

Article

Single-Component Charge-Transfer Crystals Based on Spin-Carrying TCNQ (7,7,8,8-Tetracyanoquinodimethane) Derivatives

Hideto Suzuki, Hiroki Akutsu, Jun-ichi Yamada and Shin'ichi Nakatsuji *

Graduate School of Material Science, University of Hyogo, 3-2-1 Kouto, Kamigori, Hyogo 678-1297, Japan; E-Mails: suzuki_hidemaru@yahoo.co.jp (H.S.); akutsu@sci.u-hyogo.ac.jp (H.A.); yamada@sci.u-hyogo.ac.jp (J.Y.)

* Author to whom correspondence should be addressed; E-Mail: nakatsuji@sci.u-hyogo.ac.jp; Tel.: +81-791-58-0163; Fax: +81-791-58-0164.

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Abstract: Three TCNQ derivatives carrying nitroxide radicals (**3a–3c**) were prepared and were found to form single-component charge-transfer (CT) complexes by self-assembly, in which outer nitroxide groups of a couple of different molecules work as donors and the inner TCNQ unit of another molecule as an acceptor. While the CT interactions found for the TEMPO (2,2,6,6-tetramethylpiperidin-1-oxy) derivative **3a** and the PROXYL (2,2,5,5-tetramethylpirrolidin-1-oxy) derivative **3b** are point-to-face fashion between the oxygen atom of each nitroxide group and the six-membered ring of inner TCNQ unit, the CT interactions found for the PO (2,2,5,5-tetramethyl-3-pyrrolin-1-oxy) derivative **3c** are point-to-point contacts between the oxygen atoms of outer nitroxide groups and the carbon atoms of a couple of cyano groups.

Keywords: CT complex; nitroxide; TCNQ; redox property; magnetic property; crystal structure

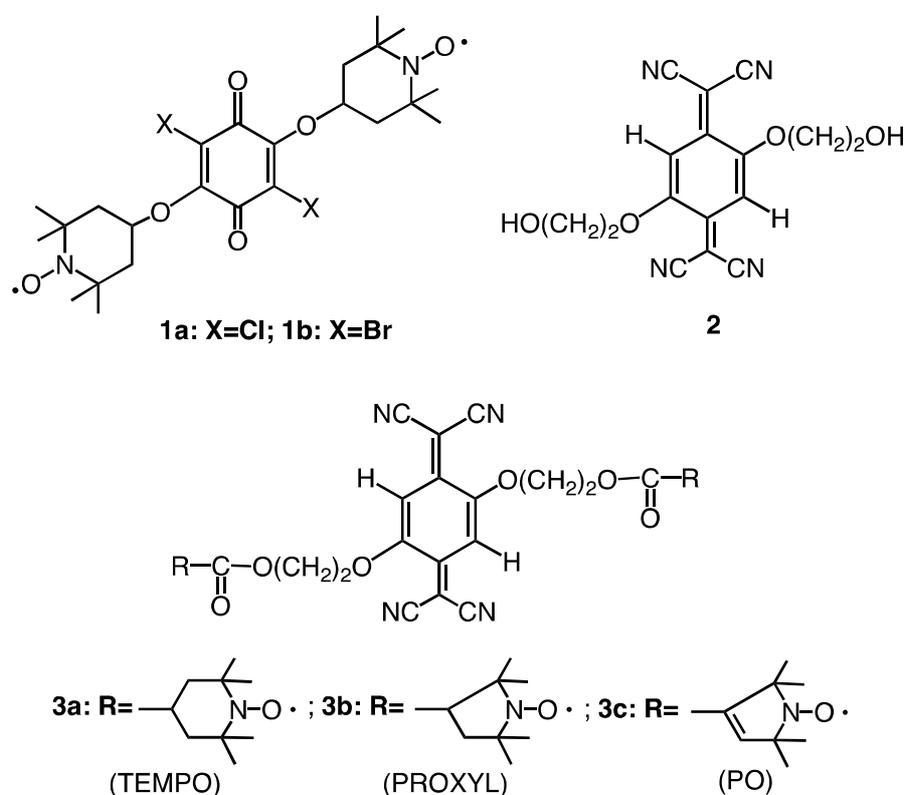
1. Introduction

CT complexes are normally known to consist of two components: a donor molecule and an acceptor molecule, and a wide variety of organic conductors such as TTF-TCNQ (TTF: tetrathiafulvalene, TCNQ: 7,7,8,8-tetracyanoquinodimethane) [1] as a typical example are composed of two-component CT complexes in general. On the other hand, several single-component molecular conductors

have been realized in recent year by Kobayashi and some other groups, e.g., [Ni(ptdt)₂] (ptdt: propylenedithiotetrathiafulvalenedithiolate) [2], [Au(ptdt)₂] [3], and [M(tmdt)₂] (tmdt: trimethylenetetrathiafulvalenedithiolate) (M = Ni, Cu, Pd, Au and Pt) families [4–7]. In turn, we found recently that some benzoquinone derivatives carrying TEMPO radical (e.g., **1a**, **1b** in Scheme 1) form single component CT complexes by assembling themselves, where benzoquinone works as an acceptor and the TEMPO group as a donor [8]. However, even if a number of TCNQ derivatives have so far been prepared to develop organic conductors or other functional materials by forming respective CT complexes with an appropriate donor molecule, to our knowledge there is no example of a TCNQ derivative carrying a stable radical and a reason will be that a stable radical works as a donor to form the corresponding CT complex [9] with TCNQ or TCNQF₄ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane) and to prevent the introduction of radical substituent on the TCNQ core as a consequence.

We wish to report in this paper the preparation, structures and some properties of the first examples of spin-carrying TCNQ derivatives (**3a–3c**), starting from the TCNQ derivative **2** with bis-hydroxyethoxy substituents (Scheme 1). The long alkoxy-substituent is beneficial to afford good solubility to an ordinary solvent and rather strong spin-spin interactions could be observed even in some biradicaloid systems with long alkoxy-substituents [10].

Scheme 1. Structural formulas of benzoquinone derivatives **1a**, **1b** and TCNQ derivatives **2**, **3a–3c**.



2. Results and Discussion

2.1. Preparation and Redox Properties of TCNQ Derivatives Carrying Nitroxide Substituents (3a–3c)

The preparation of the TCNQ derivatives carrying nitroxide substituents (**3a–3c**) was carried out by condensing 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane **2** with 4-carboxy-TEMPO (2,2,6,6-tetramethylpiperidin-1-oxy), 3-carboxy-PROXYL (2,2,5,5-tetramethylpiperidin-1-oxy), or 3-carboxy-PO (2,2,5,5-tetramethyl-3-pyrrolin-1-oxy) and DMAP (4-dimethylaminopyridine)/DCC (*N,N'*-dicyclohexylcarbodiimide). The yields were rather low mainly because of the difficulty of the tedious purification by column chromatography and recrystallization.

In order to evaluate the electron-accepting and donating properties of the derivatives, CV measurements of **3a–3c** were performed and the data are summarized in Table 1 together with those of **2** as a reference.

Table 1. CV data of TCNQ derivatives **3a–3c** and **2**.

Compound	E_1^{RED}	E_2^{RED}	E_1^{OX}
3a	0.03	−0.44	0.75
3b	0.04	−0.43	0.84
3c	0.02	−0.42	0.92
2	0.04	−0.41	

^a V vs. SCE, 0.1 M *n*-Bu₄NClO₄ in CH₃CN, Scan rate: 50 mV/s.

It is apparent from the first and second reduction potentials of **3a–3c** and the reference compound **2** that there is almost no influence of the radical substituents to the potentials, resulting in no significant difference in their electron-accepting properties. On the contrary, the first oxidation potentials due to the nitroxide groups are somewhat different, reflecting the different donating ability of the radical groups. On the whole, the co-existence of accepting and donating ability in each molecule is apparent from the CV data, enabling occurrence of some CT interaction between them.

2.2. Crystal Structures and Magnetic Properties of TCNQ Derivatives Carrying Nitroxide Substituents (3a–3c)

The X-ray analyses of the TCNQ derivatives **3a–3c** were performed by using each single crystal grown from an appropriate solvent, and the crystal data are summarized in the Experimental Section.

As shown in the crystal structure of the TEMPO-substituted derivative **3a** (Figure 1), there are two molecules in a unit cell and very close contacts are clearly observed between the centre of the TCNQ core and a couple of the oxygen atoms of nitroxide groups of the outer two molecules with the same distance of 2.906 Å for both sides. The distance of the close contacts is comparable to that observed for a black-colored spin-carrying benzoquinone (2.796 Å), in which a distinct CT band is observed in the diffuse reflectance UV-VIS spectrum in the solid state [5]. Thus, the formation of a single-component CT crystal is apparent for **3a** to reflect the black color of the crystal. Even with the stronger acceptor property of **3a** than that of **1a** ($E_1^{\text{RED}} = -0.40$ V vs. SCE in CH₃CN), the distance of the contacts is quite similar to that for **1a** (2.901 Å), suggesting the limitation of short contacts would be around 2.9 Å.

Figure 1. Crystal structure of **3a**. Three molecules are depicted and the broken lines indicate short intermolecular contacts. Hydrogen atoms are omitted for clarity and an ORTEP figure with hydrogen atoms is included in Supplementary Information (SI).

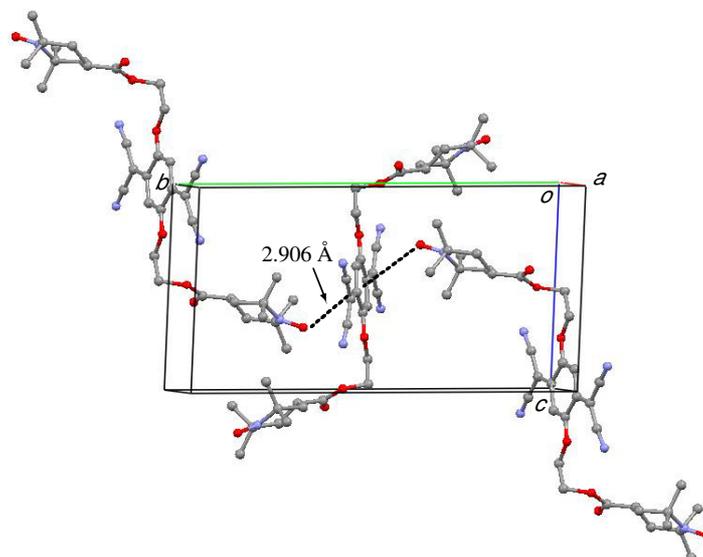
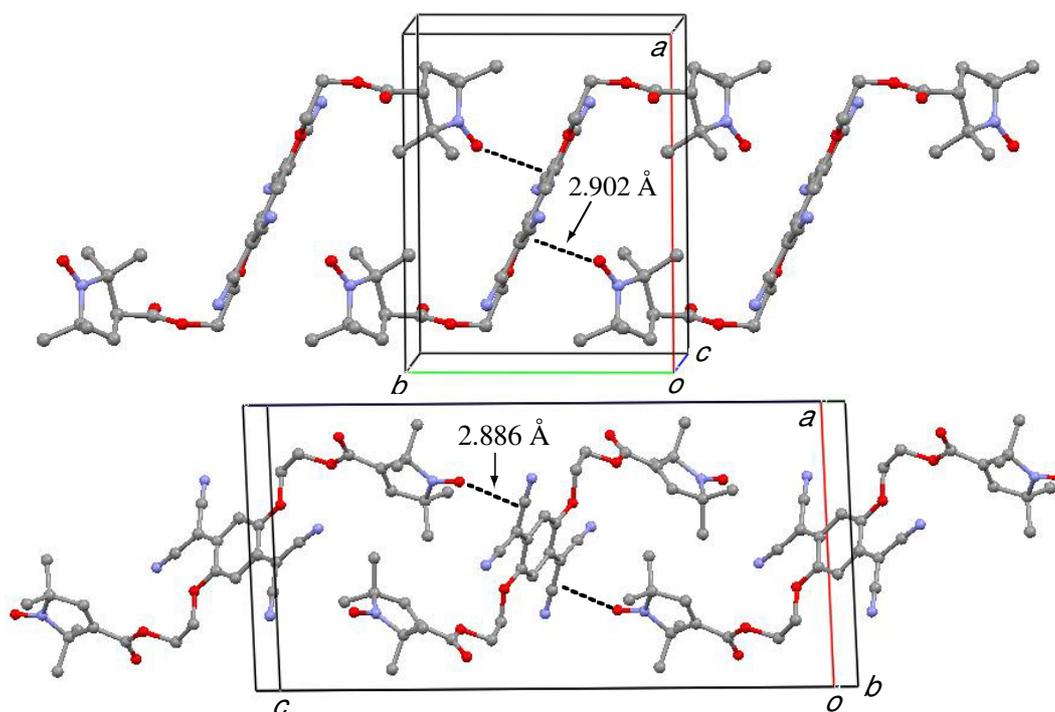


Figure 2. Crystal structure of **3b** (upper) and **3c** (lower). Three molecules are depicted and the broken lines indicate short intermolecular contacts. Hydrogen atoms are omitted for clarity and the ORTEP figures with hydrogen atoms are included in SI.



A similar structural feature is observed for the crystal structure of the PROXYL-substituted derivative **3b** to that of **3a** as shown in Figure 2 (upper), in which the oxygen-to-TCNQ contacts amount to 2.902 Å to afford a single-component CT crystal also in this case. The weaker donor property of the PROXYL group than that of the TEMPO group does not affect the distance of the short contacts. On the contrary, a rather different contacting feature is found for the PO-substituted derivative **3c** to that of **3a**

and **3b** (Figure 2b). Namely, a couple of short contacts are seen between the oxygen atoms of outer nitroxide groups and the carbon atoms of a couple of cyano groups, as shown in Figure 2 (lower) with the distances of 2.886 Å shorter than those of **3a** and **3b**. With this unique contacting feature, the derivative **3c** consequently provides another single-component CT crystal.

The magnetic measurements of the solid samples were carried out by using a SQUID susceptometer in the temperature range from 2 K to 300 K and the data for **3a–3c** are summarized in Table 2.

Table 2. Magnetic data of TCNQ derivatives **3a–3c**.

compound	magnetic interaction ^a	<i>C</i> ^b /emu K·mol ⁻¹	<i>θ</i> ^c K
3a	antiferromagnetic	0.75 (100)	-1.20
3b	antiferromagnetic	0.68 (91)	-1.40
3c	antiferromagnetic	0.59 (79)	-1.10

^a Fitting for the Curie-Weiss law. ^b Curie constant. Figures in parenthesis denote the estimated spin concentrations, by using theoretical value of 0.75 emu K·mol⁻¹ for diradicals. ^c Weiss temperature.

All of the radical compounds show paramagnetic Curie-Weiss behavior with small antiferromagnetic interactions between the spins. As no close contact is observed in their crystal structures other than those described above, the weak antiferromagnetic interactions observed are probably due to those between the spin centers mediated by a couple of TCNQ cores. The smaller Curie constants for **3b** and **3c** than the theoretical value are considered to be due to the contaminated monoradicals, which were quite difficult to separate by usual purification methods.

3. Experimental Section

3.1. Materials

Commercial grade 2,5-bis(2-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane **2** 4-carboxy-TEMPO, 3-carboxy-PROXYL, and 3-carboxy-PO [11] were used for the reactions described in the text.

3.2. Instrumentation

Melting points of the solid samples are uncorrected. The data of FAB-MS spectra were obtained by using *m*-nitrobenzylalcohol as matrix and appropriate polyethylene glycol samples as internal standard. Magnetic susceptibility measurements were carried out on a SQUID susceptometer using *ca.* 10 mg for each powdered sample. Crystal structures of all compounds were determined at room temperature. X-ray diffraction data were recorded using a CCD area detector on a diffractometer and crystal structures were solved by the direct method. The refinements were made by the full-matrix least squares methods. Anisotropic temperature factors were used for the non-hydrogen atoms and the hydrogen atoms were included in the final calculation. All the calculations were performed using the Texan crystallographic software package. Crystal data of **3a**, **3b**, **3c** and their TTF complexes have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

3.3. Preparation and Crystal Data of TCNQ Derivative 3a

To a stirred mixture of **2** (0.81 g, 2.5 mmol), 4-carboxy-TEMPO (1.00 g, 5.0 mmol) in dichloromethane (5 mL) was added DCC (1.03 g, 5.0 mmol) and DMAP (0.61 g, 5.0 mmol) at ambient temperature. After stirring for 3d, the reaction mixture was subjected without concentration to column chromatography on silica gel by using ethylacetate as an eluent. After repeated column chromatography, the solid product was recrystallized from n-hexane-dichloromethane (1:1) to give black blocks (0.24 g, 14%). mp: 215–220 °C; FAB-MS (*m/z*): 689 (*M* + 1); Crystal data: C₃₆H₄₂N₆O₈, FW = 686.76, monoclinic (P2₁/*n*), *a* = 9.143(3), *b* = 19.352(5), *c* = 10.894(3) Å, β = 106.285(5)°, *V* = 1850.3(9) Å³, *T* = 293 K, *Z* = 2, *D_c* = 1.233 mg·m⁻³, *R* = 0.0854, *wR* = 0.2980 [4166 reflections and 226 parameters with *I* > 2σ(*I*)].

In a similar manner, **3b** and **3c** were obtained albeit with low yields (5% for **3b** and 4% for **3c**) and their data are as follows; **3b**: mp: 220–225 °C; FAB-MS (*m/z*): 661 (*M* + 1); Crystal data: C₃₆H₄₄Cl₄N₆O₈ (2CH₂Cl₂ molecules are incorporated), FW = 830.59, monoclinic (P2₁/*n*), *a* = 12.890(4), *b* = 9.700(3), *c* = 16.890(5) Å, β = 102.920(5)°, *V* = 2058.3(9) Å³, *T* = 293 K, *Z* = 2, *D_c* = 1.340 mg·m⁻³, *R* = 0.0607, *wR* = 0.1906 [4586 reflections and 244 parameters with *I* > 2σ(*I*)]. **3c**: mp: 210–213 °C; FAB-MS (*m/z*): 657 (*M* + 1); Crystal data: C₄₀H₄₂N₆O₈ (C₆H₆ molecule is incorporated), FW=734.81, monoclinic (P2₁/*c*), *a* = 12.000(4), *b* = 6.7200(19), *c* = 24.400(7) Å, β = 92.210(6)°, *V* = 1966.2(10) Å³, *T* = 293 K, *Z* = 2, *D_c* = 1.241 mg·m⁻³, *R* = 0.0635, *wR* = 0.1763 [4438 reflections and 244 parameters with *I* > 2σ(*I*)].

4. Conclusions

Three TCNQ derivatives carrying nitroxide radicals (**3a–3c**) were prepared as the first examples of spin-carrying TCNQ derivatives and were found to form single component CT crystals by self-assembly, in which the TCNQ core works as an acceptor and nitroxide radical as a donor. The CT feature of **3c** with point-to-point contact was proved to be different from those of **3a** and **3b** that displayed point-to-face contact. Reflecting remote distances between the spin centers in their crystal structures, no eminent but weak antiferromagnetic properties of Curie-Weiss behavior were observed for all of the radical crystals. It is of interest to see if two-component CT complexes would be formed between the TCNQ derivatives **3a–3c** and an appropriate donor molecule such as TTF and work along this line is still in progress.

Conflict of Interest

The authors declare no conflict of interest.

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