Flexible Cyclohexane Diammonium Cations in $[Ni(dmit)_2]^-$ Salts

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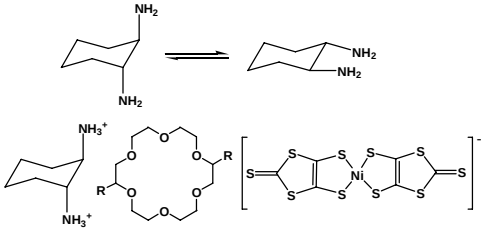
Various supramolecular magnetic compounds based on $[Ni(dmit)_2]^-$ (dmit = 2-thioxo-1,3-dithiole-4,5-dithiolate) have been studied and reported, since the $[Ni(dmit)_2]^-$ has an open-shell electronic structure with S =1/2 spin. The system can easily assemble with cationic supramolecules to construct interesting magnetic (antiferromagnetic and ferromagnetic coupling), dielectric, and potential ferroelectric material [1]. Herein, we report the novel supramolecular compounds based on $[Ni(dmit)_2]^-$ and cyclohexane diammoniums (Scheme 1), which were successfully synthesized through the standard diffusion methods in high yield. For these compounds, the conformation change of flexible cyclohexane diammonium is one of the possible ways to realize the novel dielectric $[Ni(dmit)_2]$ salts. The cyclohexane ring adopts a chair conformation in the crystal (Figure 1). Two ammoniums moieties exist in the axial position interacting with the cavity of two [18]crown-6. The temperature dependent anisotropic dielectric constants were dominated by the anisotropy of the π-electron on the $[Ni(dmit)_2]^-$ anion. The permittivity (~250) is almost frequency independence along the a- and b-axis, while that along the c-axis shows the frequency dependence behavior above 200 K. The motional freedom of flexible diammonium will related with these dielectric behavior.



Scheme 1. Orientation change in 1, 2-*trans*-cyclohexanediamine and its corresponding $[Ni(dmit)_2]^-$ salt.

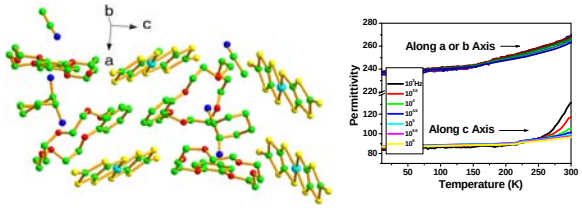


Figure 1. Crystal structure and plots of dielectric constants vs. T show frequency dependence along the c-axis, corresponding to the direction of cyclohexane rings

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[1] Akutagawa, T.; Nakamura, T. *Dalton Trans.*, **2008**, 6335.