

## 1) Synthesis of novel $\pi$ -extended oligo(imidazole)s and their hydrogen-bonded charge-transfer complexes

2,2'-Biimidazole (2,2'-H<sub>2</sub>Bim) is a redox active molecule having the similar molecular structure to TTF, and possesses the four-step redox processes coupled with proton-transfer (Figure 1). In addition, the hydrogen-bonds (H-bonds) of 2,2'-H<sub>2</sub>Bim in neutral, deprotonated and protonated state have been utilized in the construction of crystal engineering. These features of 2,2'-H<sub>2</sub>Bim have attracted attentions as a component of charge-transfer (CT) complexes (For example, see, Akutagawa, T; Saito, G.; Kusunoki, M; Sakaguchi, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2487-2511). In order to explore molecular assemblies exhibiting new functions, structures and properties based on the cooperation of CT interaction and H-bonds, we are studying the synthesis of novel H-bonded electron-donor molecules based on imidazole-ring system and the construction of their H-bonded CT complexes.

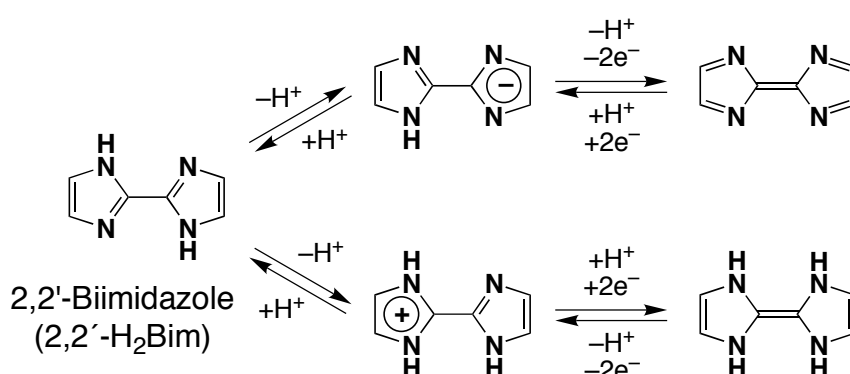


Figure 1. Redox process of 2,2'-Biimidazole coupled with proton-transfer

We have designed novel  $\pi$ -extended oligo(imidazole)s composed of imidazole-rings by direct linear ring assembly and heteroaromatic-ring bridging (Figure 2). Oligomerization across  $\pi$ -system affords the multiple redox ability, thus oligo(imidazole)s are expected to be promising candidates for the electron-donor molecules of CT complexes. Furthermore, oligo(imidazole)s possess diverse H-bonding directionalities depending on the protonated states and conformations, and are expected to construct well-defined multidimensional network structures. Introduction of H-bonds into CT complexes is recognized as an effective methodology to control molecular arrangement and to increase the dimensionality of intermolecular interactions, resulting in the exhibition of stable metallic behavior by preventing the Peierls transition and in control of electronic structures. Furthermore, the proton-donating and -accepting ability of imidazole-ring system can couple with the CT to realize the cooperative proton- and electron-transferring system.

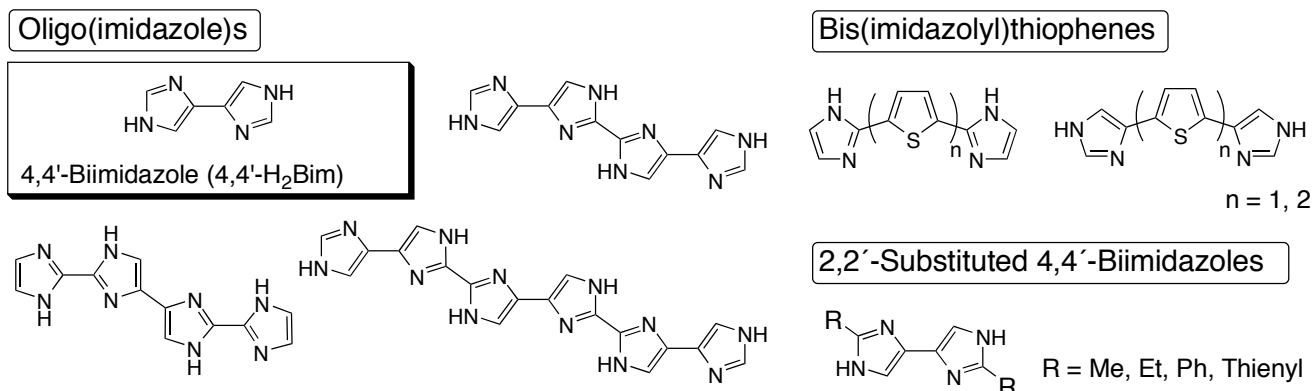


Figure 2.  $\pi$ -extended oligo(imidazole)s

The synthetic difficulties of imidazole-ring system due to the protection groups on the N–H group and the obstruction of metal-catalyzed reaction by coordination of N atoms limit the variation of reactions and prevent the synthesis of the oligomers of imidazole. Thus, oligo(imidazole)s composed of more than three imidazole-rings have been unknown, and few studies about physical properties of  $\pi$ -extended imidazoles have been reported. The synthesis of  $\pi$ -extended oligo(imidazole)s are interesting from the viewpoint of not only the cooperation between proton/electron-transfer, new molecular conductor and crystal engineering but also organic synthesis.

We have succeeded in the first synthesis of 4,4'-biimidazole (4,4'-H<sub>2</sub>Bim), an isoelectronic isomer of 2,2'-H<sub>2</sub>Bim, quarter- and sexiimidazoles [1,2]. We have succeeded in the construction of a variety of H-bonded networks in 4,4'-H<sub>2</sub>Bim system by taking the advantage of its diverse H-bonding styles depending on protonated states and conformations (Figure 3) [2,3]. Furthermore, we have disclosed that this diverse H-bonds

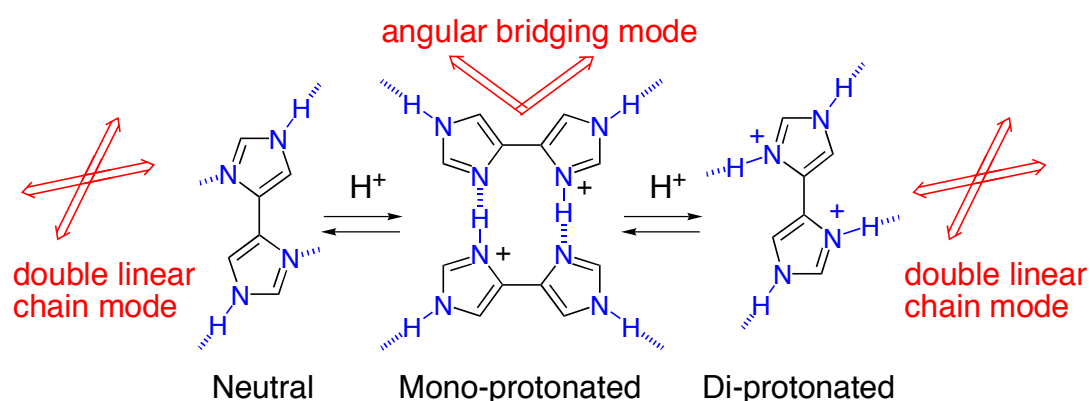


Figure 3. Diverse H-bond styles of 4,4'-H<sub>2</sub>Bim depending on the protonated state

control the molecular arrangement in the CT complexes to remarkably affect their electronic properties [3]. For example, in the TCNQ salts of 4,4'-H<sub>2</sub>Bim, the H-bonds of protonated 4,4'-H<sub>2</sub>Bim cations controlled the stacking patterns of TCNQ columns working as conduction paths, resulting in the 10<sup>3</sup> order of difference in the conductivities between TCNQ salts of mono- and di-protonated 4,4'-H<sub>2</sub>Bim cations. The angular-bridging mode of H-bonds of mono-protonated 4,4'-H<sub>3</sub>Bim<sup>+</sup> established the distorted TCNQ column, resulting in the low conductivity (10<sup>-4</sup> S cm<sup>-1</sup>) (Figure 4, left). On contrary, in the TCNQ salt of di-protonated 4,4'-H<sub>4</sub>Bim<sup>2+</sup> with double linear chain mode of H-bonds, three-dimensional H-bonding network established the TCNQ column only by ring-over-bond mode of stacking, resulting in the high conductivity (10<sup>-1</sup> S cm<sup>-1</sup>) (Figure 4, right).

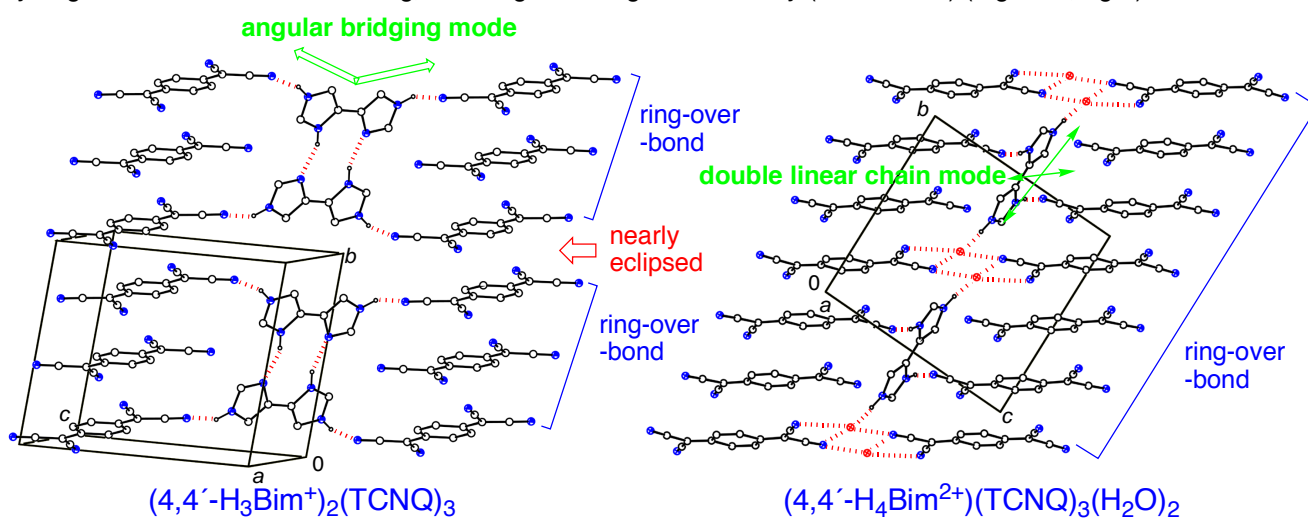


Figure 4. Crystal structures of TCNQ salts of mono-protonated (left) and di-protonated 4,4'-H<sub>2</sub>Bim (right)

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We are also studying the syntheses, H-bonded networks and CT complexes of 4,4'-H<sub>2</sub>Bim derivatives having electron-donating substituents [4] and bis(imidazolyl)thiophenes composed of imidazole- and thiophene-rings [5]. The introduction of substituents and thiophene-ring-bridging into oligo(imidazole)s increased the diversity of H-bonding directionalities, resulting in the construction of a variety of unique and well-defined assembled structures (Figure 5). Furthermore, one of the TCNQ complexes of bis(imidazolyl)thiophenes exhibited relatively high conductivity (10<sup>-2</sup> S cm<sup>-1</sup>) with semiconducting behavior [5].

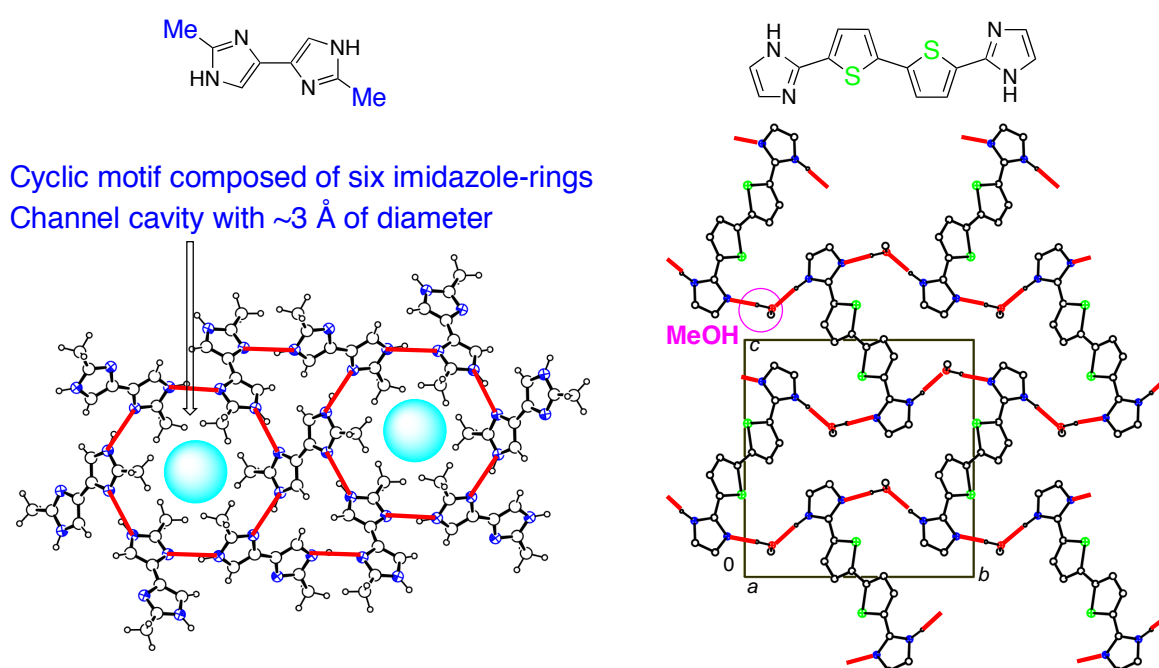


Figure 5. Crystal structures of 2,2'-dimethyl substituted 4,4'-H<sub>2</sub>Bim (left) and bis(imidazolyl)thiophene (right)

## References

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## 2) Crystal engineering on the assembled metal complexes of $\pi$ -extended oligo(imidazole)s

2,2'-H<sub>2</sub>Bim is a well-known bidentate ligand forming intermolecular H-bonds. Our research group have studied the assembled metal complexes constructing well-defined H-bonded networks using the monodeprotonated 2,2'-HBim anion (Ref: Tadokoro, M.; Nakasuji, K. *Coord. Chem. Rev.* **2000**, *198*, 205). 2,2'-H<sub>2</sub>Bim system forms the complementary or bifurcated mode of H-bonds, where two H-bonds are elongated to the same direction (Figure 6a). On the other hand, two H-bonds of metal complexes of 4,4'-H<sub>2</sub>Bim system are expected to be elongated to separated directions (angular bridging mode, Figure 6b) and to construct more diverse and higher dimensional H-bonded networks. Thus, oligomerization of imidazole-rings can increase the diversity of

H-bonding and coordination styles, and is attractive from the viewpoint of crystal engineering. Furthermore, proton-transfer process inherent in imidazole-ring system can control the electronic properties of metal atoms to bring about the dynamic properties. In order to explore the well-defined assembled structure based on the diverse H-bonds of oligo(imidazole)s and the dynamic properties coupled with proton-transfer, we are studying the construction of assembled metal complexes of  $\pi$ -extended oligo(imidazole)s as ligands.

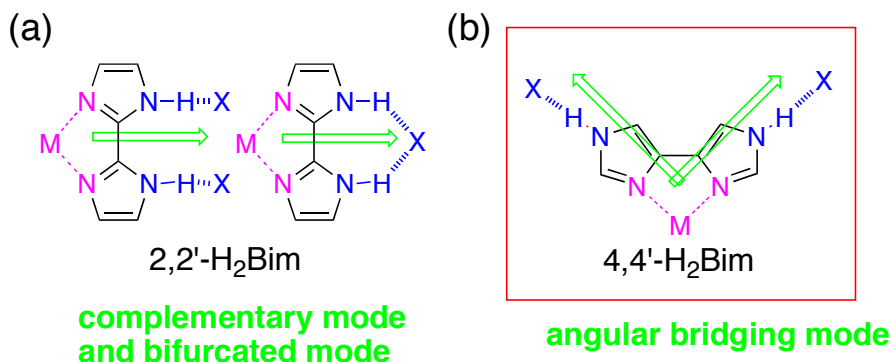


Figure 6. H-bond styles of 2,2'- (a) and 4,4'-H<sub>2</sub>Bim (b) in metal complexes

We have succeeded in the construction of a variety of H-bonded networks in the transition metal complexes of the neutral 4,4'-H<sub>2</sub>Bim and mono-deprotonated 4,4'-HBim<sup>-</sup> anion [6]. Their H-bonds with angular bridging mode established the tape-like one-dimensional structure and three-dimensional network across counter anions and solvent molecules, respectively (Figure 7). Further studies toward the construction of assembled metal complexes using quarter- and sexiimidazoles are in progress.

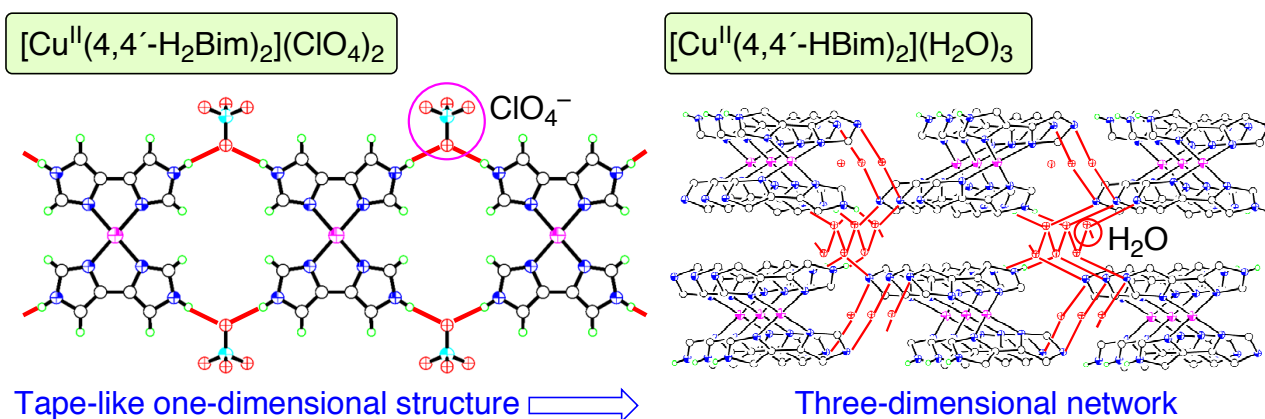


Figure 7. H-bonded networks of copper (II) complexes of neutral 4,4'-H<sub>2</sub>Bim (left) and mono-deprotonated anion 4,4'-HBim<sup>-</sup> (right)

#### References

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### 3) Macrocyclic $\pi$ -extended oligo(imidazole)s

The future target of the synthetic challenge of  $\pi$ -extended oligo(imidazole)s is macrocyclic compounds shown in Figure 8.  $\pi$ -Extended macrocyclic compounds are studied as an ideal model of infinite-chain polymers, and the extended  $\pi$ -electron around their cyclic skeletons attract is expected to exhibit intriguing electronic properties. Actually, porphyrin and phthalocyanine derivatives form complexes with a variety of transition metals, and

exhibit interesting conducting, magnetic and optical properties. Macrocyclic compounds composed of imidazole-rings, which have two-direction interaction sites, can form the H-bonds and coordination bonds directed to both inside and outside of cyclic skeletons. Thus, they are expected to bind metal ions and small molecules, and also to construct specific supramolecular structures. For example, macrocyclic octiimidazole will assemble by H-bonds and coordination bonds to built the two-dimensional sheet in the planar conformation and tubular structure in the belt conformation, respectively (Figure 8), and thus is attractive for the application into nano technology. There have been no examples of full-conjugated macrocyclic compounds constructing these supramolecular structures. Furthermore, the proton-transfer and the change of coordination styles depending on pressure, temperature and pH inherent in macrocyclic oligo(imidazole)s will cause the dynamic properties based on the binding/releasing of guest molecules and structural transformation.

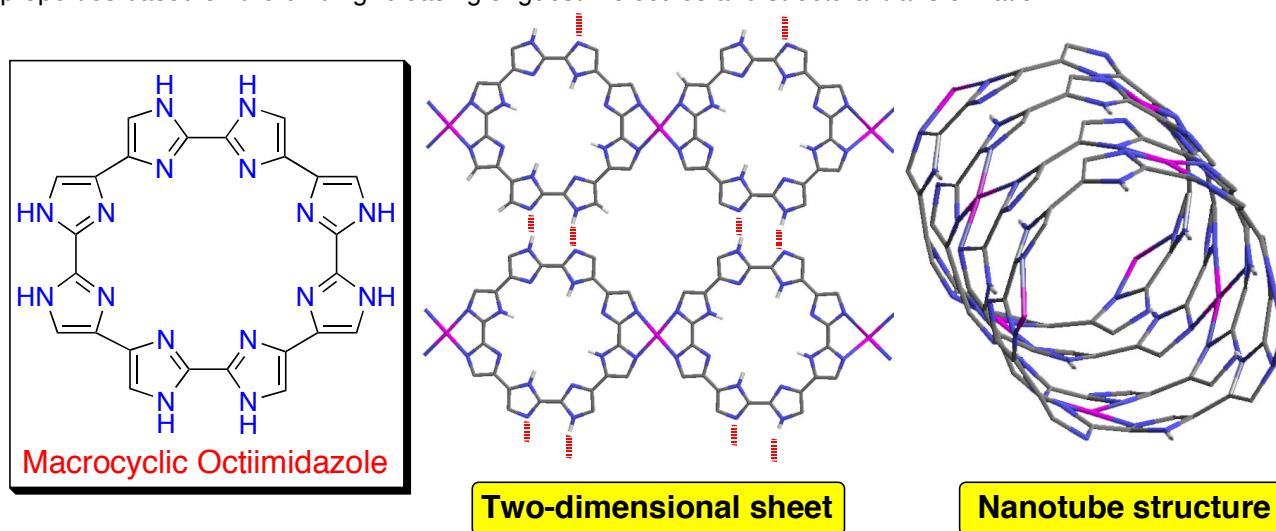


Figure 8. Molecular structure of macrocyclic octiimidazole (left) and possible supramolecular structures (center, right) by H-bond and coordination bond

#### 4) TTF-imidazoles for new molecular conductors with H-bonded structures and electronic modulation by H-bonds

We have designed the TTF-imidazoles, which are composed of imidazole-ring as H-bonding functionality and tetrathiafulvalene (TTF) derivatives widely studied in molecular conductors (Figure 9) [7,8]. The intermolecular H-bond is recognized as an effective tool to control the molecular packing and increase the dimensionality in CT complexes. Furthermore, the H-bonds between electron-donor and -acceptors can control the electronic state of each component. The coupling of electron-transfer on TTF moiety and proton-transfer on imidazole-ring may realize the cooperative proton-electron transferring system.

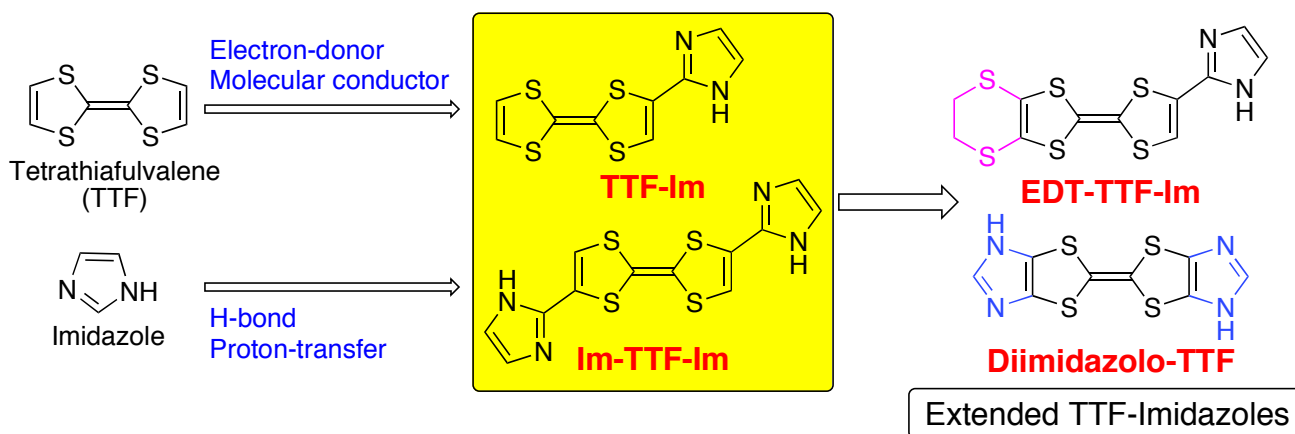


Figure 9. Strategy of molecular design for TTF-Imidazole

In the TTF-Im-*p*-chloranil complex, we have demonstrated the first purely organic metal based on CT complexes of H-bond functionalized TTF derivatives. In this complex, the H-bonds between donor and acceptor regulated the molecular packing to construct two-dimensional conduction layer and three-dimensional network. Furthermore, we have disclosed the electronic effect of H-bonds: the control of D-A ratio by forming D-A-D triad and the enhancement of the accepting-ability of acceptors. These effects resulted in the control of ionicity of electron-donor and -acceptor (Figure 10) [8]. The synthesis of extended TTF-imidazole derivatives, EDT-TTF-Im [9] and imidazole-fused TTF (Figure 10), is in progress.

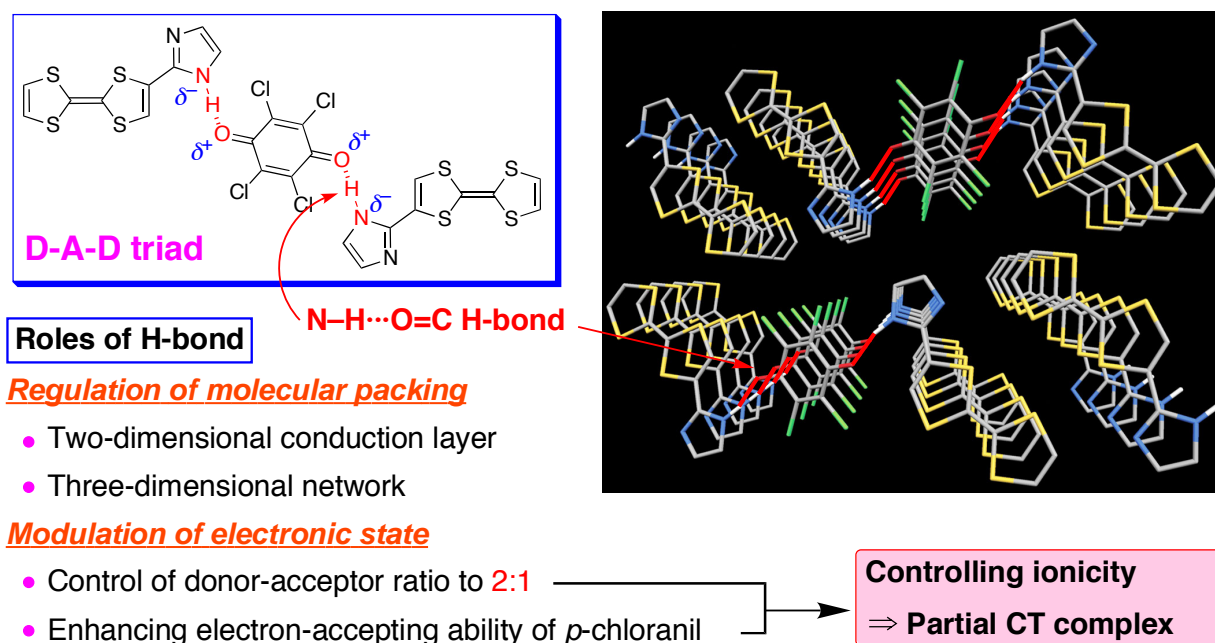


Figure 10. D-A-D triad and crystal structure of TTF-Im-*p*-chloranil complex

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