Theoretical studies on the photoisomerization-switchable second-order nonlinear optical responses of DTE-linked polyoxometalate derivatives

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ABSTRACT

The switchable second-order nonlinear optical (NLO) responses of the photoisomerized chromophore dithienylperfluorocyclopentene (DTE) derivatives, organic–inorganic systems of Lindqvist-type $[Mo_6O_{19}]^{2-}$, have been investigated by tuning open-ring and the closed-ring form. In the present paper, we performed density functional theory (DFT) combined with finite field (FF) methods to calculate the second-order NLO coefficients for these organic-inorganic compounds. The calculations with three functionals (B3LYP/CAM-B3LYP/LC-BLYP) confirm the switching behavior on NLO properties by the photoisomerization reaction. The β_{tot} value of system 2c (closed-ring form) is 10 times larger than that of its open-ring form (system 2o). And the other two pairs of systems also show good tuning properties. The ampliative ratio on second-order NLO coefficients between systems 2o and 2c (β_{2c}/β_{2o}) is 13 times as large as that of DTE ($\beta_{DTEc}/\beta_{DTEo}$). It suggests that introduction of $[Mo_6O_{19}]^{2-}$ and organic groups to the DTE monomer effectively improve the conversion ratio of second-order NLO coefficients between the open-ring and closed-ring forms.

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1. Introduction

In the past few years, molecular switching has attracted increasing attention. To date, molecular switches exhibiting changes in some properties, such as colors [1,2], luminescence [3,4], optical nonlinearity [5,6], or magnetic properties [7–9], have been reported. Among them, switching on second-order nonlinear optical (NLO) property may be a potentially important approach. It is well known that the molecule-based second-order NLO materials involving new scientific phenomena and offering potential application in emerging optoelectronic technologies [10,11] have attracted much interest. Therefore, the investigation of reversible changes in NLO properties, which are widely applied in molecular switches, possesses great significance.

Organic photochromic materials are commonly divided into the following four species: fulgide, spiropyran, azobenzene and diaryethene. Among these photochromic materials, diarylethene compounds as potential candidates for photochromic applications have attracted much attention because of their outstanding thermal stability and fatigue resistance [12,13]. The molecule undergoes reversible cyclization and cycloreversion reactions of the C—C bond in six members ring when the molecule is stimulated with UV and

visible light. Dithienylperfluorocyclopentene (DTE) (Fig. 1) with good photostability has received extensive attention [14–16]. Furthermore, the NLO properties of an organic molecule containing DTE unit have been studied by Liu using DFT method [17]. The result demonstrates that take the DTE monomer as the π-conjugated bridge can significantly enhance the second-order NLO response. As NLO materials, the organic compounds have several disadvantages, such as low thermal stability; they may undergo a facile relaxation to random orientation and so on. Although inorganic salts possessing a large transparency range are robust and available as large single crystals, the purely electronic NLO effects are often accompanied by those arising from lattice distortions; response times are slow. The limitations identified above spur us to explore new materials. The organic–inorganic hybrid materials are urgent to design and investigate.

Polyoxometalates (POMs) are compounds of early transition metals in their highest oxidation states bounded to oxygen atoms forming discrete oxygen cluster anions [18,19]. POMs as the extremely versatile inorganic building blocks for functionally active materials, covalent attachment of organic or organometallic groups via linkages constitute an extremely interesting class of organic–inorganic hybrid materials [20–22]. Furthermore, the experimental and theoretical investigations have shown that POM-based hybrid complexes hold a remarkably large NLO response [23–25]. POMs as electron acceptors enable the formation of hybrid materials in which the delocalized electrons coexist in both the organic network and the inorganic clusters. Moreover, the first- and

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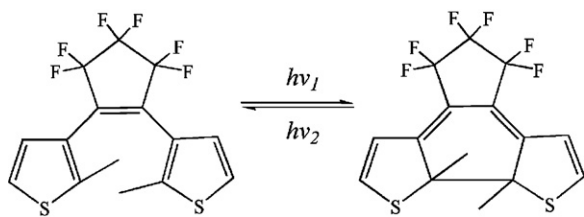
Fig. 1. Photoisomerization of the DTE.

second-order hyperpolarizabilities of POMs and derivatives have been studied by density functional theory (DFT) methods with our group [26–28].

Designing sophisticated switching NLO components that possess some advantages, such as thermal stabilities, higher photoelectric coefficient is an important goal. In this paper, we design a series of organic–inorganic hybrid systems based on Lindqvist-type $[Mo_6O_{19}]^{2-}$ and dithienylperfluorocyclopentene. In these systems, the strong electron donor N,N-bis-(4-methoxyphenyl) phenyl-amino (D) and electron acceptor 2-dicyanomethylen-3-cyano-5-phenyl-5-trifluoromethyl-3,4-dihydrofuran (A) are introduced (Fig. 2). In this paper, we named the open-ring forms with 1o–3o, and the corresponding closed-ring forms with 1c–3c. The switchable second-order NLO responses by tuning open-close ring are investigated in detail on the basis of DFT calculations. This work may provide new hybrid materials with tunable second-order NLO response.

2. Computational details

Herein, three pairs of systems were chosen and shown in Fig. 2. All of the calculations in this work were carried out by using GAUSSIAN 09W program package [29]. The ground states of all systems studied here were closed-shell singlet states and the geometries were optimized by B3LYP method [30–32]. Additionally, the basis set LANL2DZ associated with pseudo-potential was used to describe the Mo atom, and 6-31G (d) was employed for C, N, O, F, S, and H atoms. The static first hyperpolarizabilities (β_{tot}) were calculated by using the finite field (FF) method [33,34] with hybrid functional B3LYP, long range-corrected functionals CAM-B3LYP and LC-BLYP, respectively.

The static first hyperpolarizability, β_{tot} is defined by following equation:

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

where $\beta_i = (\beta_{iii} + \beta_{ijj} + \beta_{ikk})$, $i, j, k = x, y, z$.

Moreover, to obtain a more intuitive description of the trend in the second-order NLO behaviors of systems, the time-dependent density functional theory (TDDFT) method was used to calculate the excitation energies due to its efficiency and accuracy. And the calculation of the natural bond orbital (NBO) analysis is performed
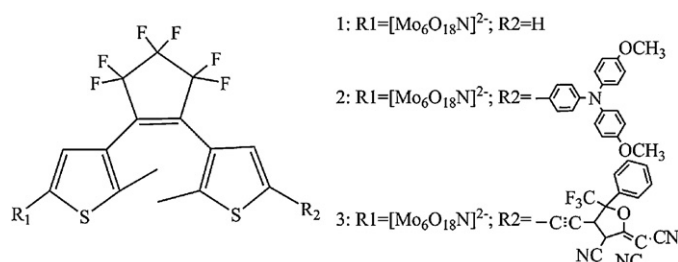

Fig. 2. Calculation models of systems 1o–3o, and systems 1c–3c defined closed forms of 1o–3o.
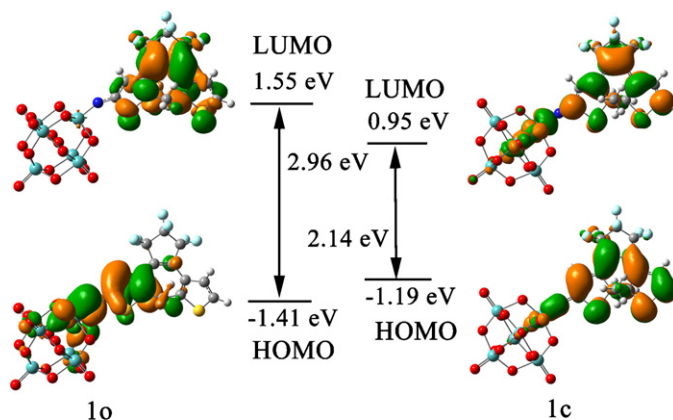

Fig. 3. The electronic structures of systems 1o and 1c.

by the NBO program [35] at the B3LYP/6-31G (d) level (LANL2DZ basis set for Mo atoms).

3. Results and discussion

3.1. Electronic and geometric structure

The strong interaction between molybdenum and nitrogen was attributed to the Mo≡N triple bond, which has been studied in arylimido-hexamolybdate [22]. In order to further confirm the covalent character of Mo≡N, we perform NBO calculations on systems 1o and 1c (Table 1). NBO analysis reveals that the Mo≡N triple bond is composed of a Mo–N σ bond and two Mo–N π bonds. Taking system 1o for an example, the Mo–N σ bond is formed by a Mo ($sd^{1.51}$) orbital and a N ($sp^{0.77}$) orbital, while the two Mo–N π bonds are made up of a hybrid Mo orbital and a pure p-N orbital, respectively. The strong Mo≡N bond that links organic and inorganic segments could lead to some interesting properties.

For all systems, the geometrical optimizations provide a clear difference in geometry between the open-ring and the closed-ring form. Two thiophene rings in DTE are non-planar for open-ring forms of systems 1o–3o, and the dihedral angle between two thiophenes is about 81°–84°. By contrast, the dihedral angle between two thiophene rings of DTE decreases to ~32° for closed-ring form. These changes in the geometry effectively improve π-conjugation for closed-ring form. For two species of open-ring and closed-ring form, the large difference in geometric structure might produce the different electronic structure.

The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for each system are displayed in Figs. 3 and 4. The HOMO of system 1o is d-p π-bond that comes from d_{yz} orbital of Mo atom and p_z orbital of N atom, and the π-bond from the p_z-carbon orbitals of the left thiophene. The large overlap for orbital populations between inorganic and organic segments is well agreement with the bond character analysis by NBO. The LUMO mainly concentrates on cyclopentene and the right thiophene. The HOMO and LUMO are significantly separated because of the non-planar geometric structure for system 1o (open-ring form). In contrast, the closed-ring form system 1c possesses a good π-conjugation because of the relevant good planar arrangement. As for other two pairs of systems, it can be found that the introduction of diverse groups (electron donor N,N-bis-(4-methoxyphenyl) phenyl-amino (D) and electron acceptor 2-dicyanomethylen-3-cyano-5-phenyl-5-trifluoromethyl-3,4-dihydrofuran) did not clearly change the electron density distribution of HOMO, while the LUMOs are affected. For example, the LUMO of system 2o mainly concentrates on the right thiophene ring of the DTE and the first phenyl ring of

Table 1
The analysis of NBO for system 1o.

Natural bond orbitals	Occupancy	Orbital coefficients and hybrids	Orbital type
Mo—N	1.94	$0.48\,(sd^{1.51})_{Mo} + 0.88\,(sp^{0.77})_N$	σ
Mo—N	1.85	$0.53\,(sd^{5.13})_{Mo} + 0.85\,(p)_N$	π
Mo—N	1.75	$0.57\,(sd^{4.76})_{Mo} + 0.82\,(p)_N$	π
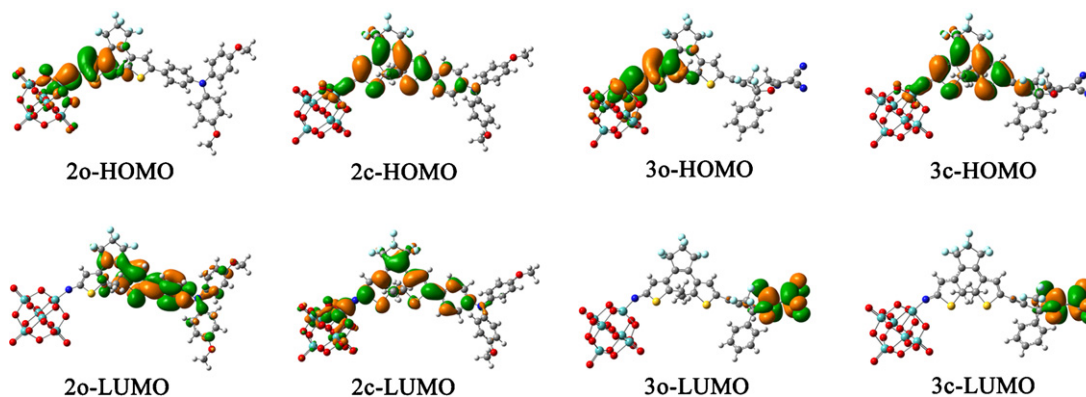
Fig. 4. The frontier molecular orbitals for systems 2o–3o and 2c–3c.

the donor group, while in system 3o, the LUMO localizes over the acceptor group.

The energy levels of HOMO and LUMO for systems 1o and 1c are shown in Fig. 3. The HOMO energy of system 1o is −1.41 eV, which is 0.22 eV lower than that of system 1c, while the LUMO energy of system 1o is higher than system 1c by 0.60 eV. It suggests that the interlinkage of the C—C bond of six members ring heightens the HOMO energy and reduces the LUMO energy. Therefore, the energy gap of HOMO–LUMO for system 1c is smaller than that of system 1o by ∼0.82 eV. In general, the lower HOMO–LUMO energy gap can give rise to larger NLO response.
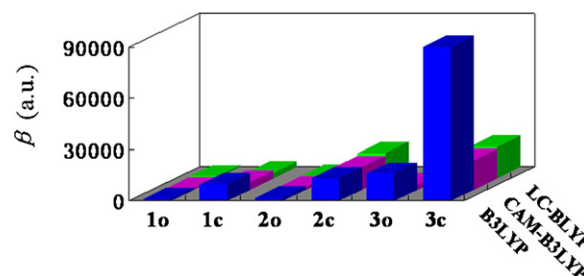
3.2. NLO properties

The static first hyperpolarizability (β_{tot}) has been calculated using the FF method at the B3LYP/CAM-B3LYP/LC-BLYP/6-31G (d) level (LANL2DZ basis set for Mo atoms) in this work. As the data showed in Table 2, the β_{tot} values of systems reveal a strong dependence on functionals. The results from hybrid functional B3LYP are larger than those of the long-range correction functionals except for systems 1c and 3c. For example, the β_{tot} value of system 2o by B3LYP is 2.08 and 3.02 times as large as those of CAM-B3LYP and LC-BLYP. It seems that the B3LYP hybrid functional overestimates the static first hyperpolarizabilities of D-π-A systems because of the incorrect long-range charge transfer behaviors

between donor and acceptor, and the long-range correction has an important effect on the first hyperpolarizabilities. For CAM-B3LYP and LC-BLYP functionals, the results are similar. It illustrates that long-range correction has more significant effect than Hartree Fock (HF) exchange on the estimation of β_{tot} value. Furthermore, we analyzed the β_{tot} values of all systems (Table 2). The β_{tot} values of system DTEo and system DTEc are 278.10 a.u. and 207.99 a.u. by functional CAM-B3LYP, and the difference in β_{tot} value between two systems is subtle. It shows that the structural change from open-ring to close-ring form does not cause the significant change on second-order NLO properties. That is, the DTE does not exhibit the effective switch for NLO in the open-closed ring conversion. Introduced POM and different organic groups to DTE, the static first hyperpolarizabilities are obviously enhanced. For instance, the β_{tot} value of system 2c is 13,174.37 a.u., which is 63.3 times as large as system DTEc according to the CAM-B3LYP calculations. We also found that the multiplying factor between the open- and closed-ring forms for systems 1o–3o and 1c–3c has significantly improved, and the close-ring forms show higher NLO responses. Fig. 5 intuitively exhibits the amplificatory relations for β_{tot} values of systems 1o–3o and 1c–3c. The calculated β_{tot} value of the closed-ring form 2c is about 8 and 10 times larger than the relevant open-ring form 2o according to B3LYP and long-range correction functionals (CAM-B3LYP and LC-BLYP), respectively. Furthermore, the multiplying factor for system 2 (β_{2c}/β_{2o}) is 10 times by CAM-B3LYP result, and is 13-fold relative to that of the system DTE ($\beta_{DTEc}/\beta_{DTEo}$). From structure-property point, the larger β_{tot} values of close-ring forms for organic-inorganic hybrid systems 1c–3c than

Table 2
Computed static second-order polarizabilities (a.u.) for systems 1o–3o and DTEo ($\beta_{tot}(O)$), relevant photocyclized species, systems 1c–3c and DTEc ($\beta_{tot}(C)$).

System	Functionals	β_{tot} (O)	System	Functionals	β_{tot} (C)
1o	B3LYP	1375.93	1c	B3LYP	9823.43
	CAM-B3LYP	806.48		CAM-B3LYP	4722.31
	LC-BLYP	1228.66		LC-BLYP	3250.66
2o	B3LYP	2003.63	2c	B3LYP	13,496.17
	CAM-B3LYP	1347.18		CAM-B3LYP	13,174.37
	LC-BLYP	1515.43		LC-BLYP	14,718.06
3o	B3LYP	16,190.77	3c	B3LYP	89,898.13
	CAM-B3LYP	2937.64		CAM-B3LYP	17,152.24
	LC-BLYP	1464.32		LC-BLYP	18,104.96
DTEo	B3LYP	355.47	DTEc	B3LYP	179.14
	CAM-B3LYP	278.10		CAM-B3LYP	207.99
	LC-BLYP	205.11		LC-BLYP	185.48

Fig. 5. Comparison of the static first hyperpolarizability of systems 1o–3o and 1c–3c.
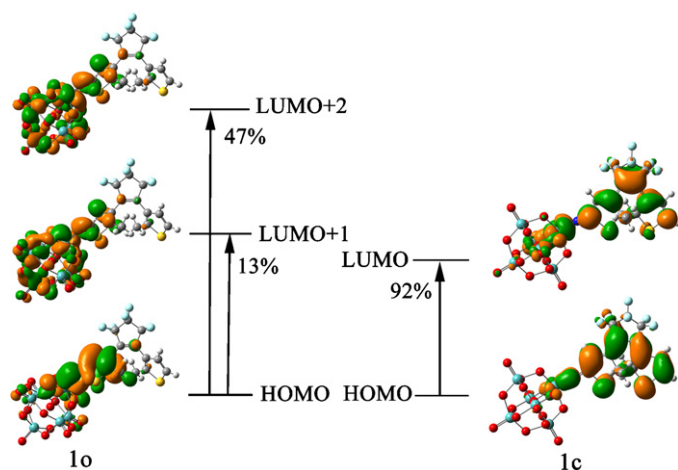
Fig. 6. The dominant electron transition of systems 1o and 1c.

those of the open-ring forms are mainly due to the better conjugated geometry structure. It proposes that the photoisomerization reaction significantly affects the static first hyperpolarizability. So this kind of complexes might be promising candidates for switching NLO materials.

3.3. TDDFT calculations

In order to elucidate the origin of second-order NLO properties of the studied systems, we have performed the TDDFT calculations on the electronic transition. The calculation results show that the crucial excited state of system 1o is mainly made up of HOMO→LUMO+2 (47%) and HOMO→LUMO+1 (13%) transitions (Fig. 6). For system 1o, the HOMO localizes on the Mo≡N triple bond and the left thiophene ring, while the LUMO+1 and LUMO+2 localize on hexamolybdate. Obviously, the electron transition only occurs on the left side of the molecule owing to the large dihedral angle between the two thiophenes. By contrast, the system 1c has better delocalized characteristics on the organic ring. The charge transfer can be assigned to the $\pi\to\pi^*$ transition of DTE, which is much different from that of system 1o. Moreover, the system 1c exhibit larger β_{tot} value than system 1o. So the $\pi\to\pi^*$ transition type may play an important role for NLO properties. To describe the charge transfer simply and effectively, the electronic difference density maps (EDDMs) are plotted in Fig. 7, and the direction of electron transition is from the purple part to the pink. It is found that systems 2o and 3o have the same electron

transfer as system 1o, and the substituted groups do not obviously exhibit its donating/accepting nature because the nonplanar structure reduces the molecular π-conjugation. However, in systems 2c and 3c, the molecule exhibits the good conjugation, which is similar to the system 1c. The charge transfer of DTE can be attributed to the $\pi\to\pi^*$ transition, which may effectively improve the static first hyperpolarizability. In other words, the photoisomerization reaction accompanied by open-ring form to closed-ring form significantly affects the characteristics of electron transfer. The extent of charge delocalization strongly depends on open-ring or closed-ring form of DTE. The degrees of electron transfer and electron delocalization are helpful for enhancing the NLO responses. For DTEo and DTEc, the intermolecular $\pi\to\pi^*$ transition does not play a significant role for the static first hyperpolarizability. This may be related to the transition energy and other factors. Therefore, the two-level formula will be employed to further discussion.

As we all known, the two-level model that linked between β_{tot} and a low-lying charge-transfer transition has been established by Oudar and Chemla [36,37],

$$\beta \propto \frac{\Delta\mu_{gm} f_{gm}}{E_{gm}^3}$$

where $\Delta\mu_{gm}$ is the difference of the dipole moment between the ground state (g) and the mth excited state (m), f_{gm} is the oscillator strength, and E_{gm} is the transition energy. The corresponding data are listed in Table 3. The first hyperpolarizability is associated with those factors, which are controlled by the electronic properties of the donor/acceptor and the nature of the conjugated bridge. In the two-level model expression, the first hyperpolarizability is proportional to the oscillator strength and inversely proportional to the third power of the transition energy. And the low transition energy is the decisive factor for β_{tot} value. As can be seen from Table 3, the transition energies of open-ring forms for systems 1o–3o are higher than those of close-ring forms 1c–3c. For example, the transition energy of crucial excitation of system 2o is 3.14(5) eV, which is 1.7 times as large as system 2c. In other words, the photoisomerization leading to the conversion from open-ring to closed-ring form significantly decrease the transition energy of the crucial excitation, and the small transition energy is in favor of the large first hyperpolarizability. Furthermore, the order of $\Delta\mu_{gm} f_{gm}/E_{gm}^3$ values is closed-ring forms larger than open-ring forms, which is in agreement with β values calculated with the TDDFT method. Although the transition energy of system DTEc is higher than that of system DTEo, while the oscillator strength is lower, this results in smaller β_{tot} value of system DTEc comparing with system
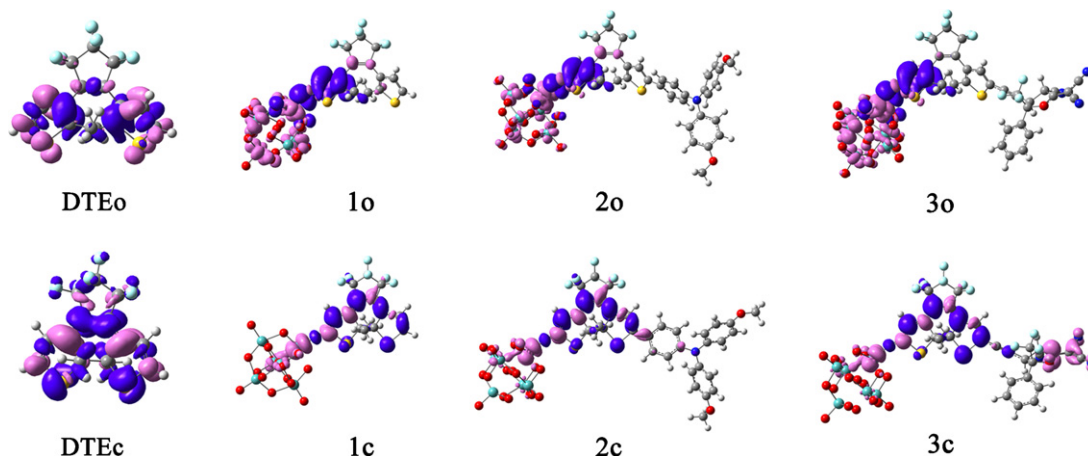

Fig. 7. The electronic difference density map of all systems.

Table 3
The transition energies (*E*, eV), oscillator strengths (*f*), and major contribution of 1o–3o and 1c–3c obtained by CAM-B3LYP.

System	Excited state	E	f	$\Delta\mu_{gm} f_{gm}/E_{gm}^3$	Major contribution
1o	S3	3.14 (8)	0.31	0.020	HOMO→LUMO+2 (47%)
					HOMO→LUMO+1 (13%)
2o	S3	3.14 (8)	0.48	0.038	HOMO→LUMO+3 (62%)
3o	S5	3.15 (5)	0.34	0.023	HOMO→LUMO+6 (57%)
DTEo	S6	5.91	0.30	0.002	HOMO→LUMO+2 (51%)
					HOMO-1→LUMO+1 (39%)
1c	S1	2.13	0.62	0.222	HOMO→LUMO (92%)
2c	S1	1.88	0.98	0.687	HOMO→LUMO (93%)
3c	S1	1.83	0.82	0.567	HOMO→LUMO+1 (76%)
					HOMO→LUMO (17%)
DTEc	S13	6.34	0.17	0.001	HOMO-4→LUMO (74%)

DTEo. The description of two-level model is well in agreement with the second-order NLO response calculation.

4. Conclusion

In this paper, we have performed DFT calculations to investigate the electronic structure and static first hyperpolarizability of the chromophore DTE and the organic–inorganic systems based on $[Mo_6O_{19}]^{2-}$. The optimized calculations showed that the photoisomerization processes significantly affect the geometrical structure that from the open-ring form to the closed-ring form. In closed-ring form of DTE, the relevant planar structure provides a good π-conjugation. Compared with the open-ring systems, the closed-ring systems possess low transition energies of the π→π* transitions, which effectively improve the static first hyperpolarizability. The β_{tot} value of system 2c (closed-ring form) is about 10 times as large as system 2o (open-ring form). In addition, introducing different groups can effectively enhance the static first hyperpolarizability and the amplification ratio between the open-ring and closed-ring forms. The β_{tot} value of system 2c is 63.3 times larger than DTEc, and the multiplying factor of system 2 (β_{2c}/β_{2o}) is 13 times as large as system DTE ($\beta_{DTEc}/\beta_{DTEo}$). On the basis of remarkable changes on the static first hyperpolarizability between open-ring and closed-ring forms, we design series organic–inorganic materials that possess photoisomerization properties, which may be well applied to the field of optical switch.

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