Coexistence of Conducting and Magnetic Electrons Based on Molecular π-Electrons in a Supramolecular Conductor (Me-3,5-DIP)[Ni(dmit)2]

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Supporting Information

Synthesis and Electrochemical Crystallization

All reagents and solvents were used without further purification.

3,5-diiodopyridine

The mixture of 3,5-dibromopyridine (5.0 g, 21.1 mmol), KI (114.7 g, 691 mmol) and CuI (10.5 g, 55.1 mmol) was placed in a three-necked flask (1 L). DMF (450 mL) was added, and the flask was heated at 180˚C under Ar. After 1 week, the flask was allowed to cool to room temperature and the reacted solution was poured onto ice-water. The precipitate was collected on a G4 glass filter by filtration and dissolved in CH₂Cl₂/pyridine (5:1) solution. Saturated Na-EDTA solution was added to remove excess Cu compound from the organic layer, and the mixture was stirred overnight. The organic layer was separated and dried over MgSO₄. After filtration, the residue was purified with column chromatography on silica gel with CH₂Cl₂. The same procedure was repeated three times until two bromine atoms were completely replaced by iodine atoms. Final purification yielded 3,5-diiodopyridine (5.42g, 77.6%) as white powder. MS (EI): 331.

(Me-3,5-DIP)BF₄

The mixture of 3,5-diiodopyridine (2.20 g, 14.9 mmol) and Me₃OBF₄ (2.15 g, 6.20 mmol) was placed in a three-necked flask (100 mL). Toluene (100 mL) was added and the flask was heated at 100˚C under Ar. After 7 hours, EtOH (20 mL) was added and filtered thorough G4 glass filter. The precipitate was washed with benzene and dissolved in MeCN. After removal of MeCN under reduced pressure, the residue was recrystallized from EtOH/CH₃CN/ n-hexsan to yield (Me-3,5-DIP)BF₄ (0.92 g, 34.3%) as colorless crystals. MS (ESI⁺): 346.

(Me-3,5-DIP)[Ni(dmit)2]

Preparation of (nBu₄N)[Ni(dmit)₂]¹ and galvanostatic electrolysis with current switching² were performed according to the literature method. Concrete procedure and condition of the crystallization are described in the main text.

Overlapping Mode in Layer II

In Layer II, Ni(dmit)$_2$ anions organize themselves into a non-columnar structure that includes two overlapping modes (Mode I: A–B and Mode II: A–D'). This is quite similar to the packing motif of $\alpha$-(Et$_2$Me$_2$N)[Ni(dmit)$_2$]$_2$ that includes the ‘spanning-overlapping mode’. However, Mode II is slightly different: the longitudinal axis of the overlapping molecules are parallel to each other in $\alpha$-(Et$_2$Me$_2$N)[Ni(dmit)$_2$]$_2$, while in the present system, Ni(dmit)$_2$ anions stack at an angle to each other.

Figure 1S. Overlapping modes of Ni(dmit)$_2$ anions in Layer II.

Band Calculation

Overlap integrals between LUMOs of adjacent Ni(dmit)2 anions were calculated with the extended-Hückel method and semiempirical parameters for Slater-type atomic orbitals. The band structure and Fermi surface were obtained by tight-binding calculations. The transfer integrals (t) can be approximated as $t \approx \varepsilon$, where $\varepsilon$ is a constant corresponding to the order of the energy level of the LUMO ($\approx -10$ eV). These calculations are based on the assumption that every Ni(dmit)$_2$ molecule has the same charge, which is supported by bond lengths analysis and the Raman spectra. HOMO-LUMO band inversion does not occur in every layer, when the HOMO-LUMO energy difference is 0.6-0.8 eV.

![Figure 2S. Calculated band structure for Layer I. $\mu$ denotes the chemical potential.](image)

![Figure 3S. Calculated Fermi surface ($a_P = (a + b)/2$, $b_P = b$, $c_P = c$) (left) and electronic band structure (right) for Layer II. $E_F$ denotes the Fermi energy.](image)