# Tuning of Intramolecular π–π Overlap Mode of Tetrathiafulvalene Bisannulated Macrocycles in the Open-Shell Electronic State

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Charge-transfer complexes of bis(methylthio)tetrathiafulvalene (DMT-TTF) bisannulated macrocycles with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($F_4$-TCNQ) were prepared. The crystal structural analysis revealed an intramolecular dimer structure with the π–π overlap of DMT-TTF units. The magnitude of intramolecular π–π overlap depends on the ring size of macrocycles.

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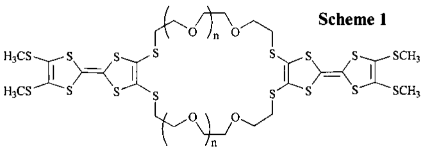
Tetrathiafulvalene (TTF) derivatives have attracted much attention as redox active organic π-systems.[1] The TTF molecular framework can take a stable open-shell electronic structure in the solid state and exhibits metallic or superconducting properties by the π–π overlaps of these open-shell molecules.[1] Hybridized supramolecular systems incorporating the redox active TTF unit and ion recognizing macrocyclic molecules have been reported for constructing novel supramolecular structures.[2-4] Likewise redox responsive TTF-based ligands have been reported.[5] The TTF multiannulated macrocycles have conformational freedom due to the flexibility in the macrocyclic part. Depending on the conformations in the macrocyclic part, the more rigid redox active TTF units can change their π-electron configurations within the molecule. The bulk physical properties, such as electrical conduction or magnetic spin ordering, significantly depend on the π–π interaction scheme of the TTF units. Therefore, knowledge of the solid state structural information of these multi π-electron linkage system, especially in the open-shell electronic state, is necessary for the design of new molecular conductors.

We have reported the crystal structures of bis(methylthio)-TTF (DMT-TTF) bisannulated macrocycle, bis(DMT-TTF)24C, in the divalent cation form as the cation radical salt and charge-transfer (CT) complex with the counter anion of $(I_3^-)(I_5^-)$ and the electron acceptor of 2,5-dicholoro-7,7,8,8-tetracyanoquinodimethane ($Cl_2$-TCNQ), respectively.[6,7] The bis(DMT-TTF)24C molecule has a macrocyclic 24-membered ring as linking two DMT-TTF units. The bis(DMT-TTF)24C found in these crystals takes a conformation of the Z-type intramolecular π–π dimer structure. The intramolecular interaction scheme of TTF bisannnulated macrocycles should depend on the size of the macrocyclic moiety. Here we employed the bis(DMT-TTF)30C having 30-membered macrocyclic ring as a linker of two DMT-TTF units (Scheme 1) and examined the crystal structure of the CT complex. The molecular conformation of the divalent bis(DMT-TTF)30C will be discussed in comparison with that of bis(DMT-TTF)24C having 24-membered ring.

Scheme 1



n=1: bis(DMT-TTF)24C, n=2: bis(DMT-TTF)30C

Bis(DMT-TTF)30C has been synthesized using the cyanoethyl protection/deprotection protocols.[8] The CT complex was obtained using the electron acceptor 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($F_4$-TCNQ). High-quality single crystals were grown from the 1 : 3 mixture of bis(DMT-TTF)30C and $F_4$-TCNQ in 1 : 1 mixed solvent of $CH_3CN$ and 1,2-dichloroethane (DCE). The stoichiometry of [bis(DMT-TTF)30C]$(F_4\text{-TCNQ})_2(\text{DCE})_{1.5}$ was determined by the X-ray structural analysis.[9] The electronic ground state of the CT complex was examined by the absorption spectrum on KBr pellet sample in the UV-vis-NIR region. The CT absorptions were observed at energies of 9500, 11000, and 13000 $cm^{-1}$. The divalent $[\text{bis(DMT-TTF)24C}]^{2+}$ molecule showed a CT transition at 9100 $cm^{-1}$ due to the $(\text{DMT-TTF})^+$ unit,[6,7] whereas the $(F_4\text{-TCNQ})^-$ monomer has the transitions at 11700 and 13300 $cm^{-1}$.[10] Since the absorption spectrum is a superimposition of completely ionized $(\text{DMT-TTF})^+$ unit and $(F_4\text{-TCNQ})^-$, the electronic ground state should be the fully charge transferred $[\text{bis(DMT-TTF)30C}]^{2+}(F_4\text{-TCNQ})^-_2(\text{DCE})_{1.5}$. The charge transferred state of the CT complex is reasonable from the negative $\Delta E$ value (-0.1 V) [$\Delta E = E_{1/2}(\text{D}) - E_{1/2}(\text{A})$] between the bis(DMT-TTF)30C [$E_{1/2}(\text{D}) = +0.46$ V] and $F_4$-TCNQ [$E_{1/2}(\text{A}) = +0.56$ V vs. SCE, 0.1 M $(n\text{-Bu})_4\text{N}{\cdot}\text{BF}_4$ in DCE], here the $E_{1/2}$ is the half-wave redox potential.[11]

Figure 1 shows the unit cell of [bis(DMT-TTF)30C]$(F_4\text{-TCNQ})_2(\text{DCE})_{1.5}$ viewed normal to the DMT-TTF plane. A half unit of bis(DMT-TTF)30C and one $F_4$-TCNQ molecule are the crystallographically asymmetric units. The bis(DMT-TTF)30C molecule adopts an intramolecular dimer structure, whereas the $F_4$-TCNQ molecules form an intermolecular dimer pair. The molecular planes of the DMT-TTF and $F_4$-TCNQ are orthogonal to each other, and the solvent molecule of DCE exists between the $F_4$-TCNQ dimers.

Figures 2a and 2b show the molecular conformation of divalent $[\text{bis(DMT-TTF)24C}]^{2+}$ and $[\text{bis(DMT-TTF)30C}]^{2+}$ found in the [bis(DMT-TTF)24C]$(I_3^-)(I_5^-)$ and [bis(DMT-TTF)30C]$(F_4\text{-TCNQ})_2(\text{DCE})_{1.5}$, respectively.[6] Although the intramolecular dimer structures are observed in both conformations, the π–π overlap modes are quite significantly different from each other. The π–π overlap in the former radical salt occurs only at the

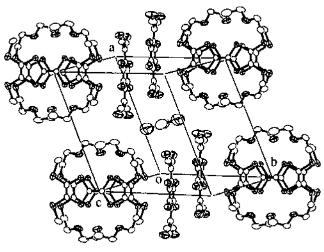


**Figure 1**. Unit cell of [bis(DMT-TTF)30C]($F_4$-TCNQ)$_2$(DCE)$_{1.5}$ viewed normal to the DMT-TTF plane.

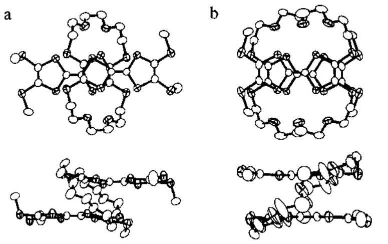


**Figure 2**. Intramolecular π-π overlap of [bis(DMT-TTF)24C]$^{2+}$ (a) and [bis(DMT-TTF)30C]$^{2+}$ (b) viewed normal to the DMT-TTF planes.

inner 5-membered ring of the DMT-TTF units, while a complete overlap of the DMT-TTF moieties is observed in the latter CT complex. This surprising ring over ring overlap mode is significantly different from the ring over bond type π–π overlap typically found in the TTF-based CT compelxes.[12] The mean interplanar distances ($d_1$ = 3.408 Å) between two TTF moieties in the bis(DMT-TTF)30C molecule is ca. 0.11 Å longer than that found in the bis(DMT-TTF)24C ($d_1$ = 3.300 Å). The intradimer transfer integrals ($t_1$) determined by the extended Hückel molecular orbital calculation are 40.3 x $10^{-2}$ and 48.2 x $10^{-2}$ for bis(DMT-TTF)24C and bis(DMT-TTF)30C, respectively.[13] The larger magnitude of the latter π–π overlap than that of the former one is due to the effective interaction within the DMT-TTF moieties. The 24-membered macrocyclic ring system is too small for the overlap of whole DMT-TTF units, while the 30-membered ring has adequate length to allowing optimal stacking of two DMT-TTF units. Thus tuning of the π–π overlap mode in TTF bisannulated macrocycle is possible by changing the length of macrocyclic unit.

Figure 3 shows the intermolecular interactions of [bis(DMT-TTF)30C]($F_4$-TCNQ)$_2$(DCE)$_2$ viewed along the a-axis. Since the intermolecular interaction ($t_2$ = -0.9 x $10^{-2}$) along the c-axis is small, each donor molecule is isolated from each other. The $F_4$-TCNQ dimer is surrounded by four bis(DMT-TTF)30C molecules, and the molecular planes of $F_4$-TCNQ dimer are orthogonal to the DMT-TTF plane. The mean interplanar distance ($d_2$) and transfer integral ($t_3$) within the $F_4$-TCNQ dimer is 3.233 Å and 20.1 x $10^{-2}$, respectively. Two kinds of intermolecular interactions between the DMT-TTF and $F_4$-TCNQ dimers were observed along the b+c ($t_4$ = -1.15 x $10^{-2}$) and b-c direction ($t_5$ = -1.99 x $10^{-2}$). The magnitude of intermolecular interactions between the donor and acceptor is much smaller than those of intradimer interactions, and each dimer unit is isolated.

In conclusion, the intramolecular dimer structure is the most stable molecular conformation in these open-shell TTF bisannulated macrocycles. The magnitude of π–π overlap between the DMT-TTF units depends on the size of macrocyclic unit. The 30-membered macrocyclic ring system as the bridging unit of two DMT-TTF units increases the effective π–π intramolecular interaction compared with the 24-membered ring system. Consequently, the control of intra and intermolecular π–π interaction scheme is possible through the design of macrocyclic parts. The CT complex formations of related TTF bisannulated macrocycles are now in progress.

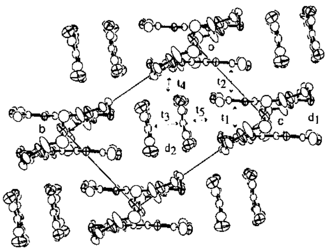


**Figure 3**. Intermolecular interactions found in the [bis(DMT-TTF)30C]($F_4$-TCNQ)$_2$(DCE)$_{1.5}$. DCE molecules are omitted in figure. Transfer integrals ($t_1$ ~ $t_5$) and mean interplanar distances ($d_1$ and $d_2$) are indicated.

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9 Crystal data for $C_{58}H_{48}O_6S_{16}N_6F_8Cl_2$, F.*M* = 1688.92, crystal dimension 0.6 × 0.4 × 0.3 $mm^2$, triclinic, $P\bar{1}$(#2), $a$ = 14.637(3), $b$ = 14.828(4), $c$ = 9.845(2) Å, $\alpha$ = 98.62(2), $\beta$ = 98.62(2), $\gamma$ = 118.58(2)°, $V$ = 1793.7(8) $Å^3$, $T$ = 298 K, $d_{calc}$ = 1.563 $gcm^{-3}$, $Z$ = 1, $\mu$(Mo-K$\alpha$) = 6.31 $cm^{-1}$, 8718 reflections measured, 8238 unique which were used in all calculations. The final $wR(F^2)$ was 0.058 ($I > 3.5\sigma(I)$) and 443 variable parameters. Parameters were refined using the anisotropic temperature factors, and the hydrogen atoms were removed from the refinements.

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