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How the alkali metal atoms affect electronic structure and the nonlinear optical properties of $C_{24}N_{24}$ nanocage

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ABSTRACT

How do the alkali metal atoms affect electronic structure and the first hyperpolarizability (β_0) of $C_{24}N_{24}$ nanocage. In this work, $M_{out}@C_{24}N_{24}$ (M = Li, Na, K) and $M_{int}@C_{24}N_{24}$ (M = Na, K) were designed and investigated in theory using density functional theory. First, two models ($M_{out}@C_{24}N_{24}$ and $M_{int}@C_{24}N_{24}$) is formed by introduction the alkali metal atoms into the $C_{24}N_{24}$ nanocage with different doping sites, the center of four nitrogen atoms and encapsulated into $C_{24}N_{24}$ nanocage. It is revealed that energy gap E_{gap} of $M_{out}@C_{24}N_{24}$ and $M_{int}@C_{24}N_{24}$ decreased obviously in contrast to $C_{24}N_{24}$ cage due to alkali metal atoms effect. Furthermore, introduction the alkali atoms lead to $M_{out}@C_{24}N_{24}$ and $M_{int}@C_{24}N_{24}$ exhibiting considerable first hyperpolarizabilities, which were 1242, 650, 1065 au for $M_{out}@C_{24}N_{24}$ (M = Li, Na, K), and 4772, 106 au for $M_{int}@C_{24}N_{24}$ (M = Na, K), respectively. It is clearly that introduction Li over the center of four nitrogen atoms get large first hyperpolarizabilities for $M_{out}@C_{24}N_{24}$ (M = Li, Na, K), while the different situation is obtained for $M_{int}@C_{24}N_{24}$ (M = Na, K), where introduction Na atom can obtain large first hyperpolarizabilities.

1. Introduction

Over the past twenty years, a great deal of work has focused on the design and synthesis of novel materials with large first hyperpolarizability in view of potential applications in many areas such as optical information processing and optical computing [1–4]. Up to now, the special molecular structures, such as prolonged π-electron molecules [5,6], distorted π-electron molecules [7], donor- π bridge-acceptor framework [8–10], the metal-ligand structures [11–13], octupolar molecules [14,15], have been considered as building blocks to design new high-performance nonlinear optical materials.

Recently, it was revealed that inducting alkali metal atom into a compounds can lead to a large nonlinear optical response due to alkali metal atom effect, where alkali metal atom can donate one electron to form loosely bound excess electrons which is decisive factor in increasing the first hyperpolarizability value. Adopting the effective method in different kinds of species, some promising excess electron compounds were designed and considered as a candidate for exhibiting excellent nonlinear optical response [16–24]. For example, by doping Li atom into a fluorocarbon chain, the $Li_n{-}H{-}(CF_2{-}CH_2)_3{-}H$ can show considerable first hyperpolarizability in the scope of 3694–76978 au, which is greatly increased by about 33–687 times than that of undoped fluorocarbon chain, in which valence electron coming from Li atom is loosely bound and form

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excess electron [18]. By substituting the H atom of adamantane with alkali metal, the compounds can also present large first hyperpolarizability up to 9468–76626 au, in which the valence electron of alkali metal was pushed to get the excess electron [19]. Moreover, previous study on the interaction between alkali metal and the π-conjugated aromatic ring prove that valence electron of alkali metal was pushed out to form the excess electron, which bring about large first hyperpolarizability [25]. In addition, when introducing alkali metal atom into the tetrahedral P_4, a new pattern, interaction between alkali metal atom and σ electron cloud, can also form diffuse excess electrons and exhibit considerable first hyperpolarizability [26].

A large number of studies have proved that introducing excess electron is an effective method to increase first hyperpolarizability. Using the effective strategy, we plan to design a new type nonlinear optical material with large first hyperpolarizability based on inorganic nanocage, which exhibit larger stability in contrast to organic compounds.

The fullerene-like nanocage, as a new nanometer material, have attracted scientists' great interest in the field of experiment and theory, in view of their wide application in catalysts [27], biochemical adsorbent [28], gas sensors [29], and hydrogen storage materials [30,31]. For example, the investigation on interaction between guanine and nanocages ($Al_{12}N_{12}$, $Al_{12}P_{12}$, $B_{12}N_{12}$, and $B_{12}P_{12}$) using density function theory show that all nano-strucyures are promising candidates for sensing of guanine molecule [28]. It is also revealed that Mg-doped $Al_{12}N_{12}$ is used to monitor SO_2 as gas sensor due to decrease in energy gap resulting in large electrical conductivity of a material [29]. Recently, Ti atoms decorated porous fullerene $C_{24}B_{24}$ increase hydrogen gravimetric density up to 8.1 wt%, which exceed the 2017 DOE objective of 5.5 wt% [32]. Transition metal decorated $C_{24}N_{24}$ also achieve excellent hydrogen adsorption capacity, which is considered as promising materials for hydrogen storage [33].

Besides above mentioned potential application, alkali metal atoms doped nanocage, as new inorganic electride compounds, can exhibit considerable first hyperpolarizabilities and will be potential applications for high-performance nonlinear optical properties [34]. In order to regulate binding energies of the compounds, superalkali is adopted to design inorganic electrides based on $Al_{12}N_{12}$, which is found to be high stability, deep-ultraviolet transparency and a large nonlinear optical response [35]. As far as we know, however, there are still few investigations on nonlinear optical response of $C_{24}N_{24}$ nano-cage.

In this paper, we intend to enhance the NLO response of $C_{24}N_{24}$ nano-cage by means of introducing alkali metal atoms. We mainly focus on the following questions. (1) How does alkali metal atoms affect the electronic property of $C_{24}N_{24}$ nano-cage? (2) How does alkali metal atoms affect the absorption spectrum of $C_{24}N_{24}$ nano-cage? (3) How does alkali metal atoms affect the first hyperpolarizability of $C_{24}N_{24}$ nano-cage? Are the first hyperpolarizability of the compound rely on the alkali atomic number (Li, Na, K) and absorption location. In order to clarify these questions, we study the equilibrium geometries, electronic property, absorption spectrum and nonlinear optical responses of $C_{24}N_{24}$ nanocage. We expect that such a theoretical study can provide helpful information for further experimental studies about nonlinear optical materials of $C_{24}N_{24}$ nanocage.

2. Computational details

When a system is in the weak and homogeneous electric field, its energy can be written as [36–38]:

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma - \ldots \tag{1}$$

Here, E^0 is the molecular total energy without the electric field, and F_α is the electric field component along α direction; μ_α, $\alpha_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the dipole, the polarizability, and the first hyperpolarizability, respectively. The dipole moment (μ_0) and polarizability (α_0) are defined as follows:

$$\mu_0 = ({\mu_x}^2 + {\mu_y}^2 + {\mu_z}^2)^{1/2}$$

$$\alpha_0 = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

The first hyperpolarizability is obtained as

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

In which

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

The geometric structures of $C_{24}N_{24}$ and alkali metal atoms doped $C_{24}N_{24}$ were optimized using the B3LYP method with the 6–31G(d) basis set. It is well known that B3LYP method can predict geometric structures of nanostructure, which has been proved by a lot of scientists spending a lot of time to study the relation between nano structures and properties. In order to confirm whether geometric structures is minima in global scope, frequency analysis were carried out at the same level.

Mention to the (hyper)polarizability of system, we have to take into consideration an appropriate method. As is known to all, MP2 method is more reliable compared with B3LYP. When we compute (hyper)polarizability of large molecular