Development of Novel Heterocyclic Compounds and Their Molecular Assemblies for Advanced Materials

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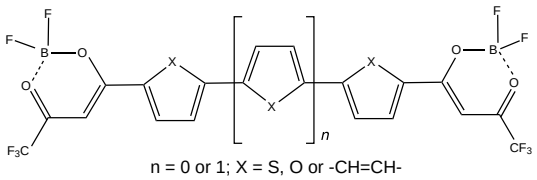
Heterocycles containing sulfur and/or nitrogen atoms are useful as components of functional organic materials since heteroatoms in their rings are helpful to stabilize ions or ion-radical species. In addition, intermolecular interactions caused by heteroatom contacts can be expected to form unique molecular assemblies. In this project, novel functional organic materials based on various heterocycles were synthesized and their physical and structural properties were investigated.

1. Synthesis and Properties of Terthiophene and Bithiophene Functionalized by BF_2 Chelation: A New Type of Electron Acceptor Based on Quadrupolar Structure[1)]

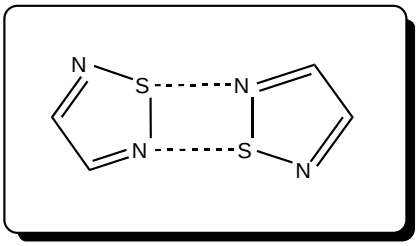
Terthiophene and bithiophene derivatives functionalized by BF_2 chelation were synthesized as a new type of electron acceptor, and their properties were compared to those of bifuran and biphenyl derivatives. These new compounds are characterized by quadrupolar structures due to resonance contributors generated by BF_2 chelation. The bithiophene derivative has a strong quadrupolar character compared with the bifuran and biphenyl derivatives because their hydrolytic analyses indicated that the bithiophene moiety has a larger on-site Coulomb repulsion than the others. The terthiophene derivative has a smaller on-site Coulomb repulsion than the bithiophene derivative due to the addition of a thiophene spacer. These BF_2 complexes exhibit long-wavelength absorptions and according to measurements of ionization potentials and absorption edges they have energetically low-lying HOMOs and LUMOs. The crystal structure of the bithiophene derivative is of the herringbone type, with short F···S and F···C contacts affording dense crystal packing. n-Type semiconducting behavior was observed in organic field-effect transistors based on these BF_2 complexes.



n = 0 or 1; X = S, O or -CH=CH-

2. Theoretical Study of Intermolecular S···N Interactions in a 1,2,5-Thiadiadole Dimer

Ab initio (HF, MP2) and DFT (B3LYP, PW91PW91) calculations with the 6-31++G(2d,2p) basis sets have been performed on a 1,2,5-thiadiazole dimer. The binding energy of the dimer by MP2 corrected BSSE and ZPE is 3.37 kcal/mol, which is comparable to those of noncovalent C–H···O and C–H···π interactions. The HF and DFT method extremely underestimated the binding energies as compared to MP2. This fact indicates that the dispersion interaction is significantly important for the intermolecular S···N interaction in the dimer. The optimized S···N distance (3.022 Å) by MP2 is in good agreement with crystallographic data.



Reference

1) K. Ono, A. Nakashima, Y. Tsuji, T. Kinoshita, M. Tomura, J. Nishida and Y. Yamashita, *Chem. –Eur. J.* **16**, 13539–13546 (2010).