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Determination of the π-Charge Distribution of the DMe-DCNQI Molecule in (DMe-DCNQI)$_2$M, M=Li, Ag, and Cu

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Solid state high-resolution NMR of ^1H and ^{13}C along with ^{15}N is analyzed to investigate the electronic states of the charge transfer salts (DMe-DCNQI)$_2$M, (M=Li, Ag, and Cu). We determined the spin/charge distribution in a DMe-DCNQI molecule of the Li-salt from the Knight shifts at each atom on the molecule. It is found that the obtained charge distribution is similar to the theoretical prediction. The charge density on the DCNQI molecules of the Ag-salt is found to be smaller by 20% *than the Li-salt, which could be an origin of differences from the Li-salt. This result is consistent with the first principle calculations* (*Miyazaki and Terakura, Phys. Rev. B* **54**, 10452, 1996).

The (2,5-R$_1$,R$_2$-DCNQI)$_2$M, (R$_1$, R$_2$ =Me, I, M=Li, Ag, and Cu) system has been intensively studied as a platform of strongly correlated electron physics. The Cu-salt provides three–dimensional Fermi-surface via strong $\pi - d$ hybridization, and extremely sensitive both to physical and chemical pressures that cause Metal–Insulator–Metal reentrant transitions.[1] The simplest system with Li-ions is known to be a quarter-filled one-dimensional π-band with $4k_F$-CDW states at room temperature (rt), followed by the spin-Peierls transition around 60 K on the basis of the dc conductivity[2] and the $4k_F$ superstructure.[3] Recently, it has been reported that the charge transport is governed both by the sliding motion and the intercolumn hopping of thermally excited hole and spin solitons in the $4k_F$-CDW gap with the expected fractional charges of $\pm e/2$.[4–6] Ag-salt is

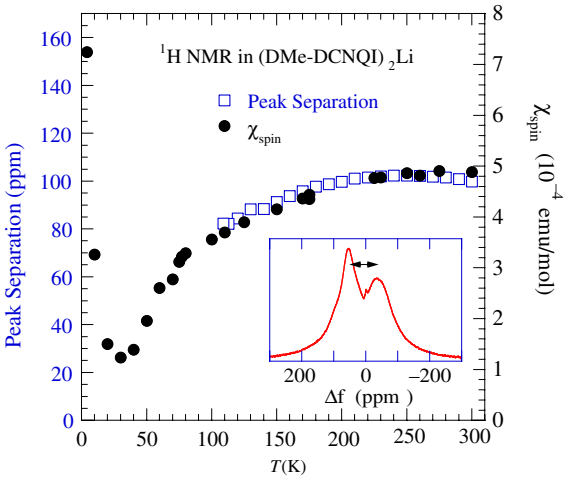

Fig. 1. The temperature dependence of the spin susceptibility measured by EPR-NMR technique and the peak separation of ^{1}H NMR splitting in Li-salt.

known as the other isostructural, quarter-filled π-band system with similar physical properties to the Li-salt, but several differences are also found. For example, the intercolumn hopping rate of the electrons in the Ag-salt is remarkably enhanced than that in the Li-salt.[6]

In this report, we studied the electron charge distribution of DMeDCNQI molecule as one of the most basic, important physical properties of the charge transfer organic conductors. We utilized the solid state high-resolution NMR to measure the Knight shift caused by the magnetization of the electron spins on the molecule. Figure 1 shows the proton NMR splitting of the broad line spectrum of the Li-salt, which is compared with the spin susceptibility measured by ESR–NMR technique.[7] A good qualitative agreement between them is a clear indication that this spilitting originated from the local field of the relevant local electron spin density. Figure 2 demonstrates Cross Polarization/Magic Angle Spinning (CP/MAS) ^{1}H NMR spectra with the d2- and the DMe-deuterated d6-Li salts to assign the spectrum to each proton site. The similar spectra of the neutral DCNQI crystals give the chemical shift of ^{1}H NMR, which corresponds to the zero Knight shift. The obtained Knight shift is related to the local spin susceptibility of the i-site as,

$$K^i = H^i_{\mathrm{hf}} \frac{\chi^i_\pi}{\mu_{\mathrm{B}}}, \tag{1}$$

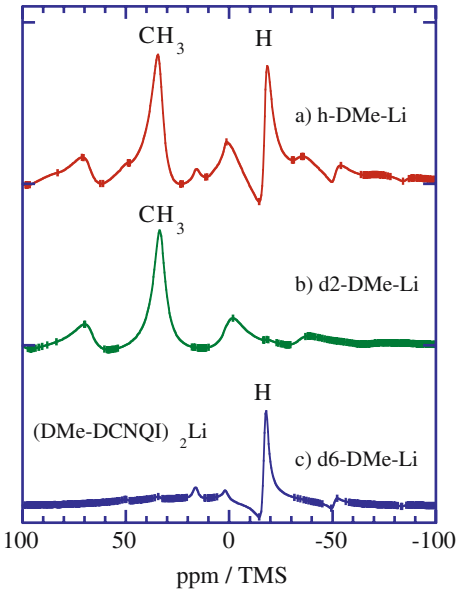

Fig. 2. MAS ^{1}H NMR spectra in Li-salt together with the two partially deuterated salts.

where H^i_{hf} is the hyperfine coupling constant per one μ_B of electron magnetization, and χ^i_π is the local π-electron spin susceptibility on the relevant carbon atom. The hyperfine coupling constant for each proton site have been well established by the analysis of EPR splittings due to the coupling with the relevant proton nucleus; $-8.2\,\mathrm{kOe}/\mu\mathrm{B}$ for CH and $+8.3\,\mathrm{kOe}/\mu\mathrm{B}$ for CH_3.[8] Figure 3 demonstrates the obtained charge distribution on each carbon or nitrogen site. The carbon sites attached with the hydrogen and the methyl group are analyzed with the Knight shift of the protons. The π-charge density at the carbon site of CN is assumed to be negligibly smaller than the other carbon sites, on the basis of the first principles calculations.[9,10] The reported anisotropic Knight shift data are used for the two nitrogen sites.[11] The density at the last carbon site, N–C<, is determined as the surplus of all the others.

In conclusion, the charge distribution of DMeDCNQI molecule in the Li-salt is successfully determined experimentally. The obtained charge distribution is consistent with the first principles calculations by Miyazaki and Terakura.[9,10] The detailed discussion on the other salts will appear elsewhere.

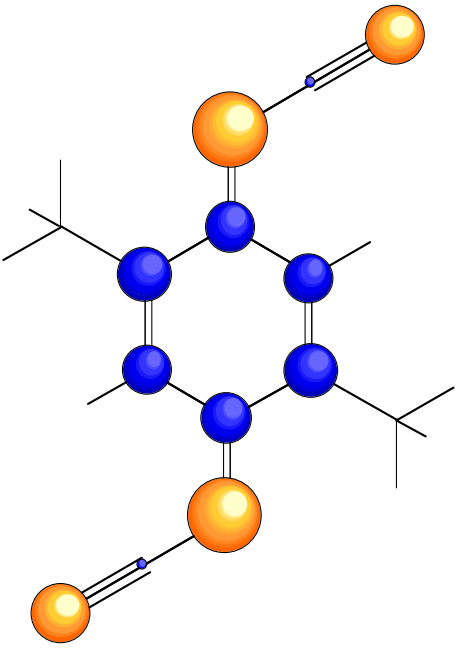

Fig. 3. The obtained charge distribution of the Li-salt. The area represents the relative charge density at each carbon or nitrogen site.

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