Supporting Information

Highly Polar 7,7-Bis(*N*, *N*-dimethylpiperazinium)-8,8-dicyano quinodimethane in $[Ni(dmit)_2]^-$ Salt; Crystal Structure and Magnetic Properties

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1. X-ray Crystal Structural Analysis

The data were collected at a temperature of 100 $\pm$ 1 K to a maximum 2θ value of 55.0°. A total of 76 oscillation images were collected. A sweep of data was done using w scans from 130.0 to 190.0° in 5.0° step, at χ=45.0° and ϕ = 0.0°. The exposure rate was 120.0 [sec./°]. A second sweep was performed using w scans from 0.0 to 160.0° in 5.0° step, at χ=45.0° and ϕ = 180.0°. The exposure rate was 120.0 [sec./°]. Another sweep was performed using ω scans from 0.0 to 160.0° in 5.0° step, at χ=0.0° and ϕ = 180.0°. The exposure rate was 120.0 [sec./°]. The crystal-to-detector distance was 127.40 mm. Readout was performed in the 0.100 mm pixel mode.

Of the 43531 reflections that were collected, 11876 were unique (R_{int} = 0.038); equivalent reflections were merged.

The linear absorption coefficient, m, for Mo-Ka radiation is 15.583 cm^{-1}. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.579 to 0.792. The data were corrected for Lorentz and polarization effects.

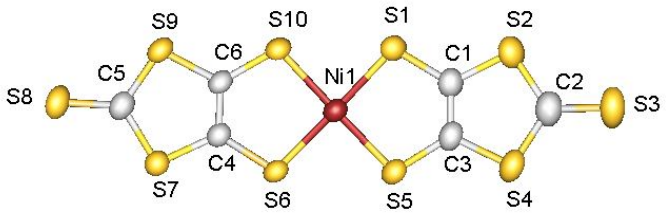
A black block crystal of $C_{35}H_{36}N_6Ni_2S_{20}O$ having approximate dimensions of 0.40 x 0.30 x 0.15 mm was mounted on a glass fiber. All measurements were made on a Rigaku RAXIS RAPID imaging plate area detector with graphite monochromated Mo-Kα radiation.

The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 8142 observed reflections and 619 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

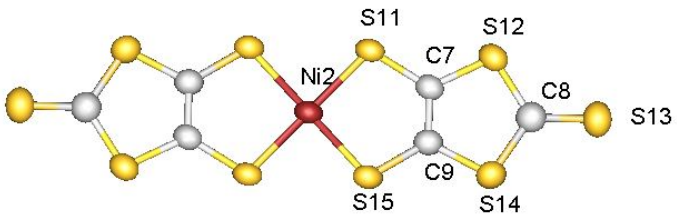
$$R1 = S \, ||Fo| - |Fc|| \, / \, S \, |Fo| = 0.0317$$

$$wR2 = [S (w (Fo^2 - Fc^2)^2)/ S \, w(Fo^2)^2]^{1/2} = 0.0510$$

The standard deviation of an observation of unit weight was 1.07. A Robust-resistant weighting scheme was used[5]. Plots of $\Sigma \, \omega \, (|Fo| - |Fc|)^2$ versus |Fo|, reflection order in data collection, sin θ/l and various classes of indices showed no unusual trends. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.49 and -0.39 $e^-/Å^3$, respectively.



[Ni(dmit)$_2$] **A**



[Ni(dmit)$_2$] **B**

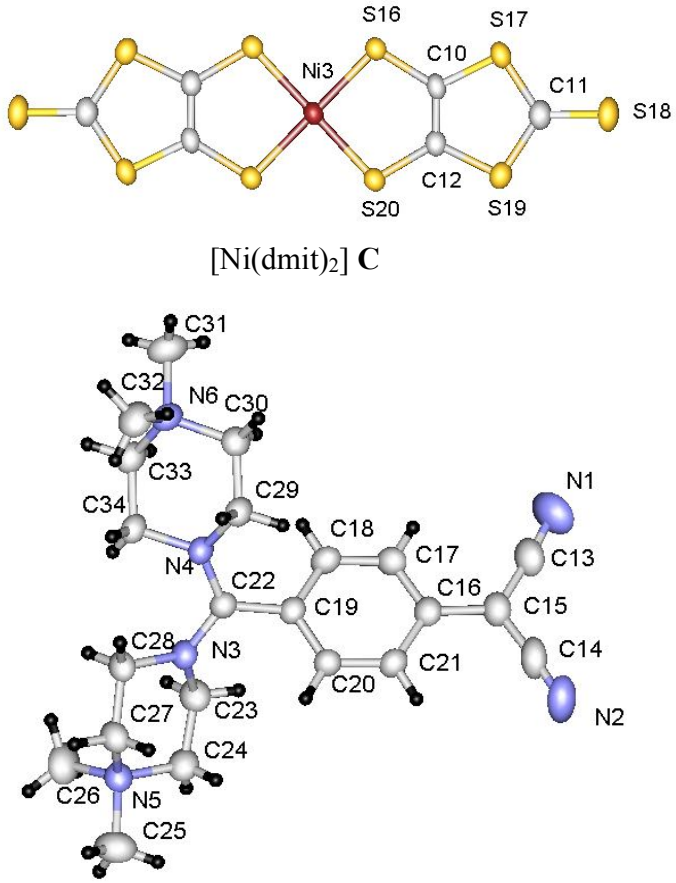


Figure S1 Atomic numbering scheme of **1** except for hydrogen atoms.

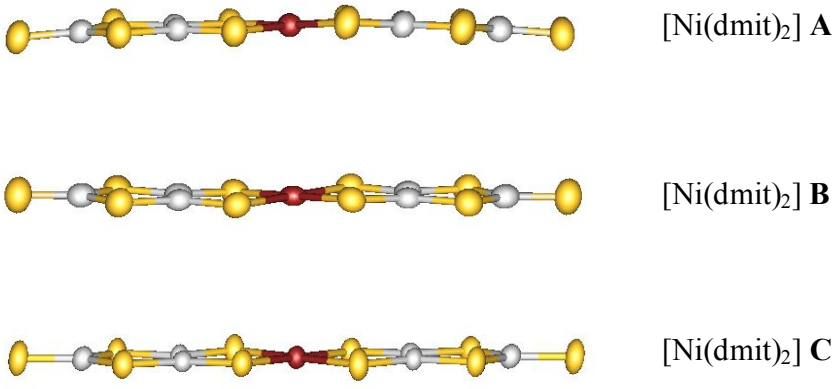


Figure S2. [Ni(dmit)$_2$] conformation in **1** viewed along the short axis.

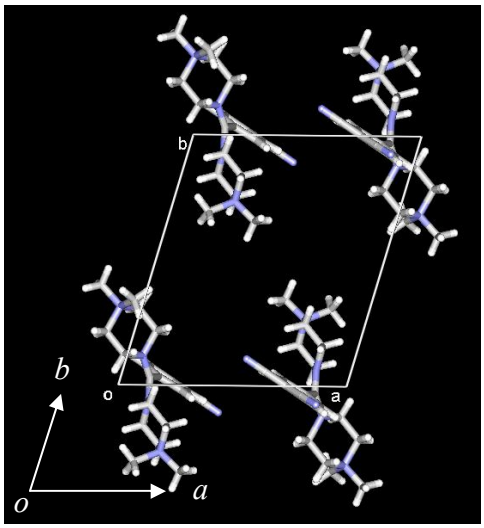


Figure S3 BDPDQ cation arrangements in the unit cell viewed along the *c*-axis.

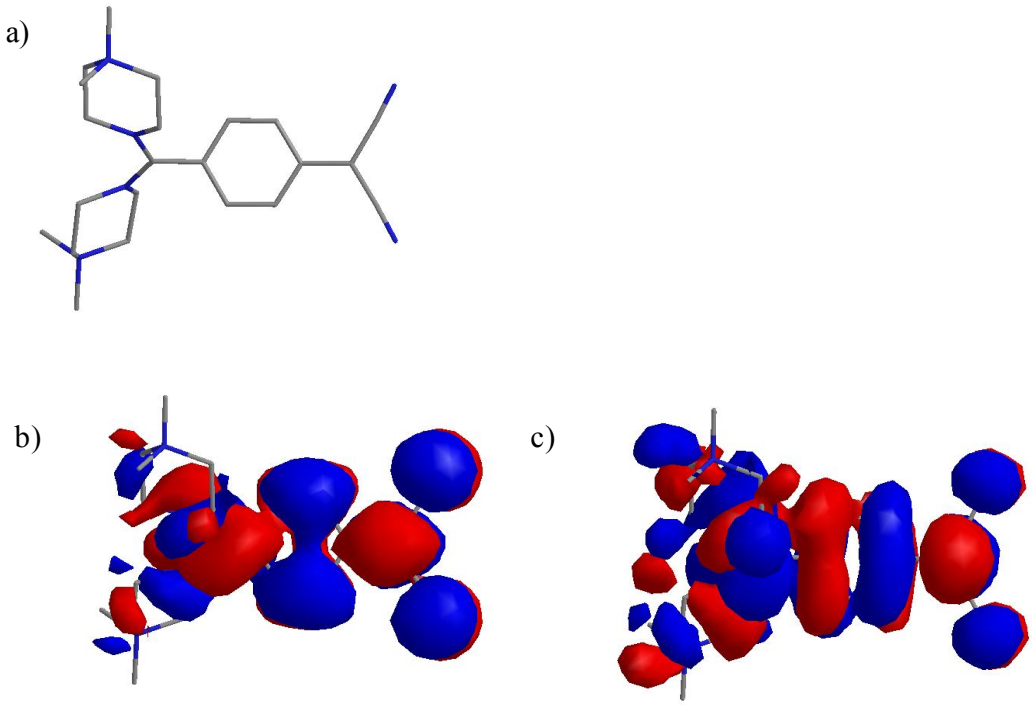


Figure S4. DFT calculation of BDPDQ cation. a) Molecular structure of BDPDQ cation. b) HOMO and c) LUMO viewed along the π-plane of BDPDQ.

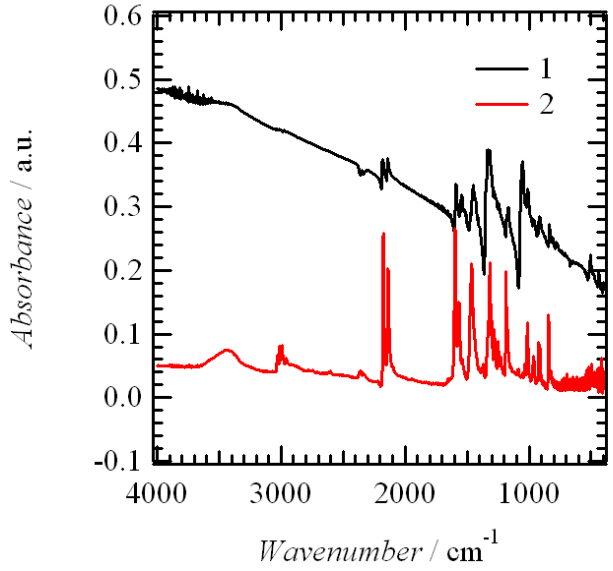


Figure S5. Vibrational spectra of crystal **1** and **2** in KBr pellets.

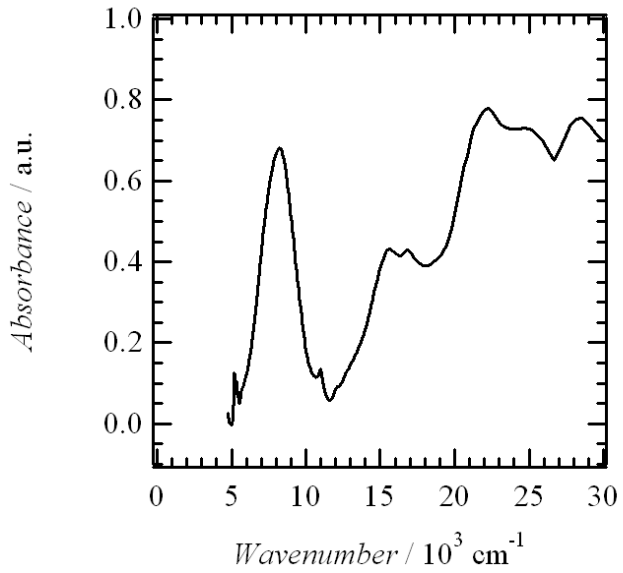


Figure S6. Electronic absorption spectrum of monovelant (tetrabutylammonium)$[Ni(dmit)_2]^-$ crystal in KBr pellet.

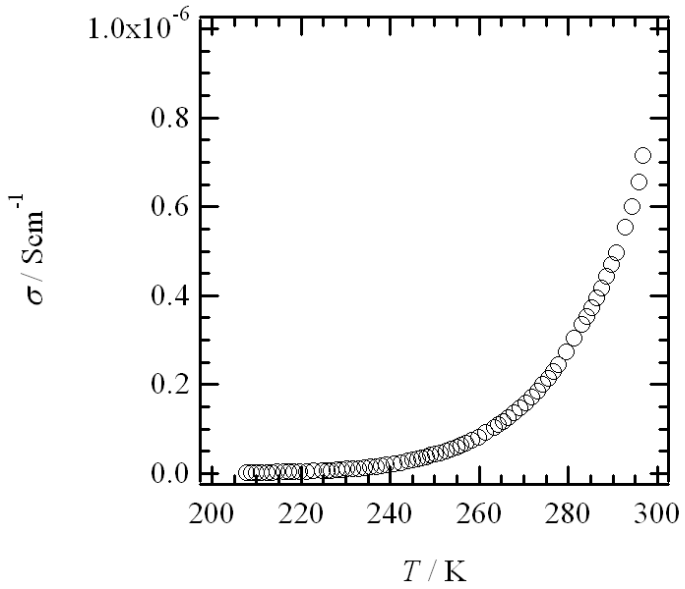


Figure S7. Temperature dependent electronic conductivity of single crystal **1**.