**Temperature-Dependent Stepwise Charge-Transfers in a One-Dimensional Chain of a Paddlewheel [$Ru_2^{II,II}$] Complex and DM-DCNQI Inducing Insulator (I)-Metal (M)/M-I Transitions with Subsequent Ferrimagnetic Spin Ordering**

Hitoshi Miyasaka, Natsuko Motokawa, Tamiko Chiyo, Masahiro Yamashita
*Department of Chemistry, Graduate School of Science, Tohoku University, Japan.*
*Email: miyasaka@agnus.chem.tohoku.ac.jp*

Charge-transfer molecular assemblies comprised of electron-donors (D) and –acceptors (A) are one of the candidates for magnetic-conducting synergic materials because of the expectation of interaction between transport electrons caused by the charge-transfer and local spins on D and/or A. While the D:A = 2:1 (or 1:2) system is possible to create a mixed-valence system with one-electron transfer [1,2], the D:A = 1:1 system is only producible either neutral (*N*) or ionic state (*I*) in the limited case. However, its partial charge-transfer systems like $D^{\delta+}A^{\delta-}$ and/or systems that occur any structural phase transition dependent on temperature are rather favorable cases among them. Only a few cases of such a system have been known such as TTF-CA (CA = chloranil) [3], but there is no example associated both with magnetic order and conductivity in the DA system. We designed one-dimensional chains composed of paddlewheel diruthenium(II, II) complexes [$Ru_2^{II,II}$] as D and *N*,*N'*-dicyanoquinonediimine (DCNQI) as A, and successfully obtained a structurally-characterized [$Ru_2$]DCNQI system, which experiences stepwise charge-transfers involving structural phase transitions (at $T_1$ and $T_2$) and subsequent ferrimagnetic order of $S = 3/2$ on [$Ru_2^{II,III}$] and $S = 1/2$ on $DCNQI^{\bullet-}$ at low temperatures. At around room temperature, this compound is assigned to the quasi-*N* state. Upon decreasing the temperature, it immediately occurs a partial charge-transfer of $\delta < 0.5$ at which involves an Insulator-Metal transition. Then, at $T_1$, at which the degree of charge-transfer is $\delta \approx 0.5$, the conductivity occurs an M-I transition. At $T_2$, the charge is varied from $\delta \approx 0.5$ to ca. 1 to induce a magnetic order of $S = 3/2$-$1/2$ at temperatures below $T_2$.

[1] H. Miyasaka *et al.*, *Angew. Chem. Int. Ed.* 39 (2000) 3831.
[2] H. Miyasaka *et al.*, *J. Am. Chem. Soc.* 128 (2006) 11358.
[3] a) J. B. Torrance *et al.*, *Phys. Rev. Lett.* 47 (1981) 1747. b) H. Okamoto *et al.*, *Synth. Met.* 27 (1988) B189. c) T. Mitani *et al.*, *Phys. Rev. Lett.* 53 (1984) 842. d) T. Mitani *et al.*, *Phys. Rev. B* 35 (1987) 427.