

Proton- Electron-Transferring system / Diazaphenalenenes

Phenalenyl possesses a highly delocalized π -conjugation and a nonbonding molecular orbital (NBMO), and its three redox species, cation, neutral radical and anion, possess high thermodynamic stability (Figure 1). In view of the recent growing studies for the construction of molecule-based organic materials such as organic magnets and organic conductors, these electronic features of phenalenyl systems have attracted much attention. Haddon and coworkers have demonstrated the phenalenyl-based molecular conductors in charge-transfer (CT) complexes sulfur-substituted phenalenyl derivatives and spiro-conjugated bisphenalenyl radicals as single-component organic conductors.

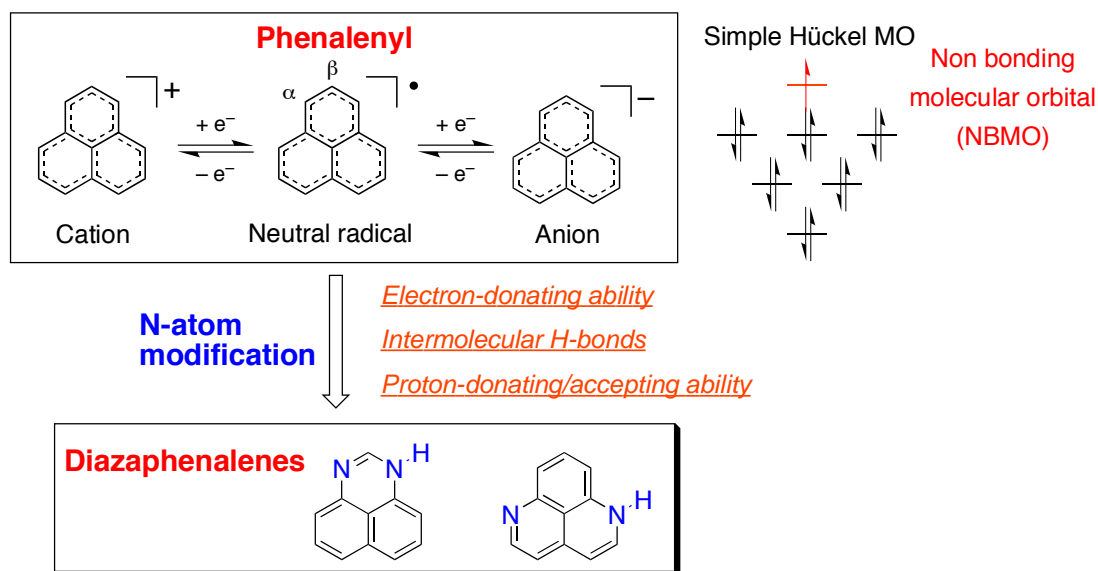


Figure 1. Three redox states of phenalenyl system and molecular design of diazaphenalenenes

Diazaphenalenenes (DAPs), where two nitrogen atoms are incorporated at the α -positions of phenalenyl skeleton, possess proton-donor (N–H) and acceptor (N) functionalities which show strong proton donating/accepting abilities. Furthermore, DAPs possess the isoelectronic structures with phenalenyl anion, are electron-rich and electronically active systems. These features indicate that DAP systems

- 1) can behave as electron-donor molecules in CT complexes
- 2) form strong intermolecular hydrogen-bonds (H-bonds) to construct assembled structures
- 3) are expected to realize the proton-electron-transferring system by the cooperation of proton-transfer at nitrogen atoms and electron transfer to acceptor molecules.

Here, we are studying the preparation, assembled structures and electronic properties of CT complexes of new H-bonded donors, 1,3- and 1,6-DAP derivatives (Figure 2).

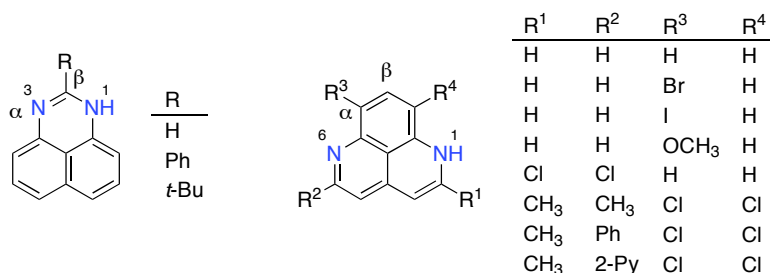


Figure 2. 1,3- and 1,6-diazaphenalenene derivatives in our study

We have succeeded in the preparation of CT complexes of 1,3- and 1,6-DAP derivatives with TCNQ. Some of these CT complexes exhibited relatively high conductivity ($10^{-2}\sim 10^{-1}$ S cm^{-1} at room temperature) with semiconductive behavior [1,2]. Furthermore, we have investigated the crystal structures of protonated salts of DAPs. In these salts, protonated DAPs formed strong H-bonds with counter anions to construct a variety of assembled structures (Figure 3) [1,3].

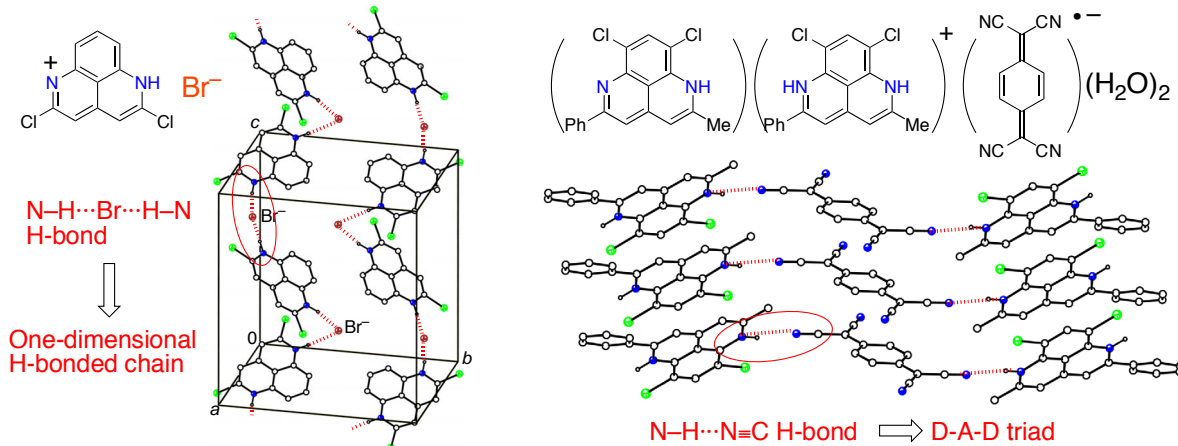


Figure 3. H-bonded structures of protonated salts of 1,6-diazaphenalene derivatives

References

- 1) Tamaki, K.; Morita, Y.; Toyoda, J.; Yamochi, H.; Saito, G.; Nakasuji, K. *Tetrahedron Lett.* **1996**, *38*, 4583.
- 2) Morita, Y.; Murata, T.; Tamaki, K.; Yamochi, H.; Saito, G.; Nakasuji, K. *Synth. Met.* **2003**, *135-136*, 657.
- 3) Murata, T.; Morita, Y.; Tamaki, K.; Nakasuji, K. *J. Low Temp. Phys.* in press.