Hydrogen-bonded charge-transfer salts of three-fold symmetric tris(alkylamino)phenalenylions with TCNQ radical anion

Phenalenyl is a highly symmetric ($D_{3h}$) odd-alternant $\pi$-electronic system exhibiting three thermodynamically stable redox species, anion, neutral radical and cation. The electronic structure of phenalenyl system is sensitive to chemical modification and external stimuli (temperature and solvent polarity, etc), and gave various dynamic and electronic functions. Furthermore, since the first proposal of the phenalenyl-based organic conductor by Haddon, electrically conducting materials were discovered in their charge-transfer (CT) complexes and zwitterionic bis(phenalenyl)boron complexes.

Hydrogen-bond (H-bond) interaction is a robust and directional intermolecular interaction and has been widely utilized as a powerful tool to control the molecular orientation in the development of molecule-based functional materials including conducting CT complexes and salts. The authors have recently investigated the nitrogen-atom incorporated phenalenyl derivatives and revealed that the introduction of intermolecular H-bond sites into the phenalenyl system afforded diverse assembled structures in the metal complexes and CT salts with TCNQ$^\cdot$.

Here the authors have newly designed and synthesized alkylamino-substituted phenalenyl derivatives, tris(alkylamino)phenalenylion (TAP), as new countercations of CT salts having three-fold symmetric intermolecular H-bond ability. The $\pi$-extension effect and strong electron-rich feature of the amino groups caused a significant negative potential shift of the redox processes in the electrochemical measurement. In the crystal structures of 1:1 fully ionic CT salts with TCNQ$^\cdot$, strong $\pi$-stacks of the TAP skeleton and intermolecular H-bonds between amino groups of TAP and CN groups of TCNQ$^\cdot$ constructed multi-dimensional network structures, claiming the structural regulation ability of this system (Fig. 1).