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Photophysical properties of chiral covalent organic cages

Qi Shi, Meng Sun, Jinmei Tian, Wenjie Zhang, Guochun Yang *

Centre for Advanced Optoelectronic Functional Materials Research and Laboratory for UV Light-Emitting Materials and Technology of Ministry of Education, National Demonstration Centre for Experimental Physics Education, Northeast Normal University, Changchun 130024, China

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ABSTRACT

Chiral organic compounds are the excellent second-order nonlinear optical (NLO) materials due to their intrinsic non-symmetric structures and combined with the merits of organic compounds. Here, the ground electron structures, excited-state electron transition, and second-order NLO property of novel chiral covalent organic cages (COCs) (Solomek et al., 2017) consisting of naphthalene-1,4:5,8-bis(dicarboximide) (NDI) units, have been fully investigated by DFT/TDDFT. The simulated electron absorption wavelengths are in good agreement with experimental ones, allowing us to assign their electron transition characters with high confidence. Based on the experimental structures, we designed eight compounds to probe the effect of different substitutions on photophysical properties. It is found that the substitution of NH_2 and NO_2 groups at opposite side of NDI and replacement of cyclohex-1,2-diyl with benzene are the most effective way to not only tune energy gaps and electron transition properties but also enhance the NLO response. For instance, the second-order NLO value of compound **2-h** is about 80 times as large as the organic urea molecule. Our work is also important for fully understanding photophysical properties and extending potential applications of chiral COCs.

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1. Introduction

Nonlinear optics (NLO) has widespread applications (e.g. telecommunications, optical storage, and all-optical computing) [1–3]. As a NLO material, large NLO response value is one of the necessary conditions for practical applications. Therefore, designing and synthesizing materials with large nonlinear optical (NLO) responses have attracted considerable attentions [4–9]. Among them, second-order NLO properties, deriving from the second-order polarization, are of the most immediate interest for practical applications. After continuous efforts and attempts, following two strategies have been proved to be greatly effective for enhancing the second-order NLO response. Specifically, one is the involvement of the electron donor and electron acceptor substitutions into the π-conjugated skeleton at appropriate positions [10–14]. In addition, second-order NLO response can be further enhanced by elevating electron-donor and electron-acceptor ability or extending the π-conjugation length [15]. The other way is the usage of chiral compounds, resulting from inherent non-symmetric structures [16]. Up to now, chiral compounds have been deemed as a valuable alternative in the search for new second-order NLO materials [17–23]. The role of chirality in second-order NLO has been reviewed [24].

Much attention has been paid to the covalent organic cages (COCs) because of their rigid structures and broad applications (e.g. selective gas separation and organic electronics) [25–29]. Very recently, a chiral COC, named as compound **3** consisting of three redox-active naphthalene-1,4:5,8-bis(dicarboximide) (NDI) units, was synthesized and well characterized (i.e. X-ray diffraction, ^1H NMR, electron absorption spectra, circular dichroism spectra, and EPR spectrum) [30]. NDI is the smallest homologue of rylene diimides, and exhibits perfectly planar, chemically robust, redox-active, electron-deficient [31,32]. NDI and its derivatives have a variety of applications, ranging from biomedicine to electronics [33,34]. It is noted that, in organic photovoltaic devices and flexible displays, NDI and its derivatives exhibit excellent thermal and oxidative stability, high electron affinity, high fluorescence quantum yield, and high carrier mobility [31,35–37]. Studies have shown that the introduction of electron-withdrawing groups at the imide position of NDI usually causes a strong π-electron polarization [38]. In compounds **3**, chiral cyclohex-1,2-diyl groups were involved into NDI and connected with aromatic imine. This special molecular architecture might offer some intriguing new opportunities for organic photoelectronic materials.

To fully understand the electron transition properties and find the potential applications, a number of compounds were studied, as show in Fig. 1. Among them, compound **1** is composed of a NDI fragment, two cyclohex-1,2-diyls and two aromatic imines, which can be considered as a basic structural unit of compounds

2 and **3**. Compound **2** is the dimerization compound **1**. The other compounds were designed to investigate the effect of donor or acceptor on second-order NLO and find the charge transfer cooperativity. In this work, with the help of density functional theory (DFT) calculations, our goal is to shed light on their frontier molecular orbitals distributions, electronic transition character, and the origin of second-order NLO.

2. Computational details

All of the calculations were carried out in GAUSSIAN 09W program package [39]. The ground state geometries of the studied compounds (Fig. 1) have been fully optimized by using the B3LYP [40] functional, which is a combination of Becke's three-parameter hybrid exchange functional [40] and the Lee–Yang–Parr [41] correlation functional. During the process of optimization, there are no symmetry or internal coordination constraints. Basis sets of 6-31G(d) were applied. There are not any imaginary vibrational frequencies for all the optimized geometries, which confirmed that the optimized geometries were the local minima. The electron absorption energies and transition properties were studied at the TD-B3LYP/6-31G(d) level. We also probed the effect of different DFT functionals on the electron absorption wavelength.

Here, the hyper-Rayleigh scattering (HRS) was used to determine the second-order NLO properties, which can be described as [42,43]:

$$\beta_{HRS} = \sqrt{\langle \beta_{ZZZ}^2 \rangle + \langle \beta_{ZXX}^2 \rangle} \tag{1}$$

The associated depolarization ratio (DR), which gives the shape information of the NLO-phore, reads as follows [44]:

$$DR = \frac{\langle \beta_{ZZZ}^2 \rangle}{\langle \beta_{ZXX}^2 \rangle} \tag{2}$$

β is also typically decomposed into the sum of dipolar ($J = 1$) and octupolar ($J = 3$) tensorial components [1]:

$$\langle \beta_{ZZZ}^2 \rangle = \frac{9}{45} |\beta_{J=1}|^2 + \frac{6}{105} |\beta_{J=3}|^2 \tag{3}$$

$$\langle \beta_{ZXX}^2 \rangle = \frac{1}{45} |\beta_{J=1}|^2 + \frac{4}{105} |\beta_{J=3}|^2 \tag{4}$$

3. Results and discussion

3.1. Molecular structures and stability

The geometric structures of the studied compounds (Fig. 1) were fully optimized at the B3LYP/6-31G(d) level of theory. The absence of the imaginary frequency confirms that the optimized structures are the local minima. Compounds **1**–**3** have been synthesized and characterized by X-ray crystallography [30]. Compound **3** is taken as an example to test the reliability of our adopted functional and basis set. The optimized bond lengths along with experimental ones were shown in Table S1. It is found that the experimental bond lengths were well reproduced by our calculations except C—N bond. Specifically, our optimized C—N bond length is 0.053 Å larger than the experimental value. Similar phenomena were also observed in the compounds containing N atoms [9,45], which might be attributed to the limitation of the current method.

3.2. Electronic structures

It is well known that the electronic and optical properties are closely related to the HOMO/LUMO energy levels, the HOMO-LUMO gaps (energy gap), and the distributions of the frontier molecular orbitals (FMOs). Therefore, it is necessary to investigate these key parameters.

First, we investigated the effect of polymerization on energy levels or gaps of compounds **1**–**3**. Their HOMO/LUMO energy levels and energy gaps are nearly the same, as shown in Fig. 2. This indicates that the coupling between the NDI units are rather weak. To
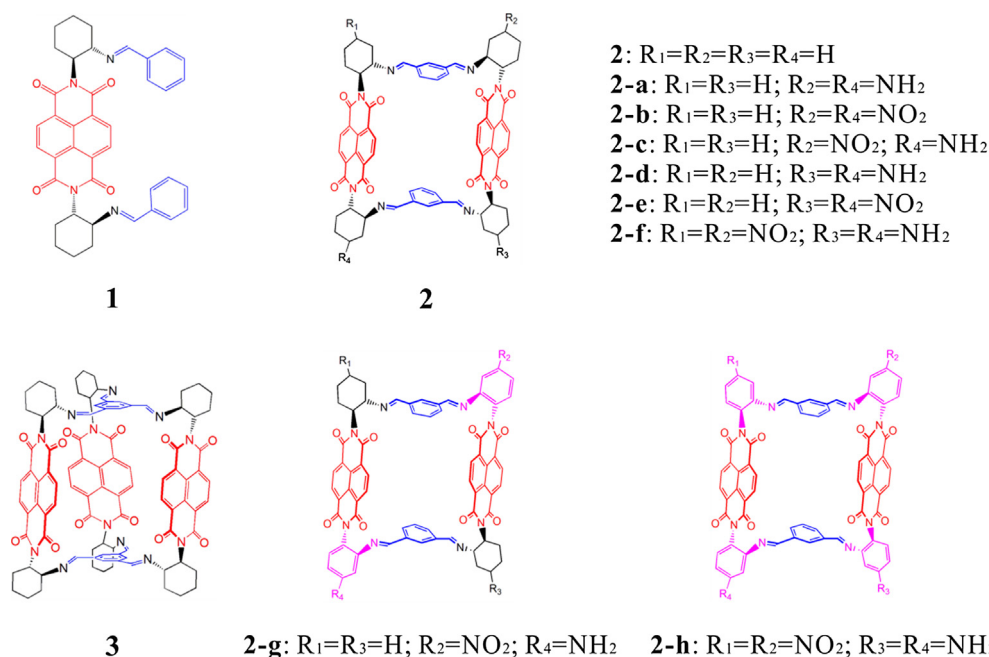

2: R₁=R₂=R₃=R₄=H
2-a: R₁=R₃=H; R₂=R₄=NH₂
2-b: R₁=R₃=H; R₂=R₄=NO₂
2-c: R₁=R₃=H; R₂=NO₂; R₄=NH₂
2-d: R₁=R₂=H; R₃=R₄=NH₂
2-e: R₁=R₂=H; R₃=R₄=NO₂
2-f: R₁=R₂=NO₂; R₃=R₄=NH₂

1 **2**

3 **2-g**: R₁=R₃=H; R₂=NO₂; R₄=NH₂ **2-h**: R₁=R₂=NO₂; R₃=R₄=NH₂

Fig. 1. Chemical structures of the studied compounds. (NDI, red; cyclohex-1,2-diyl, black; aromatic imine, blue; benzene ring, purple.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)