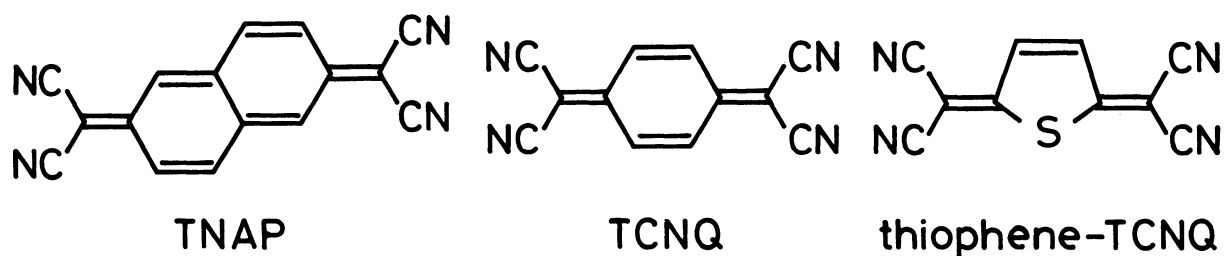


New Electron Acceptors of Condensed-Thiophene TCNQ Type

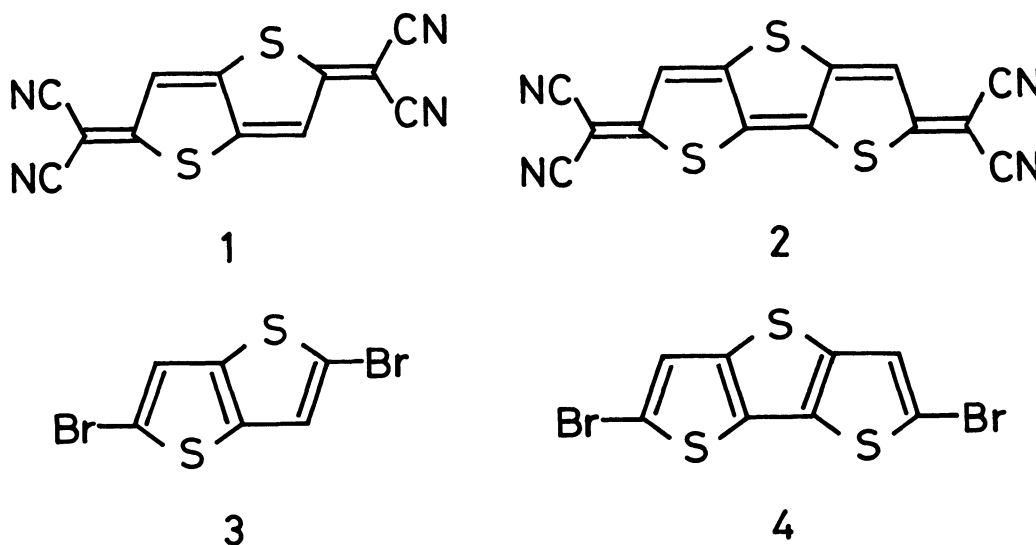
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Two conjugated homologues of thiophene-TCNQ, i.e., 2,5-bis(dicyanomethylene)-2,5-dihydrothieno[3,2-b]thiophene and 2,6-bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-b:2',3'-d]thiophene have been prepared as potential acceptors. They form charge-transfer complexes with TTF or TTT as well as complex sodium or tetrabutylammonium salts, some of which are highly conducting.

11,11,12,12-Tetracyanonaphtho-2,6-quinodimethane (TNAP), an extended conjugated homologue of 7,7,8,8-tetracyanoquinodimethane (TCNQ), has a slightly stronger electron affinity, a higher polarizability, and a smaller on-site Coulomb repulsion than TCNQ itself.¹⁾ These features make it attractive in the design of organic metals. Actually it is capable of forming metallic complexes with tetrathiafulvalene (TTF)²⁾ and hexamethylenetetraselenafulvalene (HMTSF).³⁾ 2,5-Bis(dicyanomethylene)-2,5-dihydrothiophene (thiophene-TCNQ) is a thiophene analogue of TCNQ,⁴⁾ which has been, however, attracted little attention as an electron acceptor owing to its weak electron affinity.⁵⁾ Our recent interest in search of new acceptors has directed towards an extension of thiophene-TCNQ to a



condensed system. 2,5-Bis(dicyanomethylene)-2,5-dihydrothieno[3,2-b]thiophene (1) and 2,6-bis(dicyanomethylene)-2,6-dihydrodithieno[3,2-b:2',3'-d]thiophene (2) are especially interesting as potential acceptors which might behave like TNAP. We now wish to report their syntheses and complexation.



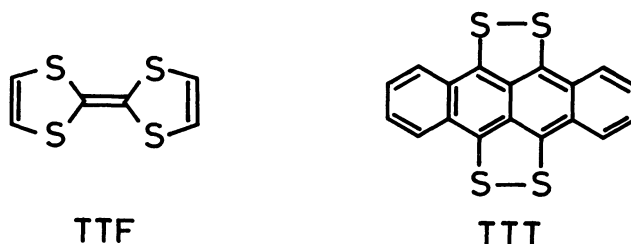
Gronowitz and Uppström found a unique reaction to afford thiophene-TCNQ.⁴⁾ A similar method was successfully applied to the syntheses of 1 and 2. Thus, 2,5-dibromothieno[3,2-b]thiophene (3)⁶⁾ was treated with excessive tetracyanoethylene oxide in 1,3-dibromopropane under reflux for 2 h, followed by silica gel column chromatography with dichloromethane and then recrystallization from acetonitrile, giving 1 as reddish brown needles in 36% yield, mp >300 °C, $\nu_{\text{C}\equiv\text{N}}$ 2223 cm^{-1} . A similar treatment of 2,6-dibromodithieno[3,2-b:2',3'-d]thiophene (4)⁷⁾ with tetracyanoethylene oxide in 1,2-dibromoethane under reflux for 1.5 h gave 2 as deep violet fine crystals in 39% yield, mp >300 °C, $\nu_{\text{C}\equiv\text{N}}$ 2219 cm^{-1} .⁸⁾

In cyclic voltammetry, condensed-thiophene TCNQs 1 and 2 show two redox waves corresponding to two one-electron reductions. Both first half-wave reduction potentials (1: +0.058 V; 2: +0.048 V) are nearly comparable to that of thiophene-TCNQ (+0.068 V).⁹⁾ On the other hand, the second ones (1: -0.355 V; 2: -0.288 V) increase with the extended conjugation, being significantly higher than that of thiophene-TCNQ (-0.544 V). This indicates an effective reduction of on-site Coulomb repulsion in the dianion states of condensed-thiophene TCNQs as expected.

Table 1. Complexation of 1 and 2

Complex	Stoichiometry ^{a)}	Appearance	D.P. °C	ν_{CN} cm ⁻¹	Conductivity ^{b)} S.cm ⁻¹
<u>1</u> ·TTF	1:1	black needles ^{c)}	157	2199	13
<u>2</u> ·TTF	1:1	deep green powder ^{c)}	184	2198	2.3
<u>1</u> ·TTT	1:1	Green powder ^{d)}	228	2216	ca. 10 ⁻⁸
<u>2</u> ·TTT	1:1	black powder ^{d)}	256	2172	3.0
<u>1</u> ·Na	10:7	black needles ^{c)}	>300	2204	3.1×10 ⁻³
<u>2</u> ·Na	— ^{e)}	dark violet powder ^{c)}	>300	2180	5.3×10 ⁻¹
<u>1</u> ·Bu ₄ N	3:1	black powder ^{c)}	279	2170	6.3×10 ⁻⁴
<u>2</u> ·Bu ₄ N	5:1	dark violet powder ^{c)}	273	2183	1.9×10 ⁻¹

a) Estimated on the basis of C, H, N elemental analyses. b) Measured on compressed pellets with a four probe method at RT. c) From acetonitrile. d) From chlorobenzene. e) Not determinable by C, H, N elemental analysis: C, 44.13; H, 0.76; N, 14.27%.



Thiophene-TCNQ forms a molecular complex with TTF, which is nearly insulating. However, it can not complex tetrathiotetracene (TTT) as another typical donor. In contrast, both 1 and 2 are capable of forming 1:1 complexes with either donor. As summarized in Table 1, all complexes except for 1·TTT are highly conducting. They are characterized by some charge-transfer, as indicated by considerable lower wavenumber shifts of their CN stretching vibrations on complexation.¹⁰⁾ On the other hand, the nonconducting complexes such as thiophene-TCNQ·TTF and 1·TTT show no such shift. As also shown in Table 1, 1 and 2 can react with sodium iodide or tetrabutylammonium iodide to give the corresponding complex salts, which are well conducting.

These results clearly indicate that 1 and 2 of an extended conjugated type, though their electron affinities are as weak as thiophene-TCNQ, are promising acceptors for organic metals. Further investigation is now in progress.

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