

Supplementary data for the article:

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Malenov, D. P.; Veljković, D. Ž.; Hall, M. B.; Brothers, E. N.; Zarić, S. Influence of Chelate Ring Type on Chelate-Chelate and Chelate-Aryl Stacking: The Case of Nickel Bis(Dithiolene). *Physical Chemistry Chemical Physics* **2019**, *21* (3), 1198–1206. <https://doi.org/10.1039/c8cp06312e>

## SUPPORTING INFORMATION

### CCSD(T)/CBS calculations; comparison of CCSD(T)/CBS and DFT energies

Helgaker extrapolation method<sup>1</sup> was applied to determine MP2 energies at complete basis set (MP2/CBS). HF and MP2 energies were calculated with aug-cc-pVDZ and aug-cc-pVTZ basis sets (aDZ and aTZ in the following equations), and from their difference CORR (correlation) energies were obtained ( $\Delta E(\text{CORR}) = \Delta E(\text{MP2}) - \Delta E(\text{HF})$ ). The HF energy at complete basis set ( $\Delta E(\text{HF}/\text{CBS})$ ) and the CORR energy at complete basis set ( $\Delta E(\text{CORR}/\text{CBS})$ ) were then obtained according to the following equations:

$$\Delta E(\text{HF}/\text{CBS}) = \frac{\Delta E(\text{HF}/\text{aDZ}) \cdot \exp(-1.63 \cdot 3) - \Delta E(\text{HF}/\text{aTZ}) \cdot \exp(-1.63 \cdot 2)}{\exp(-1.63 \cdot 3) - \exp(-1.63 \cdot 2)}$$

$$\Delta E(\text{CORR}/\text{CBS}) = \frac{3^3 \cdot \Delta E(\text{CORR}/\text{aTZ}) - 2^3 \cdot \Delta E(\text{CORR}/\text{aDZ})}{3^3 - 2^3}$$

The MP2 energy at complete basis set was then derived as the sum of HF and CORR energies at complete basis set:

$$\Delta E(\text{MP2}/\text{CBS}) = \Delta E(\text{HF}/\text{CBS}) + \Delta E(\text{CORR}/\text{CBS})$$

The CCSD(T)/CBS energies were determined by calculating interaction energies at HF and MP2 levels with aug-cc-pVDZ basis set<sup>2-4</sup> and taking into account that the basis set dependence of MP2 and CCSD(T) energies is very similar:<sup>5</sup>

$$\Delta E(\text{CCSD(T)/CBS}) = \Delta E(\text{MP2}/\text{CBS}) + \Delta E(\text{CCSD(T)}/\text{aug-cc-pVDZ}) - \Delta E(\text{MP2}/\text{aug-cc-pVDZ}).$$

Optimized nickel *bis*(dithiolene) (**0**, Figure 1) and benzene molecules have  $D_{2h}$  and  $D_{6h}$  symmetry, respectively. By displacing the molecules in the directions associated with longer (y) and shorter (x)  $C_2$  axis of molecular plane of nickel *bis*(dithiolene) (Figure 1), a total of three orientations were constructed for the calculation of CCSD(T)/CBS energies for chelate-aryl (A-C) and four orientations for chelate-chelate stacking (D-G) of nickel *bis*(dithiolenes) (Figure 1). For all of these CCSD(T)/CBS geometries the optimal normal distances were determined at B2PLYP-D3BJ/def2-TZVP level.

In orientation **A**, benzene center is above nickel atom, in orientation **B** benzene center is above chelate center, while in orientation **C** benzene center is above C-C bond center. For the construction of chelate-chelate model systems, the geometries found in the Cambridge Structural Database search of stacking interactions between two nickel *bis*(dithiolene) fragments<sup>6</sup> were used. In orientation **D**, one nickel atom is above the other nickel atom and chelate rings entirely overlap; in orientation **E** the molecules are displaced along the y axis, with nickel of one molecule above the center of the chelate of the second molecule. In orientation **F**, they are displaced along the x axis, with nickel of one molecule above the center of interligand S-S distance. In model system **G**, the molecules are displaced between the x and y axes, with nickel of one molecule above the sulfur of the other molecule.

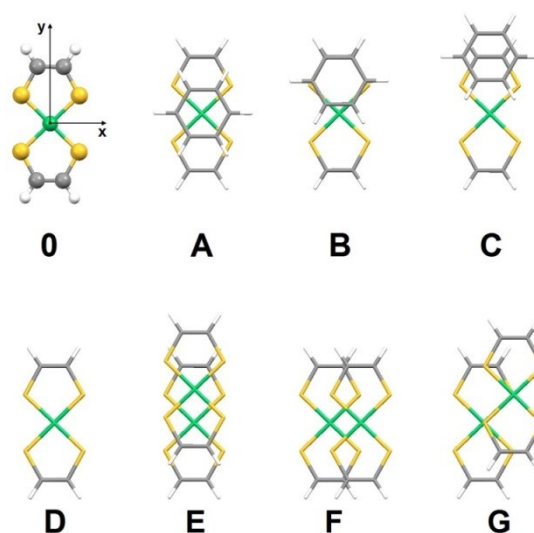


Figure S1. Nickel *bis*(dithiolene) molecule (**0**) with its  $C_2$  molecular plane axes and orientations used for the CCSD(T)/CBS calculations of chelate-aryl (**A-C**) and chelate-chelate stacking (**D-G**) of nickel *bis*(dithiolene).

The CCSD(T)/CBS calculations show strong chelate-aryl stacking between nickel *bis*(dithiolene) and benzene, and significantly stronger chelate-chelate stacking between two nickel *bis*(dithiolenes) (Table 1). This is in agreement with previously calculated stacking of *acac* type of nickel chelate, which showed stronger chelate-chelate stacking<sup>6</sup> than chelate-aryl stacking.<sup>7</sup> Chelate-aryl stacking between nickel *bis*(dithiolene) and benzene (-5.60 kcal/mol, Table 1) is similar in strength to chelate-aryl stacking between *acac* type nickel chelate and benzene (-5.75 kcal/mol).<sup>7</sup> However, chelate-chelate stacking between two nickel *bis*(dithiolenes) (-10.31 kcal/mol, Table 1) is stronger than the stacking of two *acac* type nickel chelates (-9.50 kcal/mol).<sup>6</sup> Chelate-aryl stacking of nickel *bis*(dithiolene) is the strongest when benzene center is above nickel; however, chelate-chelate stacking of two nickel *bis*(dithiolenes) is the weakest when one nickel is above the other (Table 1).

Table S1. Horizontal displacements ( $r$ ), normal distances ( $R$ ), CCSD(T)/CBS interaction energies for orientations A-F (Figure S1), and interaction energies calculated at  $\omega$ B97X-D/6-31+G(d) (A-C) and PBE0-D3BJ/6-31G(d) (D-G) levels with different basis sets

chelate-aryl	$r$ [Å]	$R$ [Å]	$\Delta E(\text{CCSD(T)/CBS})$ [kcal/mol]	$\Delta E(\omega\text{B97X-D})$		
				6-31++G(d,p) [kcal/mol]	6-31++G(d) [kcal/mol]	6-31+G(d) [kcal/mol]
<b>A</b>	1.763	3.60	<b>-5.60</b>	-5.45	-5.44	-5.43
<b>B</b>	0.000	3.75	<b>-4.03</b>	-3.93	-3.91	-3.91
<b>C</b>	2.186	3.55	<b>-4.60</b>	-4.68	-4.68	-4.66
chelate-chelate	$r$ [Å]	$R$ [Å]	$\Delta E(\text{CCSD(T)/CBS})$ [kcal/mol]	$\Delta E(\text{PBE0-D3BJ})$		
				aug-cc-pVDZ [kcal/mol]	6-31G(d,p) [kcal/mol]	6-31G(d) [kcal/mol]
<b>D</b>	0.000	3.80	<b>-6.86</b>	-7.05	-6.89	-6.87
<b>E</b>	1.763	3.55	<b>-10.31</b>	-10.82	-10.09	-10.09
<b>F</b>	1.505	3.55	<b>-8.26</b>	-8.32	-8.02	-8.02
<b>G</b>	2.096	3.50	<b>-9.31</b>	-9.79	-9.09	-9.09

It was found that  $\omega$ B97X-D density functional gives very good agreement with CCSD(T)/CBS chelate-aryl stacking energies when used with 6-31++G(d,p) basis set (Table S1). However, the same accuracy was found by using less polarization functions (6-31++G(d)). Additionally, the same agreement was obtained by reducing the number of diffuse functions (6-31+G(d), Table S1). Therefore, due to computational costs, the  $\omega$ B97X-D/6-31+G(d) method/basis set combination was used for the calculation of potential energy surfaces for chelate-aryl dithiolene stacking.

PBE0 density functional with Grimme D3 dispersion correction and Becke-Johnson damping was found to give good agreement with CCSD(T)/CBS chelate-chelate stacking energies when used with aug-cc-pVDZ basis set (Table S1), which was used in our previous benchmark paper on chelate stacking.<sup>8</sup> However, the accuracy was improved and computational costs lowered by taking the smaller 6-31G(d,p) basis set. Moreover, when basis set with less polarization functions (6-31G(d), Table S1) was used, the accuracy was the same. Therefore, the PBE0-D3BJ/6-31G(d) method/basis set combination was used for the calculation of potential energy surfaces for chelate-chelate stacking of nickel *bis*(dithiolenes).

## Optimal normal distances for chelate-aryl and chelate-chelate stacking

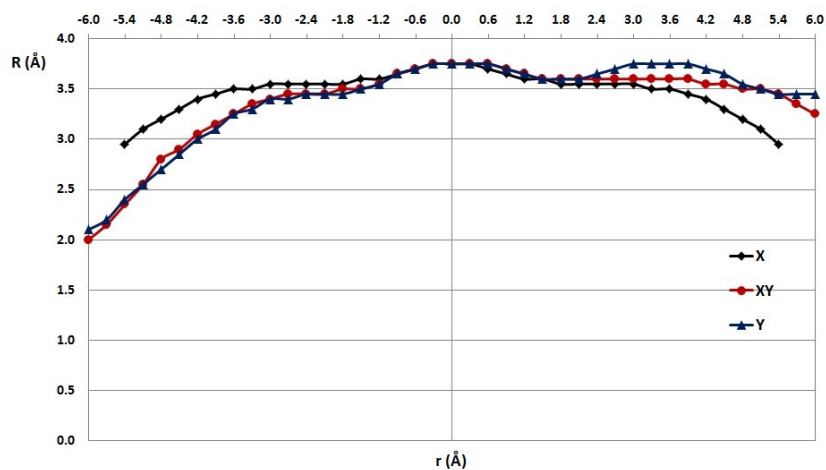
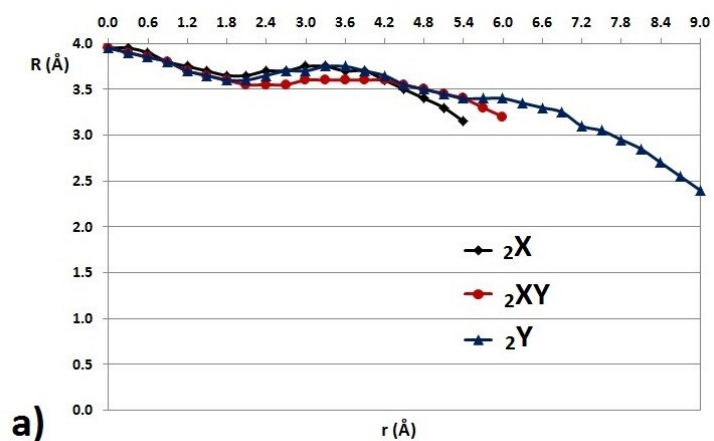
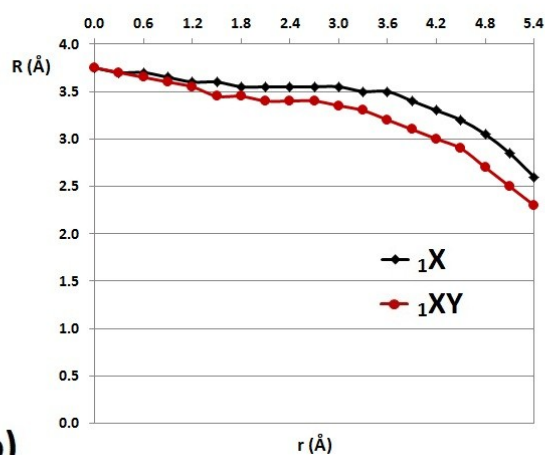


Figure S2. Optimal normal distances for chelate-aryl stacking of nickel *bis*(dithiolene) and benzene. For the geometries of model systems, see Figure 2 in the main text



a)



b)

Figure S3. Optimal normal distances for *double face-to-face* (a) and *single face-to-face* (b) chelate-chelate stacking of nickel *bis*(dithiolenes). For the geometries of model systems, see Figure 3 in the main text.

Optimized geometries of the minima at potential energy curves

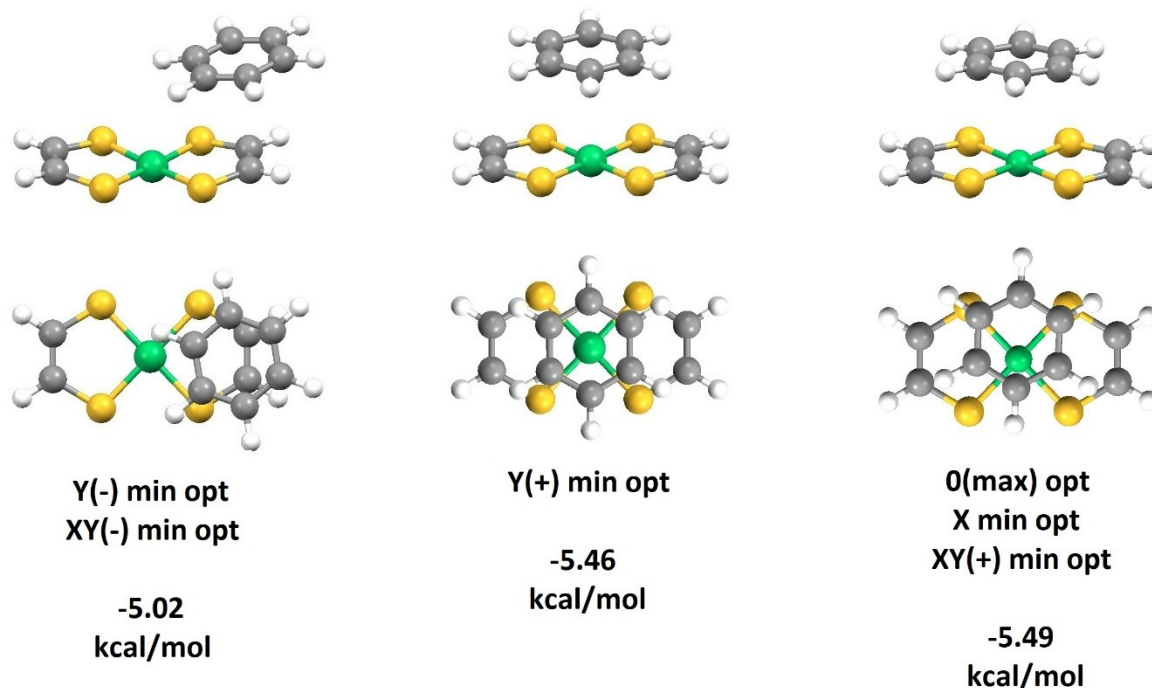


Figure S4. Two views of the optimized geometries for chelate-aryl stacking of nickel *bis*(dithiolene) and benzene. The starting geometries for each optimization are indicated. The optimizations were performed at  $\omega$ B97X-D/6-31+G(d) level. This method is in best agreement with CCSD(T)/CBS data for the chelate-aryl stacking of nickel *bis*(dithiolene) and benzene (see Table S1), and the presented interaction energies of the optimized minima were calculated with that method.

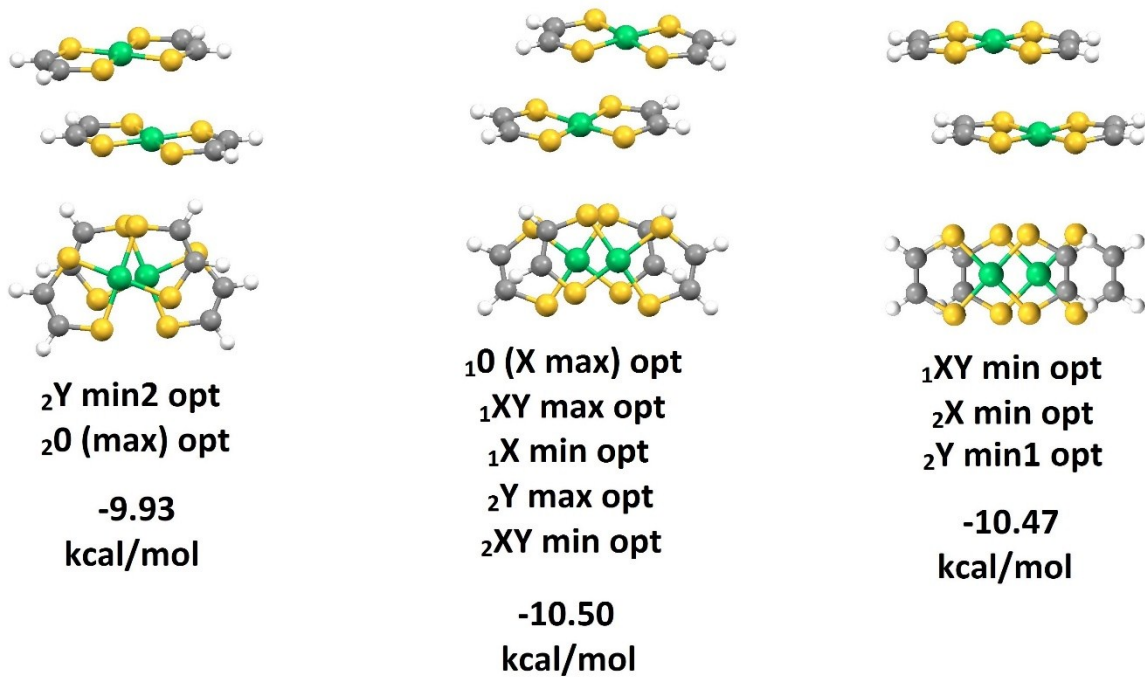


Figure S5. Two views of the optimized geometries for chelate-chelate stacking of nickel *bis*(dithiolenes). The starting geometries for each optimization are indicated. The optimizations were performed at PBE0-D3BJ/6-31G(d) level. This method is in best agreement with CCSD(T)/CBS data for the chelate-chelate stacking of nickel *bis*(dithiolenes) (see Table S1), and the presented interaction energies of the optimized minima were calculated with that method.

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