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Synthesis of Novel Electron Acceptor, 2,5-Bis[4'-(dimethylamino)pyridinio]-3,6-difluoro-7,7,8,8-tetracyanoquinodimethane Bis(trifluoromethanesulfonate), in the Form of Charge-Transfer Complex

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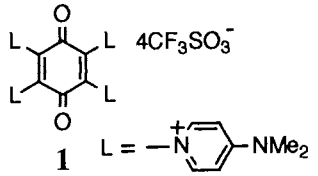
2,5-Bis[4'-(dimethylamino)pyridinio]-3,6-difluoro-7,7,8,8-tetracyanoquinodimethane bis(trifluoromethanesulfonate) was obtained as a 1:1 charge-transfer complex with 4-(dimethylamino)pyridine in the reaction of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($TCNQF_4$) with N-trimethylsilyl-4-(dimethylamino)pyridinium trifluoromethanesulfonate. Its first reduction potential was measured in cyclic voltammetry to be as high as 0.96 V (vs. Ag/AgCl), exceeding that of 2,5,7,7,8,8-hexacyanoquinodimethane ($TCNQ(CN)_2$) by 0.29 V.

7,7,8,8-Tetracyanoquinodimethane[1] (TCNQ) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone[2] (DDQ) are well-known as powerful organic electron acceptors. Moreover, 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane[3] ($TCNQF_4$) and 2,5,7,7,8,8-hexacyanoquinodimethane[3] ($TCNQ(CN)_2$) exhibit much stronger electron-accepting character than TCNQ does.[4] $TCNQ(CN)_2$ was generally accepted as the strongest organic electron acceptor. Recently, Weiss *et al.* carried out the onio-substitution reaction of *p*-chloranil to successfully obtain 2,3,5,6-tetrakis[4'-(dimethylamino)pyridinio]-1,4-benzoquinone tetrakis(trifluoromethanesulfonate) (**1**), whose electron-accepting character is much stronger than that of $TCNQ(CN)_2$, because onio group is able to draw electron much more strongly than cyano or nitro group does.[5]



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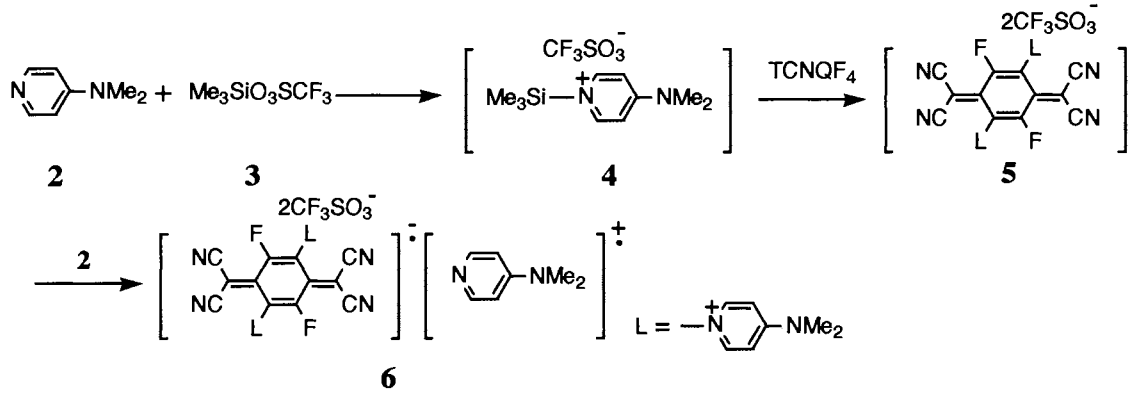
This letter described the onio-substitution reaction of $TCNQF_4$ to prepare a novel onio-substituted tetracyanoquinodimethane which is much stronger in electron-accepting character than **1**.



Onio-substitution reaction of $TCNQF_4$ was carried out according to the method of Weiss *et al.*[5] 4-(Dimethylamino)pyridine (**2**) (0.63 g, 5.2 mmol) and trimethylsilyl trifluoromethanesulfonate (**3**) (0.58 g, 2.6 mmol) were dissolved in 20 mL of dichloromethane at 35 °C. Into the solution was added 0.35 g (1.3 mmol) of $TCNQF_4$ with stirring and the reaction mixture was kept for 8 h to deposit a black viscous material which was separated by decantation and was dissolved in a small amount of acetonitrile. The resulting solution was poured into an excess of tetrahydrofuran (THF) to precipitate the product again. This dissolution-precipitation process was repeated more twice to give 0.54 g of a black solid product (**6**) with metallic luster. Mp > 250 °C. Its ^1H NMR spectrum in DMSO-d_6 showed peaks at 3.22 (s, 3H), 7.10 (d, J=7.2 Hz, 1H), and 8.05 (d, J=7.2 Hz, 1H) ppm, assignable to methyl proton of dimethylamino group, 3-, and 2-protons of pyridinium ring, respectively. Its ^{19}F NMR in acetonitrile with trichlorofluoromethane as a reference showed two singlet peaks at 79.2 and 137.1 ppm, assignable to trifluoromethyl group and fluorine on the benzene nucleus, respectively. Its IR spectrum showed absorption bands at 2152, 1280, and 1160 cm^{-1} due to C≡N, C-F, and S=O bonds, respectively (Fig. 1). Cyclic voltammogram of **6** was shown in Fig. 2. Its first reduction potential (E_1) was found to be as high as 0.96 V, which exceeds that of $TCNQ(CN)_2$ (E_1=0.67 V) by 0.29 V and also that of **1** (E_1=0.73 V) by 0.23 V. Anal. Found: C, 46.50; H, 3.87; F, 15.50; N, 15.89%. Found values nearly corresponded with the calculated ones for the 1:1 charge-transfer complex of 2,5-bis[4'-(dimethylamino)pyridinio]-3,6-difluoro-7,7,8,8-tetracyanoquinodimethane bis(trifluoromethanesulfonate) (**5**) with **2** (Calcd for $C_{35}H_{30}F_8N_{10}O_6S_2$: C, 46.57; H, 3.35; F, 16.80; N, 15.51%.). Its ESR spectrum in the solid state showed a singlet peak at g=2.007, suggesting that **6** is paramagnetic (Fig. 3). Its UV-vis spectrum exhibited absorption peaks at 208, 298, 388, and 872 nm (Fig.4). The last absorption was regarded as the charge-transfer transition band between **2** and **5**. It was concluded therefore that only two out of four fluoro groups of $TCNQF_4$ were able to be onio-substituted in the reaction of $TCNQF_4$ with N-trimethylsilyl-4-(dimethylamino)pyridinium trifluoromethanesulfonate (**4**) to obtain **5**, which reacted with **2** to form the 1:1

charge-transfer complex (**6**) to which the dative bond structure should make a great contribution. Separation of **5** as a pure compound was attempted in various ways, but a pure stable **5** was not obtainable yet as well as strong electron acceptors such as 2,2',3,3',5,5',6,6'-octafluoro-7,7,7',7'-tetracyanodiphenoquinodimethane[3] and 2,3,5,6,7,7,8,8-octacyanoquinodimethane.[6] It was conceivable that compound **5** is much more stable in the form of a charge-transfer complex with **2** rather than its pure state. At the moment the experimental data were not enough for distinguishing between 2,5- and 2,6-positions of fluorine atoms due to its poor solubility in solvent, but the former probably happens more because the corresponding nucleophilic disubstitution reaction of *p*-chloranil was reported to take place at 2,5-position.[7]

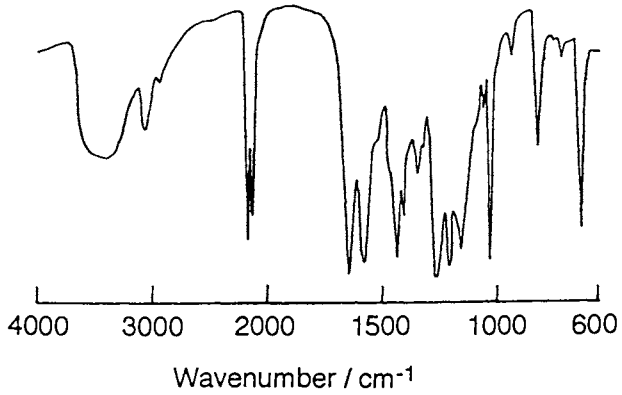


Fig.1. IR spectrum of the product (**6**).

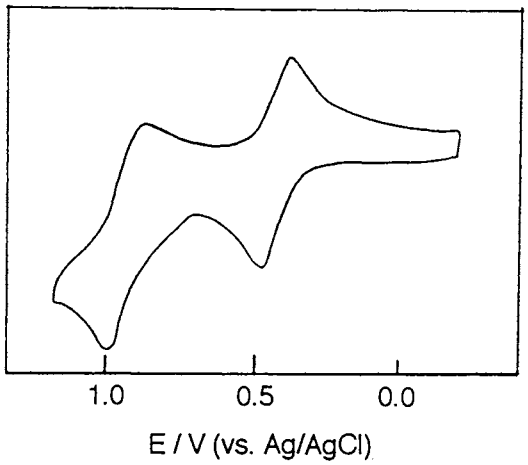


Fig.2. Cyclic voltammogram of the product (**6**) in acetonitrile solution containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate: scan rate, 100 mV s^{-1}.

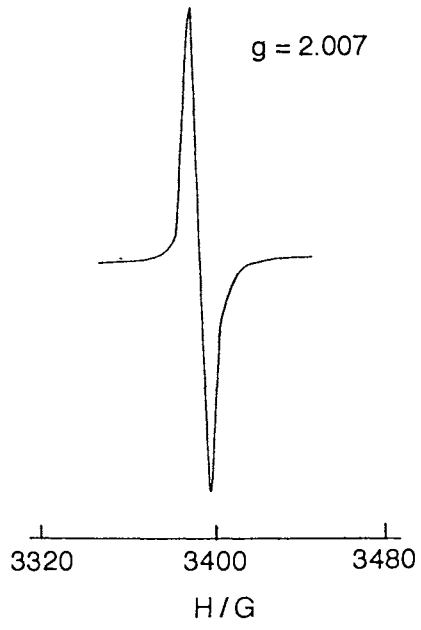


Fig. 3. ESR spectrum of the product (**6**) in the solid state at room temperature.

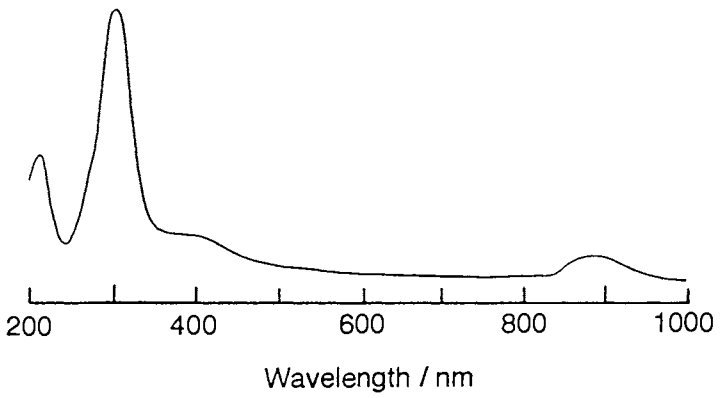


Fig. 4. UV-vis spectrum of the product (**6**) in acetonitrile.

It was found that molar ratio in feed of the onio-substitution reagent to $TCNQF_4$ plays an important role on the onio-substitution reaction. When **2** and **3** amounted to be just twice equivalent to that of $TCNQF_4$, onio-substitution did not take place at all. When **2** remained twice equivalent and **3** rose to four times equivalent to that of $TCNQF_4$, dionio-substitution eventually took place. However, when an excess of **2** and **3** were employed such as four times equivalent and eight times equivalent to $TCNQF_4$, respectively, only dionio-substitution took place, but no tetraonio-substitution did. Weiss *et al.* reported that di- and tetra-substitution reactions took place when molar amounts of **2** and **3** in feed were two times and four times equivalent to *p*-chloranil, respectively.[5] Anyhow, we could not find an experimental condition for obtaining tetraonio-substituted compound from $TCNQF_4$.

The first reduction potential values of **6**, DDQ, **1**, TCNQ, $TCNQF_4$, and $TCNQ(CN)_2$ are summarized in Table 1. It is obvious that **6**, the dionio-substituted tetracyano-quinodimethane, is the most electron accepting, probably suggesting the highest, organic electron acceptor.

Table 1. First reduction potential[a] (E_1)

compound	E_1 / V
DDQ	+0.54
TCNQ	+0.19
1	+0.73[b]
$TCNQF_4$	+0.56
$TCNQ(CN)_2$	+0.67
6	+0.96

a) Solvent, acetonitrile containing tetra-butylammonium perchlorate (0.1 mol dm^{-3}); reference electrode, Ag/AgCl; scan rate, 100 mV s^{-1}. b) Data from Ref. 5.

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