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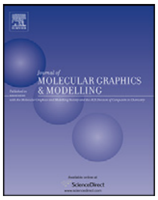

Theoretical studies on the photoisomerization-switchable second-order nonlinear optical responses of DTE-linked polyoxometalate derivatives

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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.

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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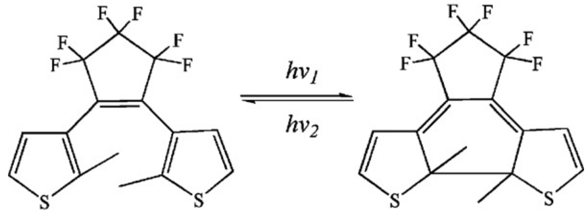

Fig. 1. Photoisomerization of the DTE.

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

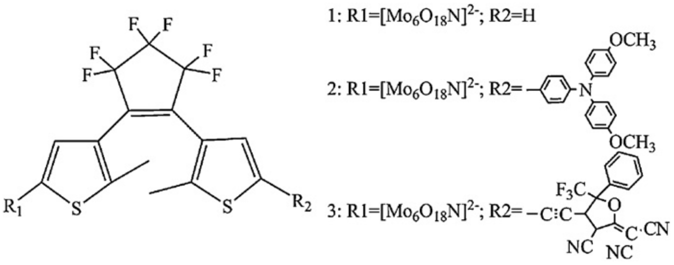

Fig. 2. Calculation models of systems 1o–3o, and systems 1c–3c defined closed forms of 1o–3o.

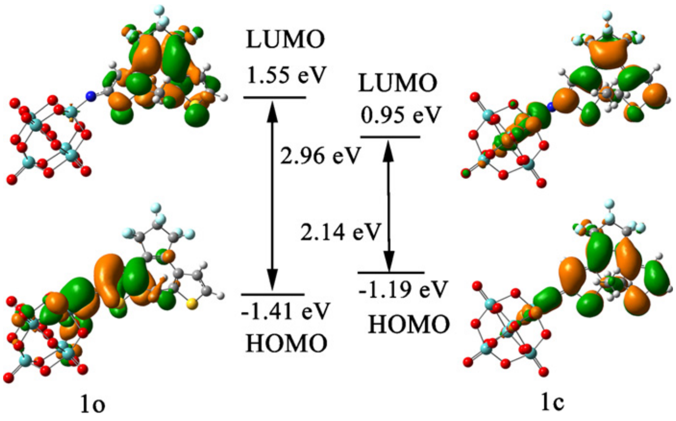

Fig. 3. The electronic structures of systems 1o and 1c.

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