Exploration of Hydrogen-Bonded Charge-Transfer Complexes

Charge-transfer (CT) complexes, molecular complexes between electron-donor and -acceptor molecules, have attracted much attention of organic chemists and materials scientists for more than 60 years, and realized various intriguing physical properties and phenomena such as electrical conduction (semiconductor, metal and superconductivity) and phase transitions (Peierls and neutral–ionic, etc). Hydrogen-bond (H-bond) interaction is a robust and directional intermolecular interaction and has been widely utilized as a powerful tool to control molecular orientation in the development of molecule-based functional materials including conducting CT complexes and salts. The authors of this account further proposed a new molecular system, cooperative proton–electron-transfer (PET) system, where the proton-transfer at H-bonding site cooperates with CT, and dynamic and multiple functions will be demonstrated by controlling the cooperativity. From these viewpoints, they have designed and synthesized various CT complexes with H-bond functionalities.

The this account reviews the authors’ recent studies on H-bonded CT complexes based on (1) tetrathiafulvalene (TTF) derivatives having nucleobase, aminobenzo and imidazole moieties, and (2) tetracyanoquinodimethane (TCNQ) radical anion salts with H-bond functionalized counter cations; nitrogen-atom incorporated phenalenyls and protonated oligo(imidazole) cations. In these CT complexes and salts, diverse supramolecular assemblies were formed by intermolecular H-bonds to control arrangements of TTF and TCNQ moieties. Furthermore, the donor/cation–acceptor H-bonds also modulated electronic structures of CT complexes and salts by the site-selective pair formation (control of component ratio) and the high polarity (enhancement of redox ability and control of charge-distribution in a conduction column). In the p-chloranil complex of an imidazole-functionalized TTF derivative, these effects of H-bonds played a key role in the realization of the first purely organic molecular metal based on CT complexes of H-bond functionalized TTF derivatives.

For details, see an article, “Cooperation of Hydrogen-Bond and Charge-Transfer Interactions in Molecular Complexes in the Solid State”, Bulletin of the Chemical Society of Japan, in press. DOI:10.1246/bcsj.20120241, by Y. Morita, T. Murata, K. Nakasuji (A05a). This is a free access article (https://www.jstage.jst.go.jp/article/bcsj/advpub/0/advpub_20120241/ article).