

## Syntheses and characterization of charge-transfer complexes based on naphthalenediimide radical

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**[Abstract]** I report synthesis and physical properties of an organic charge transfer (CT) complex  $(\text{NDIpyMe})_2\text{SiF}_6 \cdot 8\text{H}_2\text{O}$  based on Naphthalenediimides (NDI). NDI is neutral, planar, chemically robust while simultaneously electron deficient and redox active. NDI is famous molecule in supramolecular chemistry but not in conductive salt. This complex shows conductivity  $0.5 \text{ Scm}^{-1}$  that is highest among other compounds prepared in our laboratory. Moreover, it shows strong  $\pi - \pi$  stacking, distance is 3.3 Å. It's thermal stability up to 250 °C. This compound shows semiconducting behavior with unusual hysteresis. This complex is very stable in air.

**[Introduction]** A CT salt or electron-donor-acceptor complex may consists of two or more molecules or different parts of one large molecule in which a fraction of electric charge is transferred between molecular entities. The attraction in CT salt is from mainly van der waals and dipole-dipole interaction that's why much weaker than covalent forces<sup>[1]</sup>. Organic conductors have been intensively studied during the past 60 years by the scientists from multidisciplinary field, including organic and inorganic chemists, physicists, theoreticians and engineers on account of their potential applications in “unimolecular electronic devices”, “molecular electronics”, “ nanostructured materials”, and “intelligent materials”<sup>[2]</sup>. Molecule-based multifunctional materials are promising for future science thanks to the molecular intrinsic characters: electrical, magnetic and optical properties. Generally crystallinity of CT salts decreases after losing lattice solvents. In addition, precise doping is very difficult. On the other hand, Metal organic framework / porous coordination polymer have robust framework, their intrinsic insulating characteristics of organic compounds and redox inactive ligands give low conductivity. To overcome those problems, in our laboratory, we have studied porous molecular conductor (PMC) that can show high conductivity, precise doping and switching of physical property by adsorption or desorption of molecules. Here in PMCs, naphthalenediimide (NDI) has been used as an acceptor. However, relationship between structure and oxidation state of NDI is still unclear, because it is difficult to determine the oxidation state of PMCs due to the disorder of solvent and counteranion in the pores. Besides, most PMCs are gradually oxidized by oxygen in air. Owing to overcome these problems, i choose air- stable (with lower SOMO level) NDI-based CT salts.

**[Methods]** 403.6 mg (0.6 mmol) of  $\text{NDI4pyMe}(\text{CH}_3\text{SO}_4)_2$  was dissolved in 5 mL of water, then 4.06 g (22.6 mmol) of  $(\text{NH}_4)_2\text{SiF}_6$  was added into the solution. A 20  $\mu\text{A}$  constant electric current was passed during the electrolysis in a silent environment without disturbing. Few hours later, black needle-like crystals were obtained. In the synthetic process, a smaller current down to 5  $\mu\text{A}$  or a larger current up to 100  $\mu\text{A}$  is possible to get crystals. I got smaller crystal when I applied lower current . The crystals are stable in both solution and at least two months in air after removing from the electrode. The single-crystal X-ray diffraction analysis and powder X-ray diffraction analysis were performed to confirm the structures of  $(\text{NDIpyMe})_2\text{SiF}_6 \cdot 8\text{H}_2\text{O}$ . Thermogravimetry (TG) analysis was done to analyze the stabilities and the existence of lattice solvent molecules of  $(\text{NDIpyMe})_2\text{SiF}_6 \cdot 8\text{H}_2\text{O}$ . ESR measurements

were carried out to confirm the existence of radical anions in CT salt. And the conductivity was determined by electrical resistivity measurement.

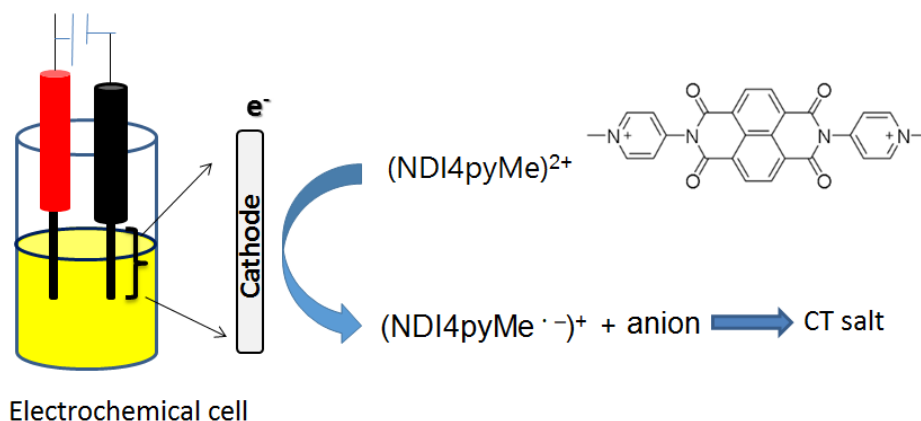


Fig. 1 electrochemical generation of  $(\text{NDIpyMe})_2\text{SiF}_6 \cdot 8\text{H}_2\text{O}$

**[Results and Discussion]** The  $(\text{NDIpyMe})_2\text{SiF}_6 \cdot 8\text{H}_2\text{O}$  crystallized in orthorhombic crystal system and space group Cccm (fig. 2). pyridine moieties were perpendicular to the central core of NDI. The oxidation state of NDI in this complex is -1. This complex shows strong  $\pi - \pi$  stacking distance that is 3.3 Å in *c* axis. Absorption spectrum proves NDI radical and CT band [3]. The most promising property of this complex is its conductivity. It shows conductivity  $0.5 \text{ S cm}^{-1}$  that is highest among other compounds prepared in our laboratory (fig. 3).

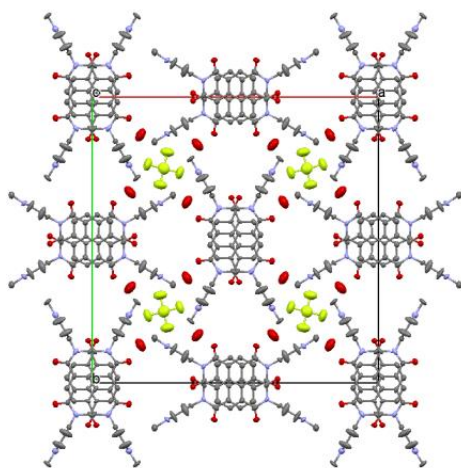


Fig. 2 Crystal structure of  $(\text{NDIpyMe})_2\text{SiF}_6 \cdot 8\text{H}_2\text{O}$

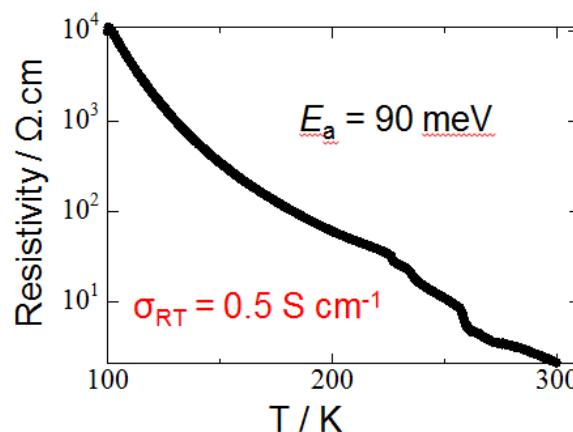


Fig. 3 Resistivity vs T plot of  $(\text{NDIpyMe})_2\text{SiF}_6 \cdot 8\text{H}_2\text{O}$

### [References]

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