New Electron Acceptors for Organic Metals: Extensively Conjugated Homologues of Thiophene–7,7,8,8-Tetracyanoquinodimethane (TCNQ)

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Two conjugated homologues of thiophene–7,7,8,8-tetracyanoquinodimethane (TCNQ) have been prepared, which form highly conductive complexes with typical electron donors such as 2,2′,5,5′- tetrathiafulvalene (TTF) or 5,6,11,12- tetrathiatetracene (TTT); these complexes have extensive conjugation.

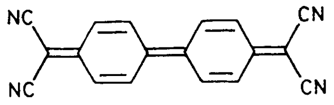
Some years ago, 13,13,14,14-tetracyanodiphenoquinodimethane (**1**) a conjugated homologue of 7,7,8,8-tetracyanoquinodimethane (TCNQ), aroused considerable interest as a promising electron acceptor, in the search for superior charge-transfer complexes with larger metallic band widths as a result of better overlap of the extended π-system, and smaller on-site Coulomb repulsion due to charge dispersal.[1,2] However, all attempts to prepare (**1**) failed although its anion and radical-anion have been reported.[2] The instability of (**1**) in the neutral state is attributable to a steric interaction between the biphenylic *ortho* hydrogens.[3] In contrast to benzenoid systems, heterocyclic systems can avoid such an interaction by assuming the *trans* conformation in the quinoid conjugation. 2,5-Bis(dicyanomethylene)-2,5-dihydrothiophene (thiophene–TCNQ) (**2**) is a typical five-membered heterocyclic analogue of TCNQ,[4] but has attracted little attention as an electron acceptor because of its weak electron affinity.[5] The quinoid conjugation of thiophene–TCNQ might be expected to improve its ability as an acceptor. We report here the syntheses and properties of the extensively conjugated homologues (**3**) and (**4**).

Gronowitz and Uppström reported the unusual formation of thiophene–TCNQ on the pyrolytic reaction of 2,5-dihalogenothiophenes with tetracyanoethylene oxide.[4] A similar method was successfully applied to the present conjugated series. Thus, treatment of 5,5′-dibromo-2,2′-bithiophene (**5**)[6] with tetracyanoethylene oxide in dry 1,2-dibromoethane under reflux for 8 h gave 5,5′-bis-(dicyanomethylene)-5,5′-dihydro-2,2′-bithiophene (**3**) as fine, deep violet crystals in 42% yield. 5,5″-Dibromo-2,2′ : 5′,2″-terthiophene (**6**)[7] similarly gave 5,5″-bis(dicyanomethylene)-5,5″-dihydro-2,2′ : 5′,2″-terthiophene (**4**) as a deep green powder in 11% yield.

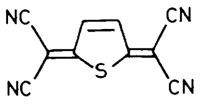
Table 1. The half-wave redox potentials of (**2**)—(**4**) and the electrical conductivities of their TTF and TTT complexes.[a,b]

	Redox potential/V		Conductivity/S cm^{-1}	
Acceptor	$E_{1/2}(1)$	$E_{1/2}(2)$	TTF complex	TTT complex
(**2**)	+0.068	−0.544	6.7×10^{-9}	No complex
(**3**)	−0.026	−0.259	2.2×10^{-4}	3.3×10^{-4}
(**4**)	−0.028		3.3×10^{-3}	7.2×10^{-1}

[a] Cyclic voltammetry was carried out in dichloromethane containing 0.1 M Bu_4NClO_4 as supporting electrolyte, with a platinum working electrode and an Ag/AgCl reference electrode. [b] Conductivities were measured on compressed pellets with a four-probe method.



(1)



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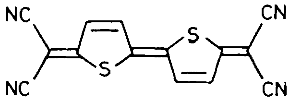
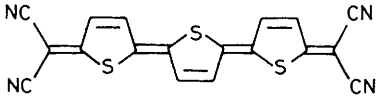
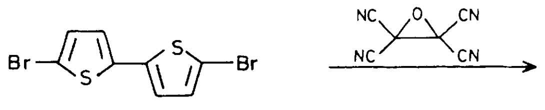


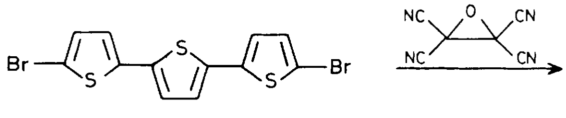
(3)



(4)



(5) (3)



(6) (4)

Both (3) and (4) are extremely stable with melting points above 300 °C.†

Table 1 shows the half-wave redox potentials of (3) and (4) together with those of thiophene–TCNQ (2) on cyclic voltammetry. The first reduction potential of (3) is somewhat lower than that of (2), but the second reduction potential is much higher, indicating an effective reduction of on-site Coulomb repulsion in the dianion state. This effect is more pronounced in the more highly conjugated acceptor (4), so that the first and second waves coalesce. Thiophene–TCNQ forms a molecular complex with 2,2′,5,5′-tetrathiafulvalene (TTF) but not with 5,6,11,12-tetrathiatetracene (TTT). The TTT complex is nearly insulating, as seen in Table 1. On the other hand, both (3) and (4) form deeply coloured complexes with either donor.‡ The conductivities of the complexes increase in line with the extensive conjugation of the acceptors. In particular, the TTT complex of (4) is highly conductive. These results indicate that, even if the conjugated acceptors do not have strong electron affinity, they are capable of forming conductive molecular complexes owing to increased overlap of their extended π-systems and effective diminution of on-site Coulomb repulsion.

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† New compounds (3) and (4) were characterized by elemental and spectrocopic analyses.

‡ All complexes except non-stoicheiomeric (3) ·TTF consist of 1 : 1 donor and acceptor components.