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Theoretical Study on the Considerable Second-Order Nonlinear Optical Properties of Naphthylimido-Substituted Hexamolybdates

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The static first hyperpolarizabilities and origin of nonlinear optical (NLO) properties of [(2-methylnaphthyl)imido]hexamolybdates derivatives have been investigated by density functional theory (DFT). The [(2-methylnaphthyl)imido]hexamolybdate has considerable large first hyperpolarizability, 6.780×10^{-30} esu, and it is larger than that of [(2,6-dimethylphenyl)arylimido]hexamolybdate due to the double aromatic rings in the naphthylimido ligand. The naphthylimido ligand acts as an electron-donor and the polyanion acts as an electron-acceptor. The substituent position on the naphthylimido is a key factor to determine the first hyperpolarizability of (naphthylimido)hexamolybdate derivatives. The derivative, which the iodine atom locates on the para nitrogen on the naphthylimido ligand, has the largest β_0 value among the iodine-substituted derivatives. It suggests that the iodine atom is quasi linear with nitrogen and Mo, which is bonded to the nitrogen atom, could generate a large static electronic field and give the large contribution to NLO response. The introducing of electron-donors significantly enhances the first hyperpolarizabilities of (naphthylimido)hexamolybdates comparing with the electron-acceptors as the electron-donating ability is significantly enhanced when the electron-donor is attached to the naphthylimido segment. The present investigation provides important insight into NLO properties of (arylimido)molybdate derivatives.

1. Introduction

Polyoxometalates (POMs) are a rich class of inorganic cluster systems and exhibit remarkable chemical and physical properties, which have been applied to a variety of fields, such as medicine, catalysis, biology, analytical chemistry, and materials science.[1] Over the past few years, there has been increasing interest in the chemistry of organically derived POMs.[2] Among the many organic derivatives of POMs, organoidimide derivatives have been drawing increasing attention in that the strong d−π interaction between the organic delocalized π electrons and the cluster d electrons may result in fascinating synergistic effects.[3] The organoimido derivatives of Lindqvist-type polyoxometalates, $[M_6O_{19}]^{n-}$, are a unique class of building blocks that are very suitable for this purpose because a Lindqvist ion has a superoctahedral structure approach to the O_h point group and the ion features its six terminal metal-oxo groups aligned along the Cartesian axes. Potential applications in molecular electronics and photonics of dumbbells and *cis*- or right-angled disubstituted derivatives have also been discussed by Peng and co-workers.[4]

The design of new molecular materials with large second-order nonlinear optical (NLO) responses has been the subject of extensive theoretical and experimental investigations for several decades because of their potential applications in low-cost, high-performance photonic and electro-optical devices.[5] Among the NLO materials, the organic compounds are of major interest because of their relatively low cost, ease of fabrication and integration into devices, tailorability that allows one to fine-tune the chemical structure and properties for a given nonlinear optical process, low dielectric constants, fast nonlinear optical response times, and off-resonance nonlinear optical susceptibilities comparable to or exceeding those of ferroelectric inorganic crystals. But organic materials have several disadvantages: low-energy transitions in the UV−vis region enhance the NLO efficiency but result in a tradeoff between nonlinear efficiency and optical transparency, they may have low thermal stability, and (in poled guest−host systems) they may undergo a facile relaxation to random orientation.[6] The limitations identified above spur the investigations on new materials.

Very recently, our group has been much interested in the investigations on the first and second hyperpolarizability of polyoxometalates and derivatives[7] using density functional theory (DFT), which has emerged as currently the most applied method to investigate the properties of POMs.[8] The main results are as follows: (1) The organoimido-to-polyanion charge transfer may be responsible for the NLO properties of this kind of compound. (2) Lengthening of organoimido π-conjugation or increasing the organoimido polyanion is helpful to enhance the β and γ values. (3) The strong interaction generates a strong electronic communication between arylimido and $[Mo_6O_{19}]^{2-}$.

Recently, the tetrabutylammonium salt of [(2-methylnaphthyl)imido]hexamolybdate, $[(n\text{-}C_4H_9)_4N]_2[Mo_6O_{18}(N\text{-}1\text{-}C_{10}H_6\text{-}2\text{-}CH_3)]$, which contains a conjugation between the d electron system of the POM and the p−π electron system of the double aromatic rings was synthesized by Wei.[9] The double aromatic rings would be helpful to the intramolecular charge transfer. So we are encouraged to investigate the NLO properties of (naphthylimido)hexamolybdates and its derivatives.

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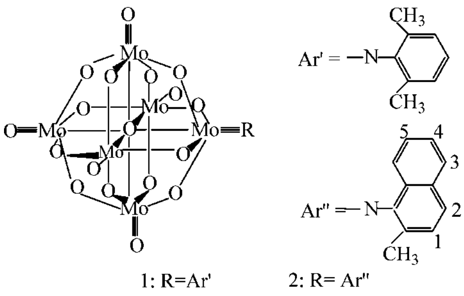

Figure 1. Calculation models.

In the present work, we performed DFT calculations on naphthylimido-substituted hexamolybdates to predict their first hyperpolarizabilities. The effect of the naphthylimido modification on the first hyperpolarizabiliy is investigated in detail. This work may provide a useful means for designing high-performance nonlinear optical materials.

2. Method and Computational Details

The DFT calculations were carried out using the ADF2006.01 program.[10] Geometries of all systems were optimized, where the initial geometric data were obtained from the crystal data.[9] The local density approximation (LDA) characterized by the Vosko−Wilk−Nusair (VWN)[11] parametrization for correlation was used. The generalized-gradient approximation (GGA) was employed in the geometry optimizations by using the Beck[12] and Perdew[13] exchange−correlation (XC) functional. The zero-order regular approximation (ZORA) was adopted in all the calculations to account for the scalar relativistic effects.[14] The basis functions were Slater-type sets. Triple-ζ plus polarization basis sets were used to describe the valence electrons of all atoms, whereas for transition metal molybdenum 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.

The NLO coefficients of all systems were calculated with the ADF-RESPONSE module[15] based on the optimized geometries. The adiabatic local density approximation (ALDA) was used and the Van Leeuwen−Baerends potential[16] (LB94) that corrects the LDA potential in the outer region of the molecule was also performed. The statistical average of orbital potentials (SAOP) by Gritsenko, Baerends et al.[17] was used to calculate the excitation energy.

3. Structures

First, system **2** ($[\mathrm{Mo_6O_{18}(N\text{-}1\text{-}C_{10}H_6\text{-}2\text{-}CH_3)}]^{2-}$) was optimized, and the structure is shown in Figure 1. The 2,6-dimethylphenyl (arylimido)hexamolybdate (system **1**) is also shown in Figure 1. The naphthylimido ligand ($\mathrm{N\text{-}1\text{-}C_{10}H_6\text{-}2\text{-}CH_3}$) is covalently bonded to a terminal position of hexamolybdate in system **2**. The short Mo−N distance and collinearity of C−N−Mo are similar to the other (arylimido)hexamolybdates (see Table 1).[4d−f]

4. Results and Discussion

4.1. Static First Hyperpolarizabilities of System 2. The static first hyperpolarizability (β_0) is denoted as

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

$$\beta_i = (3/5)\sum\nolimits_{j=x,y,z} \beta_{ijj}$$

The first hyperpolarizabilities of all systems considered in this study were calculated under the static electronic field. The β_0 value of system **1** $[\mathrm{Mo_6O_{18}R}]^{2-}$ (where R = 2,6-dimethylphenyl) is 4.732×10^{-30} esu.[8b] Here, the system **2** presents considerable large β_0 value, 6.780×10^{-30} esu, which is larger than that of system **1**. The exist of double aromatic rings in system **2** does not only prompt conjugation between the d electron system of the POM and the p−π electron of naphthylimido ligand, but more importantly, it extends the π electron system. In other words, system **2** possesses a lengthened conjugation bridge comparing with system **1**. It is responsible for the enhancement of the first hyperpolarizability.

TABLE 1: Selected Bond Lengths (Å) and Angles (deg) for System 2

	cal	exp[a]
Mo−N−C	171.685	171.520
C−N	1.356	1.392
N−Mo	1.801	1.740

[a] See ref 9.

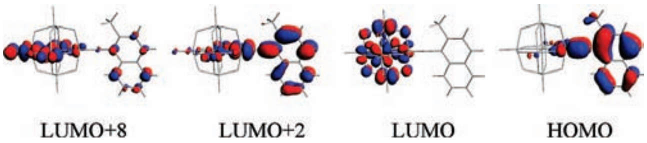

Figure 2. Frontier molecular orbitals of system **2**.

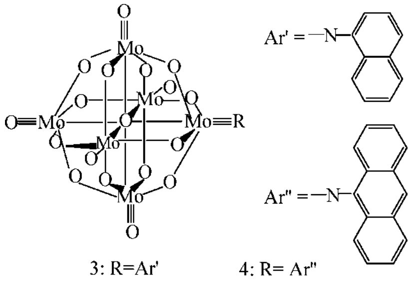

Figure 3. Calculation models.

From our previous study, the main origin of the NLO properties of system **1** is the charge transfer from organoimido to polyanion. What is the origin of NLO properties in system **2**?

The excitation energy was calculated to study the transition nature of system **2**. The transition energy of system **2** is 401 nm (the experimental value is 357 nm), which is generated by the promotion of the electron from HOMO to LUMO+2 and HOMO to LUMO+8. The frontier molecular orbitals are shown in Figure 2. These transitions can be assigned to the charge transfer from naphthylimido segment to $[\mathrm{Mo_6O_{19}}]^{2-}$. The naphthylimido ligand acts as an electron-donor and polyanion acts as an electron-acceptor. In addition, LUMO+8 and LUMO+2 have interesting points, the p−π−d−π bond in POM cluster, which would enhance the NLO responses.

In comparison, the (naphthylimido)hexamolybdate without any substituent on the naphthyl ring, which was synthesized by Wei,[18] is named as system **3** and investigated in this work. The anthracenimido-substituted hexamolybdate, system **4**, is also compared. The chemical structures of system **3** and **4** are shown in Figure 3. The calculated β_0 value of system **3** is 3.470×10^{-30} esu, which is smaller than that of system **2**. In system **2**, the $\mathrm{CH_3}$ group on the naphthyl ring attributes the electron-donating ability of organic segment, so the charge transfer is stronger than that of system **3**, and the β_0 value is larger than system **2**. As for anthracenimido-substituted hexamolybdate, there are several conformers, the system **4**, which has the lowest

TABLE 2: First Hyperpolarizabilities β_0 ($\times 10^{-30}$ esu), Transition Energy E_{ge} (nm), and the Oscillator Strength f_{eg} for Iodic-Substituted (Arylimido)hexamolybdates

system	β_0	E_{ge}	f_{eg}
2	6.780	401	0.1452
		406	0.0890
21′	2.578	402	0.0180
		398	0.0151
		397	0.0156
22′	21.584	409	0.1081
		408	0.0208
		409	0.0617
23′	4.535	406	0.0582
		360	0.0296
		405	0.0457
24′	6.899	406	0.0445
		400	0.0163
		410	0.0615
25′	4.141	360	0.0318
		378	0.0262

TABLE 3: First Hyperpolarizabilities of System 5−9 ($\times 10^{-30}$ esu)

system	**5** ($N(CH_3)_2$)	**6** (NH_2)	**7** (OCH_3)	**8** (OH)	**9** (NO_2)
β_0	42.608	28.280	17.305	16.157	14.236

TABLE 4: Excitation Energy (nm), Oscillator Strengths, Major Contribution for Systems 2 and 5−9

systems	excitation energy	f_{eg}	major contribution
			HOMO → LUMO+8 58.85%
2	401	0.1452	HOMO → LUMO+2 18.20%
5	442	0.3218	HOMO → LUMO+8 56.41%
			HOMO → LUMO+4 28.74%
			HOMO → LUMO+8 63.81%
6	450	0.1580	HOMO → LUMO+3 19.26%
			HOMO → LUMO+8 61.14%
7	418	0.2518	HOMO → LUMO+2 23.93%
			HOMO → LUMO+8 63.85%
8	420	0.1917	HOMO → LUMO+2 24.52%
			HOMO−6 → LUMO 46.33%
9	426	0.2141	HOMO−9 → LUMO 30.38%
			HOMO−5 → LUMO 10.81%

energy, is selected to study the NLO property. The calculated β_0 value of system **4** is 13.380 × 10^{-30} esu, which is larger than that of system **2** and **3**. Three aromatic rings in system **4** prompt conjugation and extend the π electron system, so the first hyperpolarizability much larger than that of system **2** and **3**.

4.2. Substituted Position Effect on the First Hyperpolarizabilities of the (Naphthylimido)hexamolybdate Derivatives. There are several ways to enhance the second-order NLO property of hexamolybdate arylimido derivatives, such as adding the organoimide segment, increasing the π-conjugation length, and so on. Is there another efficient way to modify the electron-donating ability of arylimido? As it was well-known, the properties of hexamolybdate derivatives can be modified by introducing an iodine atom to the arylimido ligand.[4d] Does the iodic arylimido modify the NLO response of hexamolybdate derivative? Which is the best substituted position in arylimido ligand?

According to the carbon atom labels of naphthyl in the naphthylimido ligand (N-1-$C_{10}H_6$-2-CH_3) (as shown in Figure 1), we denoted the iodic-substituted (naphthylimido)hexamolybdates as systems **21′**, **22′**, **23′**, **24′** and **25′** (i.e., the iodine atom locates on the position 1 of N-1-$C_{10}H_6$-2-CH_3 ligand is named as system **21′**).

The conjugation bridges of these systems are the same, but the substituted positions of iodine atom are different. The calculated first hyperpolarizabilities under the static electronic field are listed in Table 2. As a comparison, the corresponding values of their parent system (system **2**) are also shown in Table 2. From Table 2, we can find that the β_0 value of system **22′** is 3 times larger than that of its parent system, but **21′**, **23′** and **25′** are all smaller than that of system **2**. That is, the substitution in position 2 is more favorable. The iodine atom position on the naphthylimido is a key factor to determine the first hyperpolarizability. In other words, the NLO response of (naphthylimido)hexamolybdate derivatives can be modified through substituted position effect.

To understand the iodine atom position effect on the first hyperpolarizability of iodic-substituted (naphthylimido)hexamolybdate, the two-level models of first hyperpolarizability are considered.[19,20] The static first hyperpolarizability is expressed by the following expression[21]

$$\beta \propto \frac{\Delta\mu_{eg} f_{eg}}{E_{ge}^{\ 3}} \tag{2}$$

where $\Delta\mu_{eg} = \Delta\mu_e - \Delta\mu_g$ is the change of dipole moment between the ground and excited (charge transfer) state, E_{ge} is the transition energy and f_{eg} is the oscillator strength. The first hyperpolarizability is jointly determined by three quantities ($\Delta\mu_{eg}, f_{eg}, E_{ge}$). As mentioned above, our studied systems possess the same conjugation bridge, which means there is not much difference in $\Delta\mu_{eg}$ value. Therefore, the first hyperpolarizabilities for our studied systems are mainly proportional to f_{eg} and inversely proportional to the cube of E_{ge}. Hence, as a guideline, the two-level model requires well-performing NLO chromophores that possess a low-energy CT excited state with large oscillator strength.[21]

The TDDFT calculations are also carried out on iodic-substituted (naphthylimido)hexamolybdates. The transition energies (E_{ge}) and oscillator strengths (f_{eg}) are listed in Table 2. The results show that the transition energy of system **22′** is smaller than that of system **2**. In addition, the difference in oscillator strength between system **2** and system **22′** is relatively small (0.1452 for system **2**, and 0.1081 for system **22′**). According to the two-level formula, the first hyperpolarizability for system **22′** is larger than that of system **2**. For the strongest transitions in systems **21′**, **23′**, and **25′**, their transition energies are larger than that of system **2**, whereas the oscillator strength f_{eg} for **21′**, **23′**, and **25′** are 0.0890, 0.0617, and 0.0615, respectively; that is, their corresponding oscillator strengths are very weak. The f_{eg}/E_{eg}^{3} values of all these three systems are smaller than that of system **2**. That results in the relatively smaller β_0 values for these three systems.

It is quite obvious that the substituted position effect has a great influence on the second-order NLO property of hexamolybdate naphthylimido derivatives. But how does it take effect? From the analysis above, the question can be answered from the following aspects: when the iodine atom is attached to the naphthylimido ligand, it does not change the charge transfer pattern; that is, the main contribution to β_0 remains the charge transfer from naphthylimido segment to $[Mo_6O_{19}]^{2-}$. However, the f_{eg} and E_{ge} values of the excited (charge transfer) state are obviously changed. The values of f_{eg} and E_{ge} are influenced by the substituted position effect, whereas the association between f_{eg} and E_{ge} values has not been observed in our studied systems. The large β_0 value comes from the strong oscillator strength and small transition energy. The π electrons equably delocalize

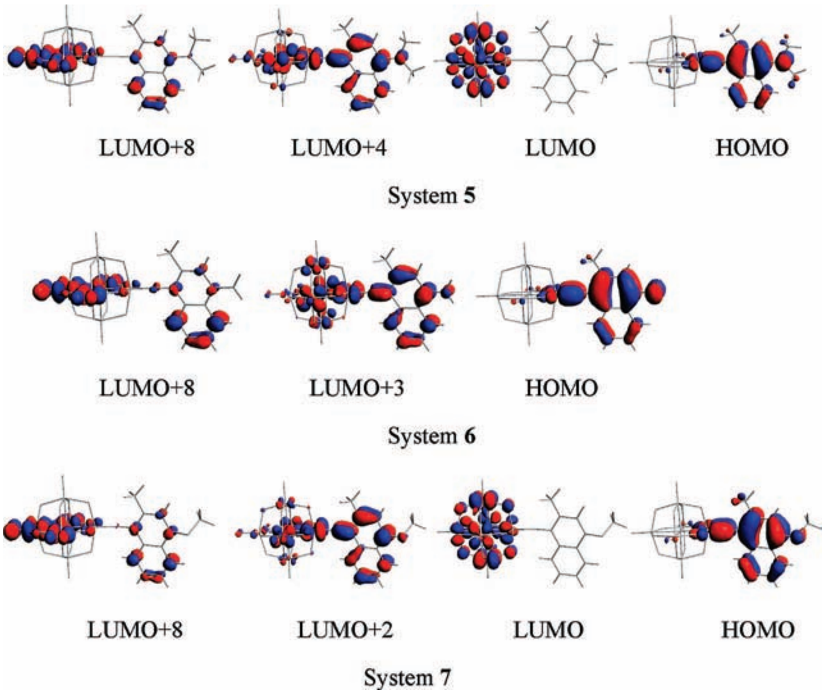

Figure 4. Frontier molecular orbitals of systems **5**−**7**.

on the naphthyl ring without any substituent, whereas the distribution of π electron is changed by the static electronic field of iodine atom. The static electronic fields, which are caused by the iodine atom in different positions, are different. Then the electron densities and energies of π system are different, as well as the first hyperpolarizabilities.

4.3. Substituent Effects on the First Hyperpolarizabilities of (Arylimido)hexamolybdate Derivatives. The three electron-donors and two electron-acceptors are chosen to investigate the substituent effect on the first hyperpolarizabilities of (naphthylimido)hexamolybdates. From the above study, the $N(CH_3)_2$, NH_2, OCH_3, OH and NO_2 are located on the position 2 of N-1-$C_{10}H_6$-2-CH_3 naphthylimido ligand and related derivatives are denoted as system **5**, **6**, **7**, **8** and **9**. The calculated first hyperpolarizabilities of systems **5** to **9** are listed in Table 3, and the substituent groups are shown in the parentheses. The β_0 values of system **5** to **9** increases as follows: system **9** < **8** < **7** < **6** < **5**. The β_0 value of system **5** is about 7 times larger than that of system **2**, and the β_0 value of system **8** is 2 times larger than that of system **2**. The results indicate that the introducing of electron-donors and electron-acceptors on naphthylimido segment leads to a substantial increment in the β_0 values. In addition, the introducing of electron-donor significantly enhances the first hyperpolarizabilities of (naphthylimido)hexamolybdates comparing with the electron-acceptor. This can be associated with the electron-donoating ability of organic ligand is enhanced when the electron-donor is attached to the naphthylimido segment. In addition, a donor group can increase the electron density in the π-conjugated system, leading to a strong interaction from the donor−acceptor combination. So the charge transfer and the electronic distribution would be changed.

The TD-DFT calculations were also performed on systems **5**−**9** to analyze the origin of a NLO property. The excitation energy, oscillator strength, and major contributions to the strongest transition are summarized in Table 4. It is found that the maximal absorption values are 442, 450, 418, 420 and 426 nm for systems **5**, **6**, **7**, **8** and **9**, respectively. They can maintain the high transparency required, which is worthy of remarks considering practical application in the NLO field. Comparing with their parent system **2**, the excitation energies decrease and the oscillator strengths increase from system **5** to **9**. So the first hyperpolarizabilities of systems **5**−**9** are increased.

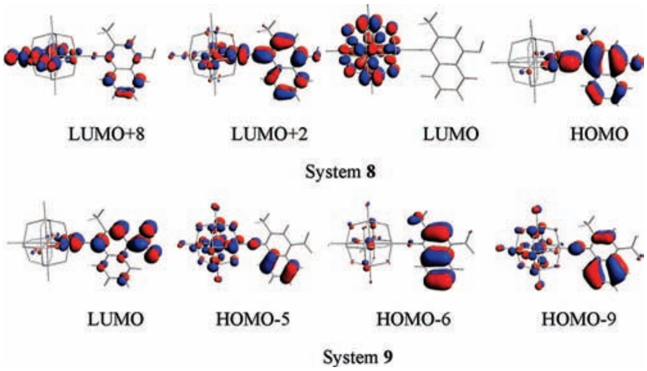

Figure 5. Frontier molecular orbitals of systems **8** and **9**.

The charge transfers of system **5** to system **7** are similar to that of system **2**. For system **5**, the transition energy is 442 nm, which is generated by the promotion of the electrons from HOMO to LUMO+4, and LUMO+8 (Figure 4). The transitions can be assigned to a charge transfer transition from naphthylimido segment to $[Mo_6O_{19}]^{2-}$, as well as the charge transfer transition intranaphthylimido segment. The charge transfer characters in systems **6** and **7** are as the same as in system **5**. It is attributed that the donors are attached on the naphthylimido ligand, so the charge transfer pattern is not changed, but the electron-donating ability is enhanced, as well as the second NLO property.

The molecular orbital diagrams involving the orbital transition of systems **8** and **9** are displayed in Figure 5. For system **8**, which the acceptor OH is attached on the naphthylimido ligand, the charge transfer is similar to that for system **2**. It suggests that the naphthylimido segment controls the charge transfer as the electron-accepting ability of OH is much weaker than that of $[Mo_6O_{19}]^{2-}$. In system **9**, which is modified by the NO_2 group, the transition can be assigned to the charge transfer from the naphthylimido segment to $[Mo_6O_{19}]^{2-}$, naphthylimido to NO_2, and naphthylimido to naphthylimido. Here, the NO_2 competes with $[Mo_6O_{19}]^{2-}$ due to the strong electron-accepting ability of NO_2 group, so the charge transfer pattern is changed.

5. Conclusions

The static first hyperpolarizabilities of [(2-methylnaphthyl)imido]hexamolybdates have been calculated by the DFT method. The substituted position and substituent effects on the first hyperpolarizabilities were first investigated. The main contributions are as follows: (1) [(2-methylnaphthyl)imido]hexamolybdate has a considerably large first hyperpolarizability, 6.780×10^{-30} esu. The naphthylimido ligand acts as an electron-donor and the polyanion acts as an electron-acceptor. The double aromatic rings in (naphthylimido)hexamolybdate could prompt the conjugation between the d electron system of hexamolybdate and the p−π electron of naphthylimido ligand, and also extend the π electron system. (2) The iodine atom position on the naphthylimido is a key factor to determine the first hyperpolarizability of (naphthylimido)hexamolybdate derivatives. The derivative, which the iodine atom locates on the para posotion of nitrogen on the naphthylimido ligand, has the largest β_0 value. It suggests that the iodine atom is quasi linear with nitrogen and Mo, which is bonded to nitrogen, could generate large static electronic field and give the large contribution to NLO response. (3) The electron-donor and electron-acceptor on the naphthylimido ligand enhance the first hyperpolarizabilities of (naphthylimido)hexamolybdates. However, the introduction of donors significantly enhances the first hyperpolarizabilities of (naphthylimido)hexamolybdates as compared with the acceptors because the electron-donoating ability is enhanced when the electron-donor is attached to the naphthylimido segment.

This work exhibits the tunable NLO behavior of (naphthylimido)hexamolybdates and may provide a new means for experimentalists to design high-performance NLO materials.

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Supporting Information Available: Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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