

Charge transfer complexes of ethylenedichalcogenothiophene (EDXT : X = O, S) and TCNQ analogs: atom-substituted effects

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Single molecular-weight organic conductors have played a crucial role in elucidating relationships between structures and their electronic transport properties to understand their underlying mechanisms. We recently focused on oligomer-based conductors that enable fine-tuning of their electronic properties via their length-elongation. The first examples were demonstrated by ethylenedioxythiophene dimer charge-transfer (CT) salts with counter anions (**2EDOT**•*A* in Figure 1, *A* = BF₄, ClO₄, PF₆).¹ The single crystals exhibited exclusively large molecular orbital overlapping along the stacking direction, reminiscent of a genuine Mott insulator state regarding their semiconducting behavior. Encouraged by the high potential of **2EDOT** as donor molecules in CT salts, we here demonstrated the effect of the encountered acceptors via the construction of CT complexes between **2EDOT** and tetracyanoquinodimethane analogs. We also explored the atom-substituted effects in donors using newly synthesized the oxygen-sulfur substituted analog, ethylenedithiothiophene dimer complexes **2EDTT**•*A*. The construction of a single-crystalline CT complex series allowed us to clarify the correlation between crystal structures and their electronic transport properties.

Neutral dimer **2EDTT** was synthesized via the copper-catalyzed homocoupling reaction of monomer units. The **2EDOT** or **2EDTT** donors were mixed with TCNQ analogs to yield single-crystalline CT complexes with similar one-dimensional structures in which donors and acceptors were alternatively π -stacked. The DFT-based band calculation of each crystal structure demonstrated strong molecular orbital interactions ($W \sim 0.8$ eV) along the stacking direction. The electrical conductivity depended on donors; **2EDTT**•*A* often showed superior conductivity than **2EDOT**•*A*. The bond length comparison in the crystal structures suggested small degrees of CT in **2EDTT**•*A* over those in **2EDOT**•*A*, which may improve conductivity. In the presentation, we will also discuss the unique atom-substituted effects in acceptor molecules in CT complexes.

1) R. Kameyama, T. Fujino, S. Dekura, M. Kawamura, T. Ozaki, H. Mori, *Chem. Eur. J.* **2021**, doi: 10.1002/chem.202005333.

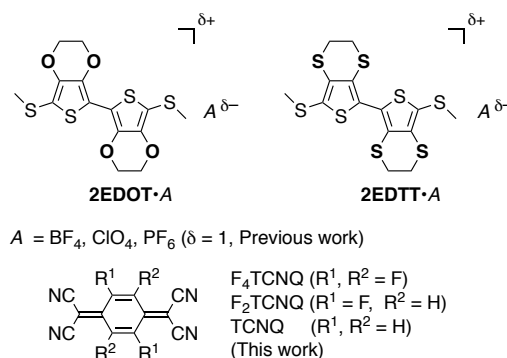


Figure 1. Structures of **2EDXT**•*A* (*X* = O, S)