Novel Donor–π–Acceptor Compounds Containing 1,3-Dithiol-2-ylidene and Tetracyanobutadiene Units

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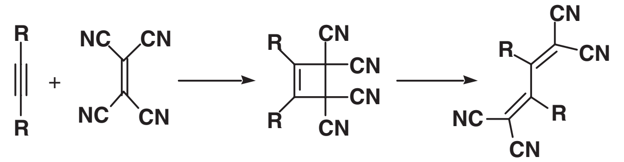
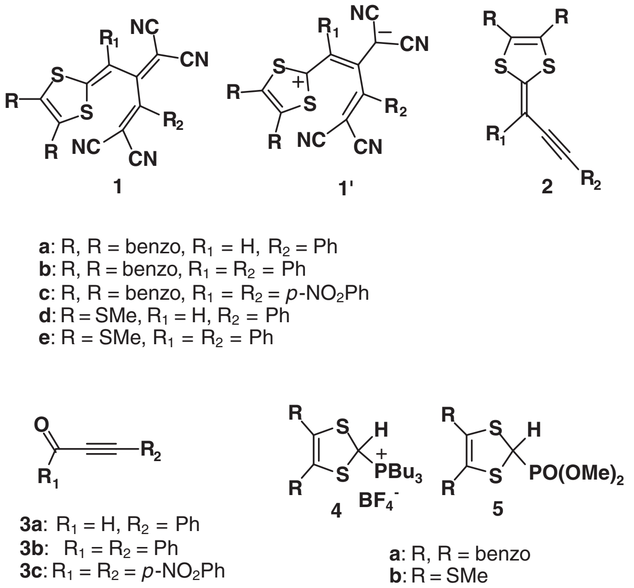
The title donor–π–acceptor compounds were prepared by the reaction of acetylenes containing a 1,3-dithiol-2-ylidene unit with tetracyanoethylene (TCNE). They showed amphoteric properties and intramolecular charge-transfer absorptions in the visible region. The molecular and crystal structures were revealed by X-ray analysis.

Donor–π–acceptor compounds have recently attracted much attention since they are expected to exhibit intrinsic semiconducting behavior due to their low band gaps[1] and efficient second-order nonlinear (NLO) properties due to their highly polarized structures.[2] They are also expected to show strong absorption and amphoteric properties which are required for organic dyes of dye-sensitized solar cells.[3] 1,3-Dithiol-2-ylidene is known as an electron-donating group and has been used as an electron-donor unit in donor–acceptor compounds.[2] On the other hand, 1,1,4,4-tetracyanobutadiene has a high electron affinity and has been used as an electron-acceptor part.[4] However, donor–acceptor compounds containing both these groups have not been reported. We have now succeeded in obtaining such compounds for the first time. We report here the facile synthesis, structure and properties of them.

It has been reported that tetracyanoethylene (TCNE) reacted with electron-rich acetylenes to afford tetracyanobutadiene derivatives,[4] which are considered to be formed by a ring-opening reaction of initially produced [2 + 2] cycloadducts as shown in Scheme 1. The target compounds **1** were synthesized according to this method. Acetylenes **2a**, **2d** containing a 1,3-dithiole moiety were prepared by a Wittig reaction of the corresponding phoshonium salts **4a**, **4b** with phenypropargyl aldehyde (**3a**) in 85 and 71% yields, respectively. Diaryl substituted derivatives **2b**, **2c**, **2e** were prepared by a Wittig–Horner reaction of phosphonate esters **5a**, **5b** with ketones **3b**, **3c** in good yields (**2b**: 62%, **2c**: 62%, **2e**: 70%). The reaction of the acetylenes **2a**–**2e** with tetracyanoethylene (TCNE) proceeded very smoothly in dichloromethane at room temperature to afford the desired compounds **1a**–**1e** in good yields (**1a**: 85%, **1b**: 73%, **1c**: 83%, **1d**: 45%, **1e**: 53%). It should be noted here that even the acetylene **2c** containing electron-withdrawing nitro groups underwent the reaction owing to the presence of the 1,3-dithiol-2-ylidene unit. This result reveals the versatility of the reaction shown here to prepare tetracycanobutadiene derivatives containing electron-donating groups.



Scheme 1. Formation of tetracyanobutadienes.



1 1' 2

a: R, R = benzo, R_1 = H, R_2 = Ph
b: R, R = benzo, R_1 = R_2 = Ph
c: R, R = benzo, R_1 = R_2 = *p*-NO_2Ph
d: R = SMe, R_1 = H, R_2 = Ph
e: R = SMe, R_1 = R_2 = Ph

4 5

3a: R_1 = H, R_2 = Ph
3b: R_1 = R_2 = Ph
3c: R_1 = R_2 = *p*-NO_2Ph

a: R, R = benzo
b: R = SMe

Scheme 2.

The new tetracyanobutadiene derivatives **1a**–**1e** are violet crystalline compounds with strong broad absorption in the visible region. Their absorption maxima are shown in Table 1. These absorptions are attributed to intramolecular charge transfer in the donor–acceptor structures and are suitable to absorb solar light.[3] Introduction of electron-donating methylthio groups makes the absorption red-shifted. On the other hand, introduction of a phenyl group of R_1 brings about blue-shifts. This fact can be explained by considering that the phenyl group disturbs conjugation between the 1,3-dithiol-2-ylidene moiety and the tetracyanobutadiene unit by a steric interaction. In nonsubstituted deriv-

Table 1. Absorption maxima[a] and redox potentials[b] of new compounds **1**

Compound	λ_{max}/nm	log ε	E^1_{red}/V	E^2_{red}/V	E_{ox}/V
1a	482	4.38	−0.39	−0.62	1.46
1b	467	4.41	−0.23	−0.56	1.36
1c	456	4.42	−0.16	−0.58	1.46
1d	523	4.51	−0.50 (2e)[c]		1.20
1e	491	4.20	−0.30	−0.60	1.40

[a]In CH_2Cl_2. [b]In MeCN containing 0.1 mol dm^{-3} *n*-Bu_4NPF_6, vs. SCE, Pt electrode, scan rate 100 mV s^{-1}. [c]Two-electron reduction.

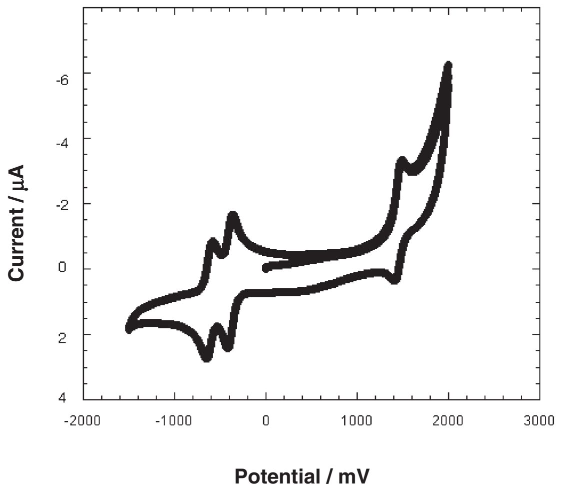


Figure 1. Cyclic voltammogram of **1a**.

atives **1a** and **1d**, the 1,3-dithiol-2-ylidene part can be coplanar with one dicyanomethylene group, which was confirmed by the X-ray structural study of **1a**.

The redox potentials were measured by cyclic voltammetry. In all compounds, both oxidation and reduction waves appeared as reversible peaks, indicating that they are amphoteric compounds. The cyclic voltammogram of **1a** is depicted in Figure 1. The redox potentials are summarized in Table 1. They are dependent on the substituents. Thus, compound **1c** shows the highest reduction potential due to the electron-withdrawing nitro groups. Introduction of a phenyl group of R_1 increases the reduction potential.

Single crystals of **1a** were obtained by recrystallization from dichloromethane. The molecular and crystal structures were revealed by X-ray structure analysis.[5] As shown in Figure 2a, the 1,3-dithiol-2-ylidene part and one of the dicyanomethylene group are nearly in a coplane (dihedral angle: 12.3°), whereas another dicyanomethyl group is twisted from the 1,3-dithiole part (dihedral angle: 102.3°). The C=C bond lengths of the C7–C8 [1.370(4) Å] and C9–C17 [1.382(4) Å] are longer than that of C10–C20 [1.356(4) Å]. The C–C bond length of C8–C9 [1.414(4) Å] is shorter than that of C9–C10 [1.498(4) Å]. These facts indicate a contribution of zwitter ionic structure **1′**. In the crystal structure (Figure 2b), the compound **1a** forms a dimer structure with an efficient overlap of the 1,3-dithiole part, where the interplane distance is 3.49 Å. A short S···S contact (3.49 Å) also exists between the dimers, resulting in a unique molecular network.

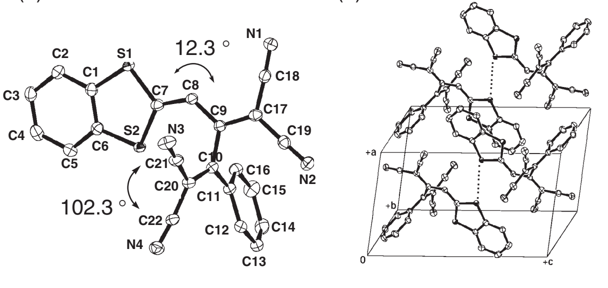


Figure 2. (a) Molecular and (b) crystal structure of **1a**. The dotted line shows a short S···S contact.

In conclusion, we have prepared novel donor–acceptor compounds by a facile one-step reaction of electron-rich acetylenes with TCNE. They showed clear amphoteric properties and the redox potential was modified by introducing substituents. They are attractive candidates for NLO materials and dyes for dye-sensitized solar cells. The studies for application purposes are currently underway.

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5 Crystal data for **1a**: $C_{22}H_{10}N_4S_2$, $M = 394.47$, triclinic, space group $P\bar{1}$, $a = 8.0598(3)$, $b = 8.9090(3)$, $c = 13.323(2)$ Å, $\alpha = 77.736(4)°$, $\beta = 82.538(6)°$, $\gamma = 83.362(2)°$, $V = 932.0(1)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 1.419\,\mathrm{g\,cm^{-3}}$, $F_{(000)} = 404$, $\mu = 3.04\,\mathrm{cm^{-1}}$, 8611 reflections collected, 4057 independent ($R_{\mathrm{int}} = 0.086$), $R_1 = 0.0456$, $wR_2 = 0.1270$ for $I > 2\sigma(I)$, $R_1 = 0.085$, $wR_2 = 0.1432$, $S = 1.021$ for all data. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The details of the crystal data have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-244924.

6 **1a**: mp 162–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90–7.94 (m, 2H), 7.70–7.50 (m, 5H), 7.42–7.32 (m, 2H), 7.13–7.08 (m, 1H); MS (EI) m/z 394 (M^+). **1b**: mp 221–222 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92–7.26 (m, Ar); EIMS m/z 470 (M^+). **1c**: mp 243–245 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45–8.32 (m, 2H), 7.93–7.91 (m, 1H), 7.77–7.72 (m, 2H), 7.68–7.63 (m, 2H), 7.57–7.52 (m, 2H), 7.47–7.34 (m, 3H), 7,15–7.10 (m, 1H); EIMS m/z 563 (M^+). **1d**: mp 170–171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.14 (m, 5H), 6.05 (s, 1H), 1.91 (s, 6H); EIMS m/z 435 (M^+). **1e**: mp 202–203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.14 (m, 10H), 1.91 (s, 6H); EIMS m/z 512 (M^+).