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Preparation, Properties, and Reduction of a Novel TCNQ-Type Thienoquinoid

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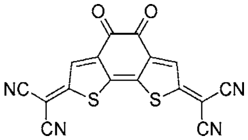
ABSTRACT



TCNQ-type bithienoquinoid condensed with a α-dicarbonyl group was synthesized. The compound revealed a reversible reduction wave at +0.32 V vs SCE. The radical anion species was cleanly generated by a reduction with Na–Hg and characterized: λ_{max} = 1027 nm in vis–NIR and a large spin density of the *β*-carbon atoms on the fused ring by EPR spectroscopy. The radical anion salts were isolated by a reduction with iodide and showed moderate conductivity.

Oligothiophenes are one of the popular *p*-type electronic materials and are widely used as the active component in many electronic devices such as FETs and LEDs.[1] A variety of cationic species of oligothiophenes have been investigated by spectroscopic and crystallographic methods to obtain an insight into doped and conducting species.[2] Recently, quinoidal oligothiophenes with dicyanomethylene terminals (QT*n*CN2: *n* refers to the number of thiophene rings) have attracted considerable attention as excellent *n*-dopable materials with unusual electronic structures (Figure 1).[3−5] For example, QT3CN2 was successfully applied for a fabrication of FET with remarkably high electron mobility and ambiopolar transport.[4] Fused-ring systems are widely investigated for FET with high carrier mobility and usually have different properties from nonfused systems because of more planar conformations, better conjugation, and more rigid structures.[1,6]

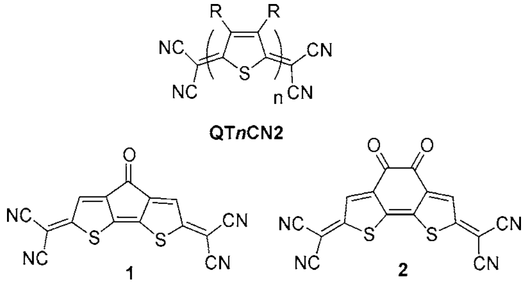


Figure 1. Quinoidal oligothiophenes with dicyanomethylene terminals.

Although the spin and charge delocalization are important for understanding unique device properties and the conduc-

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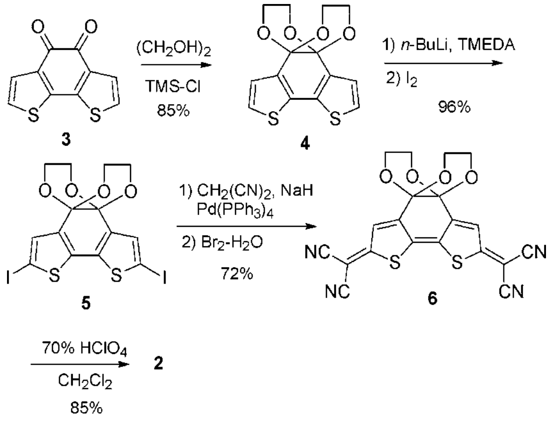
tion mechanism, there have been only a small number of papers concerning anionic species of QT*n*CN2-type compounds.[7] Takahashi and co-workers have recently reported that a carbonyl-bridged bithienoquinoid **1** exhibits high conductivity in the radical anion form.[5] However, the reduction potential of **1** ($E1_{red}$ = +0.05 V vs SCE) is not much different from that of QT2CN2 (R = H, $E1_{red}$ = −0.01 V vs SCE). This is probably because of symmetry;[8] the LUMO (delocalized in the bithiophene ring) of **1** does not have AO coeffcients on the carbonyl group. We intended to develop a synthetic method for the very readily reducible condensed thienoquinoids that would hopefully be applicable to more extended forms by oligomerization. Introduction of an α-dicarbonyl instead of the carbonyl group would stabilize the LUMO by the symmetry-allowed MO interactions. In this paper, we report preparation and fundamental properties of a novel dicarbonyl-bridged thienoquinoid with a fused ring system and dicyanomethylene terminals along with the reduction and isolation of the radical anion.

Thienoquinoid **2** was synthesized according to Scheme 1. First, compound **3** was prepared.[9] Protection of carbonyl groups was achieved in 85% yield by the reaction of **3** with ethylene glycol at room temperature in the presence of chlorotrimethylsilane (TMS-Cl).[10] Dilithiation of **4** using *n*-BuLi followed by the treatment of iodine gave compound **5** in 96% yield. The palladium catalyzed coupling reaction of **5** with sodium dicyanomethanide in dry THF followed by an oxidation with bromine solution afforded quinoidal compound **6**.[3b,11] Deprotection of the carbonyl groups with 70% perchloric acid gave **2** as a stable purple solid in 85% yield. The UV−vis spectrum of **2** was dominated by a characteristically strong $\pi-\pi^*$ absorption at 512 (log ϵ = 4.40) and 551 nm (4.71) in dichloromethane (Figure 2).

Scheme 1. Synthesis of **2**



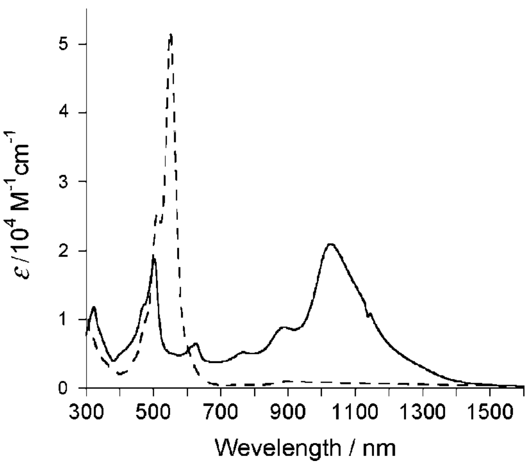


Figure 2. UV−vis−NIR spectra of neutral **2** (dashed line) and radical anion salts **2**•$(Et)_4N$ (solid line) measured in dichloromethane.

The cyclic voltammogram of **2** showed four reversible reduction waves at +0.32, −0.02, −0.73, and −1.11 V vs SCE, assigned to the successive formation of radical anion, dianion, radical trianion, and tetraanion (Figure 3). It is important to note that the first and second reduction potentials dramatically shift to the positive direction by 0.2−0.3 V compared to those of **1** ($E1_{red}$ = +0.05 V, $E2_{red}$ = −0.23 V

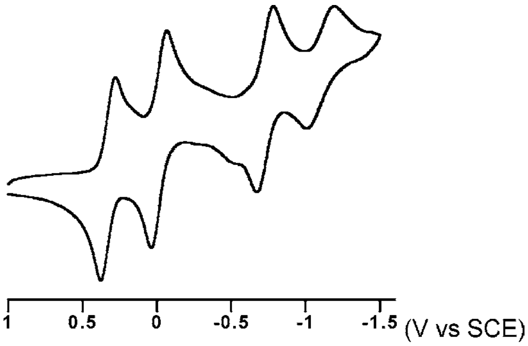


Figure 3. Cyclic voltammogram of the acceptor **2** measured using glassy carbon as a working electrode at 100 mV/s in dichloromethane containing 0.1 M tetrabutylammonium perchloride as a supporting electrolyte.

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vs SCE) or QT2CN2 (R = H, $E1_{red} = -0.01$ V, $E2_{red} = -0.24$ V vs SCE). The first reduction potential of **2** is even more positive by 0.05 V than TCNQ (+0.27 V vs SCE) and comparable to fluoroTCNQ (+0.33 V vs SCE).[12] These results clearly establish that **2** is an excellent electron acceptor and support our symmetry consideration. The difference between the first and second reduction potentials ($\Delta E = 0.34$ V) observed for **2** is significantly smaller than ΔE for TCNQ (0.61 V). The smaller ΔE values show a diminished on-site Coulombic repulsion in the dianionic species of **2**. The reversible first reduction wave and the ΔE values suggest that the radical anion species are stable and isolatable, provided that a suitable reducing method is applied.

The metal reduction of **2** using 3% Na−Hg as a reducing agent in dry acetonitrile was carried out under degassed conditions. The reduction was monitored by measuring UV−vis−NIR spectra. The spectrum change indicated the stepwise formation of the radical anion $\mathbf{2}^{\bullet-}$ (Figure 4a) and the dianion $\mathbf{2}^{2-}$ (Figure 4b). In the first stage, the intense absorption ($\lambda_{max} = 539$ nm) of neutral **2** disappeared and new absorption bands grew at 992 nm. Obviously, new absorption is ascribed to the formation of the radical anion $\mathbf{2}^{\bullet-}$. The observed NIR absorptions have vibrational progressions ($\lambda_{max} = 1100$ nm, $\epsilon = 5900$ M^{-1} cm^{-1}; $\lambda_{max} = 988$ nm, $\epsilon = 9050$ M^{-1} cm^{-1}, with $\nu_{1/2} = 1148$ cm^{-1} by fitting assuming a Gaussian band shape), indicating that these bands are charge resonance bands in class III rather than intervalence bands in class II according to the Robin and Day classification.[13] The dianion $\mathbf{2}^{2-}$ has no appreciable absorptions in the visible region (Figure 4b) but has moderate absorptions at 397 nm compatible with its aromatic VB structure.

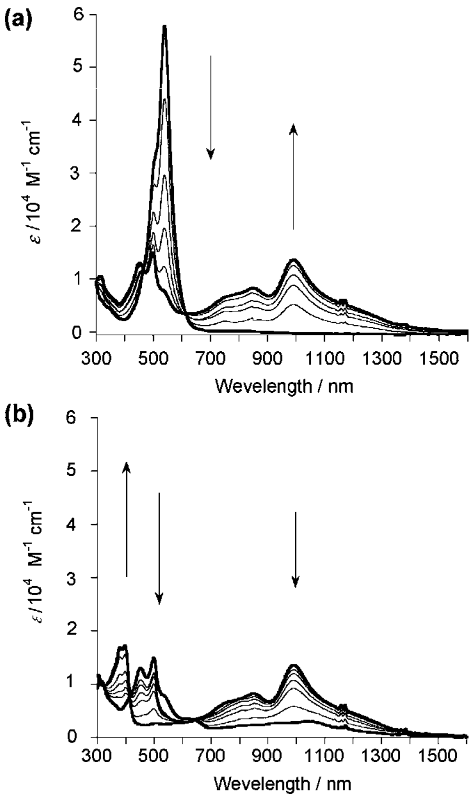

Figure 4. UV−vis−NIR spectra observed during the reduction of **2** to radical anion $\mathbf{2}^{\bullet-}$ (a) and $\mathbf{2}^{2-}$ with 3% Na−Hg in dry acetonitrile. Arrows indicate the direction of changes.

Isolation of radical anion salts of **2** (dark green powder) was achieved by mixing with 1 equiv of tetraethylammonium iodide or tetramethylphosphonium iodide in dichloromethane (Table 1). Elemental analyses of these salts showed a 1:1 composition of $\mathbf{2}^{\bullet-}$ and counter cation. Conductivities of the compressed pellets of the salts were measured at room temperature ($\mathbf{2}\cdot(Et)_4N$: 1.2×10^{-6}, $\mathbf{2}\cdot(Me)_4P$: 1.9×10^{-5} Scm^{-1}). The tetraethylammonium salt $\mathbf{2}\cdot(Et)_4N$ has intense absorption in the NIR region (1027 nm (log ϵ = 4.32)) in dichloromethane (Figure 2). The observed spectrum was nearly identical with the spectrum in the Na−Hg reduction. A negative charge in the radical anion salts caused lower wavenumber-shift of the CN stretching vibrational absorptions ($\mathbf{2}\cdot(Et)_4N$: 2197, 2185, $\mathbf{2}\cdot(Me)_4P$: 2197, 2185 cm^{-1}) compared with neutral **2** (2218 cm^{-1}). Well-resolved EPR signals assignable to $\mathbf{2}^{\bullet-}$ ($g = 2.0022$, $a_H = 4.06$, $a_N = 0.70$ G) were obtained for $\mathbf{2}\cdot(Et)_4N$ (Figure 5). The EPR spectrum reveals a 1:2:1 triplet pattern resulting from hyperfine coupling with two equivalent β-protons on thienyl units. Each

Table 1. Radical Anion Salts and CT Complexes of **2**

complex	found (calcd) % C H N	ν_{CN} /cm^{-1}	σ/S cm^{-1} [a]
$\mathbf{2}(Et)_4N\cdot{}^1/_2H_2O$	59.45, 4.55, 14.43	2197	1.2×10^{-6}
	(59.36, 4.77, 14.42)	2185	
$\mathbf{2}\ (Me)_4P\cdot H_2O$	53.06, 3.23, 11.93	2197	1.9×10^{-5}
	(52.74, 3.54, 12.30)	2185	
2TTF	47.59, 1.24, 9.92	2193	6.5×10^{-4}
	(47.98, 1.10, 10.17)	2185	
2DEP	65.51, 3.83, 13.40	2195	1.6×10^{-6}
	(65.59, 3.54, 13.11)	2185	

[a] Measured as a compressed pellet at room temperature by a two-probe method.

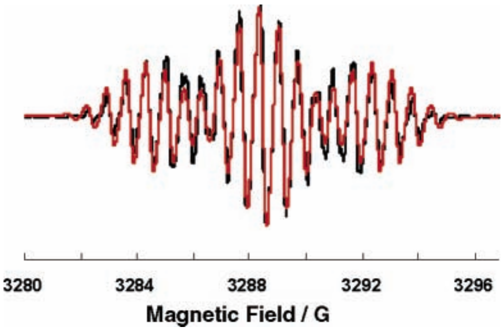

Figure 5. EPR spectra of $\mathbf{2}\cdot(Et)_4N$ measured in dichloromethane at room temperature (black line) and obtained by computer simulation (red line) ($g = 2.0022$, $a_H = 4.06$, $a_N = 0.70$ G).

line further split into 9 lines due to the coupling with four terminal nitrogen atoms. It must be noticed that the observed hyperfine coupling constants of β-protons are more than 10 times larger than the reported values for non-fused QT2CN2$^{\bullet-}$ (R = H, $g = 2.0026$, $a_{\mathrm{H}} = 0.3$, $a_{\mathrm{N}} = 0.6$ G).[7c] The higher spin density in the uncovered β-protons should facilitate intermolecular electron exchange, thus an increase in mobility is expected.

Compound **2** was mixed with strong electron donors such as TTF and diethylphenazine (DEP) (Table 1) to form corresponding CT salts with moderate conductivities (**2**·TTF (1:1): 6.5×10^{-4}, **2**·DEP (1:1): 1.6×10^{-6} S cm^{-1}). The CN stretching vibrational absorptions of the CT salts shift to a lower wavenumber (**2**·TTF: 2193, 2185, **2**·DEP: 2195, 2185 cm^{-1}) compared with neutral **2**. These values are similar to that for radical anion salts, indicating a significant charge transfer.[14] The absorption of the neutral acceptor **2** but not a radical anion band was observed in UV−vis−NIR spectrum of **2**·TTF in dichloromethane. On the other hand, absorptions for the neutral and anionic species are observed in polar solvent (dicholomethane−DMF 10:1). Consistent with this, two sets of multiplet signals each assignable to TTF radical cation[15] ($g = 2.0081$, $a_H = 1.26$ G) and **2**$^{\bullet-}$ were observed in an EPR spectrum in the same polar solvent. On the other hand broad NIR absorption was observed for **2**·TTF in KBr (see the Supporting Information).

We have also carried out DFT calculations (UB3LYP/6-31G*) for radical anions (QT2CN2)$^{\bullet-}$ (R = H), **1**$^{\bullet-}$, and **2**$^{\bullet-}$.[16] The calculated spin densities are summarized in Table 2. Radical anion **2**$^{\bullet-}$ has the largest spin densities on the β-carbons on the thiophene rings. The calculated spin density for **2**$^{\bullet-}$ ($\rho = 0.161$, corresponding to $a_{\mathrm{H}} = 3.7$ G using the McConnell equation with $Q = -23.0$ G) is in good agreement with the experimental results (4.06 G). It is also confirmed that the carbonyl oxygens have significant AO coefficients in SOMO in **2**$^{\bullet-}$, supporting strong MO interaction between the LUMO in thienoquinoid and π^*-orbitals in dicarbonyl moieties in **2** (see the Supporting Information). In contrast, SOMO of **1**$^{\bullet-}$ has a nodal plane on the carbonyl group.

Table 2. Calculated Atomic Spin Densities of Radical Anion Salts (UB3LYP/6-31G*)

	(QT2CN2)$^{\bullet-}$ (R = H)	**1**$^{\bullet-}$	**2**$^{\bullet-}$
β-C	0.118	0.086	0.161
N	0.091	0.085	0.093
	0.078	0.095	0.108
O		−0.022	−0.002
S	−0.025	−0.030	−0.031

In summary, the incorporation of the α-dicarbonyl bridging group in TCNQ-type bithienoquinoid resulted in a dramatic enhancement of electron-accepting ability. In contrast to the TCNQ-type non-fused thienoquinoid, the radical anion salts **2**$^{\bullet-}$ have a high spin density on the β-carbons on the fused ring system. Since these carbon atoms are positioned in a relatively outer region in the molecule, this would facilitate intermolecular spin-exchange interactions. Furthermore, carbonyl oxygens of **2**$^{\bullet-}$ have a significant electron density in SOMO, which leads to intramolecular charge-transfer that increases mobility. These results suggest that the α-carbonyl bridged thienoquinoid **2** is a promising *n*-dopable material for FET with high stability and good carrier mobility.

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Supporting Information Available: Detailed synthetic procedures, NMR, EPR, UV−vis−NIR spectral data, and DFT calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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