.

Fig. 4(E) and 4(F) show the corresponding STM micrographs of C2 on HOPG. At first sight, the micrographs are rather similar to those of C1, as they provide no detailed information on the molecular structure. In both cases, they indicate that aggregates of several molecules are assembled into islands with an average diameter of ~2 nm.

Fig. 5 shows the topography of the molecular islands of C1 and C2 on HOPG. The height of the islands corresponds to the thickness of the grafted molecular layers. Evidently, the thickness more than doubles, going from ~3 Å for C1 to ~7 Å for C2, illustrating the effect of extending the grafted 4-(chloromethyl)phenyl layer with 1-ethyl-4-(4′-pyridyl)pyridinium. In other words, these images show that the chemical transformation of C1 to C2 affects the already grafted areas of the surface. At the same time, there is no indication of multilayer formation originating from polymerization type reactions involving the generated aryl radicals, as opposed to procedures in which more extensive electrolysis has been applied.[15,19,20]

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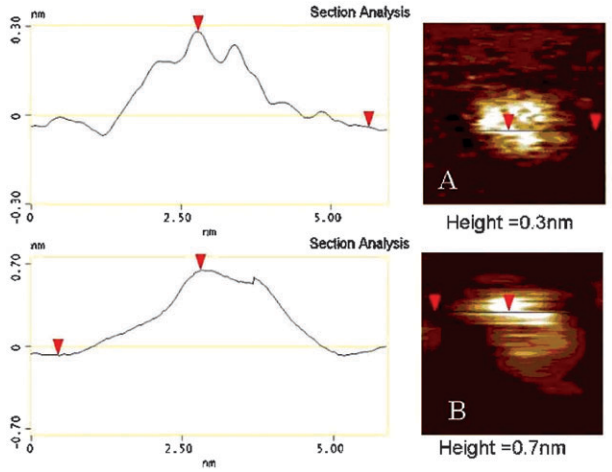

Fig. 5 Cross section profile of (A) C1 on HOPG; the thickness of the molecular structure is 0.28 nm (height scale 0.3 nm); (B) C2 on HOPG; the thickness of the molecular structure is close to 0.7 nm (height scale 0.7 nm).

Cyclic voltammograms recorded for the C2 HOPG plate exhibited the characteristic waves of the viologen redox system, although the waves were rather ill-defined because of the inefficient grafting. Nevertheless, a calculation of the coverage reveals a remarkably high number of $\sim 1.5 \times 10^{-10}$ mol cm^{-2} (110 Å^2/molecule), which clearly exceeds the number one would expect from STM analysis; as deduced from Figs. 4 and 5, less than 5% of the surface is covered by a monolayer. In turn, this would imply that the number of viologen units in the islands should be comparatively larger, which seems unlikely due to steric congestion. However, one should consider that, with STM, only the smooth basal plane is analyzed, while many of the electroactive molecules may be bound to steps or other defects, or perhaps even in multi-layers. The HOPG material employed in the molecular scale investigations is thus very different from the GC material used in the other parts of the study. In freshly cleaved HOPG the basal surface is nearly atomically smooth, which stands in sharp contrast to the GC material, which is more or less randomly oriented and shows little or no graphitic domains.[4] In particular, these differences should be kept in mind when relating the presented STM images to the other results obtained for GC.

Conclusions

In the present study, two different approaches have been presented for the introduction of an electrochemically active 4,4′-bipyridinium functionality on covalently grafted glassy carbon electrodes. In the first approach, 4-(chloromethyl)phenyl grafted electrodes were treated with monoalkylated 4-(4′-pyridyl)pyridinium salts in nucleophilic substitution reactions in aqueous solutions. The second approach consisted of a two-step procedure in which 4,4′-bipyridine was used as a nucleophile towards the 4-(chloromethyl)phenyl grafted surface, followed by a subsequent quaternization of the available nitrogen to obtain the viologen functionality. In the latter procedure both electrophilic and nucleophilic properties of the surface were used in the layer-by-layer formation of the desired surface-confined molecular structures. We found the most suitable reaction medium to be water but nucleophilic displacement still required long reaction times (up to 5 days) to surmount the kinetic retardation of such heterogeneous reactions.

The covalently modified glassy carbon electrodes were reasonably stable to repeated electrochemical sweeping in acetonitrile with only 25% decrease of the observed electroactivity after 100 sweeps at a sweep rate of 2 V s^{-1}. The coverage was determined from the electrochemical response of the 4,4′-bipyridinium moiety to be approximately 3×10^{-10} mol cm^{-2}. The presence of 4,4′-bipyridinium was also demonstrated by XPS and ToF-SIMS. Scanning images of positive SIMS indicated that 1-ethyl-4-(4′-pyridyl)pyridinium molecules were distributed uniformly over the entire surface (500×500 μm^2). STM on highly ordered pyrolytic graphite was used to follow the individual steps of the modification procedure; the nucleophilic displacement reaction was found to increase the thickness of the observed molecular aggregates from ~ 3 Å to ~ 7 Å.

Experimental

Reagents

4-(Chloromethyl)phenyl diazonium tetrafluoroborate,[23] 1-benzyl-1′-ethyl-4,4′-bipyridinium dibromide[43] and 1-benzyl-4-(4′-pyridyl)pyridinium bromide[43] were prepared and purified according to published procedures. All other chemicals were commercial and used in the highest grade available. Water was triply distilled.

The synthesis of 1-ethyl-4-(4′-pyridyl)pyridinium iodide was carried out by stirring 4,4′-bipyridine (13 mmol) and ethyl iodide (10 equiv.) in 60 ml dry diethyl ether for 3 days at room temperature, followed by filtration, drying, and recrystallization from ethanol to give 0.28 g of 1-ethyl-4-(4′-pyridyl)pyridinium iodide as yellow crystals. Yield: 10% ; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.81 (t, 3H, $J = 7.1$ Hz); 5.06 (q, 2H, $J = 7.1$ Hz); 7.68 (d, 2H, $J = 6.7$ Hz); 8.33 (d, 2H, $J = 8.8$ Hz); 8.92 (d, 2H, $J = 6.7$ Hz); 9.45 (d, 2H, $J = 8.8$ Hz); HR-ESI MS $m/z = 185.1070$ (calcd for $C_{12}H_{13}N_2^+$: 185.1079).

Electrochemical instrumentation

Glassy carbon (GC) rods (Sigradur G, HTW, diameter = 1 mm) embedded in epoxy resin, GC plates (Sigradur G, HTW, 10 mm × 10 mm × 1 mm) or highly ordered pyrolytic graphite (HOPG; NT-MDT Russia, 10 mm × 10 mm × 1.7 mm) were used as working electrodes. A platinum wire and an Ag/AgI electrode (silver wire immersed in a Pyrex tube containing 0.01 M Bu_4NI + 0.1 M Bu_4NBF_4/acetonitrile separated from the solution by a ceramic frit) were used as counter and reference electrodes, respectively. At the end of each experiment the potential of the ferricenium/ferrocene couple was measured and all other potentials were referenced against SCE using a previous determination of $E^\circ = 0.41$ V_{SCE} for the former couple.[44] For the electrochemical analysis, a home-made potentiostat interfaced with a PC was employed.[45]

Grafting procedures

Fabrication of C1. GC electrodes were carefully polished before any modification by successive treatments with diamond suspensions (grain size: 9, 3, 1, and 0.25 μm) followed by rinsing with water and 10 min ultrasound cleansing in ethanol. Initial grafting with 4-(chloromethyl)phenyl groups was carried out in a conventional three-electrode setup using a GC working electrode in acetonitrile containing 2 mM of 4-(chloromethyl)phenyl diazonium tetrafluoroborate. No supporting electrolyte was added. The cyclic voltammogram recorded at a sweep rate of 0.2 V s^{-1} was characterized by an irreversible cathodic wave (peak potential ~ -0.35 V_{SCE}). The grafting was accomplished by potentiostatic electrolysis at -0.55 V_{SCE} for 10 min. The procedure generated highly passivated electrodes (C1) as evidenced by recording of voltammograms in 0.1 M Bu_4NBF_4/acetonitrile containing 1 mM ferrocene. The criterion for a successful grafting was that the voltammograms showed low currents and were featureless in the region of the characteristic ferricenium/ferrocene redox system. Following the grafting procedure, C1 electrodes were rinsed and ultrasonicated for at least 10 min in acetonitrile.

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GC plates for XPS and ToF-SIMS analysis were rinsed ultrasonically for 10 min in hexane. The grafting was accomplished by using the plates as working electrodes in a similar manner as described above for the GC electrodes. In order to ensure that both sides of the plates had been grafted to the same extent, the electrodes were turned over halfway during a 2×10 min grafting period. The samples were ultrasonicated in acetonitrile, ethanol, water, and hexane for 10 min.

HOPG plates were used for STM imaging. The surfaces were prepared by cleaving the basal plane using adhesive tape. The electrolysis was carried out in a home-built electrochemical cell made of Teflon. HOPG samples were mounted horizontally between the bottom of the Teflon cell and a support. A small hole in the bottom surrounded by a 3 mm diameter O-ring ensured that only a small part of the basal plane of the HOPG ($\sim$0.07 cm^2) was exposed to the electrolyte. Electrical contact to the HOPG was made with a small gold spring. The 30 mm diameter Teflon cell chamber was fitted with a stopper to provide support for the reference and counter electrodes. The modification was carried out under similar conditions as described for the GC plates, apart from the ultrasonic treatment, which was omitted due to the fragile nature of HOPG. The final rinsing was made with acetonitrile and ethanol before drying in a stream of high purity argon.

Fabrication of C2, C3, and C4. The nucleophilic substitution reactions involving either 1-ethyl-4-(4′-pyridyl)pyridinium, 1-benzyl-4-(4′-pyridyl)pyridinium, or 4,4′-bipyridine and C1 to produce C2–C4 were slow, requiring reaction times of 4–5 days at room temperature in 20 mM aqueous solutions to go to completion. The 4,4′-bipyridine modified surface, that is C4, was, after rinsing and 10 min ultrasonication in acetonitrile, treated with 20 mM benzyl iodide in acetonitrile for 20 h at 60 °C to afford C3. The corresponding reaction using ethyl iodide to produce C2 was unsuccessful. Finally, the electrodes were rinsed and ultrasonicated for 10 min in acetonitrile containing the very same supporting electrolyte as would be employed in the cyclic voltammetry analysis.

Analytical techniques

XPS. XPS analyses were recorded with a SSX-100 X-ray photoelectron spectrometer (Surface Science Laboratories, USA), with an Al Kα X-ray source (1487 eV) at a power of approx. 150 W. The pressure in the main chamber during the analysis was around 10^{-8} mbar. Atomic concentrations of the elements were calculated by determining the relevant integral peak intensities using a linear type background. The systematic error is estimated to be of the order of 5–10%.

ToF-SIMS. Mass spectrometry analyses were carried out with a time-of-flight secondary ion mass spectrometer (Ion-ToF GmbH, Münster, Germany). A pulsed 25 kV Ga^+ primary ion beam incident at 45° to the surface normal was employed and the dose of primary ions was sufficiently low ($<10^{12}$ ions cm^{-2}) to ensure static conditions. The resulting secondary ions were analyzed by a time-of-flight mass analyzer equipped with a reflectron. The typical mass resolution was $M/\Delta M > 5000$. The surfaces were scanned over an area of 500×500 μm^2 and images showing the intensity of particular ion masses with respect to total ion count could be presented.

STM. STM experiments were performed using a Nanoscope IIIa STM (Digital Instruments Inc., Santa Barbara, CA. USA) using Pt-Ir (80 : 20) tips. Measurements were made at bias voltages between ±600 and ±1000 mV and tunnelling currents between 0.6 and 1 nA in air at room temperature.

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