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Superatoms (Li₃O and BeF₃) Induce Phenalenyl Radical π -dimer: Fascinating Interlayer Charge-Transfer and Large NLO Responses

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Abstract

Recently, the famous phenalenyl radical π -dimer with the fascinating 2-electron, 12-center (2e-12c) have attracted our attention. In this work, we designed two molecules Li₃O^{•••}C₁₃H₉ **1a** and BeF₃^{•••}C₁₃H₉ **1b**. Interestingly, owing to the induction of superatoms, an electron is transferred from Li₃O to phenalenyl in **1a**, while an electron is transferred from phenalenyl to BeF₃ in **1b**. Further, we employed **1a** and **1b** as building blocks to assemble two novel molecules with 2e/12c bond: Li₃O^{•••}(C₁₃H₉)₂^{•••}BeF₃ **2a** and Li₃O^{•••}(C₁₃H₉)₂^{•••}BeF₃ **2b**. Remarkably, **2a** and **2b** with novel 2e/12c bond exhibit a dramatic interlayer charge-transfer character, which results in the significant difference of dipole moments ($\Delta\mu$: 2.6804 of **2a** and 3.8019 Debye of **2b**) between the ground state and the crucial excited state. As a result, the static first hyperpolarizabilities (β_0 : 5154 of **2a** and 12500 au of **2b**) are considerably larger than 347 of **1a** and 328 au of **1b**. It is our expectation that the results of present work might provide beneficial information for further theoretical and experimental studies on the fascinating properties of molecules with the interlayer charge-transfer character.

Keywords: biphenalenyl diradical; 2e/12c bond; interlayer charge-transfer character; superatoms; first hyperpolarizability

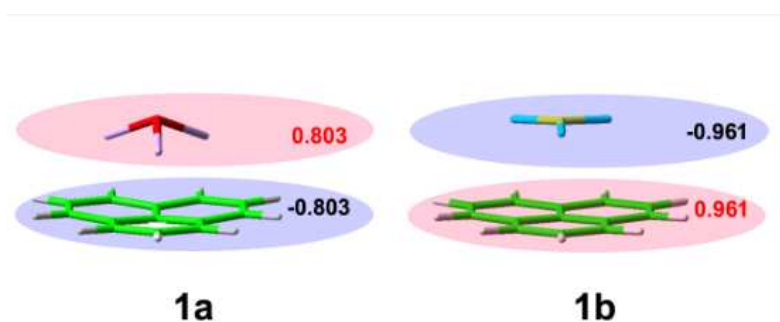
1. Introduction

Due to the fascinating structure and widely application in magnetic and conducting materials fields, a great deal of work has been carried out to study the phenalenyl radical and its derivatives.¹ In 1998, Kosaburo and coworkers synthesized and characterized a stable neutral hydrocarbon radical (2, 5, 8-Tri-tert-butyl-phenalenyl) as a good model of a pancake-bonded dimer with a 2-electron/12-center (2e/12c) bond, which has evoked enormous interest among many scientists.² On the other hand, the biphenalenyl π -dimers derivatives also aroused the interest of theoretical chemists.³ For example, in 2006, Morita and coworkers investigated the CSI-MS and NMR spectra of tri-tert-butylated biphenalenyl π -dimers for the first time.^{3a} Recently, some researchers point out that the short distance of the dimer is an effective way to enhance the electronic transport ability of the device.^{3b} Prof. Kertesz et al. performed many strategies to shorten the distances and strengthen the 2e/12c bonding of phenalenyl derivatives π -dimers, upon β -substitutions.^{3c}

Specifically, in our previous work, the structure and property of the boron/nitrogen substituted biphenalenyl was investigated, in which a novel 2e/12c bond is formed by the electron pair of occupied orbital of N substituted phenalenyl and the unoccupied orbital of B substituted phenalenyl monomers.⁴ Due to the novel 2e/12c bond, the molecules exhibit a fascinating interlayer charge transfer transitions character, which results in the significant difference of dipole moments ($\Delta\mu$) between the ground state and the crucial excited state. Significantly, our calculations demonstrated that boron/nitrogen substituted effect plays a crucial role in the large

first hyperpolarizabilities (β_0). Ever since then, an interesting question is emerging: can the pure biphenenyl also exhibit an interlayer charge-transfer character? (1--Ever since then, an interesting question is addressed: can the pure biphenenyl also exhibit an interlayer charge-transfer character? 2-- Ever since then, a new idea occurred to me: can we use the pure biphenenyl and other building blocks to assemble new molecules exhibiting an interlayer charge-transfer character?)

Fortunately, the induced effect of the superalkalies and superhalogens can give a positive response.⁵ Superalkalies have lower ionization potentials (IPs) than those (5.4-3.9 eV) of alkali atoms, which act as stronger electron donors.⁶ Superhalogens have higher electron affinities (EAs) than those (3.0-3.6 eV) of halogen atoms, which serve as stronger electron acceptors.⁷ In the present work, two molecules $\text{Li}_3\text{O}^{\cdots}\text{C}_{13}\text{H}_9$ **1a** and $\text{BeF}_3^{\cdots}\text{C}_{13}\text{H}_9$ **1b** are formed by superalkali (Li_3O) and superhalogen (BeF_3) induced the phenalenyl. As shown in Scheme 1, let's first focus on **1a**, the Natural bond orbital (NBO) charge of Li_3O is 0.803 (close to +1), indicating that an electron transfer from Li_3O to phenalenyl. However, for **1b**, the NBO charge of BeF_3 is -0.961 (close to -1), which demonstrates that an electron transfer from phenalenyl to BeF_3 .



Scheme 1 The Natural bond orbital (NBO) of **1a** and **1b**

In summary, **1a** and **1b** are used as building blocks to assemble two novel molecules $\text{Li}_3\text{O}^{\cdots}(\text{C}_{13}\text{H}_9)_2^{\cdots}\text{BeF}_3$ **2a** and $\text{Li}_3\text{O}^{\cdots}(\text{C}_{13}\text{H}_9)_2^{\cdots}\text{BeF}_3$ **2b**. The detailed structures of **2a** and **2b** can be described as follows: **1a** adopts the staggered and eclipsed positions with respect to **1b**,

respectively. For **2a**, two neighboring phenalenyls are paired and staggered in a face-to-face fashion. For **2b**, two neighboring phenalenyls are paired and eclipsed. Moreover, the two layers of phenalenyl in **2b** are slightly distorted. In addition, Li_3O and BeF_3 are located in the upper and lower position.

Owing to the induction of Li_3O and BeF_3 , two pieces of phenalenyls carry positive and negative charges, respectively. Remarkably, the pure biphenyl with novel $2e/12c$ bond indeed exhibits a dramatic interlayer charge-transfer character in **2a** and **2b**. Our work may be an important base for researchers synthesize and investigate the molecules with $2e/12c$ bond.

2. Computational Details

The hybrid meta exchange correlation functional (M06-2X) density function theory (DFT) method, has been widely used to optimize the geometries of π -dimers systems.^{3c, 8} Besides, in our previous paper, M06-2X method has been chosen for optimizing boron/nitrogen substituted the central carbons of phenalenyl radical π -dimer and azaphenalenyl radical dimers.^{4, 9} Therefore, the geometrical structures of the molecules were obtained at the M06-2X/6-31+G(d) level.

Furthermore, to correct the basis set superposition error (BSSEs), the counterpoise (CP) procedure was used in the calculations of interaction energies at the M06-2X/6-31+G(d) level.¹⁰ The interaction energy (E_{int}) was calculated as the difference between the energy of the dimer and the sum of the energies of the monomers by the following formula:

$$E_{\text{int}}(AB) = E(AB)_{AB} - [E(A)_{AB} + E(B)_{AB}] \quad (1)$$

The Wiberg bond indexes (WBI) was calculated at the M06-2X/6-31G(d) level.

For the calculation of the first hyperpolarizabilities (β_0), choosing a proper method is very important. Specifically, considering precision and cost, the MP2 method has been proposed to be

the most suitable method to calculate the first hyperpolarizabilities.¹¹ In the present work, the first hyperpolarizabilities were calculated at the MP2/6-31+G(d) level.

The static first hyperpolarizability is noted as:

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

$$\text{Where } \beta_i = \frac{3}{5}(\beta_{iii} + \beta_{ijj} + \beta_{ikk}), i, j, k = x, y, z \quad (3)$$

In this work, the M06-2X method was also employed to evaluate NBO charge. All of the calculations were performed with Gaussian 09W program package.¹²

3. Results and Discussions

3-1. Geometric Structures and Interaction Energies

The optimized geometric structures of the four molecules at the M06-2X/6-31+G(d) level are presented in Figure 1. The frequency calculations confirm that the optimized structures are at the minimum and geometric parameters are listed in Table 1. $C_1^{[a]}$ is the center carbon atom of phenalenyl which is close to Li_3O in **1a**, **2a** and **2b**. And $C_1^{[b]}$ is the center carbon atom of phenalenyl which is close to BeF_3 in **1b**, **2a** and **2b**. From Table 1, for **2a**, the distance of $C_1^{[a]} - C_1^{[b]}$ of **2a** is about 3.041 Å, it is shorter than 3.109 Å of the staggered biphenalenty diradical π -dimer. Additionally, the $C_1^{[a]} - C_1^{[b]}$ distance (3.284 Å) of **2b** is longer than that of **2a**. Compared with our previously work, it shows that the distances of $C_1^{[a]} - C_1^{[b]}$ in **2a** and **2b** are shorter (3.041 Å < 3.137 Å, 3.284 Å < 3.309 Å). This indicates that the attraction interaction of the two pieces of phenalenyls in **2a** and **2b** are stronger than that in B/N substituted the central carbons of phenalenyl radical π -dimer.⁴ In order to compare with experimental results, we took the corresponding calculation on tri-tert-butylated phenalenyl dimer. The distance of central carbon atoms is 3.477 Å, which is close to the experimental values (3.3 Å).¹³

For the purpose of investigating the stabilities of **2a** and **2b**, the interaction energy (E_{int}) was

calculated at the M06-2X/6-31+G(d) level of theory with counterpoise correction and the corresponding results were presented in Table 2. The E_{int} values of **2a** and **2b** (-21.09 and -13.66 kcal mol⁻¹) are larger than the values of the staggered and the eclipsed biphenalenyl diradical π dimer (-16.82 and -6.43 kcal mol⁻¹), which demonstrates that superatoms enhance the stabilities of biphenalenyl. Furthermore, The E_{int} values of **2a** and **2b** are even larger than B/N substituted the central carbons of phenalenyl radical π -dimer (-19.69 and -12.82 kcal mol⁻¹),⁴ which shows that **2a** and **2b** are more stable in comparison with B/N substituted the central carbons of phenalenyl radical π -dimer. In addition, compared with the E_{int} values of **2a** and **2b**, it also reveals that **2a** is more stable than **2b**. In order to draw a firm and reliable conclusion, we compare with the experimental result. We calculated the E_{int} values of tri-tert-butylated phenalenyl dimer by M06-2X (-11.31 kcal mol⁻¹), which is in good agreement with the enthalpy of dimerization measured by quantitative EPR spectroscopy (9.5 ± 1 kcal mol⁻¹).¹⁴

Moreover, the HOMO–LUMO energy gaps (E_{gap}) of the two molecules were also calculated and are listed in Table 2. A similar trend appears in the E_{gap} values, which the E_{gap} of **2a** and **2b** (3.59 and 3.04 eV) are also larger than the value of the biphenalenyl (3.38 and 2.93 eV). Hence, the unusual molecules (**2a** and **2b**) with larger interaction energy and the 2e/12c bond may encourage further investigations in theoretical and experimental aspects.

3-2. Natural bond orbital (NBO) analysis and Wiberg bond indexes (WBI)

The NBO charges were calculated at the M06-2X/6-31G(d) level. From Table 3, we first focus on **2a**, the phenalenyl close to BeF₃ carries positive charges but the phenalenyl close to Li₃O carries negative charges. A similar case can be observed in **2b**. The NBO charges analysis of **2a** and **2b** indicates that long range electron transfer from the Li₃O to BeF₃ through the 2e/12c bond. Such

charge transfer is induced by Li_3O and BeF_3 . Besides, toward a comprehensive understanding of charge transfer, it is also important to discuss their ground-state dipole moment (μ_g). As shown in Table 3, the μ_g values of **2a** and **2b** (16.2876 and 14.5899 Debye) are much larger than that of **1a** and **1b** (0.8395 and 9.0461 Debye).

To further understand the bond character, the analysis of the WBI should be performed. WBI¹⁵ were calculated with the NBO population analysis by using the M06-2X/6-31G(d) method. The WBI of C1-C2 and C3-C4 are 0.027 and 0.008 in **2a**. The total WBI is 0.17, which is the sum of the six pairs of carbon atoms in the same chemical environment as C1-C2 and the center atoms C3-C4 (in Figure 2). The total WBI of 2e-12c bond in **2a** (0.17) is equal to the previously reported 2e-12c bond, which shows **2a** also has an analogous covalent bond. For **2b**, the total wiberg bond index is 0.07, which is smaller than **2a**. It indicates that **2b** is a weaker covalent interaction than **2a**.

3-3. Static First Hyperpolarizability

The static first hyperpolarizabilities (β_0) of the four molecules were obtained at the MP2/6-31+G(d) level and the results are given in Table 3. From Table 3, the β_0 values of **1a** and **1b** are about 347 and 328 au. Interestingly, when **1a** and **1b** as building blocks are used to assemble two novel **2a** and **2b**, the β_0 values dramatically increase to 5154 and 12500 au. Besides, the β_0 of **2a** and **2b** are larger than the values (5154 and 12500 au) of the B/N substituted the central carbons of phenalenyl radical π -dimer (3516 and 12272 au)⁴, which demonstrates that superatoms enhance the β_0 value.

To further understand the origin of the β_0 values, we consider the widely used two-level model¹⁶:

$$\beta_0 \propto \frac{\Delta\mu \cdot f_0}{\Delta E^3} \quad (4)$$

Where the ΔE , f_0 and $\Delta\mu$ are the transition energy, oscillator strength and difference in the dipole moments between the ground state and the crucial excited state, respectively. According to the above expression, the β_0 is proportional to $\Delta\mu$ and f_0 but is inversely proportional to ΔE^3 . The physical quantities in the two-level model may be helpful to qualitatively understand the variation of β_0 of the four molecules.

The f_0 , ΔE and $\Delta\mu$ of the four molecules are estimated crudely by time dependent (TD) M06-2X/6-31+G(d) and the corresponding result are listed in Table 3. Since the third power of ΔE is inversely proportional to the β_0 , it is the decisive factor. We know that the order of the β_0 values is **2b** (12500) > **2a** (5154), inversely to the ΔE values (1.6697 eV for **2b** < 2.2191 eV for **2a**).

Further investigation on the transition properties, we take **2a** as an example to investigate the molecular orbitals of the crucial transition states because the 2e-12c bond of **2b** is similar to that of **2a**. From Figure 4, the crucial transition state (The crucial transition with the lower energy and higher oscillating strength^{1i, 2}) of **2a** is from HOMO to LUMO and the electron cloud to significantly moves from Li₃O to BeF₃ along the 2e-12c bond. It is worth noting that the HOMO of **2a** mainly distribute over the **1a** fragment and the LUMO are mainly distribute over the **1b** fragment resulting in the long range interlayer charge transfer transition, which may lead to the large $\Delta\mu$ value. Besides, as shown in Table 3, β_x values play a crucial role in β_0 values of **2a**, which is the same direction as the charge transfer transition. Therefore, the front molecular orbital analysis confirms that the remarkable β_0 values of **2a** can mainly be attributed to the long range interlayer charge transfer transition induced by the superatoms. The results also show that the superatom interacting with the 2e-12c bond is a new effective mode to introduce the interlayer

charge-transfer transition and obtain a large NLO response, which will be advantageous to facilitate the design of new types of high-performance NLO materials.

4. Conclusions

In the present work, the induced effects of the superatoms (Li_3O and BeF_3) on the phenalenyl radical π -dimer with the fascinating 2e/12c were investigated systematically. Two novel molecules (**2a** and **2b**) with 2e/12c bond were obtained by putting **1a** and **1b** in stagger and eclipse form, respectively. Significantly, **2a** and **2b** with pure biphenlenyl exhibit a dramatic interlayer charge-transfer character. The key points of this work are summarized as follows.

- i. The distance of $\text{C}_i^{[\text{a}]} - \text{C}_i^{[\text{b}]}$ in **2a** and **2b** are shorter than that in B/N substituted the central carbons of phenalenyl radical π -dimer ($3.041 \text{ \AA} < 3.137 \text{ \AA}$, $3.284 \text{ \AA} < 3.309 \text{ \AA}$). It indicates that the attraction interaction in **2a** and **2b** are stronger. Besides, the calculated interaction energy and HOMO-LUMO gap show that the two molecules (**2a** and **2b**) are stable.
- ii. The bonding characters are investigated by frontier molecular orbitals, Wiberg bond index and NBO analysis. It is worth noting that a long range interlayer charge transfer transition is induced Li_3O and BeF_3 , which result in the difference of dipole moments ($\Delta\mu$) between the ground states and the crucial excited states dramatically enhancing. The $\Delta\mu$ values of **2a** and **2b** are 2.6804 and 3.8019, which are larger than those (0.1709 and 0.2706 Debye) of **1a** and **1b**.
- iii. The β_0 values of **1a** and **1b** are about 347 and 328 au. Interestingly, when we used **1a** and **1b** as building blocks to assemble two novel molecules **2a** and **2b**, the β_0 values dramatically increase to 5154 and 12500 au. The order of the β_0 values is **2b** (12500) > **2a** (5154) > **1a** (347) > **1b** (328).

It is our expectation that this work can be beneficial for theoretical and experimental scientists to make further investigations on the NLO response of molecules with the interlayer charge-transfer character.

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Table 1. The selected bond distances (Å) and bond angles (°) of the four optimized structures at the M06-2X/6-31+G(d) level of theory.

	1a	1b	2a	2b
Li-C _i ^[a]	2.785		2.885	2.810-2.831
O- C _i ^[a]	2.960		2.909	2.948
Li-O	1.707		1.711	1.700
F- C _i ^[b]		3.081	3.041	3.083-3.103
Be- C _i ^[b]		2.796	2.720	2.789
Be-F		1.474	1.485	1.474
C _i ^[a] - C _i ^[b]			3.041 (3.137 ^[c])	3.284 (3.309 ^[d])
Li-O-Li	106		111	108
F-Be-F		120	120	120

[a] is the center carbon atom of phenalenyl which is close to Li₃O in **1a**, **2a** and **2b**.

[b] is the center carbon atom of phenalenyl which is close to BeF₃ in **1b**, **2a** and **2b**.

[c] the value is the distance between central atoms in B/N substituted the central carbons of the staggered phenalenyl radical π -dimer (from ref. 14).

[d] the value is the distance between central atoms in B/N substituted the central carbons of the eclipsed phenalenyl radical π -dimer (from ref. 14).

Table 2. The wiberg bond index (WBI), the interaction energy (E_{int} , kcal mol⁻¹) and the energies (eV) of HOMO, LUMO, and the energy gap (E_{gap} , eV) of **2a** and **2b** molecules.

	2a	2b
WBI	0.17	0.07
E_{int}	-21.09 (-10.74 ^[a])	-13.66 (-3.44 ^[b])
LUMO	-2.33	-2.88
HOMO	-5.92	-5.92
E_{gap}	3.59 (3.38 ^[a])	3.04 (2.93 ^[b])

[a] the energy is the staggered phenalenyl radical π -dimer (from ref. 14)

[b] the energy is the eclipsed phenalenyl radical π -dimer (from ref. 14)

Table 3. The natural bond orbital (NBO) of **2a** and **2b** molecules at the M06-2X/6-31G(d) level.

	2a	2b
Li ₃ O	0.836	0.820
phenalenyl ^[a]	-0.637	-0.734
phenalenyl ^[b]	0.784	0.899
BeF ₃	-0.983	-0.985

[a] is the phenalenyl which is close to Li₃O in **2a** and **2b**

[b] is the phenalenyl which is close to BeF₃ in **2a** and **2b**.

Table 4. The first hyperpolarizability (β_0 , a.u.) at the MP2/6-31+G(d) level; the difference of dipole moments ($\Delta\mu$, Debye) between the ground and excited state, the transition energy (ΔE , eV) and the oscillator strength f_0 at the TD-M06-2X/6-31+G(d) level.

	1a	1b	2a	2b
β_x	0	0	-5154	12498
β_y	0	0	-1	16
β_z	347	-328	-2	-229
β_0	347	328	5154 (3516 ^[a])	12500 (12272 ^[b])
f_0	0.1428	0.5532	0.2514	0.1584
ΔE	3.2810	6.7710	2.2191	1.6697
μ_c	2.2968	8.5099	18.9680	18.3918
μ_g	0.8395	9.0461	16.2876	14.5899
$\Delta\mu$	1.4573	0.5362	2.6804	3.8019
$\Delta\mu f_0 / E^3$	0.0059	0.0009	0.0617	0.1294

[a] the value is the β_0 of B/N substituted the central carbons of the staggered phenalenyl radical π -dimer (from ref. 14).

[b] the value is the β_0 of B/N substituted the central carbons of the eclipsed phenalenyl radical π -dimer (from ref. 14).

Figure 1. The optimized structures of the four molecules

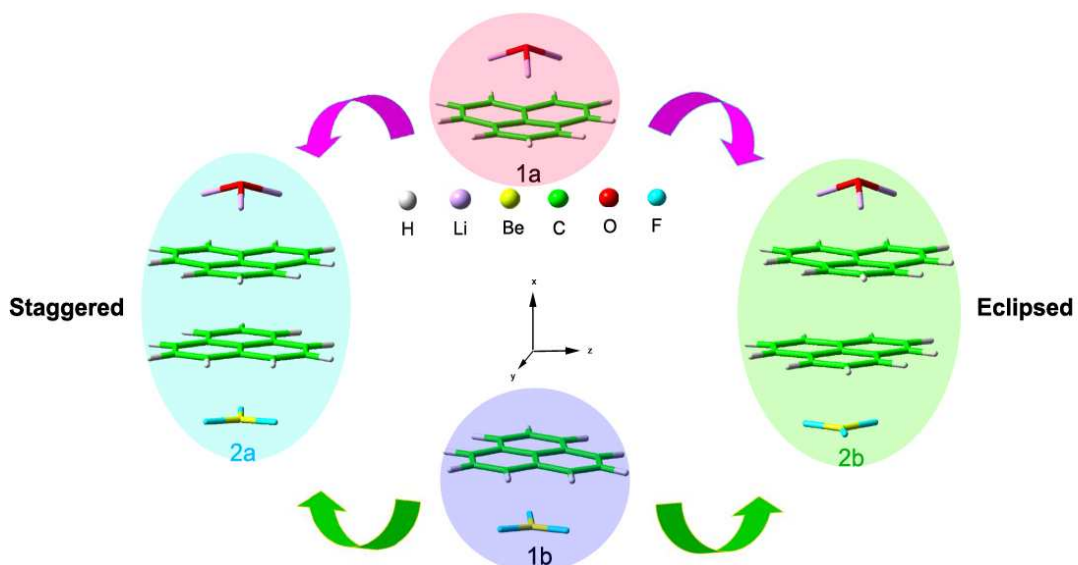


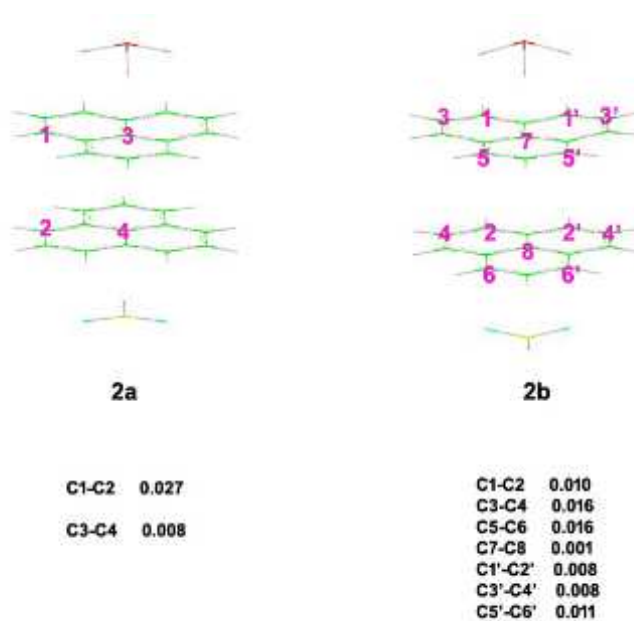
Figure 2. The Wiberg bond indices (WBI) of the **2a** and **2b**

Figure 3. The qualitative molecular orbital diagram for the frontier molecular orbital overlap of the two fragments of **2a** and **2b**

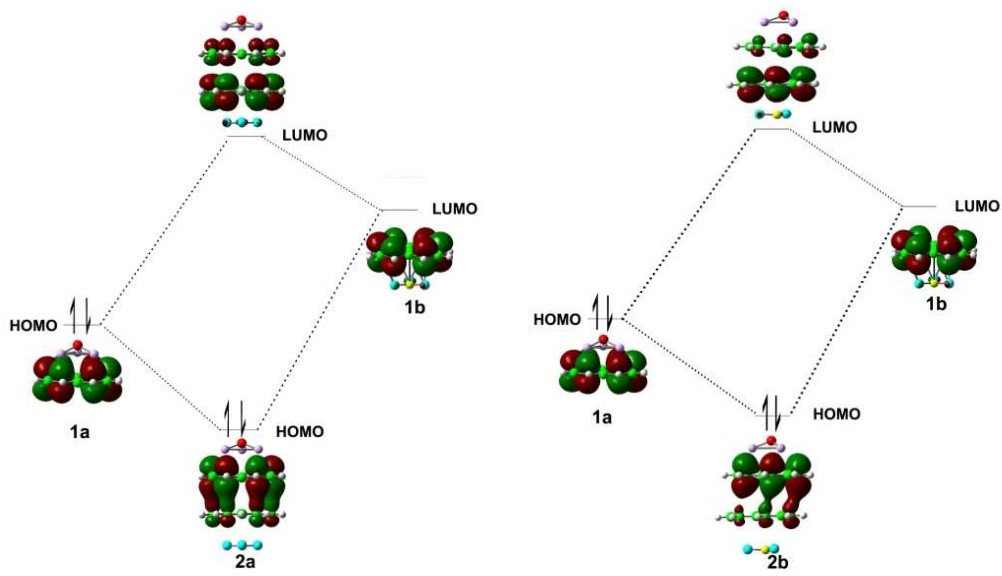


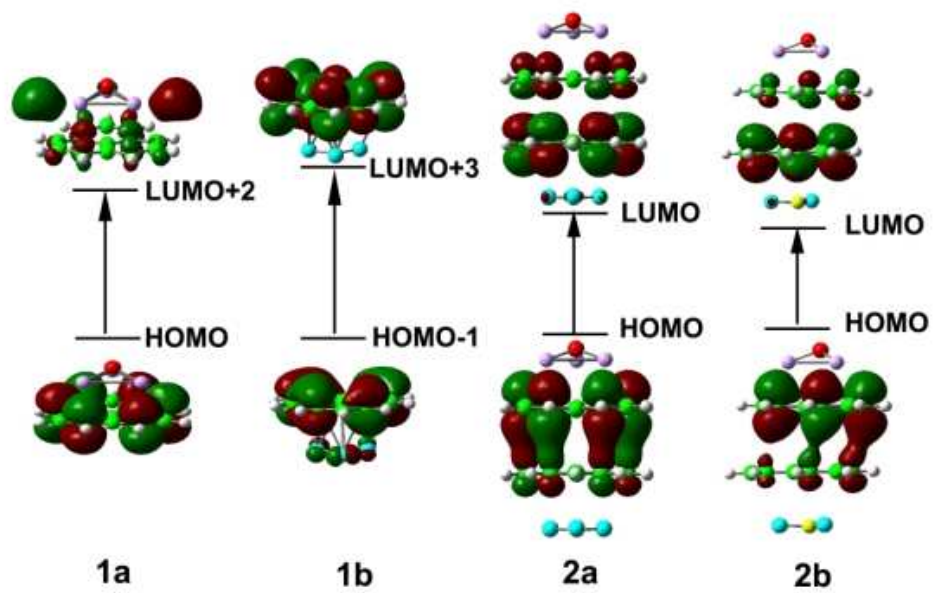
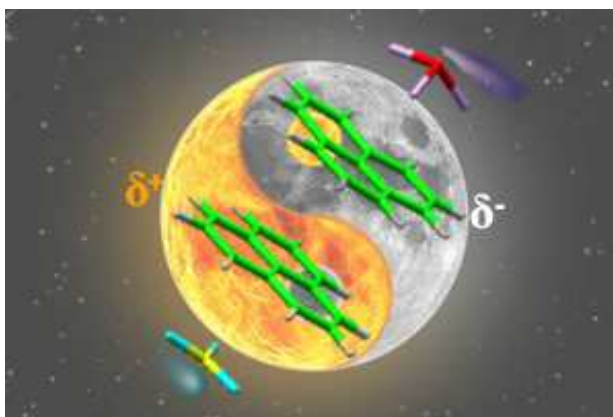
Figure 4. The crucial transitions of the four molecules

Table of Contents



Can the phenalenyl radical π -dimer with the fascinating 2-electron/12-center ($2e/12c$) possess the interlayer charge-transfer character? The induced effect of the superatoms (Li_3O and BeF_3) can give us a positive response. Significantly, the two pieces of phenalenyls in **2a** and **2b** carry positive and negative charges, respectively. Remarkably, **2a** and **2b** with novel $2e/12c$ bond exhibit a dramatic interlayer charge-transfer character, which results in the significant $\Delta\mu$ and considerably larger first hyperpolarizabilities.