# Supporting Information

# Ferromagnetic Coupling of $[Ni(dmit)_2]^-$ Anions in (*m*-Fluoroanilinium)(dicyclohexano[18]crown-6)$[Ni(dmit)_2]$

*Tomoyuki Akutagawa,*[*, †, ‡] *Daisuke Sato,*[‡] *Qiong Ye,*[‡] *Shin-ichiro Noro,*[†, ‡] *and Takayoshi Nakamura*[*, †, ‡]

Full list of all authors in Ref. 10
Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.;. Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *GAUSSIAN 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

**Preparation of salt 1.** The crystals of salt **1** was grown via slow diffusion of ($n$-$Bu_4N$)$[Ni(dmit)_2]$ and (*m*-fluoroanilinium$^+$)($BF_4^-$) - dicyclohexano[18]crown-6 in *H*-shaped cell charged with $CH_3CN$ (ca. 50 mL). ($n$-$Bu_4N^+$)$[Ni(dmit)_2]$ (30 mg), (m-fluoroanilinium$^+$)($BF_4^-$) (~60 mg), and dicyclohexano[18]crown-6 (100 mg) were introduced into *H*-shaped cell (50 mL $CH_3CN$). The plate-shape single crystals were obtained by slow diffusion. The stoichiometry of crystal **1** was determined by X-ray structural analysis and the elemental analysis. Elemental analysis. Calcd. C: 41.06, H: 4.63, N: 1.50. Found. C: 40.95, H: 4.67, N: 1.42.

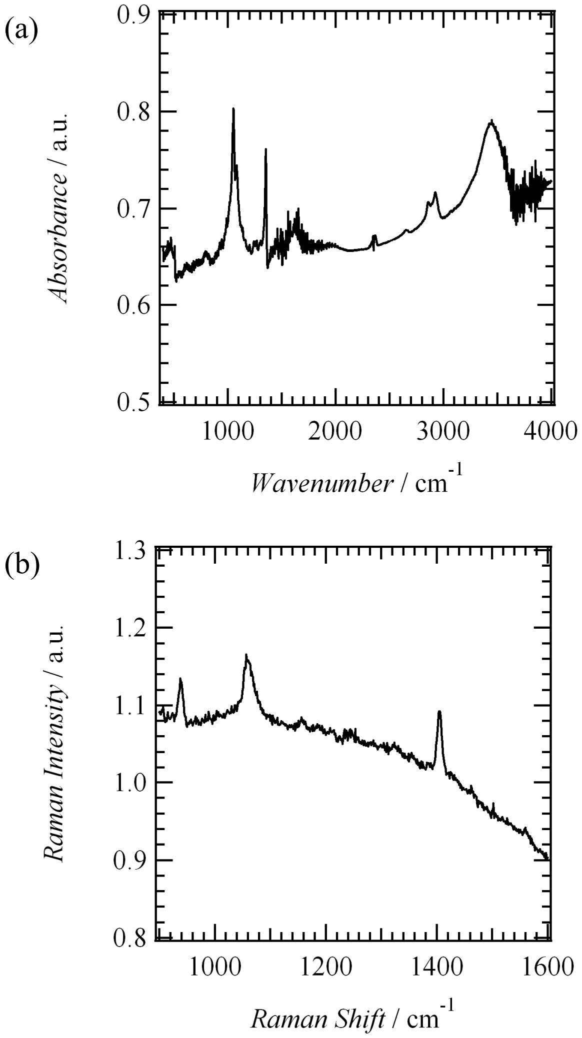

**Fig. S1**. Vibration spectra of salt **1**. a) IR and b) Raman spectra.

**Table S1**. Crystal data, data collection, and reduction parameter of salt **1** at 300 and 100 K.

| | **1** ($T$ = 300 K) | **1** ($T$ = 100 K) |
|---|---|---|
| Chemical formula | $C_{32}H_{43}N_1O_6FS_{10}Ni$ | $C_{32}H_{43}N_1O_6FS_{10}Ni$ |
| Formula weight | 935.99 | 935.99 |
| Space group | $P$-1 (#2) | $P$-1 (#2) |
| $a$, Å | 12.4557(10) | 12.3990(6) |
| $b$, Å | 12.7411(9) | 12.5367(5) |
| $c$, Å | 14.2746(10) | 14.1216(6) |
| $\alpha$, deg | 94.509(2) | 95.4297(12) |
| $\beta$, deg | 104.813(2) | 104.7569(14) |
| $\gamma$, deg | 105.509(2) | 104.5606(13) |
| $V$, Å$^3$ | 2083.9(3) | 2024.78(14) |
| $Z$ | 2 | 2 |
| $D_{calc}$, g·cm$^{-1}$ | 1.492 | 1.535 |
| $\mu$, cm$^{-1}$ | 10.124 | 10.420 |
| *Reflections measured* | 20345 | 19625 |
| *Independent reflections* | 9365 | 9072 |
| *Reflections used* | 5496 | 6969 |
| $R1$ [a)] | 0.0414 | 0.0340 |
| $wR2$ ($F^2$) [a)] | 0.0611 | 0.0510 |
| GOF | 1.114 | 1.160 |

[a] $R = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$ and $R_w = (\Sigma\omega|F_o| - |F_c|)^2 / \Sigma\omega F_o^2)^{1/2}$.

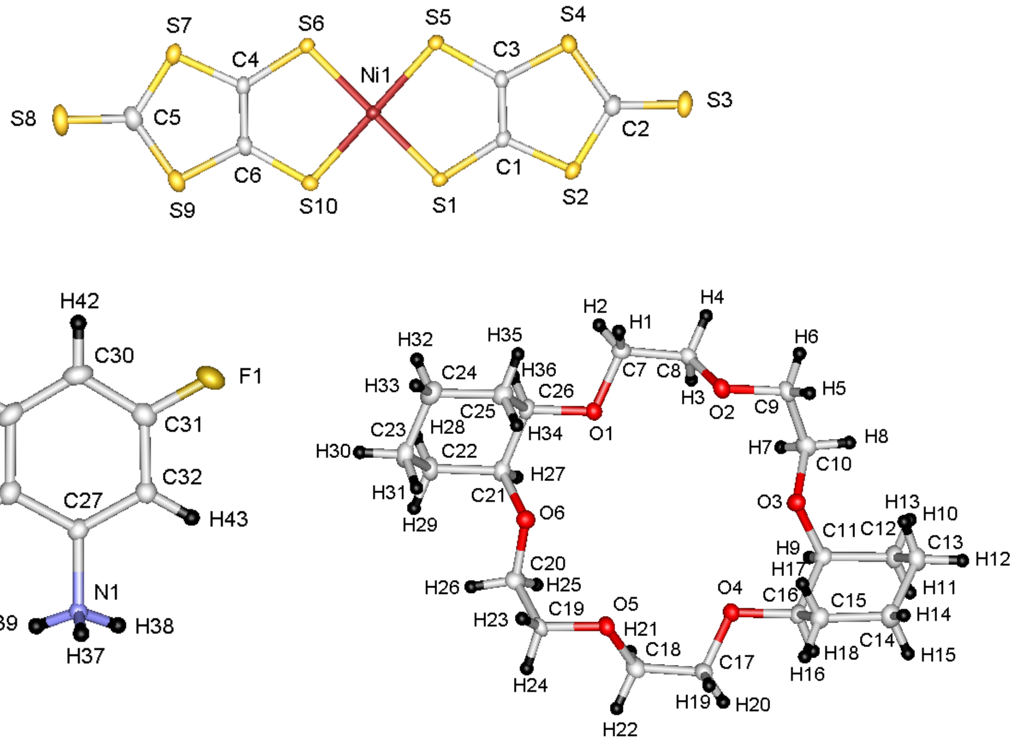

**Fig. S2**. Atomic numbering scheme of independent molecules in salt **1**.

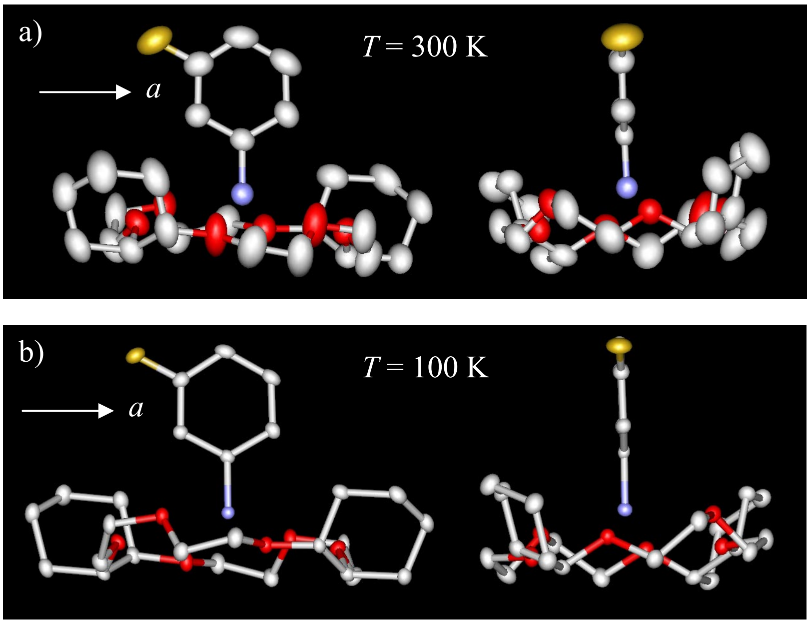

**Fig. S3**. Supramolecular cation structure of (*m*-Ani$^+$)(DCH[18]crown-6) at 300 and 100 K.

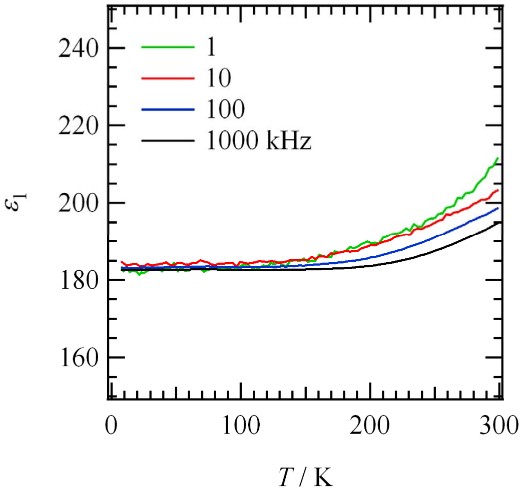

**Fig. S4.** Temperature- and frequency-dependent dielectric constants along the *c*-axis.

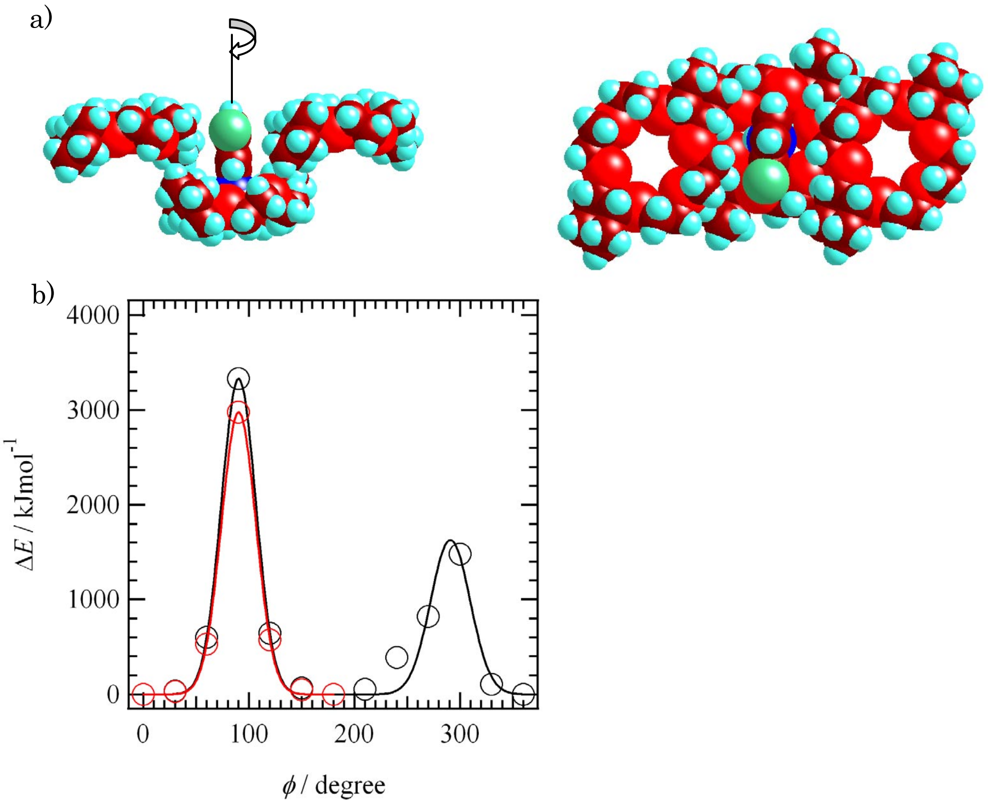

**Fig. S5.** Potential energy curve of *m*-FAni$^+$ rotation in the (*m*-FAni$^+$)(DCH[18]crown-6)$_3$ structure. Relative energy of (*m*-FAni$^+$)(DCH[18]crown-6)$_3$ was obtained by the *ab-initio* method of RHF/6-31G(*d*) basis set (black) and B3LYP / 6-31+G(d,p) one (red). The rotational angle ($\phi$) around the C-N bond of *m*-FAni$^+$ (a) was incremented by 30º, and the single point energy was calculated at each angle. The dashed curve is a guide for the eye.

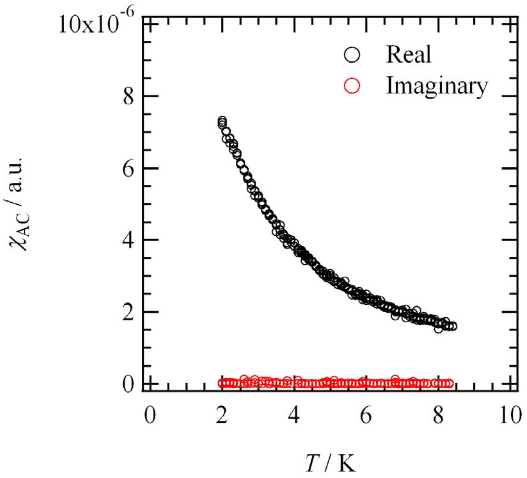

**Fig. S6.** Temperature dependent AC magnetic susceptibility of salt **1**. The measurement frequencies were 1, 10, 100, and 1000 kHz.

**Table S2**. Calculated magnetic exchange energy (*J*) of four kinds of [Ni(dmit)$_2$] dimers. The UB3LYP method was employed for the calculations, and the atomic coordinates of the X-ray structural analysis at 100 K were used for the calculations. The basis set for of Ni atom was LanL2-TZ(f) (TZ triple zeta basis set designed for an ECP + f polarization), and those of S and C atoms were Aug-cc-pVDZ.

| **interaction** | ***E*(S),** hartree | ***E*(T),** hartree | $S^2$**(S)** | $S^2$**(T)** | ***J*, eV** |
|---|---|---|---|---|---|
| $t_1$ | -8758.96271756 | -8758.97902899 | 0 | 2.0108 | -8.112x10$^{-3}$ |
| $t_2$ | -8758.96244309 | -8758.97866921 | 0 | 2.0108 | -8.069x10$^{-3}$ |
| $t_3$ | -8758.97769817 | -8758.99659194 | 0 | 2.0105 | -0.018893 |
| $t_4$ | -8758.98442703 | -8759.00478016 | 0 | 2.0104 | -0.020353 |