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A Quantum Mechanical Study of the Second-Order Nonlinear Optical Properties of Aryldiazenido-Substituted Hexamolybdates: A Surprising Charge Transfer

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The second-order polarizabilities, transition moments, and density of states of aryldiazenido hexamolybdates derivatives were investigated by density functional theory (DFT). System **2** $[Mo_6O_{18}(N_2C_6H_5)]^{3-}$ has a considerably large second-order polarizability, 14.50×10^{-30} esu, and it is larger than that of system **1** $[Mo_6O_{18}(N_2C_6H_4NO_2)]^{3-}$ due to the absence of nitro group in the aryldiazenido ligand. The aryldiazenido ligand acts as an electron donor and the polyanion acts as an electron acceptor. The substitution of an amino (-NH_2) group in the *ortho*/*para* positions on the aryldiazenido segment leads to a substantially higher nonlinear optical (NLO) response. The introduction of an electron donor (-NH_2) in the *ortho*, *meta*, *para*, and *ortho*/*para* positions on the aryldiazenido ligand significantly enhances the second-order polarizabilities of aryldiazenido hexamolybdates in comparison to the electron acceptor (-NO_2) as in system **1**, because the electron-donating ability was reasonably enhanced when the electron donor is attached to the aryldiazenido ligand. Furthermore, orbital analysis shows that incorporation of another phenyl (aromatic) ring in the aryldiazenido ligand leads to a maximum NLO response by reverting the direction and degree of charge transfer (CT), which might result from the C=C π-conjugated bridge. System **8** $[Mo_6O_{18}(N_2C_{14}H_{11})]^{3-}$ possesses a strikingly large and conspicuous static second-order polarizability (β_{vec}) computed to be 210.21×10^{-30} esu. The NLO response can be tuned by subtle changes in the aryldiazenido segment; the present investigation provides important insight into the NLO properties of (aryldiazenido) hexamolybdate derivatives.

Introduction

Polyoxometalates (POMs) are remarkable for their molecular and electronic structural diversity, versatility, and their significance in quite diverse disciplines, including catalysis, medicine, and materials science.[1–5] These species also play an important role in the design of new materials with novel electronic, magnetic, and topological properties.[6] Additionally, the functionalization of POMs (i.e., the replacement of one or several oxido ligands by other ligands) has drawn tremendous attention in the past decade, and recently a new area of interest is the design and fabrication of hybrid supramolecular arrays based on POM building blocks and various organic ligands.[3,7–11] Extensive theoretical and experimental investigations have been directed to the design of new molecular materials with large second-order nonlinear optical (NLO) responses because of their potential applications in low-cost, high-performance photonic, and electrooptical devices.[12–16] Among the NLO materials, organic compounds are of major interest because of their relatively low cost, ease of fabrication and integration into devices, tailorability, which allows one to finetune 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. Organic materials, however, 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 host–guest systems) they may undergo facile relaxation to random orientation.[17] The limitations identified above provoke investigation of new materials. Presently, our group is investigating first and second hyperpolarizability of POMs[18,51–55] and its derivatives by using density functional theory (DFT), which has been proven to be a consequential tool to explore the properties of POMs.[19–27]

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Among POM structures, one of the prototypes is the so-called Lindqvist structure, which is adopted by hexametalates $[M_6O_{19}]^{n-}$ (M = Mo,[28] W,[29] Nb,[30] Ta,[31] and V[32]) as well as by various mixed-metal analogues. The Lindqvist structure consists of a central oxygen atom, about which six metal atoms are arrayed in an octahedral geometry. Each metal bears one terminal oxygen atom and shares an additional four μ_2-oxygen atoms with adjacent metal atoms. In general, the overall symmetry of these Lindqvist ions approaches O_h. In the case of aryldiazenido hexamolybdates as in our present work, the aryldiazenido ligand exhibits the characteristic feature of the singly bent coordination mode with short Mo–N and N–N bond lengths indicative of multiple bond character leading to C_s symmetry. The functionalization of POMs (i.e., the replacement of one or several oxido ligands by other ligands) allows their properties to be tuned and provides a route to their application in supramolecular chemistry through the introduction of suitable pendent functions.[33,34] With regard to the functionalization of POMs, interest in the replacement of terminal oxido ligands by other multiply bonded ligands such as nitrosyl,[35] imido,[36,37] and nitride[38] ligands may provide better understanding about aryldiazenido hexamolybdates. However, Lindqvist-type aryldiazenido hexamolybdates have been synthesized by Bustos et al.[39]

In the present theoretical research work, for the first time we performed DFT calculations on aryldiazenido hexamolybdates to predict their first hyperpolarizabilities (second-order polarizabilities). The effect of an electron donor ($-NH_2$) in the *ortho*, *meta*, *para*, and *ortho*/*para* positions on the aromatic ring of the aryldiazenido ligand with respect to the first hyperpolarizability was investigated. Moreover, the presence of a second phenyl ring (aromatic ring) connected through a π-conjugated bridge (C=C bond) on the aryldiazenido ligand surprisingly altered the direction of charge transfer, leading to a maximum NLO response. This effort may provide a useful means to experimentalists for designing high-performance NLO materials based on aryldiazenido hexamolybdates.

Methodology

The DFT calculations were carried out by using the ADF2006.01 suite of programs.[40] The zero-order regular approximation (ZORA) was adopted in all the calculations to account for scalar relativistic effects.[41] The generalized-gradient approximation (GGA) was employed in the geometry optimizations by using the Beck[42] and Perdew[43] (BP86) exchange-correlation (XC) functional. For the calculations, we made use of the standard ADF TZP basis set, which is a triple-ζ plus polarization STO basis set. Triple-ζ plus polarization basis sets were used to describe the valence electrons of all atoms, whereas for the transition-metal molybdenum atom, a frozen core composed of 1s to 3spd shells was described by single Slater functions. In calculations of the polarizability, second-order polarizability, and excitation properties, the RESPONSE and EXCITATION modules[44] implemented in the ADF program were used on the basis of the optimized geometries. The van Leeuwen–Baerends XC potential (LB94) was chosen for calculations of all the response properties.[45] The reliability of the LB94 potential to calculate polarizabilites and hyperpolarizabilities has already been proven and is well documented.[46–49] The adiabatic local density approximation (ALDA) was applied for the evaluation of the first and second functional derivatives of the XC potential. Moreover, the value of the numerical integration parameter used to determine the precision of numerical integrals was 6.0. GaussSum[50] was used to calculate the density of states (DOS). The functional and basis set choices for our studied inorganic–organic hybrid compounds were supported by research work that has already been published.[51–55]

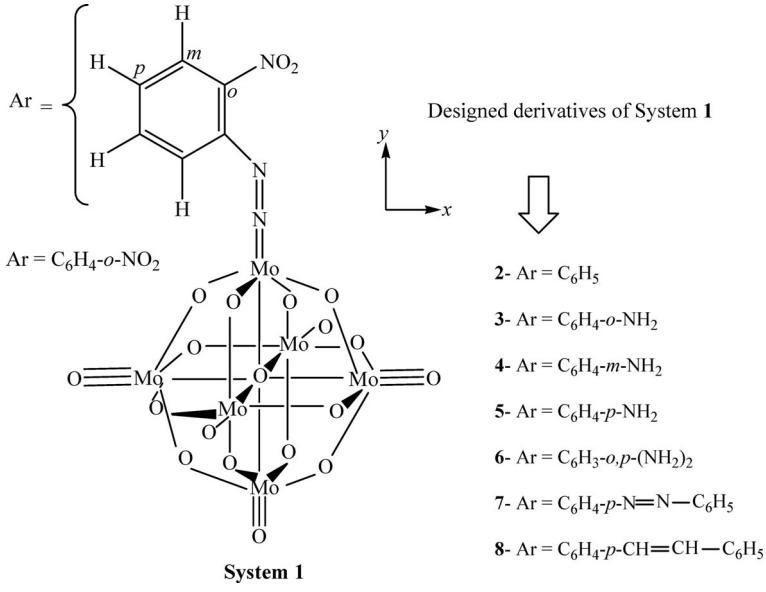

Figure 1. Orientation and calculation models for systems **1**–**8**.

Calculation Models

The geometry optimization of systems **1**–**6** under symmetry constraint C_s was carried out, where as initial geometric data were from the crystal data.[39] Their structures are sketched in Figure 1 and the optimized bond lengths are given in Table 1. The agreement between experimental and calculated metrical parameters of system **1** gives us confidence that the present study is consequential for this research work.

Table 1. Bond lengths [Å] and angles [°] calculated by DFT for systems **1**–**6**.

	1	2	3	4	5	6
Mo–N	1.807(1.751)[a]	1.799	1.798	1.798	1.800	1.801
N–N	1.282(1.285)	1.286	1.286	1.285	1.283	1.283
Mo–N–N	174.55(173.91)	176.21	178.77	177.34	177.22	177.93

[a] The experimental values are in parentheses.[39]

Results and Discussion

On the basis of system **1** we were keen to design different kinds of systems with an improved NLO response, as it is obvious from the structural configuration of system **1** that it shows an acceptor–donor–acceptor (A-D-A) relationship due to the presence of the NO_2 group in the *ortho* position of the aryldiazenido ligand and the POM cluster at the other end. Owing to the electron accepting ability of both the POM cluster (polyanion) and the nitro group (-NO_2), the β_{vec} value of system **1** was computed to be 1.59×10^{-30} esu. This insignificant NLO response might be enhanced by small changes at the molecular level. In order to meet this objective, we designed different types of systems (i.e., **2**–**8**) with the prospect to get enhanced NLO responses.

Static Second-Order Polarizability

The static second-order polarizability (β_{vec}) is termed as the zero-frequency hyperpolarizability and is an estimate of the intrinsic molecular hyperpolarizability in the absence of resonance effect. The computed β_{vec} values and their individual components of systems **2**–**6** are shown in Table 2. There are 14 components of the second-order polarizability owing to the C_s symmetry. The β_{yyy} component has the largest value in our studied systems except system **4**, where the substitution of the amino (-NH_2) group in the *meta* position of the aryldiazenido ligand has no considerable effect (see Figure 2, no electron density on the amino group when it was substituted in the *meta* position). Hence, the major contribution to the second-order polarizability is the β_{yyy} component, and the major charge transfer is also along the *y* direction. As shown in Table 3, all systems have larger second-order polarizability coefficients. For example, the computed β_{vec} value of system **6** is about 515 times larger than the average second-order polarizability of the organic urea molecule[56] and 11 times larger than the measured value for highly π-delocalized phenyliminomethyl ferrocene complex.[57] This reveals that studied systems **2**–**6** have an excellent second-order NLO response.

Table 2. Transition moments, M_x^{gm}, M_y^{gm} [a.u.];[a] the β_{xxx} and β_{yyy} components; and the computed static second-order polarizabilities, β_{vec} [1×10^{-30} esu] of systems **2**–**6**.

	2	3	4	5	6
M_x^{gm}	0.064	0.053	1.076	0.121	–0.073
M_y^{gm}	1.038	–1.151	0.022	1.200	–1.201
β_{xxx}	0.598	2.377	–28.969	0.837	2.301
β_{yyy}	19.274	42.586	–0.362	50.956	75.946
β_{vec}	14.505	27.591	19.904	33.937	49.164

[a] $M_z^{ng} = 0$.

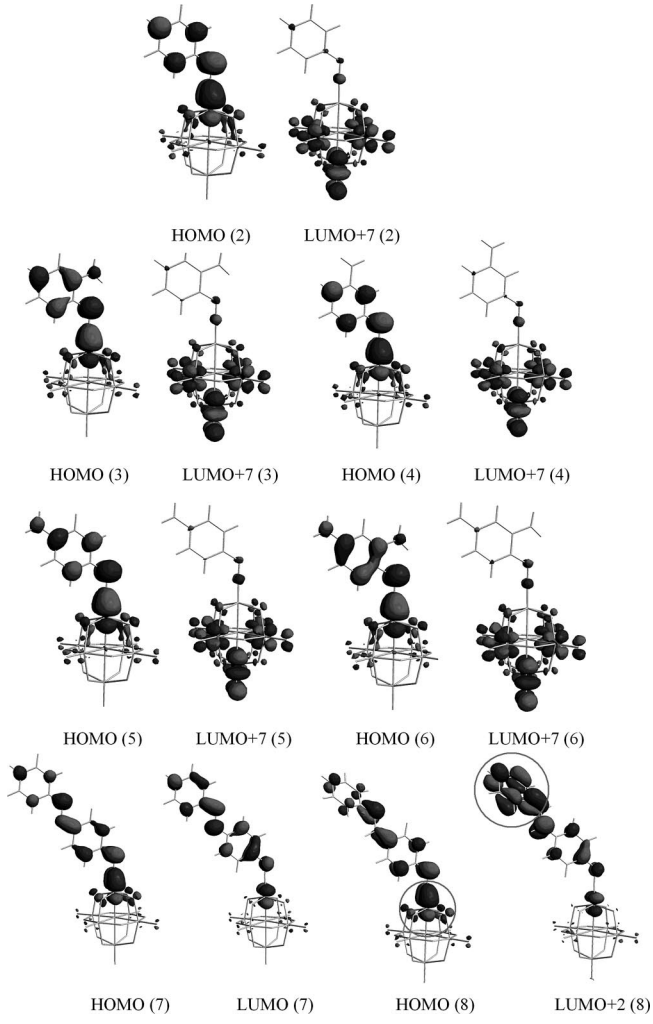

Figure 2. The Frontier molecular orbitals of systems **2**–**8** involved in the dominant electron transitions obtained by LB94/TZP calculations.

As determined by the TD-DFT calculations, the electron transition of system **2** mainly commences from the aryldiazenido ligand (HOMO) to the polyanion (LUMO+7) along the *y* direction, and this character of charge transfer similarly occurs on systems **3**–**6** (HOMO to LUMO+7). The molecular orbitals involved in the dominant electron transitions in systems **2**–**6** are shown in Figure 2.

Under the C_s symmetry constraints, electronic transitions from the ground state to the singlet A' (y direction) excited states are electric dipole allowed for our studied systems. For the present calculated systems (i.e., **2**–**6**), the dominant electron transitions have A' symmetry (see Table 3). The major charge transfer originates from the aryldiazenido ligand to polyanion along the y axis. This trend exhibits that the aryldiazenido ligand acts as a donor and polyanion (hexamolybdates) acts as an acceptor.

As a result of charge transfer along the y axis in our studied systems, the computed β_{vec} values of these systems show that the NLO response is as follows: system **6** > **5** > **3** > **4** > **2**, whereas the β_{xxx} component is a vital determinant in system **4**. The β_{yyy} component of system **6** has the highest value, as it shows the largest β_{vec} for systems **1**–**6**. However, the β_{vec} values of systems **3** and **5** are two times larger than system **2**, whereas system **2** is nine times larger than system **1**. The β_{vec} value of system **6** is 3 times and 32 times larger than systems **2** and **1**, respectively. In system **3**, the donating ability of the aryldiazenido ligand was improved by incorporation of an electron donor (-NH_2) in the *ortho* position of the phenyl ring, and this effect is further ameliorated by introducing an electron donor (-NH_2) in the *ortho* and *para* positions simultaneously in the aryldiazenido ligand in system **6**. System **6** has a strikingly large NLO response, as the donating ability of the aryldiazenido ligand was enhanced by the incorporation of two amino groups in the *ortho* and *para* positions, as shown in Figure 2. In system **3**, the presence of an NH_2 group in the *ortho* position improves the donating ability of the aryldiazenido ligand, so the β_{vec} value increased from 14.50×10^{-30} esu (for system **2**) to 27.59×10^{-30} esu (for system **3**). System **6** has the highest NLO response among all six systems, and this indicates that substitution of the amino group (-NH_2) in the *ortho*/*para* positions simultaneously is more important to enhance the optical nonlinearity; system **6** has the leading edge as compared to the others, as it shows the highest NLO response among all the studied systems (i.e., **1**–**6**) by showing an *ortho*/*para* NLO-enhanced substitution effect. The degree of charge transfer and synergistic effect between the aryldiazenido ligand (D) and the polyanion (A) were appealingly enhanced by the introduction of two amino groups (-NH_2) in the *ortho*/*para* positions (see system **6**). The NLO properties of our studied systems were improved strikingly through the introduction of a donor in the *ortho*, *para*, and *ortho*/*para* positions of the aryldiazenido ligand. Particularly, for our studied organic–inorganic hybrid materials, their NLO properties were increased through the introduction of a donor at different positions. This incorporation is helpful to enhance the degree of charge transfer by decreasing the excited energy, which leads to a conspicuous increase in the first hyperpolarizability, as it is much pronounced in system **6**, where the β_{vec} value computed to be 49.16×10^{-30} esu (see Figure 2 and Tables 2 and 3).

To spread further light on the origin of the second-order NLO properties of the studied compounds, the elucidation of a structure–property relationship is prerequisite. How does it bring about fluctuations in the computed β_{vec} values? From the complex sum-over-states (SOS) expression, the two-state paradigm model that links β and a low-lying charge transfer transition was formulated.[58] For the static case, the following model expression is employed to estimate β_{CT} [Equation (1)].

$$\beta_{CT} \propto \frac{\Delta\mu_{gm} f_{gm}}{E_{gm}^3} \quad (1)$$

where f_{gm}, E_{gm}, and $\Delta\mu_{gm} = \Delta\mu_m - \Delta\mu_g$ are the oscillator strength, the transition energy, and the change of the dipole moment between the ground state (g) and the m-th excited (charge transfer) state (m), respectively. The first hyperpolarizability is jointly determined by three quantities ($\Delta\mu_{gm}$, f_{gm}, and E_{gm}). As our studied systems possess the same conjugation bridge, which means there is not a large difference in the $\Delta\mu_{gm}$ values. Therefore, the first hyperpolarizabilities for our studied systems are mainly proportional to f_{gm} and inversely proportional to the cube of E_{gm}. 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.[59] Therefore, for the studied compounds, the low excitation energy is the decisive factor in the β value. As it can be found from Table 3, the excitation energies are related to the structural character of the studied compounds. The computed M_y^{gm} values increase from system **2** to **3**, **3** to **5**, and then **5** to **6** in accordance with the β values (see Tables 2 and 3), where the excitation energy values are as follows: system **6** < **5** < **3** < **4** < **2**. The redshift in the absorption band is attributed to the substitution of the donor in the *ortho*, *para*, *meta*, and *ortho*/*para* positions. From Equation (1), this behavior significantly enhances the β_{vec} value. Intelligibly, the excitation energy will tend to make a dominant contribution to the β_{vec} values of the studied compounds. As we have already discussed that the β value is directly proportional to the oscillator strength and inversely proportional to the transition energy, the low excitation energy is the decisive factor in determining the β value, as it has been observed in systems **2**–**6** that low-lying transition energy is a decisive/commanding factor to determine the NLO response (Table 3). However, the oscillator strength f_{gm} for systems **2**–**6** are 0.0398, 0.0469, 0.0422, 0.0498, and 0.0471, respectively. System **6** has the lowest value of excitation energy, which leads to the highest NLO response among our studied systems, that is, we may say that low-lying excitation energy has power to assign the NLO response while comparing these systems. Therefore, in these systems, low-lying excitation energy is a key factor for increasing the β_{vec} value.

Concisely, the large β_{vec} values come from the strong oscillator strength and small transition energy as shown in Table 3. It is also noticeable that substitution of the donor in the *ortho*/*para* positions has a mighty influence on the second-order NLO properties in our studied systems. From these results, it can be summarized that incorporation of an electron donor (-NH_2) in the aryldiazenido ligand is helpful to enhance the β value. In system **6**, another important fac-

Table 3. LB94/TZP calculated excitation energy [eV]; E [a.u.]; oscillator strengths, f; symmetry, S; and corresponding dominant MO transitions of systems **2**–**6**.

	Excitation energy	E	f	S	MO Transition
2	1.502	0.055	0.039	A'	HOMO → LUMO+7 (95.68%)
3	1.440	0.052	0.046	A'	HOMO → LUMO+7 (95.49%)
4	1.485	0.054	0.042	A'	HOMO → LUMO+7 (95.97%)
5	1.398	0.051	0.049	A'	HOMO → LUMO+7 (96.14%)
6	1.329	0.048	0.047	A'	HOMO → LUMO+7 (96.82%)

tor is the introduction of an amino group in the *ortho*/*para* positions simultaneously, which enhances the β_{vec} value by decreasing the energy difference between the ground and charge-transfer excited state. Nevertheless, the larger β_{vec} values are generated as electron transitions originate from the aryldiazenido ligand (D) to the polyanion (A) along the y axis.

The HOMO–LUMO energy gap of system **1** (1.05 eV) has the highest value, which leads to the lowest NLO response. As for as the HOMO–LUMO energy gaps of systems **1**–**6**, it can be seen in Figure 3 that the HOMO–LUMO energy gap of system **6** has the smallest value of 0.46 eV, which registers the highest NLO response. The low-lying HOMO–LUMO energy gap might enhance the molecular second-order NLO properties. The HOMO–LUMO energy gaps decrease in the following order: system **1** > **2** > **4** > **3** > **5** > **6**, whereas the NLO response increases accordingly as follows: system **1** < **2** < **4** < **3** < **5** < **6**. This means system **6** has the smallest energy gap, which gives rise to the highest NLO response among all the studied compounds (Figure 3).

The total density of states (DOS) of systems **1**–**6** are shown in Figure S1 (Supporting Information) to more easily and vividly observe the varieties of the HOMOs, LUMOs, and energy gaps. The investigated systems are particularly interesting for nonlinear optical properties, appropriately operating by the substitution of the donor and phenyl ring. With the appropriate changes in the studied systems, one can also vary the NLO properties. Thus, one requires reliable data about the band structure, which could be collected from the DOS diagram. DOS calculation was carried out by using GaussSum,[50] and it was employed to convolute DOS spectra from the molecular orbital data for the studied systems.

After having a detailed discussion on systems **1**–**6**, we were driven to probe the role of another phenyl ring (aromatic ring) substituted at the end of the aryldiazenido ligand, and that is why we have also explained systems **7** and **8**. The second phenyl ring was incorporated into the existing aryldiazenido ligand through the N=N and C=C bonds in systems **7** and **8**, respectively, as shown in Figures 1 and 2. System **8** shows a greater NLO response relative to that of system **7**, which indicates that the C=C conjugated bridge has a greater influence on increasing the second-order polarizability. This means the presence of an N=N bond linkage between the two phenyl rings has a significant influence on the second-order NLO response, as shown in Table 4 and Figure 2, whereas a C=C bond linkage has a strikingly large effect on the NLO response, and that is why system **8** offers the highest β_{vec} value in all of our studied systems. The β_{vec} value was computed to be 210.21×10^{-30} esu, which is the result of the existence of a charge-transfer transition from the polyanion (hexamolybdate) to the aryldiazenido ligand along the y direction, leading to an appealingly large NLO response. System **7** has a much higher β_{vec} value in comparison to those of systems **1**–**6**, whereas system **8** has an NLO response that is more than two times higher than that of system **7**. Systems **7** and **8** investigated here show C_s and C_1 symmetry, respectively. Moreover, charge transfer in system **7** arises from (HOMO→ LUMO), and this type of charge transfer similarly occurs in system **8** (HOMO → LUMO+2). The molecular orbitals involved in the dominant electron transitions in systems **7** and **8** are shown in Figure 2.

The calculated β_{vec} values of system **7** and **8** are 83.80×10^{-30} and 210.21×10^{-30} esu, respectively. For systems **7** and **8**, the main contribution of β_{vec} is in the y direction and the β_{yyy} components have larger values than those

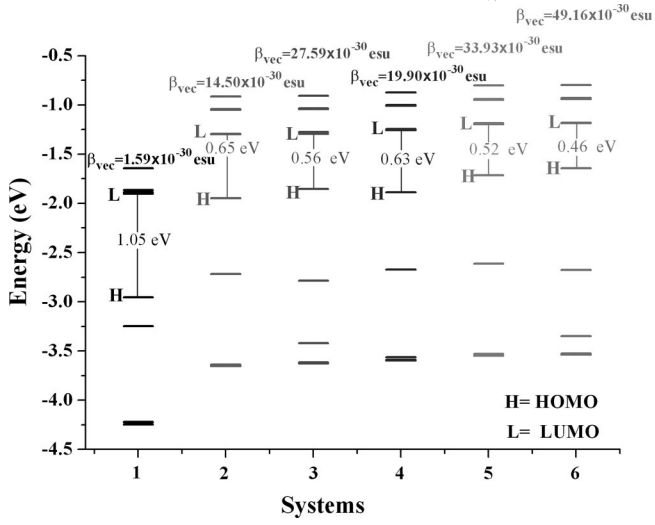

Figure 3. Molecular orbital energy diagram with HOMO–LUMO energy gaps of systems **1**–**6** and the corresponding β_{vec} values.

Table 4. LB94/TZP calculated excitation energy, E [eV]; symmetry, S; transition moments M_x^{gm}, M_y^{gm}, and M_z^{gm} [a.u.]; the β_{yyy} components, computed static second-order polarizabilities, β_{vec} [1×10^{-30} esu]; and the corresponding dominant MO transitions for systems **7** and **8**.

	E	S	M_x^{gm}	M_y^{gm}	M_z^{gm}	β_{yyy}	β_{vec}	MO transition
7 (N=N)	2.014	A'	0.445	4.645	0.000	129.47	83.80	HOMO → LUMO (55%)
8 (C=C)	1.857	A_1	0.592	4.313	0.452	329.28	210.21	HOMO → LUMO+2 (52%)

of the other tensors. In system **8**, the main contribution of β_{vec} is in the *y* direction so the β_{yyy} component has larger values among the 27 tensors; this point is in accord with the direction of the charge transfer (see Figure 2), whereas the β_{yyy} component of system **7** has also its maximum value among its 14 tensors due to its C_s symmetry. Moreover, the transition energy of system **8** is less than that of system **7**, as shown in Table 4. This low-lying transition energy might also be an authoritative factor towards the higher NLO response of system **8**.

The present theoretical investigation gives insight into the NLO properties of aryldiazenido hexamolybdates and attempts to reveal the origin of the considerably large NLO properties of this family of organic–inorganic hybrid compounds, which are interesting and appealing in design and synthesis of new promising NLO material. For our studied systems, the incorporation of an electron donor (-NH_2) leads to a larger β value, whereas introduction of another phenyl (aromatic) ring through the N=N and C=C π-conjugated bridge at the end of the aryldiazenido ligand leads to appealingly large and conspicuous β values (Figure 4).

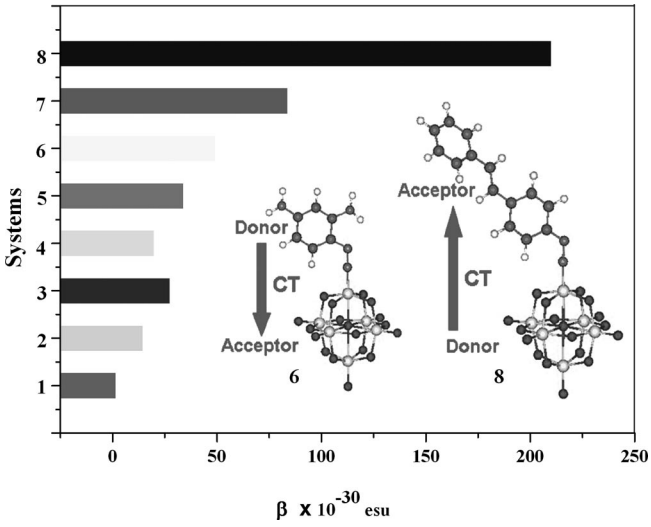

Figure 4. Horizontal bars showing the incremental increase in the β values from systems **1** to **8**.

These organic–inorganic hybrid molecules can become an excellent kind of NLO materials in the field of optoelectronics. The electron donor in the aryldiazenido ligand enhances the first hyperpolarizability, whereas the second phenyl ring in the aryldiazenido ligand appealingly increases the first hyperpolarizability. In our studied systems (i.e., **1**–**6**) the polyanion (A) acts as an acceptor and the aryldiazenido ligand (D) acts as a donor. The direction of charge transfer is reversed in systems **7** and **8**, where the polyanion (D) acts as a donor and the aryldiazenido ligand (A) acts as an acceptor. Therefore, larger β_{vec} values are generated, as the electronic transition originates from the polyanion (hexamolybdates) to the aryldiazenido segment. The NLO properties of our studied systems were improved strikingly through the increase in the conjugation path (as in systems **7** and **8**) and the introduction of a donor at different positions in aryldiazenido ligand (as in systems **1**–**6**).

Conclusions

The second-order polarizabilities of aryldiazenido hexamolybdates were calculated by the DFT method. Interestingly, a reversal in the role of the hexamolybdate fragment from electron acceptor (systems **1** through **6**) to electron donor (systems **7** and **8**) was observed. Firstly, the second-order polarizabilities were investigated by substituting an electron donor (-NH_2) in the *ortho*, *meta*, *para*, and *ortho*/*para* positions. Secondly, β values were also computed by incorporation of a second phenyl ring in the preexisting aryldiazenido ligand. In the framework of this theoretical study, we can jump to the following majestic points: (1) System **2** $[Mo_6O_{18}(N_2C_6H_5)]^{3-}$ has a considerably large first hyperpolarizability, 14.505×10^{-30} esu. The aryldiazenido ligand acts as an electron donor and the polyanion acts as an electron acceptor. (2) $[Mo_6O_{18}(N_2C_6H_4NO_2)]^{3-}$ (system **1**) shows a weak NLO response as it undermines the donating ability of the aryldiazenido ligand due to the acceptor–donor–acceptor (A-D-A) configuration. (3) The electron-donor (-NH_2) in the *ortho*, *para*, *meta*, and *ortho*/*para* positions on the aryldiazenido ligand enhances the first hyperpolarizabilities of (aryldiazenido) hexamolybdates. However, the introduction of donors (-NH_2) significantly enhances the first hyperpolarizabilities of aryldiazenido hexamolybdates relative to of the electron acceptor (-NO_2) because the electron-donating ability is enhanced when the electron donor is attached to the aryldiazenido segment. (4) The substitution of the amino (-NH_2) group in the *ortho*/*para* positions simultaneously in the aryldiazenido ligand leads to a substantially higher NLO response. (5) The substitution of the amino (-NH_2) group on the aryldiazenido ligand leads to an increase in the NLO response in the following order: *ortho*/*para* > *para* > *ortho* > *meta*. (6) System **8** shows the highest NLO response among all the studied systems, as the direction of the charge transfer was altered and the degree of charge transfer was reasonably increased by the addition of another aromatic ring in aryldiazenido ligand through the C=C bond. (7) The second-order NLO response of such types of organic–inorganic hybrid materials could be enhanced not only by including strong donor groups (-NH_2) but also by introducing a second phenyl through the N=N and C=C bonds as in systems **7** and **8**, respectively. (8) The presence of a C=C bond has a much greater influence on the NLO response than does the N=N bond. The increased length, resulting from introduction of the π-conjugated bridge, reverses the direction of charge transfer, as the polyanion acts as a donor and the aryldiazenido segment acts as an acceptor in systems **7** and **8**.

However, the present calculations on aryldiazenido derivatives of hexamolybdates provide the quantum mechanical framework in which CT and NLO properties may be understood as the introduction of a donor group (-NH_2) significantly enhances the first hyperpolarizabilities of (aryldiazenido) hexamolybdates relative to that of the acceptor because the electron-donating ability is enhanced when the electron donor is attached to the aryldiazenido ligand,

whereas the introduction of another phenyl ring through the C=C bond strikingly enhances the NLO response. This work exhibits the tunable NLO behavior of aryldiazenido hexamolybdates and may provide a new means for experimentalists to design high-performance NLO materials.

Supporting Information (see footnote on the first page of this article): Calculated DOS spectra for systems **1**–**6**.

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