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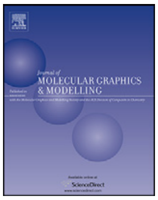

The structure–property relationship of chiral 1,1′-binaphthyl-based polyoxometalates: TDDFT studies on the static first hyperpolarizabilities and the ECD spectra

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ABSTRACT

In this paper, density functional theory is used to investigate the linear optical and nonlinear optical (NLO) properties of a series of Λ-type chiral compounds composed of two Lindqvist-type polyoxometalates (POMs) linked by 1,1′-binaphthyl derivatives through arylimido. It shows that compound **1** which has two POMs on 6-6′-sites of 1,1′-binaphthyl possesses large static first hyperpolarizability and the strongest two-dimensional NLO response among studied compounds. The organic substituents on 2-2′-sites of 1,1′-binaphthyl twofold control the NLO responses of studied compounds. They act as electron acceptors or donors therefore suppress or enhance the NLO responses of studied compounds, and they restrain the torsion angles between two naphthyl rings at certain degrees which are inversely proportional to the NLO responses. Compound **6** with remarkable NLO response is obtained as ferrocene substitutes on 2-2′-sites of 1,1′-binaphthyl. Additionally, the electronic circular dichroism (ECD) spectra of studied compounds are simulated with CAM-B3LYP and B3LYP hybrid functionals. The results agree well with the experimental ECD spectra. The charge-transfer transitions from organic fragment to POM are responsible for the ECD differences between molecular hybrids and their precursors. It is confirmed that these Λ-type chiral compounds are potentially high-dimensional NLO materials and the structure–property relationship of these compounds is presented.

1. Introduction

Polyoxometalates (POMs) are early transition-metal (usually W^{VI}, Mo^{VI}, and V^{V}) oxide with the extensive capability of attaching organic groups on the surface of the cluster [1]. If suitable organic ligands are available, they can be exploited to make chiral POM derivatives. These chiral derivatives have attracted much attention in scientific research fields due to their merits in asymmetric catalysis [2], molecular recognition [3], and marvelous structures [4]. Recently, many chiral POM derivatives have been synthesized and characterized by electronic circular dichroism (ECD) spectra [5–8]. In spite of the splendid studies in experiment, the quantum chemical studies of chiral POMs are few [9]. Moreover, chiral molecules have been exploited and modified to show nonlinear optical (NLO) responses [10]. It is prior that chiral molecules seldom pack into crystals in center space group due to their inherent noncentrosymmetry, which is necessary to generate electric-dipole-allowed second-order NLO response. In the cases of helical-shaped molecules, the magnetic-dipole and quadrupole contributions to NLO responses are significant compared with the electric-dipole contributions, therefore the NLO responses are further enhanced [11]. Another interesting character of chiral molecule in nonlinear optics is that the optical activity can be observed based on nonlinear process [12]. The NLO activity is more sensitive than linear optical activity. Thus techniques based on nonlinear optical activities are increasingly applied to detect the surface chirality [13] and the second-order structures of protein and DNA [14,15].

In 1996, the NLO response of POM was firstly observed by Niu et al. in noncentrosymmetric-space-group crystal of Keggin-type POMs and organic substrates, and the third-order susceptibilities were studied [16]. Traditionally, large NLO response molecules are those chromophores composed of electron donors and acceptors, which are linked through an intervening π-bridge [17]. POMs have been the subject of NLO studies [18–20]. The NLO responses of POMs were improved through directional design and synthesis [21–23]. The theoretical studies on NLO properties of POM-based compounds have been systematically carried out by our group using time-dependent density functional theory (TDDFT) methods [24,25]. The π-bridge lengths were optimized to improve the second-order NLO response [26], and different organic substituents

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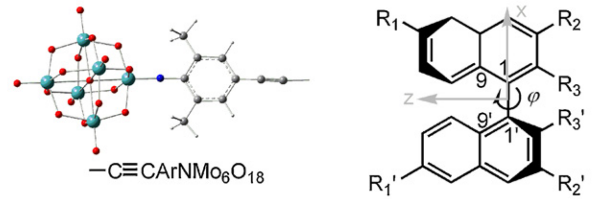
1: $R_1 = R_1' = -C{\equiv}CArNMo_6O_{18}$; $R_2 = R_2' = H$; $R_3 = R_3' = OEt$ **2**: $R_1 = R_1' = H$; $R_3 = R_3' = OEt$; $R_2 = R_2' = -C{\equiv}CArNMo_6O_{18}$



$\mathbf{3}_{30^\circ}$, $\mathbf{3}_{70^\circ}$, and $\mathbf{3}_{100^\circ}$: $R_1 = R_1' = -C{\equiv}CArNMo_6O_{18}$; $R_2 = R_2' = R_3 = R_3' = H$; $\varphi = 30°, 70°$, and $100°$

4, **5**, and **6**: $R_1 = R_1' = -C{\equiv}CArNMo_6O_{18}$; $R_2 = R_2' = H$; $R_3, R_3' = -COO-$, $=SiMe_2$, or $-CpFeCp-$

Fig. 1. The calculation models.

combined with the π-bridge were studied to give different electron transitions and NLO responses [20]. Recently, we investigated the NLO properties of Λ-type POM derivatives, which are based on the reversible metal-centered redox process. The results show that this kind of derivatives is promising candidates for two-dimensional-NLO (2D-NLO) materials [27].

1,1′-Binaphthyl has been widely used to generate novel chiral materials [28,29]. It can be used as a bridge to link two Lindqvist-type polyanions through π-bridge arylimido, therefore Λ-type compounds **1** and **2** are formed (Fig. 1) [30]. These chiral compounds are potentially multifunctional materials bearing NLO responses. On the basis of this structural regime, we design several analogs (compounds **4**, **5**, and **6** in Fig. 1) by introducing different electron acceptors and donors on 2,2′-sites of 1,1′-binaphthyl to investigate the influence of electron acceptor–donor substitutions on NLO responses. Moreover, the torsion angle between two naphthyl rings is fixed at different degrees (compounds $\mathbf{3}_{30^\circ}$, $\mathbf{3}_{70^\circ}$, and $\mathbf{3}_{100^\circ}$ in Fig. 1) to detect the influence of conjugation on NLO responses. In this work, the second-order NLO properties of Λ-type binaphthyl–hexamolybdate compounds are investigated by using TDDFT methods. The linear optical activities of compounds **1** and **2** and their precursors 1,1′-bi-6,6′-ethynyl-2,2′-binaphthol ($\mathbf{1}_{\text{ligand}}$) and 1,1′-bi-3,3′-ethynyl-2,2′-binaphthol ($\mathbf{2}_{\text{ligand}}$) [30] are discussed by ECD calculations. We aim to address the structure–property relationship of Λ-type POM derivatives. Our work provides a novel idea to design high-dimensional POM-based NLO materials combining with chirality.

2. Computational methods

2.1. Molecular structures

Compounds **1** and **2** were synthesized, while the crystal structures were not available [30]. The structures of compounds **1** and **2** were constructed based on the structures of 1,1′-bi-6,6′-ethynyl-2,2′-binaphthol [31] and arylimido-substituted Lindqvist-type polyoxomolybdate [32]. Compounds $\mathbf{3}_{30^\circ}$, $\mathbf{3}_{70^\circ}$, and $\mathbf{3}_{100^\circ}$ were generated by removing the ethoxyl groups from compound **1**, and the torsion angles between two naphthyl rings (φ-9-1-1′-9′ in Fig. 1) were restrained to 30°, 70°, and 100°, respectively. On the basis of the optimized structure of compound **1**, the structures of compounds **4**, **5**, and **6** were constructed via replacing the ethoxyl groups on 2-2′-sites of 1,1′-binaphthyl by electron donors dimethylsilane [33], ferrocene [34] and acceptor lactone [35], respectively. Compound **4** was optimized without any symmetrical constraint, and other compounds were optimized under C_2 symmetry. According to the crystal structures of 1,1′-binaphthyl derivatives, compound **4** was of *R* stereochemistry, while other compounds were of *S* stereochemistry.

2.2. The static first hyperpolarizability calculations

Geometry optimizations were carried out using ADF2008.01 program [36]. The local density approximation (LDA) characterized by the Vosko–Willk–Nusair (VWN) parametrization [37] for correlation was used. The generalized-gradient approximation (GGA) was employed by using the Becke [38] and Perdew [39] exchange correlation (XC) functional. The zero-order regular approximation (ZORA) [40] was adopted in all the calculations to account for the scalar relativistic effects. The basis functions were Slater-type sets. Triple-ζ plus polarization (TZP) basis sets were used to describe the valence electrons of all atoms. For transition metal Mo atom, a frozen core composed of 1s to 3spd shells was described by means of single Slater functions. Moreover, the value of the numerical integration parameter used to determine the precision of numerical integrals was 6.0. All the structures were optimized in a model solvent accounted for with the conductor-like screening model (COSMO) [41] implemented as part of the ADF code. To define the cavity surrounding molecules, we used the solvent-excluding-surface method and a fine tesserae. The ionic radii, which actually define the size of the solvent cavity the target molecule remains, were chosen to be 1.26 Å for Mo atom, and 1.52 Å, 1.70 Å, 1.55 Å, and 1.20 Å for O, C, N, and H, respectively. The dielectric constant (ε) was set to be 37.5 for modeling the effects of acetonitrile. The following TDDFT calculations were carried out in acetonitrile solvent. The static first hyperpolarizabilities were calculated by the RESPONSE module and the excited state calculations were carried out under the EXCITATIONS module in ADF. The "gradient-regulated connection potential" (GRAC) [42] corrects the Kohn–Sham potential in the outer "asymptotic" region therefore leads to improved virtual orbitals. Our previous work confirmed the efficiency of GRAC on calculating the excited states of large POM systems [43]. Thus GRAC was used to calculate the static first hyperpolarizabilities and electron transitions of studied compounds.

2.3. ECD calculations

Coulomb-attenuating method (CAM-B3LYP) [44] was developed to overcome the deficiencies of B3LYP in dealing with Rydberg and charge-transfer (CT) excitations. The CAM-B3LYP functional improves the ECD calculations of conjugated systems than traditional density functionals, such as B3LYP [44]. For the past few years, the CAM-B3LYP functional has been applied to study the excited properties of large metal-containing systems [45–48]. The ECD spectra of compounds **1** and **2** and their precursors $\mathbf{1}_{\text{ligand}}$ and $\mathbf{2}_{\text{lignad}}$ were calculated by TDDFT/CAM-B3LYP ($\alpha = 0.19$, $\beta = 0.46$, and $\mu = 0.33$) method [49] from the standpoints that DFT are computational cost agreeable for calculating large POMs and these compounds are expected to be CT-excitation-dominated systems [27]. The effective core potential (ECP) basis set LANL2DZ [50] was used to describe the electrons of all atoms in compounds **1** and **2**, while SVP basis set was used to describe all atoms in $\mathbf{1}_{\text{ligand}}$ and $\mathbf{2}_{\text{lignad}}$. For comparison, the ECD spectra of $\mathbf{1}_{\text{ligand}}$ and $\mathbf{2}_{\text{lignad}}$ were also discussed by B3LYP functional. Solvent effect, which proves to have great influence on molecular ECD spectrum [51], was considered with polarizable continuum model (PCM) [52] in acetonitrile reaction field. The lowest 150 excited states were calculated for simulating the ECD spectrum of compounds **1** and **2**, and 40 excited states for $\mathbf{1}_{\text{ligand}}$ and $\mathbf{2}_{\text{ligand}}$. The ECD calculations were carried out in Gaussian 09 program package [53].

To consolidate the absorption spectrum calculations, the UV–Vis and the ECD spectra of compounds $\mathbf{1}_{\text{ligand}}$, $\mathbf{2}_{\text{ligand}}$, **1**, and **2** were also simulated at the GRAC/TZP level by using ADF2008.01 program [54].