**π-Dimeric structures and magnetic properties of air-stable 6-Oxophenalenoxy neutral radicals**

The control of intermolecular exchange interactions between stable organic open-shell molecules is a crucial issue in the design and development of molecule-based magnetic materials. Molecular design approaches to the establishment of stronger ferromagnetic exchange interactions within molecular open-shell entities, such as molecular high spins, have been well tested from both theoretical and experimental sides. Recent trends in open-shell chemistry are towards the weakening of exchange coupling leading to electromagnetic control of molecular spins for spin qubits in quantum computing/quantum information technology. The control of intermolecular exchange couplings between organic open-shell entities in solids is still a challenging issue in chemistry and materials science.

The tri-tert-butylphenalenyl (TBPLY) radical exists as a π dimer in the crystal form with perfect overlapping of the singly occupied molecular orbitals (SOMOs) causing strong antiferromagnetic exchange interactions (Figure 1). 2,5-Di-tert-butyl-6-oxophenalenoxy (6OPO) is a phenalenyl-based air-stable neutral π radical with extensive spin delocalization and is a counter analogue of phenalenyl in terms of the topological symmetry of the spin density distribution (Figure 1). X-ray crystal structure analyses showed that 1 and 2 (X = I, Br) also form π dimers in the crystalline state (Figure 1). The π-dimeric structure of 1 is seemingly similar to that of TBPLY even though its SOMO-SOMO overlap is small compared with that of TBPLY. The 8-(p-XC₆H₄) derivatives 2 form slipped stacking π dimers in which the SOMO-SOMO overlaps are greater than in 1, but still smaller than in TBPLY. The solid-state electronic spectra of 1 and 2 show much weaker intradimer charge-transfer bands, and SQUID measurements for 2 (X = Br) show a weak antiferromagnetic exchange interaction in the π dimer. These results demonstrate that the control of the spin distribution patterns of the phenalenyl skeleton switches the mode of exchange interaction within the phenalenyl-based π dimer.

![Figure 1. Chemical structures, spin density distributions, and π-dimeric structures of TBPLY, 1, and 2 (X = Br).](image)