TTF–Cytosine Dyad as an Electron-donor Molecule Having Proton-accepting Ability: Formation of Hemiprotonated Cytosine Dimer in I_3^- Salt

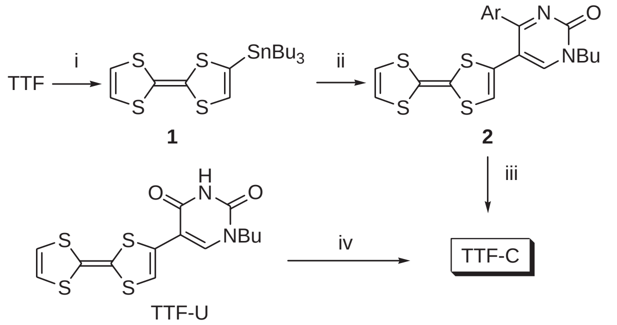
Eigo Miyazaki,[1] Yasushi Morita,*[1,2] Yumi Yakiyama,[1] Suguru Maki,[1] Yoshikazu Umemoto,[1]
Makoto Ohmoto,[1] and Kazuhiro Nakasuji*[3]
[1]*Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043*
[2]*PRESTO, Japan Science and Technology (JST), 4-1-8 Hon-cho, Kawaguchi 332-0012*
[3]*Fukui University of Technology, 3-6-1 Gakuen, Fukui 910-8105*

(Received June 15, 2007; CL-070650; E-mail: morita@chem.sci.osaka-u.ac.jp)

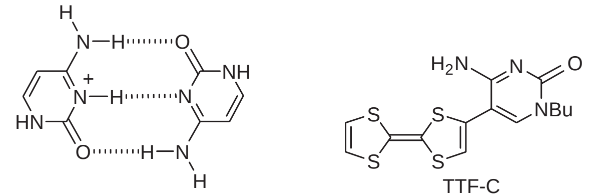
A tetrathiafulvalene (TTF) derivative with a cytosine moiety was designed and synthesized as a bi-functional molecule with both electron-donating and proton-accepting abilities. In the crystal of I_3^- salt, TTF–cytosine dyad formed a hemiprotonated dimer through triple hydrogen-bonds with radical cationic state of the TTF moieties.

An attractive application based on the bio-molecule inspired functional molecular systems are rapidly spread in the field of materials science.[1] Cytosine possesses a self-assembling nature to form a hydrogen-bonded (H-bonded) dimer having double N–H···N interactions under neutral condition.[2] Interestingly, due to a proton-accepting ability, two cytosine molecules catch one proton under acidic condition, forming a hemiprotonated cytosine dimer with triple H-bonds (Chart 1).[3] This unique self-assembling ability was utilized in charge-transfer (CT) salt of pristine cytosine with TCNQ derivative, in which the dimer acted as cationic part in the salt.[4] Our previous study on H-bonded CT complex of TTF–imidazole (D) with *p*-chloranil (A) revealed the new role of H-bond to control electronic structure by regulating electron-accepting ability of *p*-chloranil and the donor/acceptor ratio by forming a D–A–D triad.[5] In order to expand examples involving these new roles of H-bonds, recent our attention is concentrating on nucleobase systems with TTF moieties, i.e. TTF-U (Scheme 1).[6] Focusing on the hemiprotonated cytosine dimer, we have designed a novel TTF–cytosine dyad (TTF-C) in this study (Chart 1). Here, we report the syntheses and crystal structures of TTF-C and a hemiprotonated cytosine dimer in its I_3^- salt, demonstrating a high potential of TTF-C for H-bonded electron-donor molecule in a complementary triple H-bonded cationic dimer.

TTF-C was obtained as an orange powder by the Stille cross-coupling reaction of $SnBu_3$-substituted TTF **1** with iodo derivative of 1-*n*-butylpyrimidin-2-one followed by treatment of aqueous NH_3 solution (Scheme 1).[7] As an alternative method, a transformation of TTF-U[6a] by two steps (mesitylenesulfonylation and substitution by ammonia) also gave an effective way to TTF-C. Notably, this molecule possesses a reasonable solubility toward common organic solvents in spite of a cytosine derivative. Cyclic voltammetry (CV) measurement of TTF-C in a DMF solution showed two-stage one-electron oxidation waves (see Supporting Information).[8] The first oxidation potential exhibited a positive shift (0.06 V) compared with that of TTF, indicating that the cytosine moiety worked as a weak electron-withdrawing group.



Scheme 1. Reagents and conditions: i) *n*-BuLi then Bu_3SnCl, $-78\,^{\circ}C$, ii) 1-*n*-butyl-5-iodo-4-(*o*-nitrophenoxy)pyrimidin-2-one, $Pd(PPh_3)_4$, Ar = *o*-nitrophenoxy, iii) aqueous NH_3 solution, THF, rt, iv) 2-mesitylenesulfonyl chloride, dimethylaminopyridine, and triethylamine, rt, then aqueous NH_3 solution.



hemiprotonated cytosine dimer

TTF-C

Chart 1.

Single crystals of TTF-C containing crystal water, TTF-C•H_2O, were obtained as orange blocks by vapor-diffusion method using hexane–CH_2Cl_2.[9] Dihedral angle between TTF and cytosine moieties is 31.8°. TTF-C forms complementary quadruple H-bonds, two of which are direct N–H···N bonds (2.98 Å) and the other two bonds are through water molecules (Figure 1). The H-bonded dimer was connected by intermolecular O···S contacts and $\pi\cdots\pi$ interactions, resulting in the formation of a two-dimensional network.[8] In the IR spectrum measured by KBr pellet, the absorption band of $1674\,cm^{-1}$ is attributed to C=O stretching mode.[8] The broad N–H stetching absorptions are observed around $3080\,cm^{-1}$ due to N–H···N and N–H···O H-bonds. IR data and H-bonding distances of the cytosine moiety of TTF-C•H_2O are similar to those reported for 1-methylcytosine.[8,10]

A I_3^- salt of TTF-C was obtained as black platelets by the diffusion method using TTF-C and I_2 in 1,2-dichloroethane solution.[11] This I_3^- salt was composed of crystallographically equivalent two $TTF^{\bullet +}$-C, and three I_3^- as determined by X-ray structure analysis (Figure 2).[8,12] Furthermore, considering the total balance of charge, a proton with 0.5 of site occupancy factor was disordered into two cytosine moieties. This proton might be derived from HI which was generated from contami-

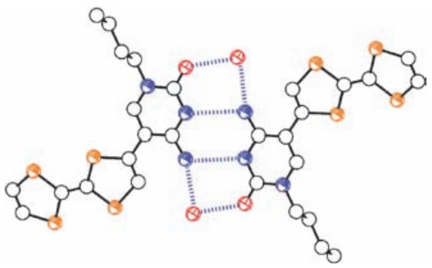


Figure 1. Crystal structure of TTF-C•H_2O. H-bonded dimer structure through complementary quadruple H-bonds including H_2O molecules. Hydrogen atoms are omitted for clarity.

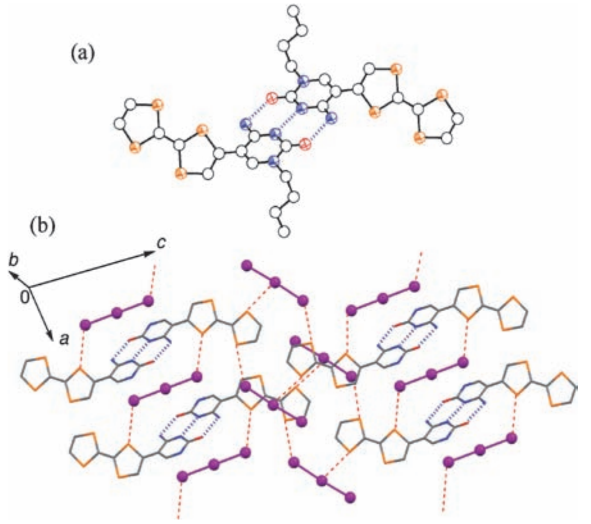


Figure 2. Crystal structure of $(\mathrm{TTF}^{\bullet+}\text{-C})_2\cdot\mathrm{H}^+\cdot(\mathrm{I}_3{}^-)_3$. (a) Hemiprotonated dimer through complementary triple H-bonds. (b) Two-dimensional network through the I···S contacts (red color line) and H-bonds (blue color line). Hydrogen atoms (a and b) and the *n*-butyl group of the cytosine moiety (b) are omitted for clarity.

nated H_2O and decomposed I_2. Consequently, the molecular formula of the $\mathrm{I}_3{}^-$ salt was determined as $(\mathrm{TTF}^{\bullet+}\text{-C})_2\cdot\mathrm{H}^+\cdot(\mathrm{I}_3{}^-)_3$, confirming a formation of the hemiprotonated cytosine dimer through complementary triple H-bonds (Figure 2a). The N–H···O and N–H···N distances between the cytosine moieties were 2.79 and 2.83 Å, respectively, which are almost the same as those of the known hemiprotonated cytosine dimers.[8,13] The IR spectrum in KBr also corroborated the formation of this dimer structure: The absorption band attributed to C=O stretching mode was observed in 1733 cm^{-1}. This data was similar to that of reported hemiprotonated cytosine dimers.[8,13] The radical cationic state of TTF-C may influence the molecular structure: The larger dihedral angle of 131° between TTF and cytosine moieties than that of neutral TTF-C•H_2O indicates the effect of electrostatic repulsion between the TTF radical cation and the cationic hemiprotonated cytosine dimer. In the crystal structure, there were some I···S contacts of 3.55–3.75 Å between $\mathrm{TTF}^{\bullet+}$-C and $\mathrm{I}_3{}^-$, resulting in the construction of a two-dimensional network (Figure 2b).[8]

In summary, TTF-C was newly synthesized as an electron-donor molecule with proton-accepting ability. Reflecting such features, TTF and cytosine moieties adopted the radical cationic state and the hemiprotonated dimer in the $\mathrm{I}_3{}^-$ salt, respectively. These results open a new possibility for preparing a highly conductive CT complex having a partial CT state of TTF moiety in the hemiprotonated cytosine dimer motif by using an appropriate electron-acceptor molecule. Current studies are carried out in this direction.

This work was partially supported by PRESTO-JST, Grant-in-Aid for Scientific Research (No. 16350074) from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by grants of the Asahi Glass Foundation and CASIO Science Promotion Foundation.

References and Notes

1 For example, see E. Katz, I. Willner, *Angew. Chem., Int. Ed.* **2004**, *43*, 6042.

2 a) F. S. Mathews, A. Rich, *Nature* **1964**, *201*, 179. b) G. A. Jeffrey, Y. Kinoshita, *Acta Cryst.* **1963**, *16*, 20.

3 a) T. J. Kistenmacher, M. Rossi, L. G. Marzilli, *Biopolymers* **1978**, *17*, 2581. b) K. Gehring, J.-L. Leroy, M. Guéron, *Nature* **1993**, *363*, 561. c) D. Armentano, G. D. Munno, R. Rossi, *New J. Chem.* **2006**, *30*, 13.

4 a) G. G. Sheina, E. D. Radchenko, I. P. Blagoi, B. I. Verkin, *Dokl. Akad. Nauk SSSR* **1978**, *240*, 463. b) T. Murata, G. Saito, *Chem. Lett.* **2006**, *35*, 1342. c) T. Murata, K. Nishimura, G. Saito, *Mol. Cryst. Liq. Cryst.* **2007**, *466*, 101.

5 T. Murata, Y. Morita, K. Fukui, K. Sato, D. Shiomi, T. Takui, M. Maesato, H. Yamochi, G. Saito, K. Nakasuji, *Angew. Chem., Int. Ed.* **2004**, *43*, 6343.

6 a) Y. Morita, S. Maki, M. Ohmoto, H. Kitagawa, T. Okubo, T. Mitani, K. Nakasuji, *Org. Lett.* **2002**, *4*, 2185. b) E. Miyazaki, Y. Morita, Y. Umemoto, K. Fukui, K. Nakasuji, *Chem. Lett.* **2005**, *34*, 1326. c) Y. Morita, E. Miyazaki, Y. Umemoto, K. Nakasuji, *J. Org. Chem.* **2006**, *71*, 5631.

7 Selected physical data of TTF-C: mp 169–170 °C (dec). ^{1}H NMR (270 MHz, DMSO-d_6): δ 0.88 (t, $J = 7.4$ Hz, 3H), 1.17–1.31 (m, 2H), 1.49–1.60 (m, 2H), 3.85 (t, $J = 7.2$ Hz, 2H), 6.68 (s, 1H), 6.73 (s, 2H), 7.85 (s, 1H). Anal. Calcd for $(\mathrm{C_{14}H_{15}N_3OS_4})(\mathrm{H_2O})_{0.5}$: C, 44.42; H, 4.26; N, 11.10%. Found: C, 44.36; H, 3.90; N, 10.98%.

8 Supporting Information is electronically available on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

9 Crystal data for TTF-C•H_2O: $\mathrm{C_{14}H_{17}N_3O_2S_4}$, fw 387.55, monoclinic, space group, $P2_1/c$ (no. 14), $a = 11.7943(9)$, $b = 5.6155(3)$, $c = 26.1325(16)$ Å, $\beta = 100.683(2)°$, $V = 1700.78(19)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.506$ g/cm^{-3}, μ(Mo Kα) = 5.70 cm^{-1}, $T = 200(2)$ K, 3902 unique reflections ($R_{\mathrm{int}} = 0.128$). The structure was refined to $R_1 = 0.079$, $wR_2 = 0.190$ for 2305 reflections with $I > 2\sigma(I)$ and 224 parameters, goodness-of-fit = 1.02. The data was deposited in Cambridge Crystallographic Data Centre (CCDC-652831).

10 In the case of 1-methylcytosine, complementary double H-bonds of N–H···N were formed.[2a]

11 Selected physical data of $(\mathrm{TTF}^{\bullet+}\text{-C})_2\cdot\mathrm{H}^+\cdot(\mathrm{I}_3{}^-)_3$: mp 182–183 °C (dec); Anal. Calcd for $(\mathrm{C_{14}H_{15}N_3OS_4})_2(\mathrm{H})(\mathrm{I_3})_3$: C, 17.87; H, 1.66; N, 4.46%. Found: C, 18.25; H, 1.63; N, 4.66%.

12 Bond lengths analyses indicate TTF moieties are oxidized to be +1. Crystal data for $(\mathrm{TTF\text{-}C}^{\bullet+})_2\cdot\mathrm{H}^+\cdot(\mathrm{I}_3{}^-)_3$: $\mathrm{C_{14}H_{15.5}N_3OS_4I_{4.5}}$, fw 941.11, triclinic, space group, $P\bar{1}$ (no. 2), $a = 7.83(1)$, $b = 8.11(1)$, $c = 20.42(3)$ Å, $\alpha = 80.71(4)$, $\beta = 78.70(4)$, $\gamma = 84.43(5)°$, $V = 1252(2)$ Å^3, $Z = 2$, $D_{\mathrm{calcd}} = 2.496$ g/cm^{-3}, μ (Mo Kα) = 59.41 cm^{-1}, $T = 200.2$ K; 5305 unique reflections ($R_{\mathrm{int}} = 0.040$). The structure was refined to $R_1 = 0.044$, $wR_2 = 0.082$ for 2145 reflections with $I > 1\sigma(I)$ and 241 parameters, goodness-of-fit = 0.92. CCDC-652830.

13 In the hemiprotonated cytosine dimer of the reported compounds,[3c,4b] N–H···O and N–H···N distances were determined to be 2.78–2.84 Å, and C=O stretching absorptions in the IR spectra were observed in 1725 and 1731 cm^{-1}.

Published on the web (Advance View) July 28, 2007; doi:10.1246/cl.2007.1102