Electronic Supplementary Material for Dalton Transactions

Supporting information

Quasi-one-dimensional molecular magnets based on derivatives of (fluorobenzyl)pyridinium with $[M(mnt)_2]$ monoanion (M = Ni, Pd or Pt; mnt^{2-} = maleonitriledithiolate): Syntheses, crystal structures, magnetic properties

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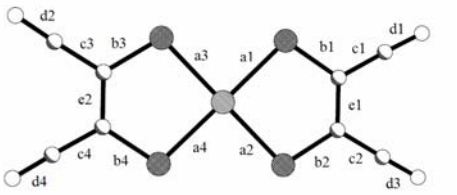
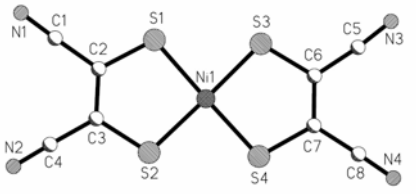
Table S1. Bond lengths (Å) in the moiety of an anion for **1**-**4**



	1	**2**	**3**	**4**
a_1	2.1505(6)	2.2661(15)	2.2683(17)	2.1374(7)
a_2	2.1429(8)	2.2740(15)	2.2633(18)	2.1385(7)
a_3	2.1516(8)	2.2797(15)	2.2680(17)	2.1368(8)
a_4	2.1544(6)	2.2703(14)	2.2698(18)	2.1477(7)
b_1	1.7174(18)	1.695(6)	1.694(7)	1.708(2)
b_2	1.7106(18)	1.705(5)	1.700(7)	1.709(2)
b_3	1.7133(18)	1.720(5)	1.705(7)	1.710(2)
b_4	1.7143(18)	1.708(5)	1.707(7)	1.722(2)
c_1	1.435(2)	1.448(7)	1.431(9)	1.483(3)
c_2	1.438(2)	1.433(8)	1.436(10)	1.429(3)
c_3	1.437(2)	1.459(8)	1.437(9)	1.423(3)
c_4	1.432(2)	1.416(7)	1.433(9)	1.433(3)
d_1	1.147(2)	1.135(7)	1.139(9)	1.133(3)
d_2	1.147(2)	1.128(7)	1.155(9)	1.138(3)
d_3	1.148(2)	1.148(7)	1.147(9)	1.141(3)
d_4	1.150(2)	1.143(7)	1.154(9)	1.129(3)
e_1	1.371(3)	1.375(7)	1.381(9)	1.357(3)
e_2	1.373(2)	1.382(7)	1.373(9)	1.361(3)

Table S2. Spin density distributions in a monomer of $[Ni(mnt)_2]^-$

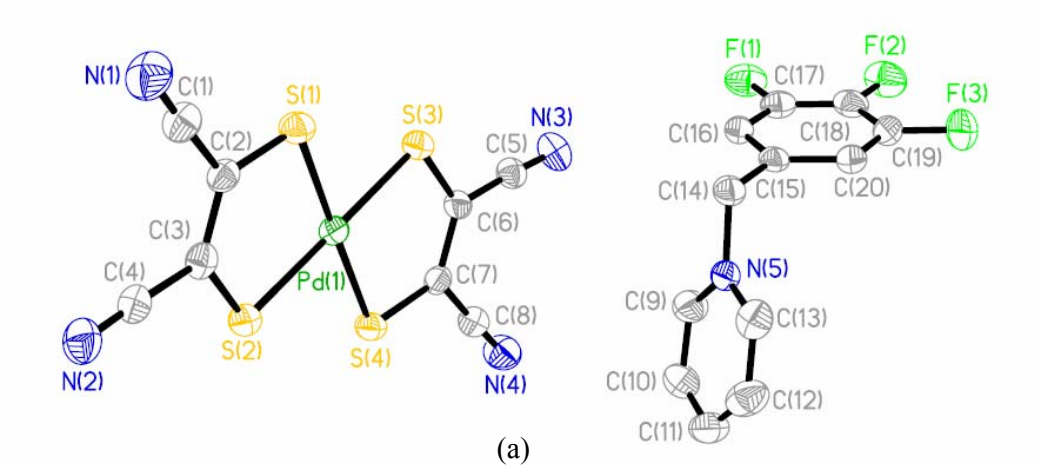


	ub3lyp/3-21g*	ub3pw91/3-21g*	ub3lyp/lanl2dz	ubpw91/lanl2dz
Ni (1)	0.838363	0.815970	0.151345	0.214193
S(1)	0.039982	0.044998	0.194027	0.165855
S(2)	0.043804	0.049760	0.198118	0.169891
S(3)	0.041772	0.049067	0.195901	0.167510
S(4)	0.041277	0.044857	0.194515	0.167024
N(1)	0.000402	-0.000406	0.009597	0.011906
N(2)	-0.000014	-0.000013	0.011113	0.013006
N(3)	-0.001385	-0.000417	0.008220	0.011012
N(4)	0.001111	-0.001273	0.011021	0.012760
C(1)	-0.000024	0.000605	-0.005379	-0.005737
C(2)	-0.000400	-0.001461	0.011372	0.022304
C(3)	-0.002784	-0.001874	0.013217	0.023009
C(4)	0.000459	0.001223	-0.006113	-0.006032
C(5)	0.001180	0.001974	-0.004405	-0.005178
C(6)	-0.004217	-0.002062	0.008993	0.020353
C(7)	0.000885	-0.001889	0.014690	0.024212
C(8)	-0.000412	0.000942	-0.006231	-0.006091

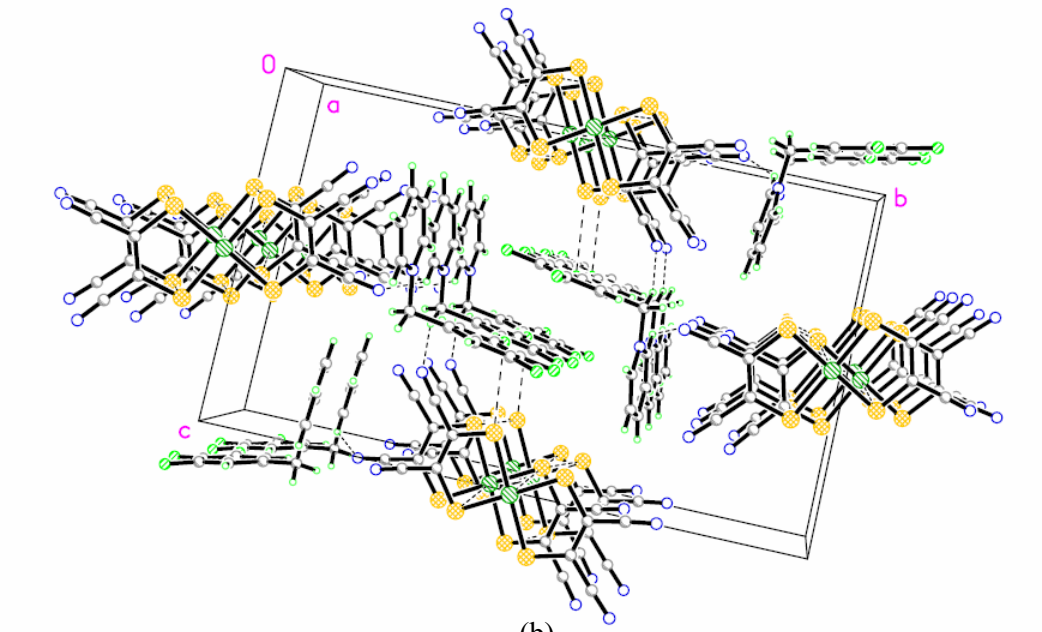
Detail of DFT calculations. The whole non-modelized molecular structure of the real complex **4** was taken directly from X-ray crystallography complete structure, and the unrestricted density functional theory (DFT) calculations at several levels are performed for the spin density population in a monomer of $[Ni(mnt)_2]^-$ utilizing the GAUSSIAN 98 program[1] on the SGI 3800 workstation. The results are almost the same as that for a dimer of $[Ni(mnt)_2]^-$.[2]

References

1. Gaussian 98, Revision A.11, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, P. Salvador, J. J. Dannenberg, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2001.
2. Z. P. Ni, X. M. Ren, J. Ma, Z. D. Chen, J. L. Xie, C. L. Ni, Q. J. Meng, *J. Am. Chem. Soc.* 2005, **127**, 14330.



(a)



(b)

Fig. S1 (a) ORTEP of **2** (with displacement ellipsoids at 30% probability level) and H-atom omitted for clarity; (b) packing of **2** shows the anionic stacks along the direction of *a*-axis.

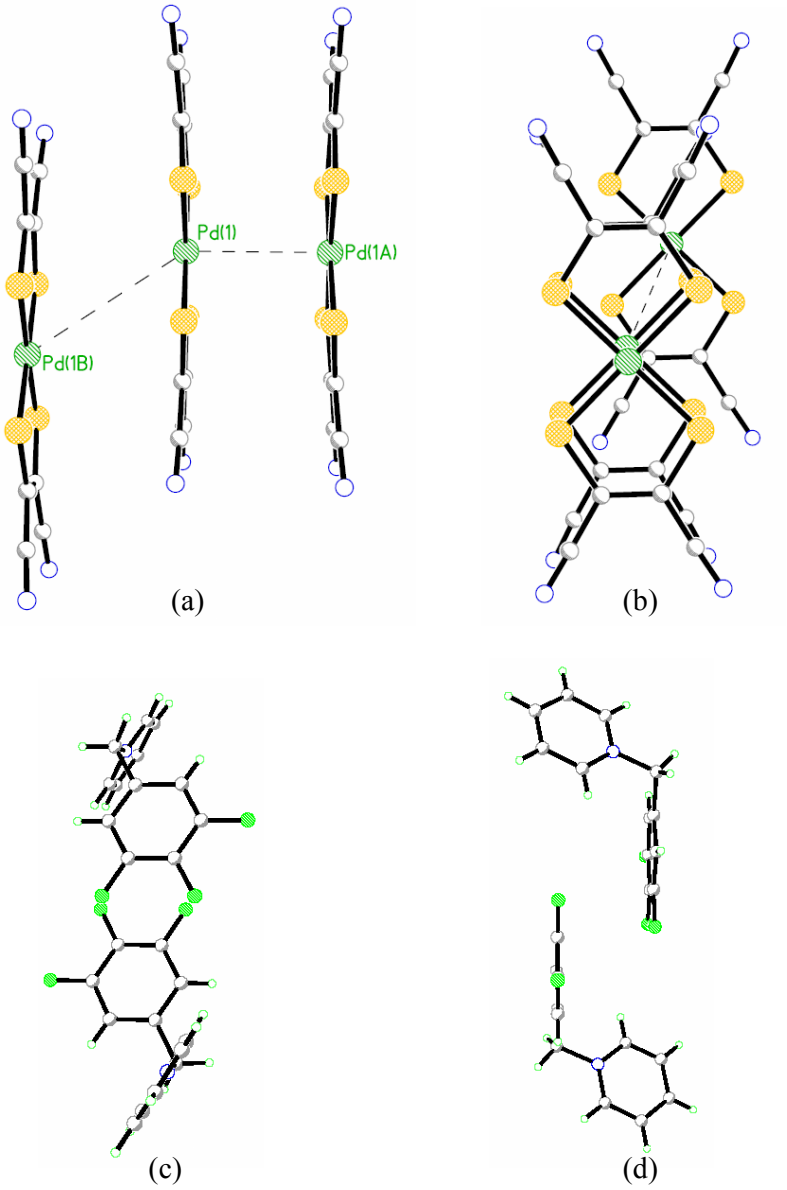
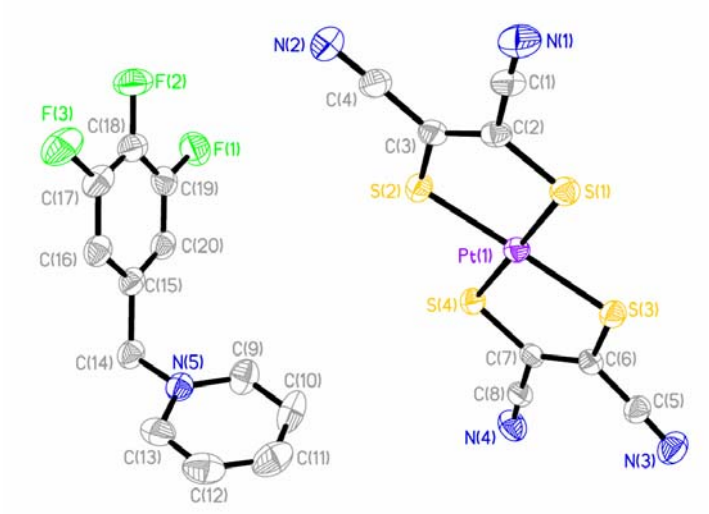
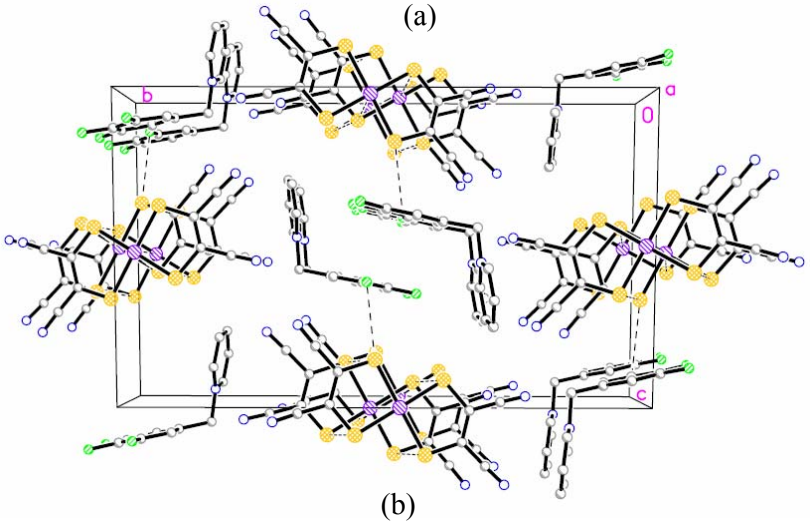


Fig. S3 Anionic arrangement patterns (a) side and (b) top views (Symmetry codes: 1A = 1-x, -2-y, 1-z; 1B = 2-x, -2-y, 1-z); cationic arrays (c) side and (d) top views in **2**.



(a)



(b)

Fig. S3 (a) ORTEP of **3** (with displacement ellipsoids at 30% possibility level) and H-atom omitted for clarity; (b) packing of **3** shows the anionic stacks along the direction of *a*-axis.

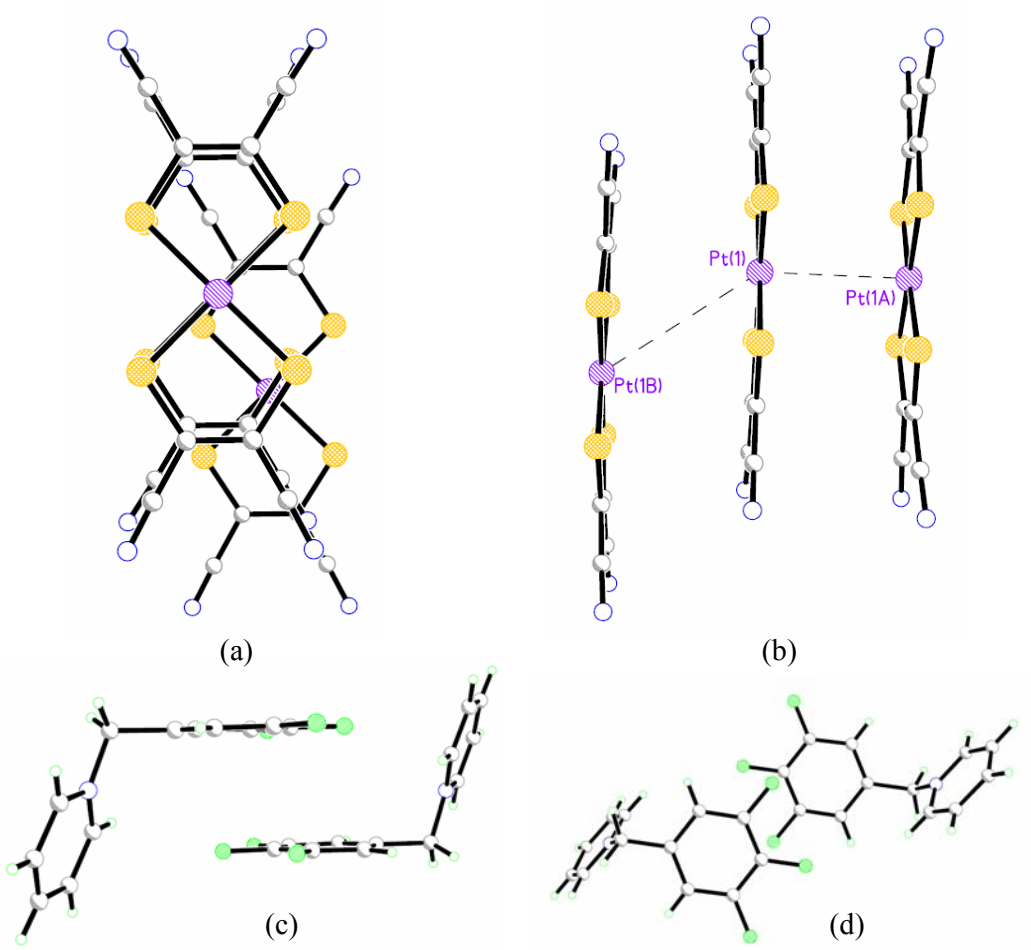
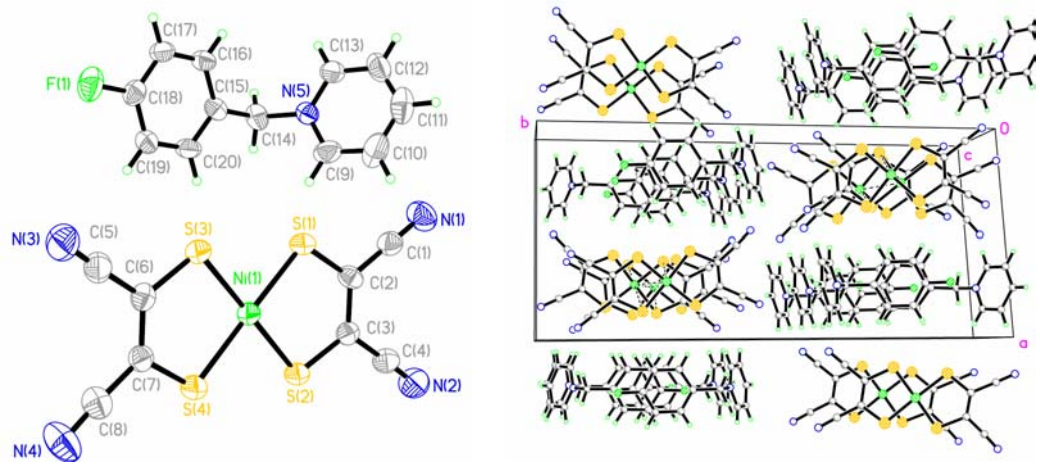


Fig. S4 Anionic arrangement patterns (a) side and (b) top views (Symmetry codes: 1A = 1-x, 2-y, 1-z; 1B = 2-x, 2-y, 1-z); cationic arrays (c) side and (d) top views in **3**.



(a) (b)

Fig. S5 (a) Molecular structure of **4** (b) segregated stacks of cations and anions along the direction of *c*-axis.

Crystal Structure at 293K.[8k] The molecular structure and packing diagram of **4** are depicted in Fig. 1a and 1b, respectively. The stack of anions runs parallel to ***c***-axis, and each of these stacks is surrounded by the cationic stacks. The adjacent anions overlap in a fashion of slipped nickel-over-sulfur in a stack, the separations of Ni…Ni between neighbors are exactly identical (3.953(1) Å), the contacts of Ni(1)…S(1)^{i} and Ni(1)…S(2)^{j} (i = 1+x, -0.5-y, 0.5+z; j = 1+x, -0.5-y, -0.5+z) are 3.646(39) and 3.598(34) Å, respectively. The nearest separation of Ni…Ni between stacks is 12.013(108) Å, which is much longer than that in a stack. Therefore, the anionic stacking column constructs a perfect regular one-dimensional magnetic chain from the viewpoint of crystal structure.

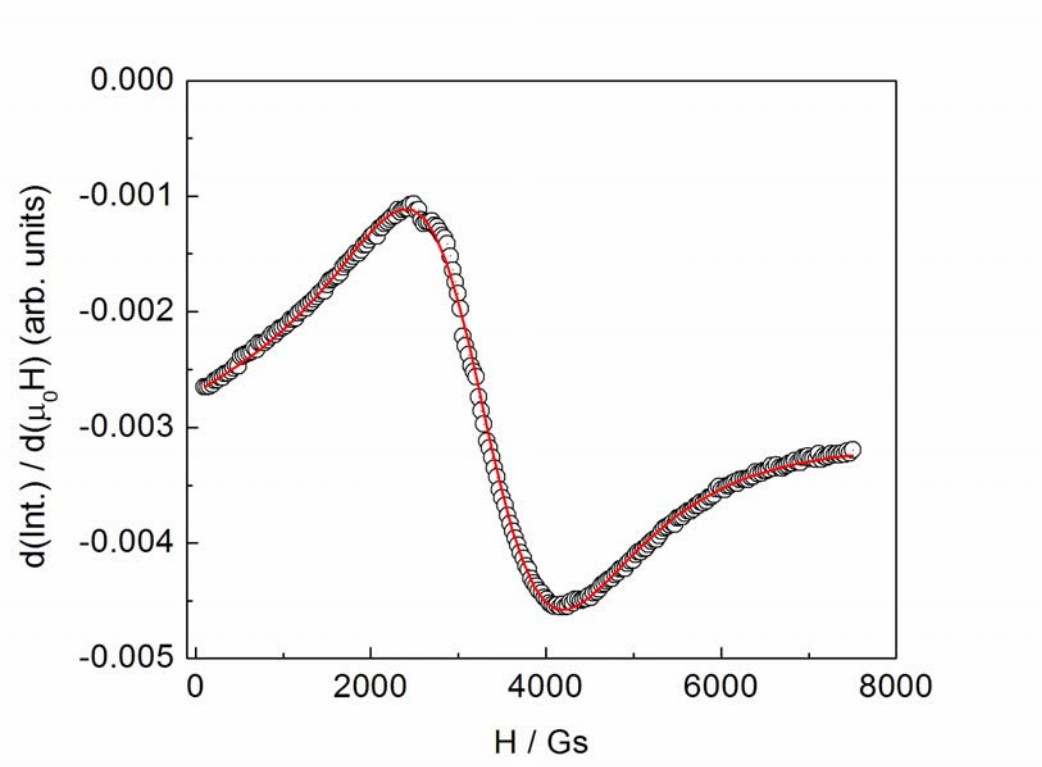


Fig. S6 EPR spectra of **4** with polycrystalline sample at room temperature: open circle representing experimental data and solid line fitting. [**EPR** measurement at room temperature was performed using polycrystalline sample with Bruker ER 200D-SRC spectrometer near 9 GHz. The spectrum was modeled by taking the field derivative of both the $+\omega$ and $-\omega$ absorption signal into consideration. The fits reveal a typical linewidth of ~1542 Gs, the *g*-factor of 2.035, which is about 1.6% larger than the free electron value indicating small orbital contributions to the magnetic moment].