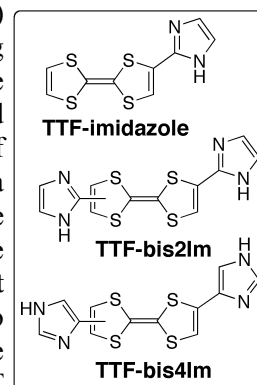


Synthesis, Crystal Structure, and Charge-Transfer Complexes of TTF Derivatives Having Two Imidazole Hydrogen-Bonding Units

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Regulation of molecular orientation and electronic state of charge-transfer (CT) complexes is the most essential issue to explore new materials and intriguing functions in the study of organic conductors. Recently, we have focused on the imidazole-ring system as a hydrogen-bonding (H-bonding) unit, and demonstrated its high potential to regulate molecular orientation in CT complexes of oligo(imidazole)s [1]. In addition to such structural viewpoint, our research on a TTF derivative having an imidazole-ring, TTF-imidazole, disclosed for the first time the ability of H-bond to produce conductive CT complexes by the selective formation of D-A-D H-bond pair and electrostatic perturbation [2]. In the present study, we have designed and synthesized new TTF derivatives having two imidazole-rings, TTF-bisimidazoles (TTF-bis2Im and TTF-bis4Im), which are the combination of oligo(imidazole)s and TTF-imidazole. We also investigated their CT



complexes and the crystal structure of TTF-bis2Im. TTF-bisIm's were synthesized by the Stille type cross-coupling reaction between poly(tributylstannyl)TTF and excess *N*-protected iodo-imidazoles followed by the deprotection reaction. TTF-bis2Im formed a two-dimensional sheet by N-H...N H-bonds, and stacked to form a uniform column (Fig. 1). The CT complex formation of TTF-bis2Im afforded 1:1 completely ionic CT complexes ($\sigma_{RT} = \sim 10^{-6} \text{ S cm}^{-1}$), and TTF-bis4Im yielded semiconductive partial CT complexes with TCNQ and *p*-chloranil ($\sigma_{RT} = 10^{-3} - 10^{-2} \text{ S cm}^{-1}$).

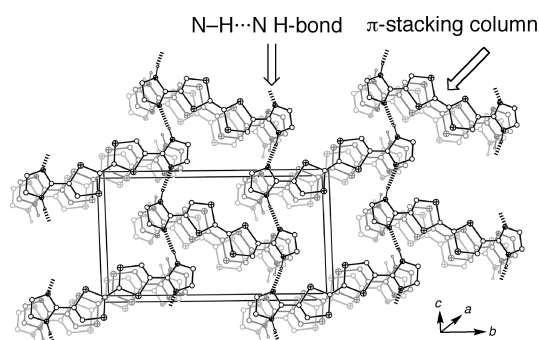


Fig. 1. Crystal structure of TTF-bis2Im.

- [1] Y. Morita *et al.*, *J. Org. Chem.* 70 (2005) 2739; T. Murata *et al.*, *Cryst. Growth Des.* 8 (2008) 3058.
[2] T. Murata *et al.*, *Angew. Chem. Int. Ed.* 43 (2004) 6343; T. Murata *et al.*, *J. Am. Chem. Soc.* 129 (2007) 10837.