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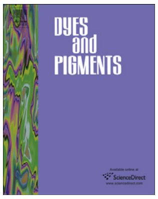

Li doped effect of through novel noncovalent charge transfer on nonlinear optical properties

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ABSTRACT

In the present work, three complexes(**1-Li–NO$_2$**, **1-Li-Mid** and **1-Li–NH$_2$**) were designed by doping Li atom into the different location(above, middle and below) of the novel noncovalent "through-space" electronic interaction (S) of Donor-S-Acceptor (**1**) to explore their structure-property relationships. The results show that doping Li atom can obviously enhance the first hyperpolarizability (β_{tot}) of **1**. Interestingly, the crucial transition direction of **1-Li–NH$_2$** is from donor group to acceptor group, which is opposite to those of **1-Li–NO$_2$** and **1-Li-Mid**. The highest occupied molecular orbital (HOMO) of **1-Li–NH$_2$** shows that doping one Li atom enhances the π–π interaction resulting in the largest β_{tot} value (1.50×10^5) which is about 16 times larger than that of **1**(9.13×10^3) and is also obviously larger than those of **1-Li-Mid**(5.81×10^4) and **1-Li–NO$_2$**(6.45×10^4 au). The results indicate that **1-Li–NH$_2$** can be considered as a novel high-performance NLO material and the location of Li atom can modulate NLO response.

1. Introduction

The last two decades have witnessed progress in the design and synthesis of high-performance nonlinear optical (NLO) materials for their potential use in telecommunication, information storage, optical computing, optical switching, and signal processing [1–15]. Among these investigations, the most typical molecular engineering schemes are based on intramolecular charge transfer processes from a donor toward an acceptor moiety through a π-electron conjugated path, which can be expressed as D–π–A [10–15]. Significantly, in 2000, a new molecular engineering strategy (D-S-A) for NLO introduced by Zyss is different from that of D–π–A [16]. In D-S-A form, S is referred to "through-space" electronic interaction (a novel kind of noncovalent charge transfer [17]), such as arene–arene interaction.

From a more general perspective, arene–arene interactions are key factors in the field of in the selective complexation of π-neutral guests inside cyclophane moieties and molecular clefts [18,19]. Such through-space electronic interactions have aroused increasing attention among scientists in many fields [20–25]. For example, Bartholomew reported clear experimental evidence that through-space octupolar contributes to the first hyperpolarizability β tensor of various multipolar donor-acceptor paracyclophane (PCP) derivatives [23]. And then, Hong demonstrated that through-space delocalization across the [2.2]PCP core is more polarizable in the excited state [24]. Furthermore, on the basis of substituted [2.2]PCP, the impact of extended interchain interactions on the photophysics of π-stacked systems was investigated by Mukhopadhyay [25].

On the other hand, doping Li is an important method to enhance the NLO responses. Many valuable papers show that the NLO responses can be dramatically enhanced by doping Li atoms [26–31]. For example, Yu reported the first attempt on the interaction between the Li atom and the π-conjugated aromatic ring. As a result, the first hyperpolarizabilities of Li-doped aromatic rings are obviously enhanced [30]. What's more, Papadopoulos confirmed that the lithiation effect can lead to an enormous increase in the second hyperpolarizability of the smaller π-conjugated benzene [31].

From the above reports and appealing features of novel noncovalent "through-space" electronic interaction, we are inspired to probe into the research of the interaction between the Li atom and the intermediate cavity of D-S-A. This question is not solved yet, although many papers on the NLO properties of molecules and materials have been published [26–31].

2. Methods

It is well known that the choice of a suitable method is crucial to generate reliable and accurate results. According to previously reported investigations, the global hybrid generalized gradient

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approximation M06-2X functional recommended by Truhlar and Zhao performs well in aromatic–aromatic stacking and main group chemistry [32,33]. The M06-2X functional is a highnonlocality functional with double the amount of nonlocal exchange (2X), which is suitable for medium interaction system [32,33]. Therefore, the optimized geometric structures of all molecules were performed at the M06-2X/6-31G(d) level. All of the geometries were characterized as energy minima at the same level. The values of nucleus independent chemical shifts (NICS) were obtained at the CAM-B3LYP/6-311++G (d,p) level. Furthermore, the calculation of the natural bond orbital [34,35] (NBO) charges was performed at the M06-2X/6-31G(d) level.

In our previous work [36], the interaction energy (E_{int}) calculated by the M06-2X method is almost equal to that calculated by the MRMP2/CASSCF(2,2) method. Therefore, E_{int} in this work was calculated at the M06-2X/6-31 + G(d) level. E_{int} is calculated as the difference between the energy of the Li-doped **1** molecules and the sum of the energies of the Li and **1** according to the equation:

$$E_{\text{int}} = E_{ab}(X_{ab}) - [E_a(X_{ab}) + E_b(X_{ab})]$$

With regard to the calculation of the (hyper)polarizability, choosing a proper method is important. In calculating (hyper) polarizability, the MP2 method is more reliable, but it is quite costly for large systems. Fortunately, because of modest accuracy and computational cost, the coulomb-attenuated hybrid exchange-correlation functional (CAM-B3LYP) has been widely used to predict the optoelectronic properties of charge transfer processes [37–39], which combines the hybrid qualities of B3LYP and the long-range correction presented by Tawada [40]. Recently, the CAM-B3LYP method has been proposed specifically to calculate the first hyperpolarizabilities of π-conjugated systems compared with the other methods [41]. Moreover, the CAM-B3LYP has been proved to be proper in NLO research for Li atom doped systems [42–44]. Therefore, in the present paper, the CAM-B3LYP is employed to explore the first hyperpolarizability with analytical third energy derivatives. The 6–31 + G(d) basis set is employed for all atoms. We have shown that the basis sets chosen in this work for our purpose are adequate. As one can see from Table S1 of the Supporting Information, the β_{tot} value (6.45×10^4) obtained from the 6–31 + G(d) basis set is only about 1% different from the β_{tot} value (6.36×10^4 au) obtained from 6–311 + G(d,p) for structure **1-Li–NO$_2$**. In addition, in this work, a test calculation shows that the trend of the β_{tot} values of our systems (See Table S2 and Figure S1 in the Supporting Information) obtained by BH and HLYP is similar to that of CAM-B3LYP.

The first hyperpolarizability is noted as:

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

Where $\beta_{\text{i}} = \beta_{\text{iii}} + \beta_{\text{ijj}} + \beta_{\text{ikk}}, i,j,k = x,y,z$

All of the above calculations were performed with Gaussian 09W program package [45]. In addition, the hyper-Rayleigh scattering (HRS) response $\beta_{\text{HRS}}(-2\omega;\omega,\omega)$ were evaluated by NLO Calculator program [46,47]. The $\beta_{\text{HRS}}(-2\omega;\omega,\omega)$ is described as:

$$\beta_{\text{HRS}}(2\omega;\omega,\omega) = \left(\left\langle\beta_{zzz}^2\right\rangle + \left\langle\beta_{zxx}^2\right\rangle\right)^{1/2}$$

3. Results and discussions

3.1. Geometric structures

3.1.1. Geometric structures of D-S-A

It is known to all that the structure of a molecule largely determines its chemical properties. Thus, it is very important to select an appropriate structure. For this reason, the D-S-A "model" compound 4-(4-dihexylaminostyryl)-16-(4-nitrostyryl)[2.2]PCP synthesized by Zyss attracted our attention [16]. Taking into account the amount of calculation, molecule **1** was obtained by using the donor (NH$_2$) instead of the donor N(Hex)$_2$ in D-S-A and the new molecular model is shown in Fig. 1. In molecule **1**, the substituted PCP is connected with two sp^3-hybridized linkages. For comparison purposes, molecule **1'** is theoretically designed in which the lateral vertical linkages are two sp^2-hybridized CH=CH. As shown in Fig. 1, the β_{tot} value of **1** is 9.13×10^3 au. Interestingly, when lateral vertical linkages of substituted PCP is replaced by sp^2-hybridized CH=CH in which the conjugacy is enhanced, but the β_{tot} value of **1'** (9.16×10^3 au) change little compared with **1**. The results indicate that two lateral vertical linkages have little influence on β_{tot} values. Thus, the intramolecular charge transfer processes from a donor toward an acceptor moiety is mainly through-space electronic interactions in our designed D-S-A systems.

3.1.2. Geometric structures of Li-doped D-S-A

The above discussions show that noncovalent through-space electronic interaction plays an important role in charge transfer of the D-S-A system. Is there any effective method to modulate the interesting arene–arene interactions? Inspired by the published work [26–31], Li atom is employed to explore the interaction with intermediate cavity of **1** (See Fig. 1). The molecule **1** is divided into two parts. Part I is the upper moiety with the acceptor group (NO$_2$) and Part II is the nether moiety with the donor group (NH$_2$). With the help of Gaussian 09W program [45], three interesting structures (**1-Li–NO$_2$**, **1-Li-Mid** and **1-Li–NH$_2$**) with all real frequencies were obtained. The differences of three molecules are the locations of Li atoms. **1-Li–NO$_2$** is obtained by locating the Li atom above the benzene ring (I) of Part I. In **1-Li–NH$_2$**, Li atom is placed below the benzene ring (II) of Part II. **1-Li-Mid** is obtained by locating one Li atom between benzene ring (I) and benzene ring (II). The energies of the three models are also shown in Table 1. It is worthy of note that the energy ranges from −1502.972 to −1502.984 au. The maximal difference is about 7 kcal mol^{-1}. This indicates that the electronic structures of Li-doped molecules might be different even though their geometries are similar.

3.2. The nucleus independent chemical shifts (NICS)

As we all know, aromaticity is a central concept in chemistry, which is a very crucial property of conjugated cyclic molecules in the determination of their stability. However, aromaticity cannot be measured directly experimentally. Luckily, some valuable papers show that nucleus independent chemical shift (NICS) has a strong

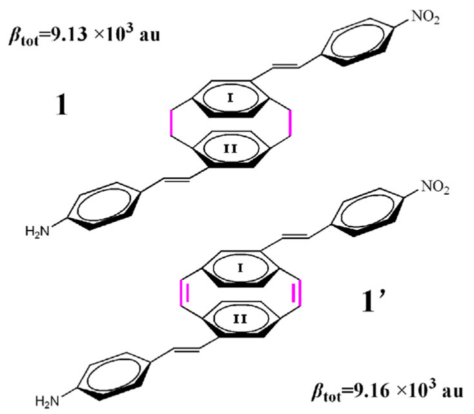

Fig. 1. The optimized structures and β_{tot} values of **1** and **1'**.