Supplementary data for the article:

SUPPORTING INFORMATION

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

Helgaker extrapolation method[1] 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 ($\Delta E(CORR) = \Delta E(MP2) - \Delta E(HF)$). The HF energy at complete basis set ($\Delta E(HF/CBS)$) and the CORR energy at complete basis set ($\Delta E(CORR/CBS)$) were then obtained according to the following equations:

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

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

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

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

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

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

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[6] 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.
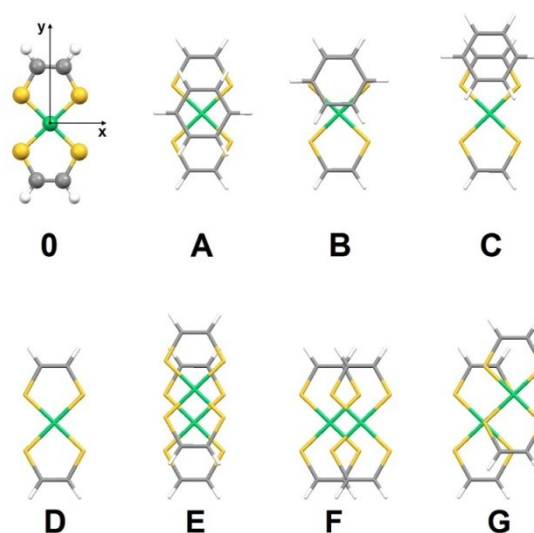
Figure S1. Nickel *bis*(dithiolene) molecule (**0**) with its C_2 molecular plane axes and orientations used for the CCSD(T)/CBS calculations of chelate-aryl (**A-C**) and chelate-chelate stacking (**D-G**) of nickel *bis*(dithiolene).

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*(ditholenes) (Table 1). This is in agreement with previously calculated stacking of *acac* type of nickel chelate, which showed stronger chelate-chelate stacking[6] than chelate-aryl stacking.[7] 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).[7] 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).[6] 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 ωB97X-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]	ΔE(CCSD(T)/CBS) [kcal/mol]	ΔE(ωB97X-D)		
				6-31++G(d,p) [kcal/mol]	6-31++G(d) [kcal/mol]	6-31+G(d) [kcal/mol]
A	1.763	3.60	**-5.60**	-5.45	-5.44	*-5.43*
B	0.000	3.75	**-4.03**	-3.93	-3.91	*-3.91*
C	2.186	3.55	**-4.60**	-4.68	-4.68	*-4.66*
chelate-chelate	r [Å]	R [Å]	ΔE(CCSD(T)/CBS) [kcal/mol]	ΔE(PBE0-D3BJ)		
				aug-cc-pVDZ [kcal/mol]	6-31G(d,p) [kcal/mol]	6-31G(d) [kcal/mol]
D	0.000	3.80	**-6.86**	-7.05	-6.89	*-6.87*
E	1.763	3.55	**-10.31**	-10.82	-10.09	*-10.09*
F	1.505	3.55	**-8.26**	-8.32	-8.02	*-8.02*
G	2.096	3.50	**-9.31**	-9.79	-9.09	*-9.09*

It was found that ωB97X-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 ωB97X-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.[8] 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).

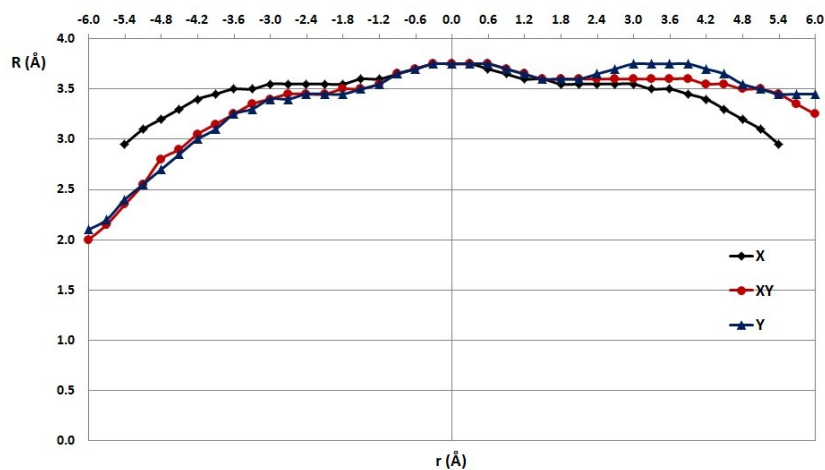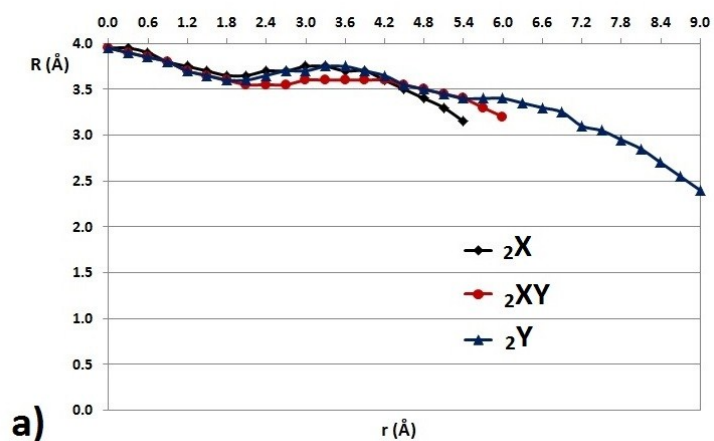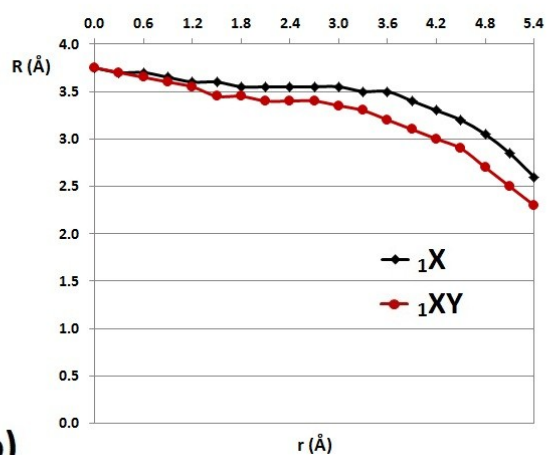*Optimal normal distances for chelate-aryl and chelate-chelate stacking*

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

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

Y(-) min opt
XY(-) min opt

-5.02
kcal/mol

Y(+) min opt

-5.46
kcal/mol

0(max) opt
X min opt
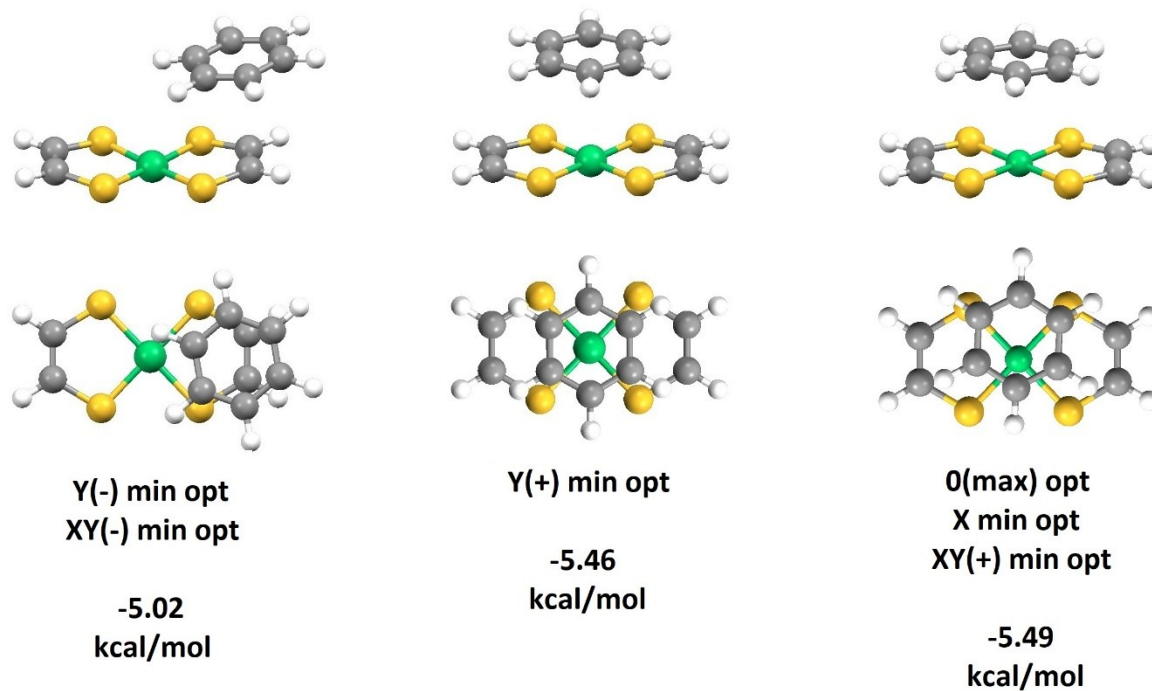**XY(+) min opt**

-5.49
kcal/mol

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 ωB97X-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.

$_2$Y min2 opt
$_2$0 (max) opt

-9.93
kcal/mol

$_1$0 (X max) opt
$_1$XY max opt
$_1$X min opt
$_2$Y max opt
$_2$XY min opt

-10.50
kcal/mol

$_1$XY min opt
$_2$X min opt
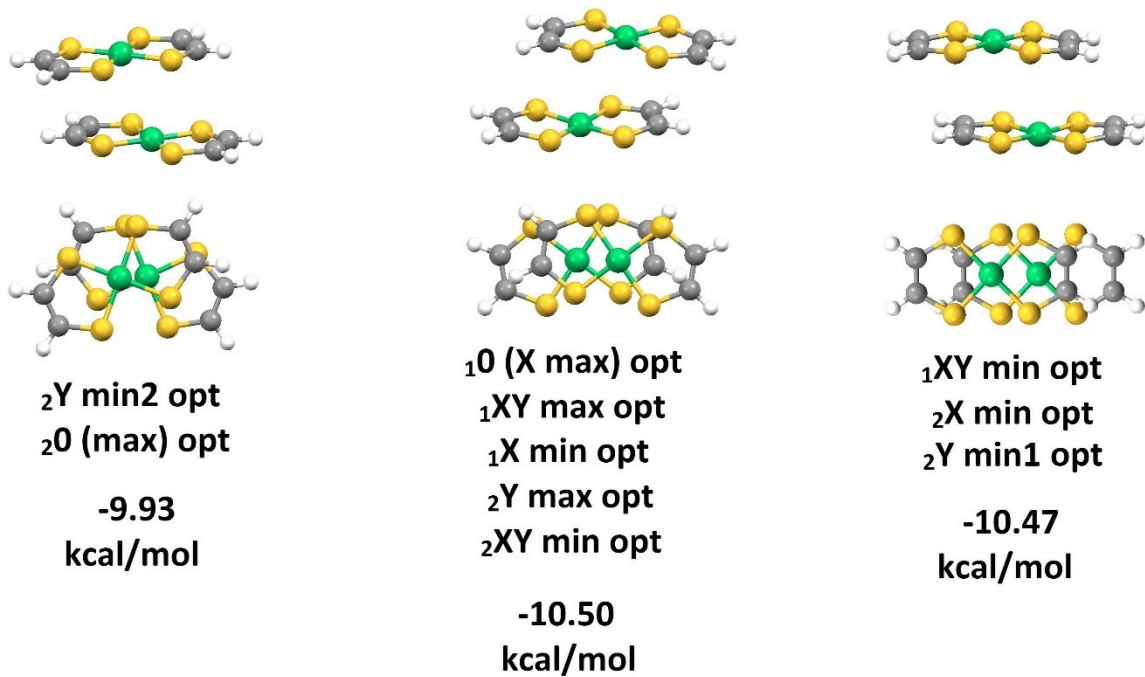$_2$Y min1 opt

-10.47
kcal/mol

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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