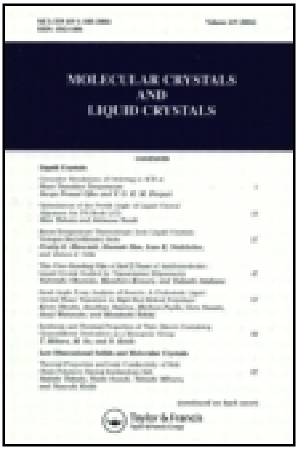

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Crystal Structures of Tetrathiafulvalene Multiannulated Macrocycles in Open-Shell Electronic State

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Crystal Structures of Tetrathiafulvalene Multiannulated Macrocycles in Open-Shell Electronic State

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Crystal structures of dimethylthio-tetrathiafulvalene (DMT-TTF) multiannulated macrocycles, bis(DMT-TTF) and tris(DMT-TTF), were examined. The intramolecular dimerization was a common structural feature for these multi-TTF macrocycles in open-shell electronic state.

Keywords: Multiannulated-TTF; Macrocycles; Cation Radical Salts

INTRODUCTION

Dimethylthio-tetrathiafulvalene (DMT-TTF) multiannulated macrocycles are an interesting component for constructing molecular conductors and supramolecular entities.[1] The DMT-TTF mutiannulated macrocycles have multi redox active TTF units and structurally flexible macrocyclic part within a molecule.[2] Since the packing arrangement of redox active DMT-TTF units within the crystals is structurally restricted by the intramolecular linkers, the formation of unique stacking arrangements is expected by using DMT-TTF multiannulated macrocycles as an electron donor of molecular conductors. However, the molecular conformation of these donors in the solid state is not clear due to the difficulties in crystal preparations. We report here the crystal structures of cation radical salts based on the bis(DMT-TTF) and tris(DMT-TTF) macrocycles (Fig. 1), in which unusual molecular packing is observed.[3,4]

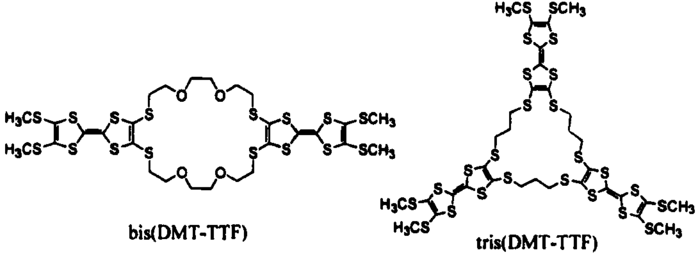

FIGURE 1. Molecular structures of bis(DMT-TTF) and tris(DMT-TTF).

RESULTS AND DISCUSSION

The cation radical salts of [bis(DMT-TTF)](I_3^-)(I_5^-) **1** and [tris(DMT-TTF)](I_3^-)(1,2-dichloroethane)$_{1.5}$ **2** were prepared by the standard electrocrystalliztaion method. From the results of X-ray structural analysis, the charged states of bis(DMT-TTF) and tris(DMT-TTF) are the completely oxidized [bis(DMT-TTF)]$^{2+}$ and partially oxidized [tris(DMT-TTF)]$^{+}$, respectively.[3,4] Figs. 2a and 2b show the molecular conformations of divalent [bis(DMT-TTF)]$^{2+}$ and monovalent [tris(DMT-TTF)]$^{+}$ found in the salts **1** and **2**, respectively.

The [bis(DMT-TTF)]$^{2+}$ molecule has an intramolecular dimer structure, in which the π–π overlap was observed between the inner 5-membered ring of DMT-TTF units.

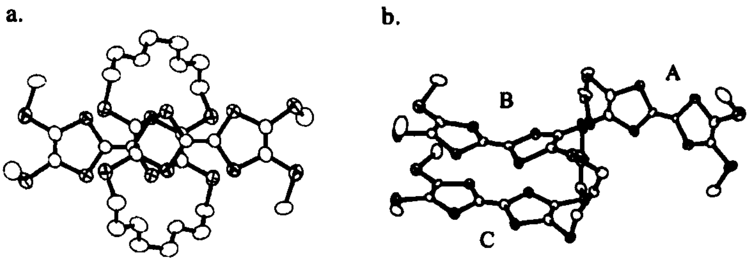

FIGURE 2. Molecular conformations of the open-shell a) [bis(DMT-TTF)]$^{2+}$ and b) [tris(DMT-TTF)]$^{+}$ within the cation radical salts.

Three kinds of DMT-TTF units, **A**, **B**, and **C**, are crystallographically asymmetric unit in the crystal **2**. A non-planar conformation through the folding of the central propyl linkers is observed. As a result, the C_3 molecular symmetry of tris(DMT-TTF) is broken. The molecular plane of **B** unit is parallel to that of the **C**, while that of the **A** unit is orthogonal to those of the **B** and **C**. A pair of **B** and **C** units form an intramolecular dimer structure through face-to-face π–π overlap with the intramolecular S ~ S contacts shorter than the van der Waals interaction. The π–π overlap mode is the double ring over ring type. The **A** unit is completely isolated from the **B** and **C** units without intramolecular interactions.

CONCLUSION

The molecular conformations of [bis(DMT-TTF)]$^{2+}$ and [tris(DMT-TTF)]$^{+}$ were regulated by macrocyclic linkers in the crystal and the

DMT-TTF units formed intramolecular dimer units. The C_2 and C_3 molecular symmetries of these multi-TTF annulated donors were broken through the formation of intradimer structures.

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