Temperature-Dependent Stepwise Charge-Transfers in a One-Dimensional Chain of a Paddlewheel $[\text{Ru}_2^{\text{II,II}}]$ Complex and DM-DCNQI Inducing Insulator (I)-Metal (M)/M-I Transitions with Subsequent Ferrimagnetic Spin Ordering

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Charge-transfer molecular assemblies comprised of electron-donors (D) and -acceptors (A) are one of the candidates for magnetic-conducting synergetic 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 $[\text{Ru}_2^{\text{II,II}}]$ as D and $N,N'$-dicyanoquinonediimine (DCNQI) as A, and successfully obtained a structurally-characterized $[\text{Ru}_2^{\text{II,II}}]$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 $[\text{Ru}_2^{\text{II,II}}]$ and $S = 1/2$ on DCNQI$^-$ 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 $S = 3/2$ at temperatures below $T_2$.