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LETTERS

Preparation and Redox Properties of Longitudinally Twinned TCNQ: Hexacyanostilbenequinodimethane Dianion

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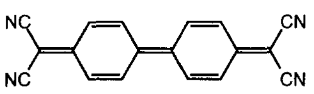
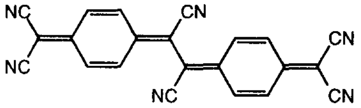
Abstract: A new extended π-conjugated TCNQ, hexacyanostilbenequinodimethane, was isolated as a dianion salt. Its cyclic voltammograms show that the dianion is reduced reversibly to a trianion radical, while the oxidized species, a monoradical anion, dimerizes to give the dimer dianion, which is further electrochemically oxidized to a neutral polymer.

Structural modification of 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) has been extensively explored to obtain new materials with enhanced conducting properties. Extended TCNQ analogues bearing π-conjugated spacers between the dicyanomethylene moieties have been the focus of much recent attention because they possess a more reduced on-site Coulombic repulsion than TCNQ and thereby enhance the conductivities of their anion radical salts.[1] Tetracyanodiphenoquinodimethane **1** is a relevant example of such structural modification,[2] whereas the neutral species of **1** is unstable, probably owing to twisting about the central double bond due to the repulsion between the *ortho* hydrogens. As a new π-extended TCNQ derivative which possesses little steric interaction and high electron-accepting property, we have now designed a longitudinally twinned TCNQ derivative, hexacyanostilbenequinodimethane (**2**). We report here the preparation of **2** as the dianion salt and its multistage redox behavior.



1



2

Among several synthetic approaches, the one that incorporates a *t*-butyl group in the early step to protect the benzylic hydrogen gave the most satisfactory results (Scheme 1). Thus, compound **4** was obtained by the reaction of 4-fluoronitrobenzene **3** with *t*-butylmalononitrile,[3,4] which was then reduced to the amine and subsequently converted to iodide **5** in 54% yield. The reaction of **5** with the ethyl cyanoacetate anion in the presence of copper(I) iodide in HMPA afforded ester **6**.[5] To avoid destruction of the cyano groups, hydrolysis of the ethoxycarbonyl group and the subsequent decarboxylation were carried out under neutral conditions; **6** was heated at 130 °C together with NaCl in a DMSO-H_2O mixture to give benzyl cyanide **7** in 76% yield from **5**.[6] The stilbene framework of **8** was constructed in 74% yield by oxidative coupling of **7**. The *t*-butyl groups was removed by heating **8** in diphenyl ether for 3 h,[3] giving **9** as a precursor of **2**.

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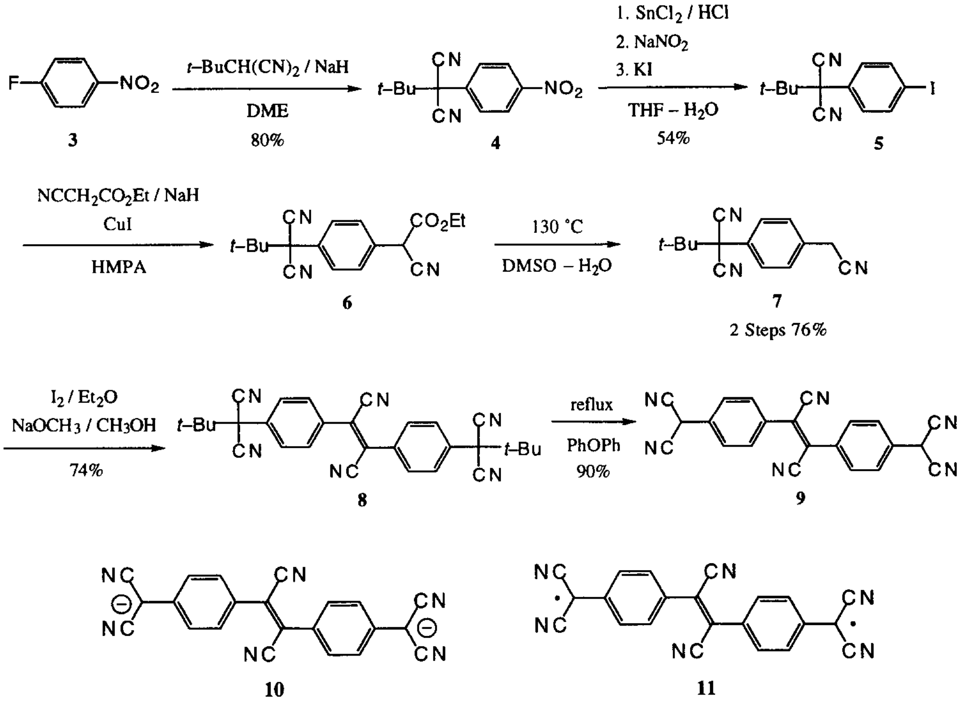
Scheme 1



Compound **9** was treated with a variety of oxidizing agents including Br_2-H_2O, NBS, NBS-pyridine, NBS-Et_3N, DDQ, PbO_2, $Pb(OAc)_4$, and CAN; however, the desired transformation to **2** could not be achieved in any case. Then, our efforts were directed to the isolation of the dianion salt of **2** rather than the neutral species. Thus, compound **9** was added in a 5% $NaHCO_3$ aqueous solution. The resulting dark-blue solution was treated with Et_4NBr to afford the tetraethylammonium salt (**10**) as metallic lustered leaflets. The solid of **10** is stable under an inert atmosphere for several weeks, whereas in solution it decomposes gradually within a few days. The structure of **10** was established by the microanalysis and spectral data.[7,8] The IR spectrum of **10** exhibits the stretching cyano band at 2214, 2163, and 2126 cm^{-1}, the latter two being attributed to the four terminal cyano groups which should be highly conjugated with the anionic center. The UV/Vis spectrum of **10** in CH_3CN shows λ_{max} at 590 nm (ε=41500). Oxidation of **10** with iodine in MeOH did not yield **2** but resulted in the formation of highly insoluble colorless solids which appeared to be polymeric materials.

The electrochemical properties of **10** were investigated by means of cyclicvoltammetry in DMF (0.1 M *n*-Bu_4NBF_4) at room temperature (Figure 1). The voltammograms show a reversible reduction wave (-1.26 V vs Ag/AgCl) and two irreversible oxidation waves (+0.53, +0.77 V vs Ag/AgCl); irreversibility of the oxidation waves is deduced from the absence of the corresponding reduction peaks upon reversing the direction of sweep. At the second sweep a new irreversible reduction wave appears at −1.0 V (Figure 1b). The current of this wave gradually increases with repetitive potential scans, indicating that **10** undergoes polymerization at the electrode surface.

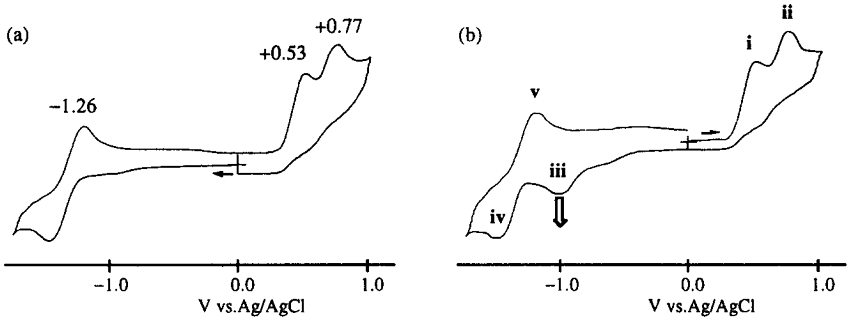
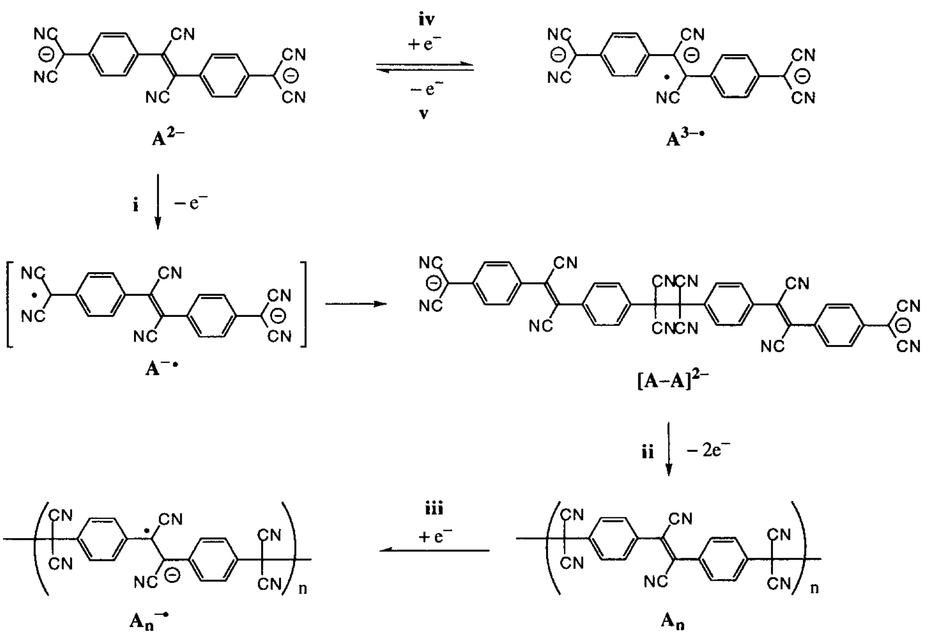


Figure 1 Cyclic voltammograms of **10** in DMF. (a) First Sweep. (b) Second sweep.

Based on the above observation, the redox behavior of dianion A^{2-} can be summarized as shown in Scheme 2. Radical anion $A^{-\bullet}$ is generated at the first oxidation wave (**i**). The coupling of two radical ions $A^{-\bullet}$ would irreversibly produce dimer dianion $[A\text{-}A]^{2-}$, as observed frequently in electrochemical redox process. Dianion $[A\text{-}A]^{2-}$ has two independent electron pools linked via the σ bond and hence is converted to diradical $[{}^{\bullet}A\text{-}A^{\bullet}]$ at the second oxidation wave (**ii**).[9] The diradical undergoes polymerization to give polymer A_n. The polymer thus formed is reduced to its radical anion $A_n^{-\bullet}$ at the reduction wave (**iii**), which deposits at the electrode surface increasingly with repetitive scans. The reversible redox waves (**iv** and **v**) are independent of the electropolymerization and attributed to the reversible redox reaction between dianion A^{2-} and trianion radical $A^{3-\bullet}$.

Scheme 2



In summary, we have demonstrated that hexacyanostilbenequinodimethane **2** is an unstable compound, being isolated only as the dianion species. Judging from its ready polymerization, neutral **2** should be represented by the canonical structure of a diradical such as **11** rather than a quinonoid structure.

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References and Notes

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7. The crystal structure of **10** was not determined, since a single crystal suited for an X-ray analysis could not be obtained in spite of our all efforts.
8. Characteristic spectral data for **7**, **8**, **9** and **10** are as follows.

   7: mp 121–122 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.577 (d, 2H, J = 8.3 Hz), 7.459 (d, 2H, J = 8.3 Hz), 3.822 (s, 2H), 1.204 (s, 9H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 131.97, 129.41, 128.76, 128.27, 117.00, 114.68, 52.51, 41.22, 25.62, 23.22; IR (KBr) 2254 (C≡N) cm^{-1}; MS *m/z* 237 (M^+). Anal. Calcd for $C_{15}H_{15}N_3$: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.74; H, 6.40; N, 17.61.

   8: mp > 255 °C (decomp.); ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.980 (d, 4H, J = 8.4 Hz), 7.770 (d, 4H, J = 8.4 Hz), 1.256 (s, 18H); ^{13}C NMR ($CDCl_3$, 126 MHz) δ 133.40, 132.99, 129.10, 129.03, 125.21, 115.76, 114.28, 52.73, 41.73, 25.76; IR (KBr) 2253 (C≡N), 2223 (C≡N) cm^{-1}; MS *m/z* 470 (M^+). UV-Vis (CH_2Cl_2) λ_{max} 327 (ε=25000), 238 (ε=9500) nm; Anal. Calcd for $C_{30}H_{26}N_6$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.28; H, 5.74; N, 17.62.

   9: mp > 230 °C (decomp.); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.01 (d, 4H, J = 8.2 Hz), 7.76 (d, 4H, J = 8.2 Hz), 5.20 (s, 2H); IR (KBr) 2266 (w, C≡N), 2231 (m, C≡N) 2177 (m, C≡N) cm^{-1}; MS *m/z* 358 (M^+). UV-Vis (CH_2Cl_2) λ_{max} 320, 239 nm.

   10: mp 231–236 °C; ^{1}H NMR (CD_3CN, 500 MHz) δ 7.6–6.7 (m, 8H), 3.15 (q, 16H, J = 7.3 Hz), 1.20 (t, 24H, J = 7.3 Hz); IR (KBr) 2214, 2163, 2126 cm^{-1}; UV-Vis (CH_3CN) λ_{max} 590 (ε=41500), 307 (ε=25600) nm; Anal. Calcd for $C_{38}H_{48}N_8$: C, 73.99; H, 7.84; N, 18.17. Found: C, 73.80; H, 7.73; N, 18.21.
9. The peak profile of this wave corresponds to the one-electron transfer, since the dimerization reduces the concentration of its monomer precursor to one-half.