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Registry No. 1a, 18928-00-2; **2**, 83380-29-4.

Supplementary Material Available: Table of atomic positional parameters with estimated standard deviations (1 page). Ordering information is given on any current masthead page.

Tetracyanoquinodimethane-Modified Electrodes

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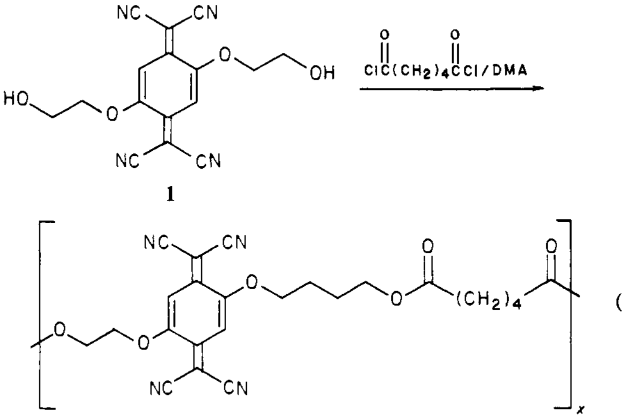
Herein we report on the preparation and characterization of modified electrodes based on the widely studied tetracyanoquinodimethane (TCNQ) acceptor molecule. The electrodes are fabricated in the usual way[1] by adsorption on a platinum-coated quartz substrate, by using novel TCNQ oligomers in which the electron-exchange sites are incorporated in the molecular backbone. In contrast to other acceptor film modified electrodes, which are water and air sensitive[2] or complicated by slow charge transfer between redox sites,[3] these TCNQ electrodes are stable upon repeated electrochemical cycling between the zero and −1 oxidation states in aqueous electrolytes, and the amount of charge accepted by the films is proportional to film thickness over the range 10–1000 nm. Thus these electrodes complement donor polymer film electrodes such as the poly(vinylferrocene)[4] and tetrathiafulvalene[5] (TTF) electrodes in that cathodic intercalation of cations into the TCNQ film is readily achieved from aqueous solutions.

The $(TCNQ)_x$ was synthesized by treatment of the dioxydiethanol TCNQ monomer (**1**) of Hertler[6] with a stoichiometric amount of adipoyl chloride in *N*,*N*-dimethylacetamide (DMA) at room temperature for more than 24 h. A light red-purple powder was obtained after the reaction mixture was poured into ethanol.[7] The average molecular weight of the resulting $(TCNQ)_x$ oligomeric mixture was estimated to be 2200 by the "universal" gel permeation chromatography method of Grubisic et al.[9]



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(1)

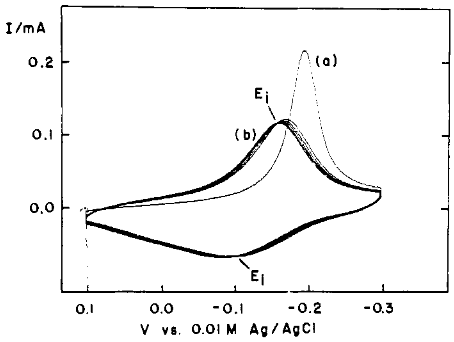

Figure 1. Cyclic voltammogram of a 800-nm $(TCNQ)_x$ film at 0.02 V/s in aqueous 0.5 M $NaClO_4$, 0.01 M NaCl: (a) first sweep; (b) repetitive cycles (E_i isopotential points).

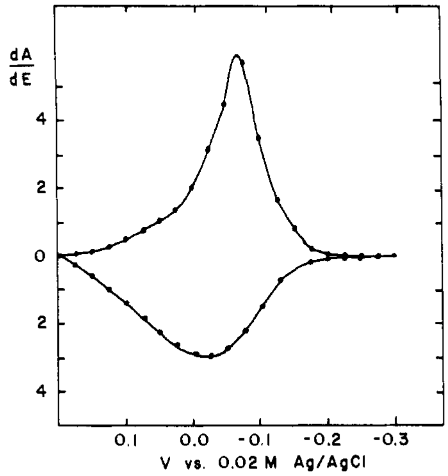

Figure 2. Derivative cyclic voltabsorptometry of a 800-nm $(TCNQ)_x$ film at 0.001 V/s in aqueous 0.5 M $LiClO_4$, 0.02 M LiCl; points are experimental; λ 735 nm; d*A*/d*E* given in absorbance units per volt.

Cyclic voltammograms of solutions of $(TCNQ)_x$ in acetonitrile revealed the expected quasi-reversible reduction waves

$$(TCNQ)_x \overset{xe^-}{\rightleftharpoons} (TCNQ^-)_x \overset{xe^-}{\rightleftharpoons} (TCNQ^{2-})_x \qquad (2)$$

($E_{1/2}{}^{0/-} = 0.06$ and $E_{1/2}{}^{-/2-} = -0.39$ V vs. SCE) for noninteracting electron-transfer sites, in agreement with the reversible waves observed for the monomer. Peak heights for the $(TCNQ)_x$ waves were attenuated due to the smaller diffusion coefficients of the oligomeric species.[10,11] The absorption spectrum of the neutral $(TCNQ)_x$ featured two peaks at λ_{max} 408 nm (log ϵ 5.06) and 430 (log ϵ 5.06), while the electrogenerated $(TCNQ^-)_x$ polyanion spectrum showed bands at λ_{max} 445 nm (log ϵ 4.30), 660 (log ϵ 3.38), 728 (log ϵ 3.92), and 812 (log ϵ 4.20). These data are consistent with the corresponding spectra of the substituted monomeric TCNQ[12] and its radical anion.[13]

Films that were spin-coated (solvent: tetrahydrofuran) onto platinum-on-quartz substrates and baked for 2–3 min at 130–140 °C were studied in aqueous electrolytes. These films were found to be insoluble in water in both the zero and −1 oxidation states

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(7) Reaction times from 25 h to approximately 1 week have been employed for this and related polymerizations. (In a typical procedure, 0.42 g of $(TCNQ)_x$ was realized from the first crop (53% yield).) Condensation polymerizations of this type are thoroughly treated by Morgan.[8]

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and yielded voltammograms of the type shown in Figure 1. While the cyclic voltammograms exhibit some subtle features, the evidence indicates that the charging process involves the formation of $\mathrm{TCNQ}^{-}\cdot$ radical anion sites. First, derivative cyclic voltabsorptometry[14] at the 735-nm band, which has been assigned to the $\mathrm{TCNQ}^{-}\cdot$ monomer species,[15] produced dA/dE curves of the same form as the conventional cyclic voltammograms obtained simultaneously; see Figure 2. Second, reduction of a $(\mathrm{TCNQ})_x$ film (dip-coated on Pt grid) in an ESR cavity by using the intra muros technique[16,17] yielded a signal ($g = 2.0031$, $\Delta H_{\mathrm{pp}} = 0.4$ mT) that increased in intensity in direct proportion to the charge passed. In addition, the two-step EE process (eq 2) is evident in the voltammograms for which the potential is scanned to more negative values, although repeated cycling past the second wave destroys the film electroactivity. However, if the potential excursions are maintained within the limits of Figure 1, the $(\mathrm{TCNQ})_x$ film retains full electrochemical activity over a period of days. Also, the ESR signal intensity and the voltammetric waves did not decrease when the reduced films were exposed to the laboratory atmosphere.

Similar voltammetric behavior was observed in both $NaClO_4$ and $LiClO_4$ electrolytes. In the presence of 0.1 M tetraethylammonium perchlorate, however, the cathodic peak current was significantly attenuated and the corresponding anodic peak was more drawn out than shown in Figure 1. Similar electrolyte effects have been found for donor polymer films.[18,19] Thus the $(\mathrm{TCNQ})_x$ reduction process in aqueous electrolytes can be viewed as "cation controlled" and written as an ionic intercalation of cations into the film phase:

$$(\mathrm{TCNQ})_x + x\mathrm{M}^+ + x\mathrm{e}^- \rightleftharpoons (\mathrm{TCNQ}^-\mathrm{M}^+)_x \qquad (3)$$

In this regard, the electrode processes for the $(\mathrm{TCNQ})_x$ films are akin to those observed for TTF–TCNQ "organic metal" electrodes in aqueous media.[20] In the presence of 0.5 M $NaClO_4$ or $LiClO_4$, chronocoulometric experiments indicate rapid diffusion-controlled charging processes for both reduction and oxidation with Cottrell slopes of 1.2×10^{-3} C cm^{-2} s$^{-1/2}$.

The cyclic voltammograms have several features that indicate slow potential-dependent changes in the film structure and/or uptake of electrolyte that are similar to those observed for TTF polymer films.[21] Initial potential scans in the negative direction resulted in a narrow cathodic peak (peak width ca. 50 mV), which was replaced by a broader peak (width 90 mV) on subsequent cycles; see Figure 1. Holding the potential at 0.2–0.3 V for 3–5 min restored the film to the original state. Simultaneous absorption measurements at 735 nm demonstrated that a slow oxidation of the radical anion sites occurred on this time scale. In addition, upon repeated cycles, isopotential points[22] indicative of a two-state system developed in the multicyclic voltammograms as shown in Figure 1. The causes of this behavior are under further study. In spite of these variations, the total charge accepted by a $(\mathrm{TCNQ})_x$ film remained constant, indicating the overall reversibility of the process.

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Registry No. **1**·ClC(O)$(CH_2)_4$C(O)Cl copolymer, 83462-96-8; **1**·ClC(O)$(CH_2)_4$C(O)Cl repeating unit, 83462-97-9; Pt, 7440-06-4; $LiClO_4$, 7791-03-9; $(\mathrm{TCNQ})_x$, 26810-79-7.

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Use of Trichlorodimethylethyl as a Protecting Group and Tributylphosphine as a Deprotecting Agent in Oligonucleotide Synthesis

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Phosphite triester chemistry[1] provides a means for rapid synthesis of oligonucleotides. In this approach 2,2,2-trichloroethyl[1,2] and methyl[3] have been the groups of choice for protecting P–O internucleoside links, the latter proving particularly useful in syntheses conducted on insoluble supports.[4] We describe here two developments that simplify some operations and broaden the scope in syntheses of oligonucleotides by the phosphite approach: (1) use of the bulky 2,2,2-trichloro-1,1-dimethylethyl group for protecting P–O; (2) a new reaction of tributylphosphine useful in cleaving trihaloethyl phosphotriesters.

^{31}P NMR studies show that 2,2,2-trichloro-1,1-dimethylethyl phosphorodichloridite reacts *selectively* with 5′-O-protected deoxyribonucleosides at −78 °C in that the first halogen in the dichlorodite is displaced before the second reacts. Consequently, solutions of active nucleoside reagents (**1**, Chart I) free of dichloridite can be prepared simply by adding a slight excess of the 5′-O-protected nucleoside to $Cl_3CC(CH_3)_2OPCl_2$ in CH_2Cl_2 or THF in the presence of pyridine at −78 °C. In contrast, CH_3O-PCl_2 is unselective, and $Cl_3CCH_2OPCl_2$ exhibits only moderate selectivity in reactions carried out under comparable conditions.

The potential of $Cl_3CC(CH_3)_2OPCl_2$ in synthesis was examined by preparing **2** and **3**. Phosphite **2**[7] (^{31}P NMR, δ −151.29, −151.02)[8] was obtained (70%) by reaction of **1** (base = thymine) with excess thymidine in THF–C_5H_5N (−78 → 0 °C). Oxidation with I_2–H_2O converted it quantitatively to the corresponding phosphate, **3**[7] (^{31}P NMR, δ −10.36, −10.23)[8] which was relatively stable to alkaline solutions (no reaction in 4 h with NH_4OH at 25 °C).

The stability of the trichlorodimethylethyl phosphotriesters to alkali permits oligonucleotide triester derivatives to be removed from insoluble supports intact, as demonstrated by synthesis of d-(DMTr)$[\mathrm{T}_{\mathrm{TCDM}}]_n$T,[9] $n = 1$–5, on a silica support. The procedure of Matteuci and Caruthers[4a] was adapted to the syringe technique,[4e] and $Cl_3CC(CH_3)_2OPCl_2$ was used in place of CH_3OPCl_2. Aliquots of loaded silica were removed at the end of each cycle and treated with NH_4OH (∼23 °C, 3 h) to liberate the oligomers. In each case a dominant spot was observed on reverse-phase TLC[10] corresponding to the nucleoside triester derivative for that stage (R_f 0.45, 0.40, 0.35, 0.29, 0.24, 0.22 for $n = 0$–5, respectively). The hexamer **4** was identical in properties with d-(DMTr)$[\mathrm{T}_{\mathrm{TCDM}}]_5$T prepared independently in solution by stepwise condensations of dimer **5** with oligomer blocks, starting with d-$\mathrm{T}_{\mathrm{TCDM}}$T(OAc). In confirmation of the structure, successive treatment with zinc and aqueous HOAc converted **4** to d-$(\mathrm{Tp})_5$T,

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(9) TCDM refers to the internucleoside 2,2,2-trichloro-1,1-dimethylethyl phospho triester link.

(10) 7:3 Me_2CO–H_2O on Whatman MKC_{18} plates.

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