Supporting Information

Switchable NLO Response Induced by Rotation of Metallacarborane [$\mathrm{Ni}^{\mathrm{III/IV}}(\mathrm{C_2B_9H_{11}})_2]^{-/0}$ and C-, B-functionalized Derivatives

Na-Na Ma,[a] Shu-Jun Li,[b] Li-Kai Yan,[a] Yong-Qing Qiu,*[a] and Zhong-Min Su*[a]

General Comments

S1. Computational details

The ground state of $[Ni^{III}(C_2B_9H_{11})_2]^-$ (**1T**) is open-shell because of d^7 (one unpaired electron) electronic configuration, and $[Ni^{IV}(C_2B_9H_{11})_2]$ (**1C**) is closed-shell compound because of d^6 electronic configuration.[1] Thus the electronic configurations of their derivatives can be determined. **1C** and **1T** maintain their solid-state structures in solution, therefore the geometries were optimized at the B3LYP/6–31+G(d)/Lanl2DZ(for metal Ni) level on the studied compounds in gas phase. The calculated dipole moment of **1C** is 5.54 D, which is close to the experimental one (6.16 D). To obtain accurate electronic properties, the solvent effect was employed by the continuum solvation model SMD[2] involving non-electrostatic interaction. Therefore, a single point calculation in acetonitrile solution was followed by the geometry in gas phase. Calculations of the absorption spectra were performed within the time-dependent density functional theory (TDDFT). Also, to consider the solvent effects in the energy and excitation properties, the SMD model in cyclohexane solution was employed in TDDFT calculations. Four functionals (ωB97X, CAM-B3LYP, PBE0 and M062X) combined with 6–31+G(d) (LanL2DZ basis set for metal Ni) were tested to obtain a rational result that is in accordance with the experimental data. According to the calculated results, the CAM-B3LYP functional has a satisfactory simulation with experimental spectra (Table S1).

The theoretical prediction of redox potential requires the difference of the free energy (ΔG) associated with the process:

$$M^{IV}\ (C) + e- \rightarrow M^{III}\ (T)$$

The ΔG of the reduction process in solution can be obtained by frequency calculations of **1C**–**6C** and **1T**–**6T**. The solvent effects of acetonitrile were included with the SMD model by single point calculations on the basis of the optimized geometries, i.e. at B3LYP/6–31+G(d)/Lanl2DZ level. Therefore, the electronic and thermal free energies in solution, G_{sol}, were obtained by taking account the thermodynamic corrections to the energy in solution, as the equation listed in the following:

$$G_{\mathrm{sol}} = E_{\mathrm{SMD}} + (G - E)_{\mathrm{g}}$$

The ΔG value associated with the reference normal hydrogen electrode (NHE) half-reaction has been calculated to be –4.48 V (in acetonitrile).[3] So the reference standard calomel electrode (SCE) should be –4.72 V. The reduction potentials ($E_{1/2}$) can be calculated according to the Nernst equation $E_0 = -\Delta G_0/nF$.

1. L. F. Warren, Jr. and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1970, **92**, 1157–1173.
2. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396
3. C. P. Kelly, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2007, **111**, 408–422

Table S1 The absorption wavelengths calculated by four functionals to agree with the experimental data

Compound	**M062X**	**ωB97X**	**PBE0**	**CAM-B3LYP**	**Exp.**
1C	450	439	426	433	425
	304	295	299	297	297
2C	415	467	413	459	457
	308	300	301	302	302
3C	--	498	--	503	465
	341	329	418	353	370
	287	271	296	282	289

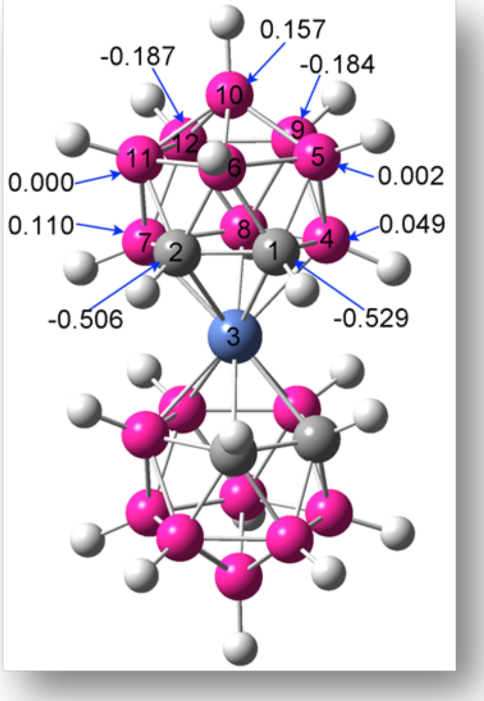
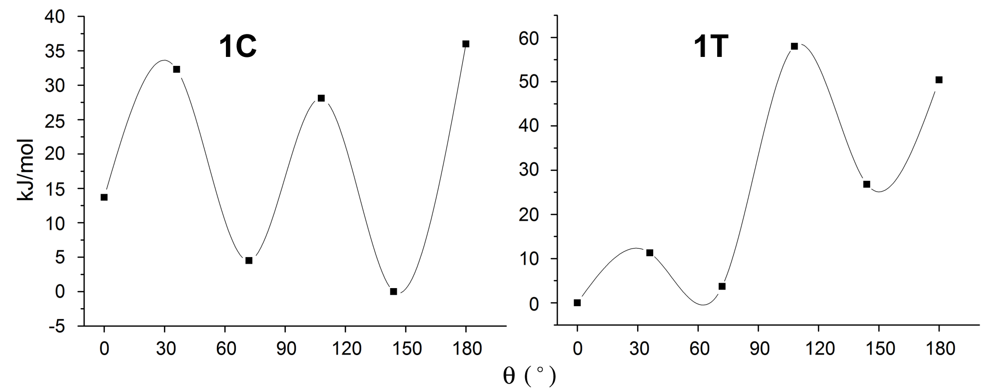
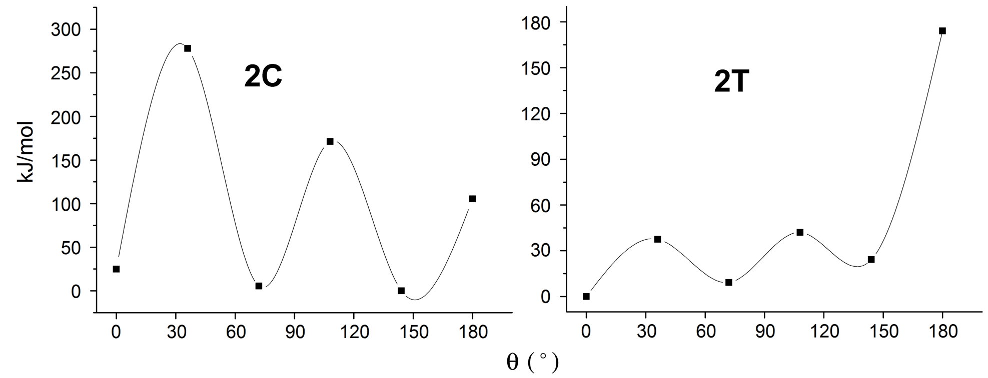


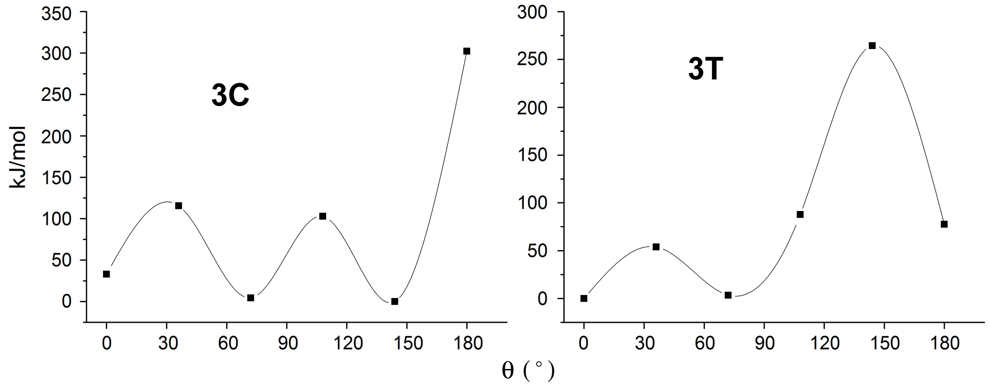
Fig. S1 Natural charge of each atom of **1C**.


1C
1T
kJ/mol
40
35
30
25
20
15
10
5
0
-5
60
50
40
30
20
10
0
0
30
60
90
120
150
180
θ (°)

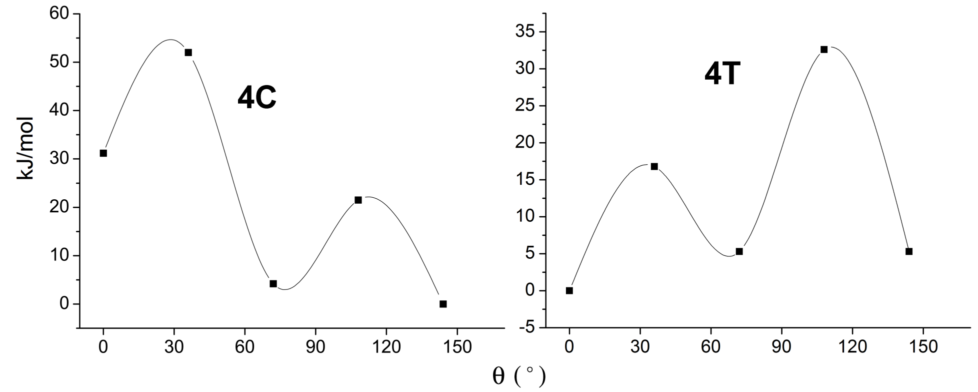
(1)


2C
2T
kJ/mol
300
250
200
150
100
50
0
180
150
120
90
60
30
0
0
30
60
90
120
150
180
θ (°)

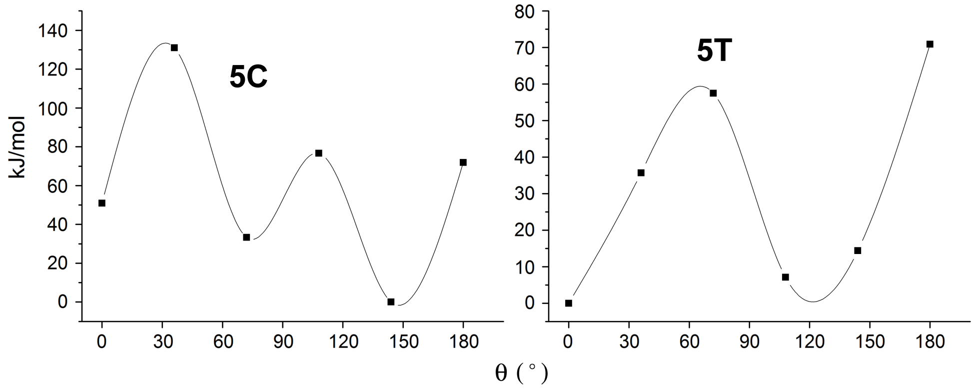
(2)


3C
3T
kJ/mol
350
300
250
200
150
100
50
0
300
250
200
150
100
50
0
0
30
60
90
120
150
180
θ (°)

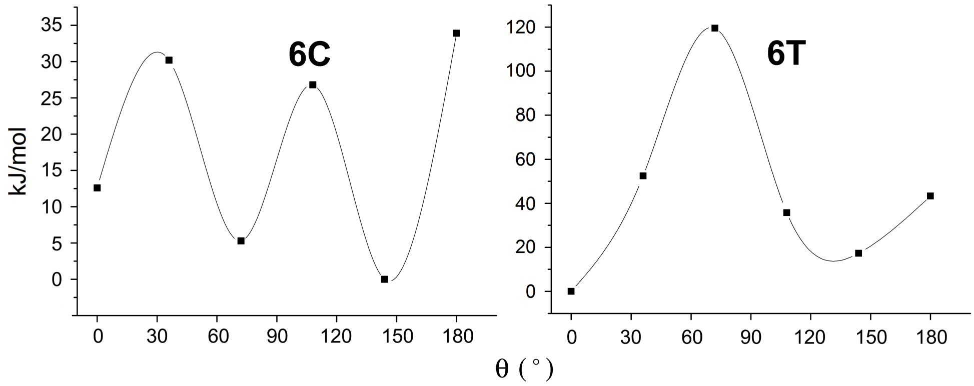
(3)


4C
4T
kJ/mol
60
50
40
30
20
10
0
35
30
25
20
15
10
5
0
-5
0
30
60
90
120
150
θ (°)

(4)



(5)



(6)

Fig. S2-(1-6) Calculated relative energies of the Ni(III) and Ni(IV) compounds **1C**/**1T**–**6C**/**6T**.

For the Ni(IV) compounds, minima are found for θ values equal or close to 0°, 72°, 144°, *i.e.*, with a staggered conformation of the two dicarbollide ligands. Whereas transition states are found for θ values near 180°, 108°, and 36°, *i.e.*, with eclipsed ligands. For the **1T**–**4T** of Ni(III) compounds, the minima are also found for θ values equal or close to 0°, 72°, 144°, and transition states are found for θ values near 180°, 108°, and 36°. There are only two transition states at θ values equal or close to 72°, 180° for the **5T** and **6T**.

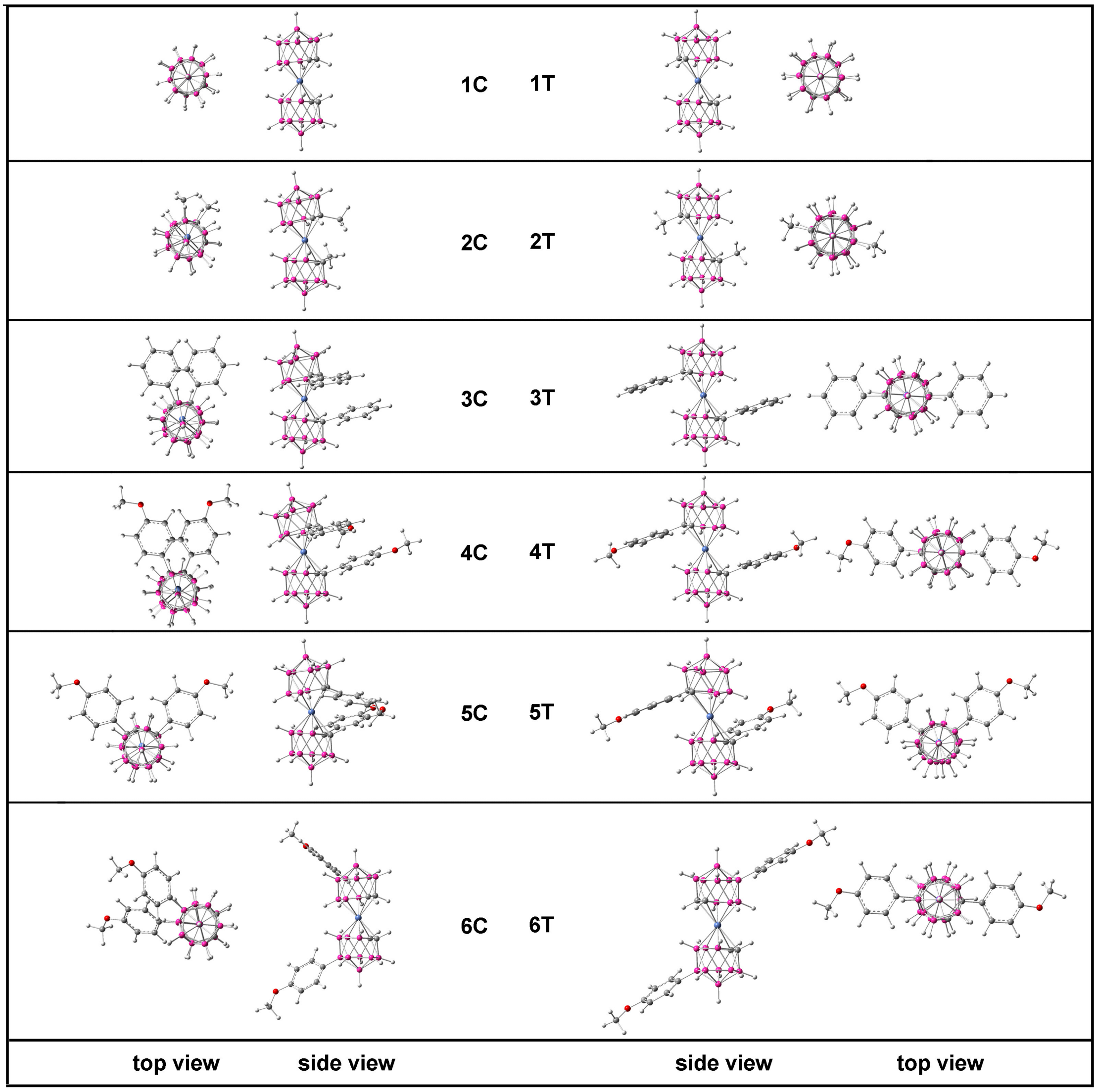


Fig. S3 The optimized geometries of stable states for all studied compounds.

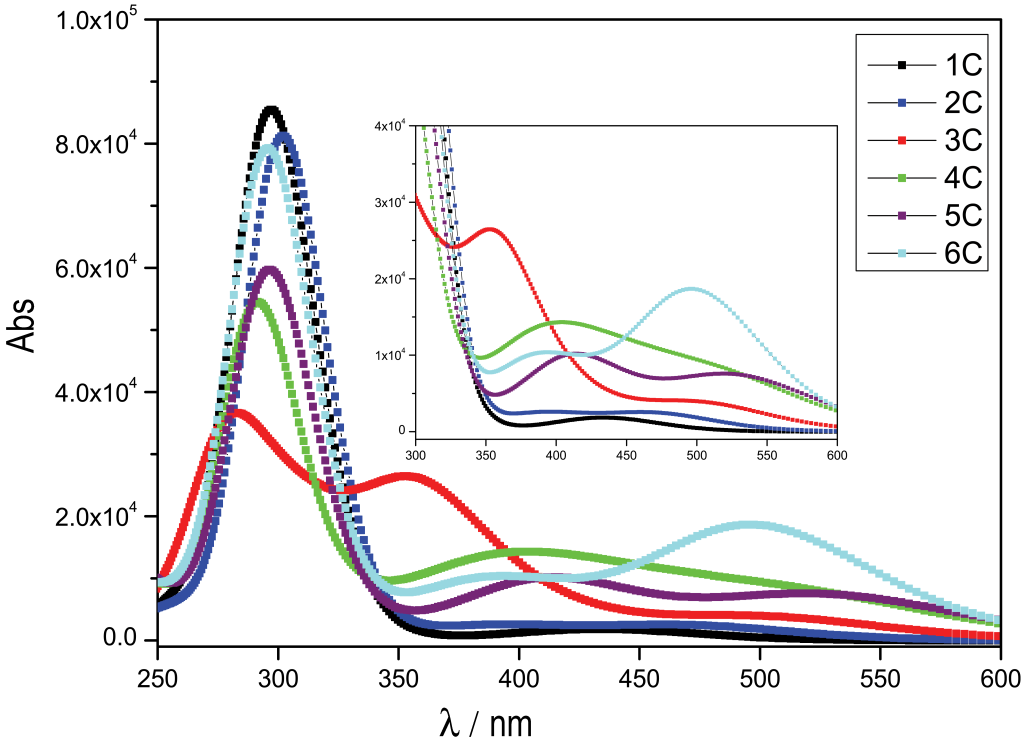


Fig. S4 The absorption spectra of compounds **1C–6C** obtained by CAM-B3LYP/6–31+G(d)/Lanl2DZ.