Supporting Information

Magnetostructural relationships in [Ni(dmit)$_2$] $^-$ radical anions

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a)

$(\pi_2 + \pi_2)$

$(\pi_1 + \pi_1)$

$3d_{z^2}$

$3d_{xz}$

$3d_{xy} + (\sigma_1 + \sigma_1)$

$(\pi_1 - \pi_1)$
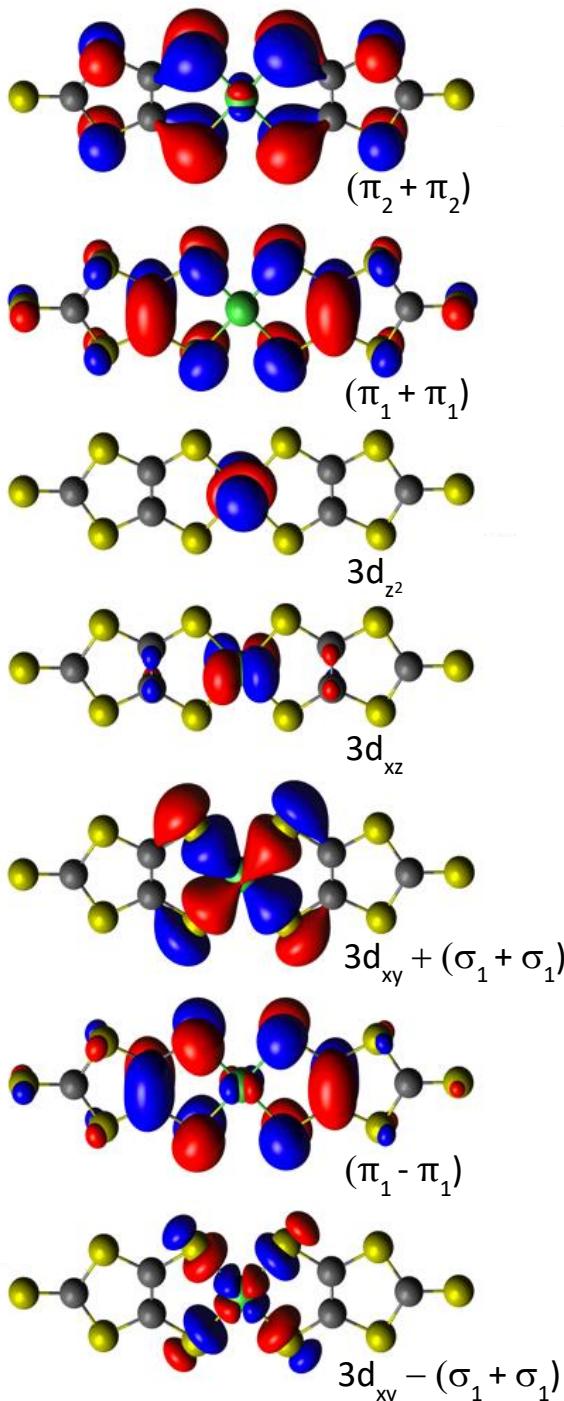
$3d_{xy} - (\sigma_1 + \sigma_1)$

CAS(11,7) dominant configuration	
MOs	Occupation
$(\pi_2 + \pi_2)$	2.00
$(\pi_1 + \pi_1)$	2.00
$3d_{z^2}$	1.99
$3d_{xz}$	1.94
$3d_{xy} + (\sigma_1 + \sigma_1)$	1.83
$(\pi_1 - \pi_1)$	1.02
$3d_{xy} - (\sigma_1 + \sigma_1)$	0.17

b)

$3d_{yz}$

$3d_{z^2}$

$3d_{xz}$

$3d_{xy} + (\sigma_1 + \sigma_1)$

$(\pi_1 - \pi_1)$

$3d_{xy} - (\sigma_1 + \sigma_1)$

$4d_{xz}$

$4d_{xy}$
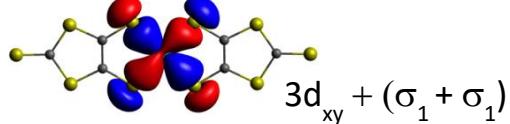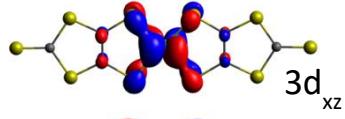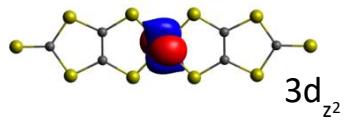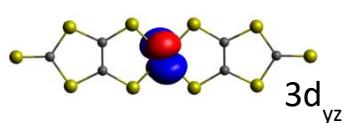
$4d_{z^2}$

$4d_{x^2-y^2}$

$4d_{yz}$

CAS(9,11) dominant configuration	
MOs	Occupation
$3d_{yz}$	1.97
$3d_{z^2}$	1.96
$3d_{xz}$	1.93
$3d_{xy} + (\sigma_1 + \sigma_1)$	1.88
$(\pi_1 - \pi_1)$	1.06
$3d_{xy} - (\sigma_1 + \sigma_1)$	0.15
$4d_{xz}$	0.01
$4d_{xy}$	0.00
$4d_{z^2}$	0.03
$4d_{x^2-y^2}$	0.00
$4d_{yz}$	0.01
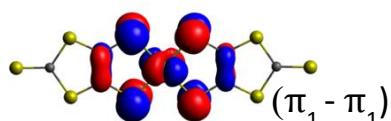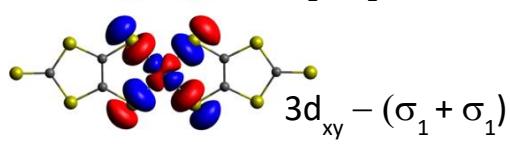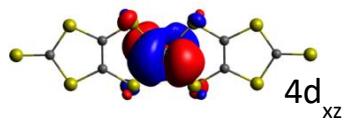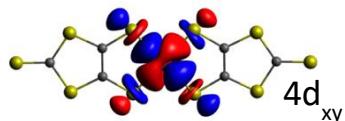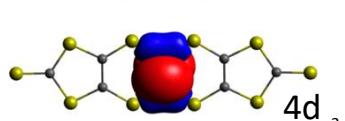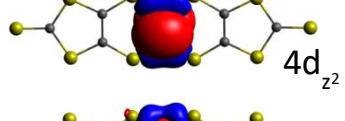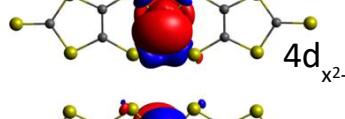
c)

$(\pi_1 + \pi_1)$

$(\pi_1 - \pi_1)$

| CAS(3,2) dominant configuration	
MOs	Occupation
$(\pi_1 + \pi_1)$	2.00
$(\pi_1 - \pi_1)$	1.00
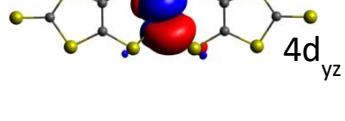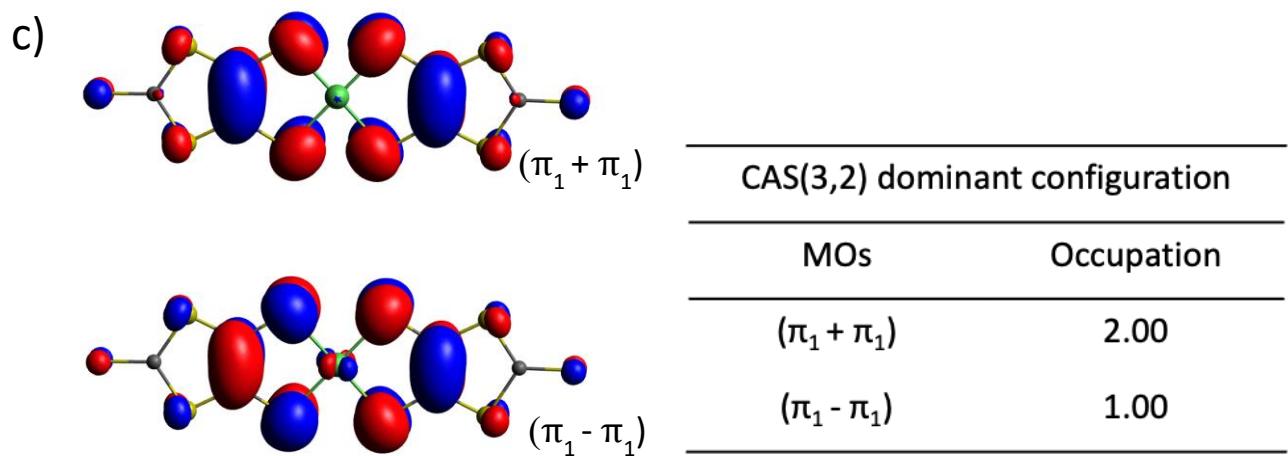
Figure S1. Active MOs at a) CASSCF(11,7), b) CASSCF(9,11), and c) CASSCF(3,2) for the [Ni(dmit)$_2$]$^-$ anion. The SOMO is mostly localized on the antibonding π orbital of the dmit ligands.
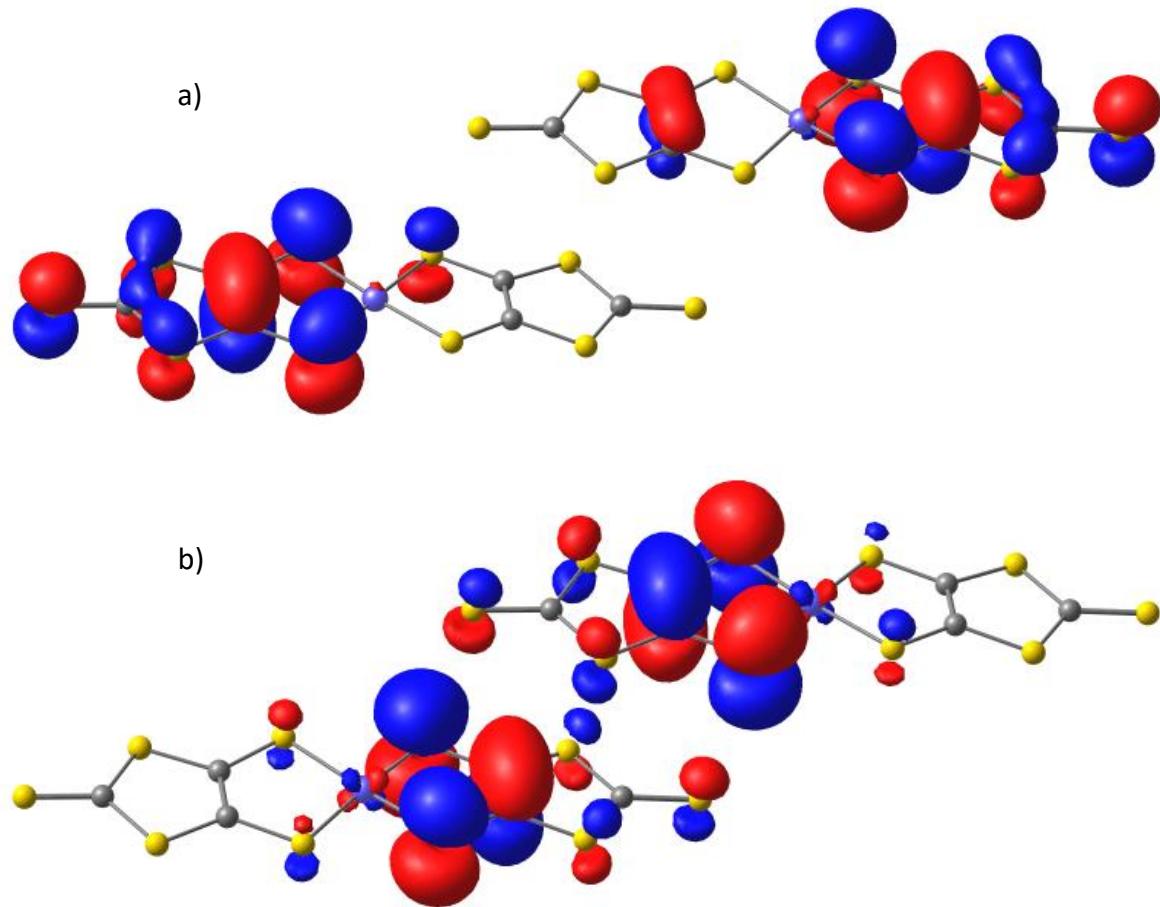
Figure S2. Active orbitals at CASSCF(6,4) level for $[Ni(dmit)_2]^{2-}$ dimer in compound B described in Ref. 16 in main text. Compound B consists of a chain of equidistant $[Ni(dmit)_2]^-$ units. All the dimers that can be chosen along the chain have to be then equivalent. The active orbitals of the dimer at this level are asymmetrically distributed in the anion. The orbitals with occupation numbers close to 2.00 (Figure S2a) placed the electronic density in the more distant dmit ligands of two different units, while those with occupation close to 1.0 (Figure S2b) locate the density on the adjacent dmit ligands (short-range interaction). This solution minimizes the repulsions of the six electrons on the four dmit π-orbitals. However they do not correctly represent the electronic distribution in the real system, since they are not compatible with the translational symmetry of the chain.

a) slippage 0.0
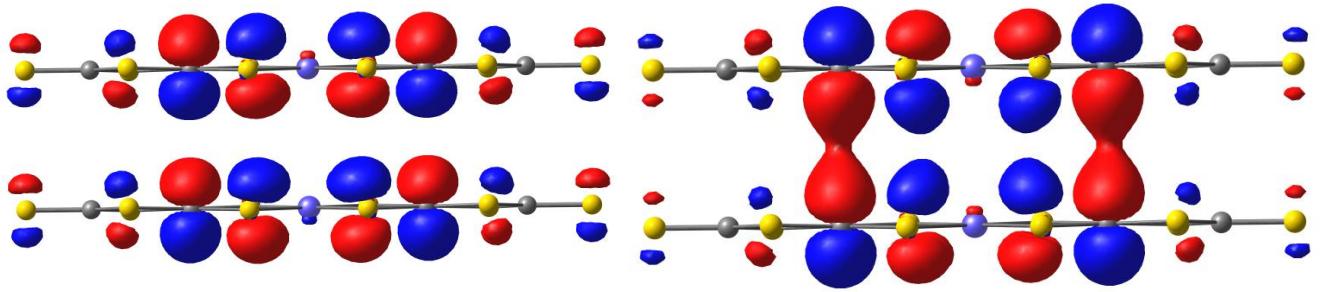
b) Slippage 2.5x
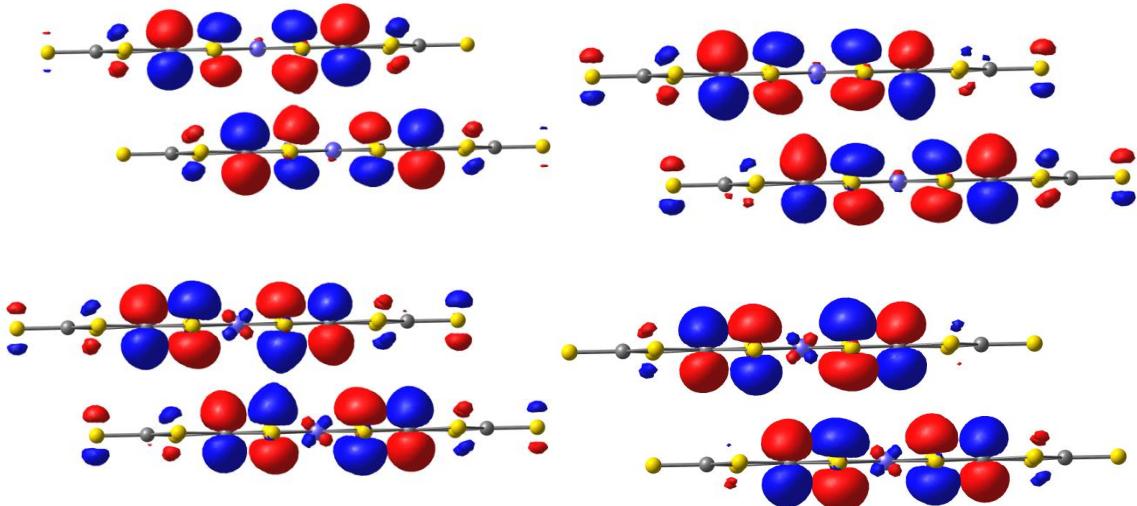
Figure S3. Active orbitals for the neutral dimer at CASSCF (4/4) level for slippage 0.0 (a) and slippage of 2.5A in x axis (b). In both sets, the two top MOs correspond to the combination of the ($\pi_1+\pi_1$) orbitals of the dmit ligands, while the two bottom MOs result from the combination of the ($\pi_1- \pi_1$) dmit orbitals.

Intradimer interaction in Compound D   Interdimer interaction in Compound D
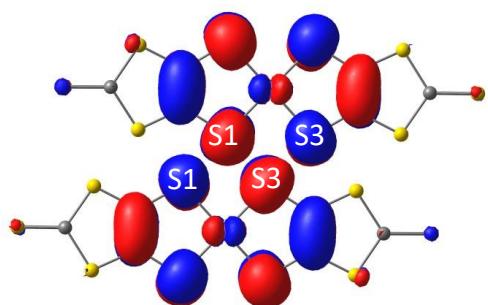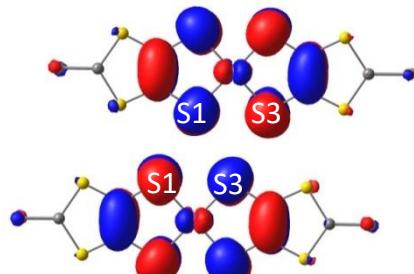
Figure S4. Top views of the out-of-phase combination of the two active orbitals for the intradimer and interdimer interaction in compound **D**.

Table S1. Slippage distances, Ni-Ni distances, and shortest S⋯S contact of S atoms coordinated to Ni in the studied $[Ni(dmit)_2]_2^{2-}$ dimers.

	Distances (Å)										
d_{slip}^{x}	0.50	1.50	2.50	3.50	4.50	5.50	7.50	8.50	9.50	10.50	
Ni-Ni	3.54	3.80	4.30	4.95	5.70	6.52	8.30	9.19	10.12	11.07	
S⋯S	3.54	3.80	3.53	3.54	3.82	4.32	5.72	6.54	7.40	8.30	
d_{slip}^{y}	1.00	2.00	3.00	4.00	5.00	6.00	7.00	8.00	9.00		
Ni-Ni	3.64	4.03	4.61	5.32	6.10	6.95	7.83	8.73	9.66		
S⋯S	3.64	3.75	3.58	3.67	4.02	4.57	5.25	6.02	6.86		
d_{slip}^{xy}	0.50	1.50	2.50	3.50	4.50	5.50	6.50	7.50	8.50	9.50	10.50
Ni-Ni	3.54	3.81	4.30	4.95	5.70	6.52	7.39	8.27	9.19	10.13	11.06
S⋯S	3.54	3.81	4.02	3.67	3.58	3.76	4.18	4.77	5.49	6.29	7.12