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Supplementary

Regulating the Optoelectronic Properties of Nickel Dithiolene by the Substituents: A Theoretical Study

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Verification of the Computational Method

In order to choose reasonable basis functional for this work, we compared some simulation results with the available experimental data in the literature. We chose four kinds of basis functionals (M06, M06L, B3LYP, PBEPBE) to perform geometry optimization for $Ni(S_2C_2H_2)_2$, $Ni[S_2C_2(CH_3)_2]_2$ and $Ni[S_2C_2(CN)_2]_2$ and performed TD-DFT calculation for $Ni(S_2C_2H_2)_2$. We chose the same basis set with the literature for Ni [1], in which the LANL2DZ basis set was adopted for Ni, the two outermost p functions were replaced by a (41) split of optimized p polarization function of Ni and an f function was added to Ni as it is more helpful for predicting excited states accurately. The 6-311 + G* was adopted for other atoms except Ni.

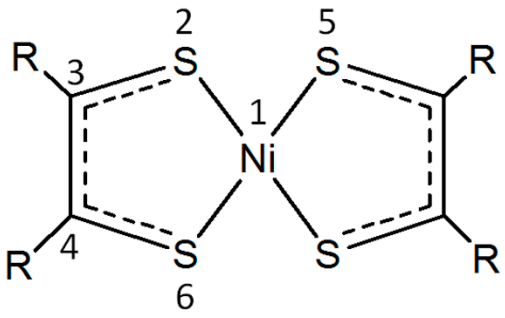


Figure. S1 Chemical structure of substituted nickel dithiolenes. (R=–CN, –H, $–CH_3$).

Table S1 The bond lengths (Å) and bond angles (°) of $Ni(S_2C_2R_2)_2$. (R = –CN, –H, $–CH_3$) using different functionals (the available experimental data is in italics).

Substituent	Functional	C3–S2	S2–Ni1	C3–C4	∠S2Ni1S6	∠S2Ni1S5
R=–H	M06	1.705	2.178	1.373	92.08	87.92
R=–H	M06L	1.704	2.178	1.373	92.08	87.91
R=–H	PBEPBE	1.705	2.178	1.373	92.08	87.92
R=–H	B3LYP	1.705	2.178	1.373	92.08	87.91
Experimental data [2]		*1.71*	*2.15*		*92*	*88*
R=–CH_3	M06	1.706	2.161	1.385	91.73	88.27
R=–CH_3	M06L	1.707	2.178	1.388	90.92	89.08
R=–CH_3	PBEPBE	1.721	2.174	1.395	91.01	88.98
R=–CH_3	B3LYP	1.715	2.169	1.389	90.95	89.05
Experimental data [3]		*1.714*	*2.128*	*1.365*	*91.35*	
R=–CN	M06	1.701	2.164	1.393	92.96	87.04
R=–CN	M06L	1.703	2.180	1.401	92.11	87.89
R=–CN	PBEPBE	1.718	2.178	1.409	92.25	87.75

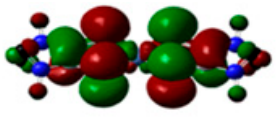
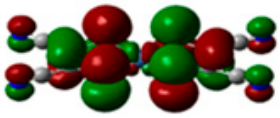
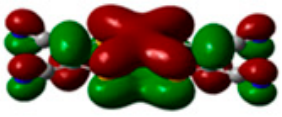
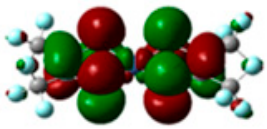
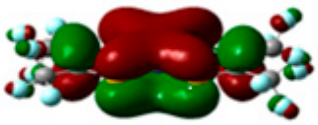
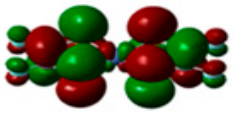
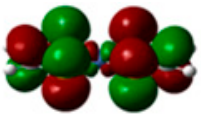
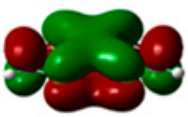
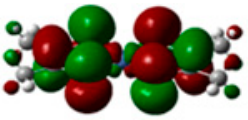
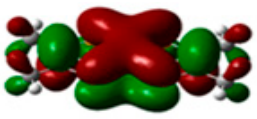
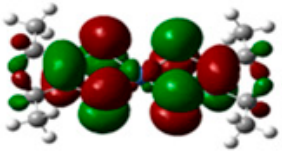
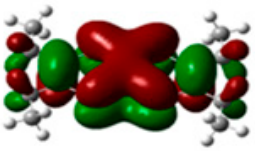
R=–CN	B3LYP	1.711	2.171	1.400	92.12	87.88
Experimental data [2]		*1.72*	*2.15*	*1.37*	*92.5*	*87.5*

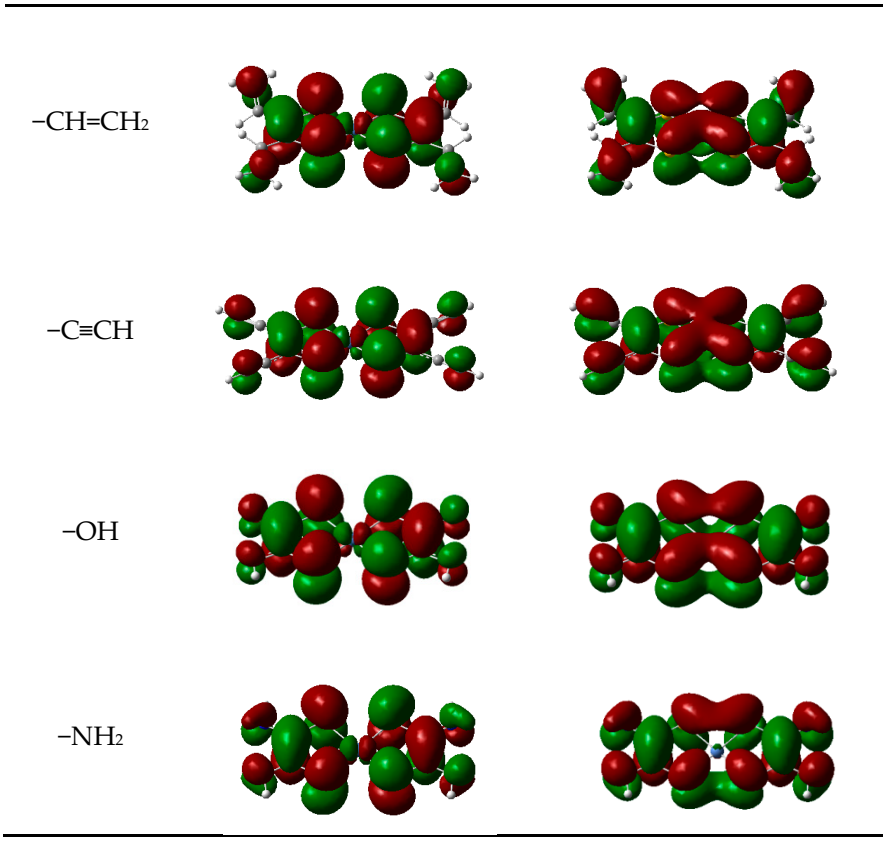
Table S2 The maximum absorption wavelength (cm^{-1}) of $Ni(S_2C_2H_2)_2$ in hexane (the available experimental data is in italics).

	Functional	λ/nm
R=–H	M06	748.59
R=–H	M06L	856.37
R=–H	PBEPBE	841.78
R=–H	B3LYP	714.15
Experimental data [4]		*719*

The Contour of Frontier Molecular Orbitals

Table S3 The frontier molecular orbitals of $Ni(S_2C_2R_2)_2$ optimized by Gaussian 09 software. (R=–NO_2, –CN, –CF_3, –F, –H, –CH_3, –C_2–H_5, –CH=CH_2, –C≡CH, –OH, –NH_2).

Substituent	LUMO	HOMO
–NO_2		
–CN		
–CF_3		
–F		
H		
–CH_3		
–C_2H_5		



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