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Quantum Mechanical Design of Efficient Second-Order Nonlinear Optical Materials Based on Heteroaromatic Imido-Substituted Hexamolybdates: First Theoretical Framework of POM-Based Heterocyclic Aromatic Rings

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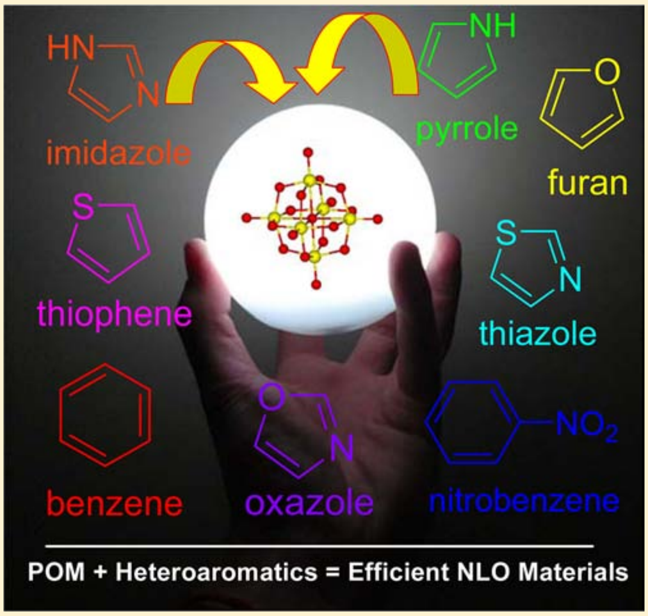
Supporting Information



ABSTRACT: This work was inspired by a previous report (Janjua et al. *J. Phys. Chem. A* **2009**, *113*, 3576−3587) in which the nonlinear-optical (NLO) response strikingly improved with an increase in the conjugation path of the ligand and the nature of hexamolybdates (polyoxometalates, POMs) was changed into a donor by altering the direction of charge transfer with a second aromatic ring. Herein, the first theoretical framework of POM-based heteroaromatic rings is found to be another class of excellent NLO materials having double heteroaromatic rings. First hyperpolarizabilities of a large number of push−pull-substituted conjugated systems with heteroaromatic rings have been calculated. The β components were computed at the density functional theory (DFT) level (BP86 geometry optimizations and LB94 time-dependent DFT). The largest β values are obtained with a donor (hexamolybdates) on the benzene ring and an acceptor ($-NO_2$) on pyrrole, thiophene, and furan rings. The pyrrole imido-substituted hexamolybdate (system 1c) has a considerably large first hyperpolarizability, 339.00×10^{-30} esu, and it is larger than that of (arylimido)hexamolybdate, calculated as 0.302×10^{-30} esu (reference system 1), because of the double aromatic rings in the heteroaromatic imido-substituted hexamolybdates. The heteroaromatic rings act as a conjugation bridge between the electron acceptor ($-NO_2$) and donor (polyanion). The introduction of an electron donor into heteroaromatic rings significantly enhances the first hyperpolarizabilities because the electron-donating ability is substantially enhanced when the electron donor is attached to the heterocyclic aromatic rings. Interposing five-membered auxiliary fragments between strong donor (polyanion) or acceptor ($-NO_2$) groups results in a large computed second-order NLO response. The present investigation provides important insight into the NLO properties of (heteroaromatic) imido-substituted hexamolybdate derivatives because these compounds exhibit enhanced hyperpolarizabilities compared to typical NLO arylimido hexamolybdates and heterocyclic aromatic rings reported in the literature.

1. INTRODUCTION

Polyoxometalates (POMs) are a rich class of inorganic clusters and display incredible chemical and physical properties, which have been applied to a variety of fields, for instance, medicine, catalysis, analytical chemistry, and materials science.[1−4] For a few years, there had been increasing interest in the chemistry of organically derivatized POMs.[5] In many organic derivatives of POMs, organoimido derivatives have been drawing much interest in that the strong d−π interaction between the organic delocalized π electrons and the cluster d electrons may result in synergistic effects.[6] The organoimido derivatives of Lindqvist-type POMs, $[M_6O_{19}]^{n-}$, are a distinctive 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.[7] The design of new molecular materials with large second-order nonlinear-optical (NLO) responses has been the subject of extensive theoretical and experimental explorations for several decades because of their potential applications in

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low-cost, high-performance photonic and electrooptical devices.[8]

There is an increasing need for organic polymeric electro-optical materials because of their potential applications in new photonic technologies such as optical data processing.[9] The development of such materials chiefly depends on the optimization of molecular as well as material second-order NLO responses. In the past, sizable progress has been made in understanding the factors that affect the molecular and material properties.[10−12] Molecular NLO response (β, first-order hyperpolarizability) is usually observed in donor−acceptor-substituted π-conjugated molecules holding built-in dipole moments. In such molecules, π conjugation provides a pathway for the redistribution of electronic charge under the influence of an electric field, while the donor and acceptor substituents provide the required ground-state charge asymmetry. Structure−property relationships that have been established indicate that β increases with increasing donor and acceptor strengths and with increasing π-conjugation length.[13,14] Polyenes are frequently used as π-conjugating units because they offer the most effective pathway for efficient charge transfer between the donor and acceptor groups.[15] Inclusion of benzene rings into the push−pull polyenes is observed to limit or saturate the molecular nonlinearity but to enhance the thermal stability.[16] The barrier due to the aromatic delocalization energy of the benzene ring is supposed to be accountable for the reduced or saturated β values. To overcome the problem of saturation of the molecular nonlinearity, numerous groups have developed systems that contain easily delocalizable five-membered heteroaromatic rings.[1−3]

In our group, there has been much interest to investigate the first and second hyperpolarizabilities of POMs and derivatives[17,18] using density functional theory (DFT), which has emerged as currently the most applied method to investigate the properties of POMs.[19] 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 in enhancing the β and γ values. (3) The strong interaction generates a strong electronic communication between arylimido and $[Mo_6O_{19}]^{2-}$.

Recently, the organoimido-substituted hexamolybdates, which contain a conjugation between the d electron system of the POM and the p−π electron system of the aromatic rings, have been reported extensively in which polyanion-to-organoimido charge transfer was responsible for the NLO properties of such kinds of compounds.[18] The double aromatic rings could be helpful in enhancing the intramolecular charge transfer. So, we are encouraged to investigate the NLO properties of (heteroaromatic) hexamolybdates and their derivatives. For the first time, in this account, we performed DFT calculations on heteroaromatic imido-substituted hexamolybdates to predict their first hyperpolarizabilities (β). The effect of the heteroaromatic modification on the first hyperpolarizabiliy is investigated in detail to provide a comprehensive picture of the effect of heteroaromatics on the second-order NLO properties. Using thiophene, pyrrole, furan, thiazole, oxazole, and imidazole as conjugating segments, we studied several classes of donor−acceptor compounds indicating that thiophene substitution causes a significant enhancement of the β value. This work may provide a useful means for designing high-performance NLO materials.

2. COMPUTATIONAL DETAILS

The DFT calculations were carried out using the *ADF2010.01* suite of programs.[20] The zero-order regular approximation was adopted in all of the calculations to account for the scalar relativistic effects.[21] The generalized gradient approximation was employed in the geometry optimizations using the Beck[22] and Perdew[23] (BP86) exchange-correlation (XC) functional. For the calculations, we made use of the standard ADF TZP basis set, which is the 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 a transition-metal molybdenum atom, a frozen core composed of 1s to 3spd shells was described by means of single Slater functions. The cores (C, N, and O 1s) were kept frozen. In calculations of the polarizability, second-order polarizability, and excitation property, the *RESPONSE* and *EXCITATION* modules[24] implemented in the ADF program were used based on the optimized geometries. The van Leeuwen−Baerends XC potential (LB94) was chosen for calculations of all of the response properties.[25] The reliability of the LB94 potential to calculate polarizabilites and hyperpolarizabilities has already been well-documented.[26−28] The adiabatic local density approximation was applied for 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. The functional and basis set choices for our studied inorganic−organic hybrid compounds were based on the research work that has already been reported.[17,18,29]

3. MOLECULAR STRUCTURES

Although many experimentally studied molecules contain a dialkylamino electron-releasing group, inspired by the previously studied systems as shown in Figures 1 and 2, the hexamolybdates cluster was chosen as a donor for the purpose of calculations, primarily to introduce a new class of NLO materials. The nitro ($-NO_2$) group serves as a conventional electron acceptor in all of the studied systems. Molecular structures examined in this study are shown in Figure 3, while their hypothetical representation is sketched in Scheme 1.

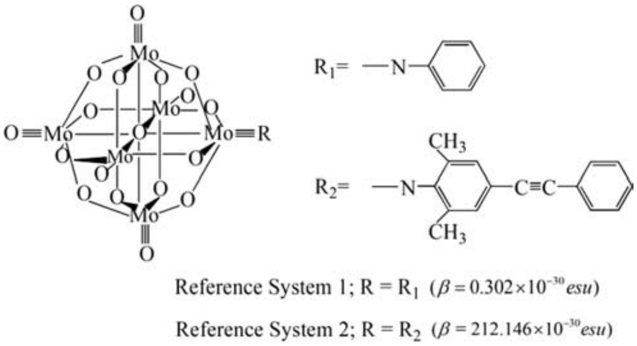


Figure 1. Calculation model represented as the reference system (R).[18]

The heteroaromatic derivative systems (**1**−**5**) were designed to understand the role of the heteroaromatic ring/rings in influencing the NLO response. Series **1a**−**1c** and **2a**−**2c** represent systems derived from the substitution of rings containing one heteroatom (such as thiophene, furan, and pyrrole), whereas series **3a**−**3i** are made up of two cyclic rings (such as thiophene, furan, and pyrrole). Series **4a**−**4c** and **5a**−**5c** contain a permanent pyrrole with thiazole, oxazole, and imidazole heteroatoms. All of the molecular structures were first optimized at the DFT level assuming C_1 (systems **1** and **2**) and C_s (systems **3**−**5**) geometries, whereas the initial geometric data were obtained from the crystal data.[30] Their structures are

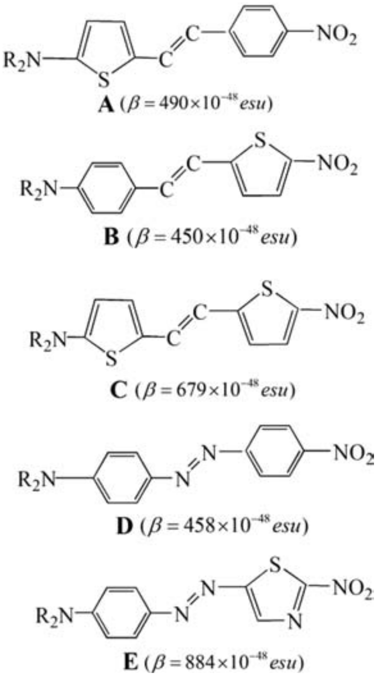


Figure 2. Experimentally studied representative thiophene- and thiazole-containing donor−acceptor compounds (**A**−**E**).[14−16]

drawn in Figure 1, and the optimized bond distances are given in Table 1, which are in reasonable agreement with reported experimental data. This agreement between the experimental and calculated parameters gives us confidence that the present study is consequential for this research work. The symmetry axis is along the x axis for systems **1** and **2** and the y axis for systems **3**−**5**.

4. RESULTS AND DISCUSSION

The nature of hexamolybdates $[Mo_6O_{19}]^{2-}$ was changed from acceptor to donor by replacing one aromatic ring with double aromatic rings in our previous reports,[18,31] which has driven us to probe into the presence of double heteroaromatic rings in hexamolybdates. From the results, it can be inferred that the first hyperpolarizabilities (β) of heteroaromatic-substituted hexamolybdates are highly dependent on the molecular structures. Furthermore, the relationship between the molecular hyperpolarizability and structure was elucidated based on the theoretical calculation of molecular orbitals (MOs). To produce heteroaromatic NLO materials, the heteroaromatic stilbenes have already been studied experimentally[1−3] while monoaromatic and diaromatic rings had already been introduced through imido linkage in hexamolybdates, as shown in Figure 1. Why are the various heteroaromatic rings chosen in imido-substituted hexamolybdates? Our previous studies[18,31] have shown that the replacement of a single aromatic ring by double rings can remarkably increase the second-order NLO response by changing the nature of hexamolybdates as a strong donor; this is attributed to a large amount of charge transfer from POM to the end of the aromatic rings.[18] Inspired by that work, this report has shown charge transfer from POM to the end of the aromatic rings bearing a nitro ($-NO_2$) group as an acceptor. The orbital features associated with MO transitions are shown in Figures 4 and S1 and S2 in the Supporting Information (SI), which offer some interesting results. The time-dependent DFT (TDDFT) results show that the electronic transitions of systems **1**−**5** mainly arise from POM (highest occupied molecular orbital, HOMO) to the end heteroaromatic ring (lowest unoccupied molecular orbital, LUMO) along the x or y direction.

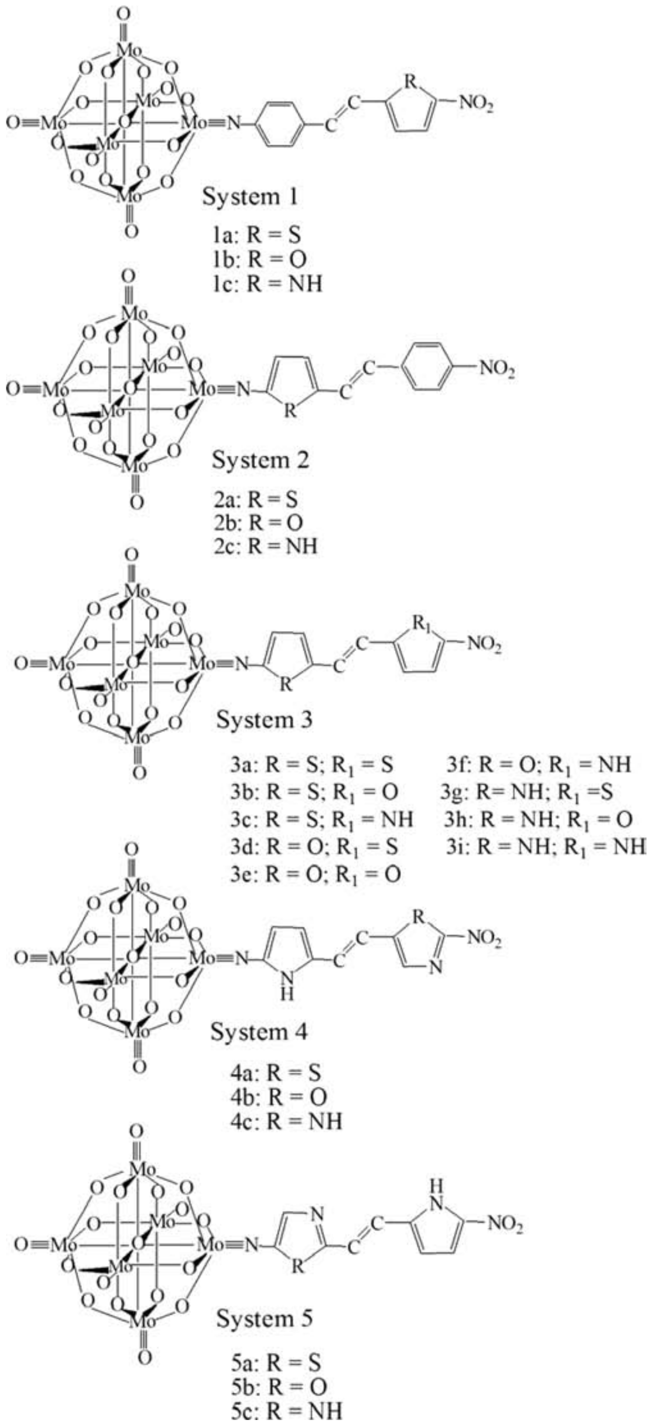


Figure 3. Donor−acceptor structures examined in the present study by combining Figures 1 and 2.

Systems **1** (**1a**−**1c**) and **2** (**2a**−**2c**) investigated here show C_1 symmetry, and the main charge transfer arises from HOMO → LUMO. The MOs involved in the dominant electron transitions are shown in Figure 4. The calculated β values of systems **1** and **2** are shown in Table 2. For these systems, the main contribution of β is in the x direction and the β_{xxx} components have larger values than those of the other tensors.

Scheme 1. Conceptional Donor−Acceptor Model Examined in the Present Study for Figure 3

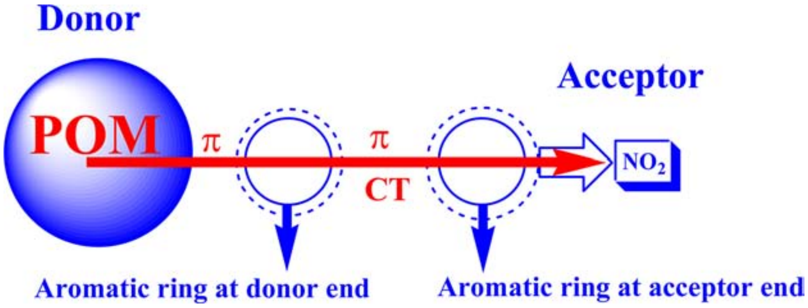


Table 1. Bond Lengths (Å) and Angles (deg) Calculated by DFT for Reference Systems (R)

	calcd		
parameter	reference system **1**	reference system **2**	exptl[a]
C1−N1	1.357	1.349	1.381
Mo1−N1	1.800	1.814	1.744
Mo1−O1	2.226	2.240	2.211
N1−Mo1−O1	180	180	178.28

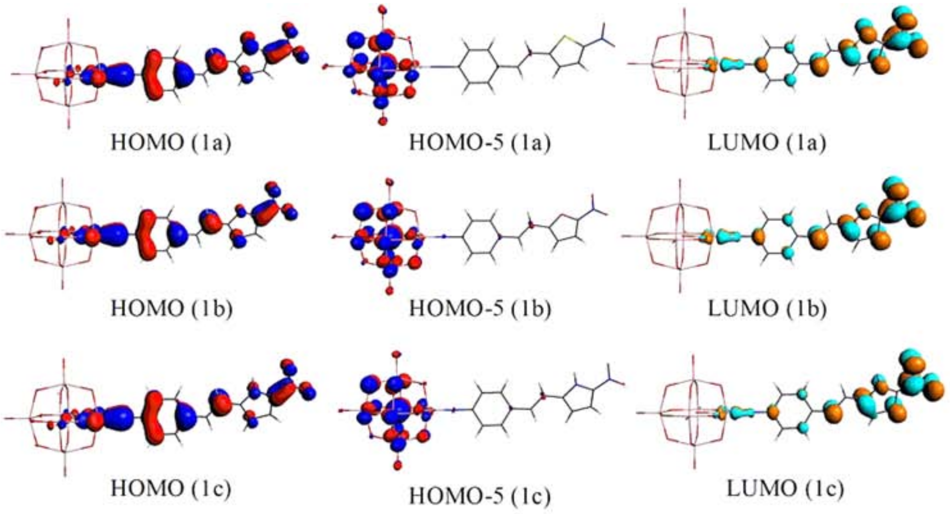
[a] Experimental values are taken from ref 30.

In system **1**, the β values in series increase as **1b** < **1a** < **1c**, which corresponds to β_{xxx} values in the same order of **1b** < **1a** < **1c**. The same trend in β and β_{xxx} values has been observed in system **2** as follows: **2b** < **2c** < **2a**. In system **1c**, the presence of a nitro group on the pyrrole ring has produced considerably large first hyperpolarizability calculated as 339.00×10^{-30} esu, highest among all of the studied systems, while the presence of thiophene and furan rings has also influenced the NLO response in an elegant way.

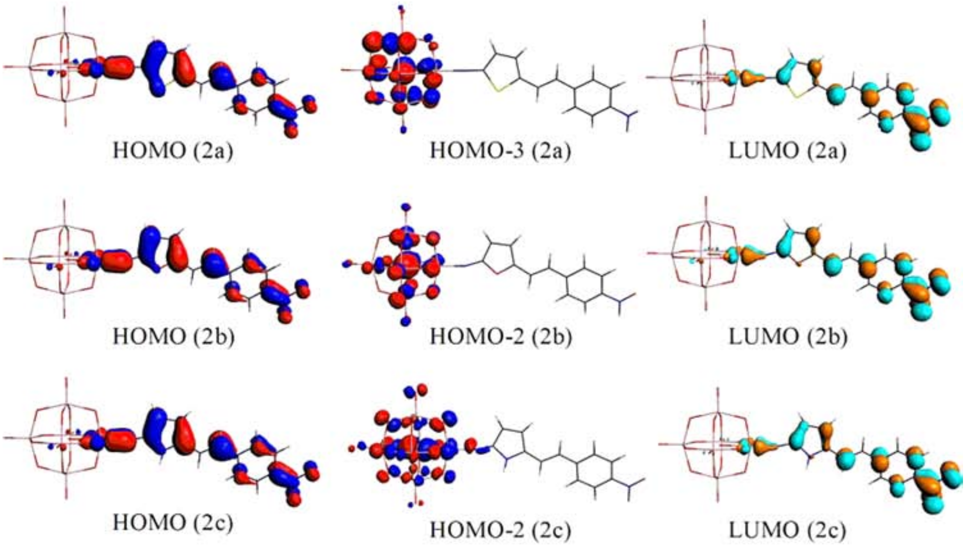
Under the C_s symmetry constraints, electronic transitions from the ground state to the singlet A' (y direction) excited states are electric-dipole-allowed for our studied series of systems **3** (**3a**−**3i**), **4** (**4a**−**4c**), and **5** (**5a**−**5c**). For the present calculated systems (i.e., **3**−**5**), the dominant electron transitions have A' symmetry (see Table 3). The major charge transfer originates from polyanion (hexamolybdates) to heteroaromatic rings along the y axis. This trend exhibits that the polyanion acts as a donor and the end heteroaromatic ring acts as an acceptor and conjugating bridge as well. As a result of charge transfer along the y axis in these studied systems, the computed β values of these systems show that the NLO response increases in accordance with the β_{yyy} values. In system **3**, the β values in series increase as **3e** < **3d** < **3g** < **3h** < **3f** < **3b** < **3i** < **3a** < **3c**, which corresponds to β_{yyy} values in same order of **3e** < **3d** < **3g** < **3h** < **3f** < **3b** < **3i** < **3a** < **3c**. The same trend in the β and β_{yyy} values has been observed in systems **4** and **5** as follows: **4b** < **4a** < **4c** and **5b** < **5c** < **5a**, respectively.

The frontier MOs involved in the dominant electron transitions in systems **1**−**5** are shown in Figures 3 and 4 and S1 in the SI. From these calculations, the frontier MOs of systems **1**−**5** involved in the dominant electron transitions imply strong electronic interactions between imido-substituted hexamolybdate anions and π-electron-conjugated heteroaromatic bridges. The p−π electron of the Mo≡N bond extends the π-electron-conjugated bridge. The conjugation is extended and the delocalization is further improved by introducing various heteroaromatic rings with an electron acceptor ($-NO_2$) at the end of heteroaromatic stilbenes. The heteroaromatic conjugated rings along with an electron acceptor increase the degree of charge transfer. The various heteraromatic rings are responsible for enhancement of the second-order polarizability. It can also be seen that the delocalized π bond coming from the carbon atoms of arylimido and the d−p π bond from the d_{xz} orbital on the molybdenum atom that links the nitrogen atom and the p_x orbital on nitrogen largely contribute to the HOMO. The LUMO mainly localizes at the end of heteroaromatic rings. According to the TDDFT calculations, the crucial transition state that dominates the optical nonlinearity is generated from Mo≡N to the end of heteroaromatic ring bearing a nitro group. This behavior further indicates that the hexamolybdate acts as a donor and the heteroaromatic rings act as an acceptor and conjugating bridge as well. This kind of D−π−A structure, as shown in Scheme 1 and Figure 3, generates a strong electronic communication, which results in a large intramolecular charge transfer and a high-performance NLO response, while a noncentrosymmetric structure is a prerequisite for crystals to exhibit efficient second-order NLO effects that enable the manufacture of second-harmonic-generating, electrooptical, and photorefractive devices. There are many examples[32−34] in the literature where the compound/structure crystallizes in the noncentrosymmetric triclinic space group $P1$ (No. 1) with excellent NLO response, which explains the relationship between the NLO response and space group of the studied parental system with noncentrosymmetric triclinic space group $P1$ (No. 1). Experimentally, the parent compound **1** in Figure 1, formulated as $[Mo_6O_{18}(NC_{16}H_{13})]^{2-}$, crystallizes in the noncentrosymmetric triclinic space group $P\bar{1}$.[35] In our theoretical prediction, it exhibits distinct NLO properties that correspond to various previous reports.[32,33,36]

The computed β values indicate that the replacement of one aryl ring with heteroaromatic rings significantly alters the first hyperpolarizability. The magnitude of the increase or decrease of β depends on both the nature of the heteroaromatic ring and its position in the molecular framework. The replacement of the benzene ring on the donor end (POM cluster) and one heteroaromatic ring such as thiophene, furan, or pyrrole on the acceptor end ($-NO_2$) results in the highest β values, as shown by system **1**: Substitution by pyrrole results in a larger effect than that by thiophene, which, in turn, has a larger effect than furan (Table 2: **1c** > **1a** > **1b**). On the other hand, in molecular systems where the same heteroaromatic rings are present on the donor end, the trends are as in Table 2 for **2a** > **2c** > **2b**. These results indicate that pyrrole when placed on the acceptor end causes significant enhancement in the molecular nonlinearity but lowers the activity when it is on the donor end. Furan substitution at the donor end is also effective but leads to a large enhancement at the acceptor end. The presence of thiophene is also valuable at the acceptor end compared to the donor end (Table 2: **1a** > **2a**). The magnitude of the increase



System 1



System 2

Figure 4. Frontier MOs of systems **1** and **2** involved in the dominant electron transitions.

Table 2. Calculated Static Second-Order Polarizabilities (1×10^{-30} esu), the Most Contributing Nonzero Component of the β Tensor (β_{xxx}), Symmetry ($S = A$), Excitation Energy (ΔE_{ge} = eV), Oscillator Strength (f_{os}), Transition Moments (M_x^{gm}), and MO Transitions for Systems 1 and 2

system	series	β_{xxx}	β	S	ΔE_{ge}	f_{os}	M_x^{gm}	MO transition
1	**1a**	529.42	318.47	*A*	1.65	0.92	4.76	HOMO → LUMO HOMO−5 → LUMO
	1b	468.34	282.72	*A*	1.72	0.84	4.46	HOMO → LUMO HOMO−5 → LUMO
	1c	562.82	339.00	*A*	1.80	0.74	4.07	HOMO → LUMO HOMO−5 → LUMO
2	**2a**	266.37	163.48	*A*	1.66	0.84	4.54	HOMO → LUMO HOMO−3 → LUMO
	2b	142.49	91.23	*A*	1.79	0.73	4.06	HOMO → LUMO HOMO−2 → LUMO
	2c	178.15	110.64	*A*	1.79	0.75	4.11	HOMO → LUMO HOMO−2 → LUMO

Table 3. Calculated Static Second-Order Polarizabilities (1×10^{-30} esu), the Most Contributing Nonzero Component of the β tensor (β_{yyy}), Symmetry ($S = A'$), Excitation Energy (ΔE_{ge} = eV), Oscillator Strength (f_{os}), Transition Moments (M_y^{gm}), and MO Transitions for Systems 3−5

system	series	β_{yyy}	β	S	ΔE_{ge}	f_{os}	M_y^{gm}	MO transition
3	**3a**	154.27	93.82	A'	1.77	0.79	4.26	HOMO → LUMO HOMO−2 → LUMO
	3b	129.71	79.58	A'	1.95	1.01	4.58	HOMO → LUMO HOMO−2 → LUMO
	3c	194.50	118.07	A'	2.11	0.73	3.75	HOMO → LUMO HOMO → LUMO+3
	3d	52.73	35.37	A'	1.86	1.07	4.86	HOMO → LUMO HOMO−2 → LUMO
	3e	47.98	32.84	A'	1.92	1.17	4.98	HOMO → LUMO HOMO−2 → LUMO
	3f	105.76	66.27	A'	1.88	0.59	3.58	HOMO → LUMO HOMO−2 → LUMO HOMO−3 → LUMO
	3g	82.54	51.36	A'	1.85	0.95	4.58	HOMO → LUMO HOMO−2 → LUMO HOMO−3 → LUMO
	3h	94.49	59.01	A'	1.91	0.90	4.37	HOMO → LUMO HOMO−2 → LUMO
	3i	146.16	89.90	A'	2.17	0.58	3.31	HOMO → LUMO HOMO−2 → LUMO HOMO−4 → LUMO
4	**4a**	103.42	62.91	A'	1.75	0.88	4.53	HOMO → LUMO HOMO−2 → LUMO HOMO−4 → LUMO
	4b	95.83	58.55	A'	1.81	0.95	4.62	HOMO → LUMO HOMO−2 → LUMO
	4c	154.89	94.09	A'	2.18	0.84	3.98	HOMO → LUMO HOMO−2 → LUMO HOMO−4 → LUMO
5	**5a**	260.77	158.52	A'	2.15	0.81	3.92	HOMO → LUMO HOMO−2 → LUMO HOMO−4 → LUMO
	5b	206.76	126.75	A'	1.78	0.74	4.13	HOMO → LUMO HOMO−2 → LUMO HOMO−4 → LUMO
	5c	244.28	148.89	A'	2.25	0.73	3.63	HOMO → LUMO HOMO−2 → LUMO HOMO−4 → LUMO

or decrease of β with respect to that of the model systems **1** and **2** depends on both the nature of the heteroaromatic ring and its position in the molecular framework. This indicates that thiophene when placed on the acceptor end causes significant enhancement in the molecular nonlinearity but lowers the activity when it is on the donor end. Thus, the increase or decrease of the molecular nonlinear activity in these systems depends on the nature as well as the location of the heteroaromatic ring. The same type of ring present on either side of the molecule evidently induces conflicting responses. The ring that enhances the nonlinearity at the donor end is comparatively less effective at the acceptor end and vice versa. One of the parameters affecting the coupling between the donor and acceptor substituents is the energy barrier imposed by the conjugating bridge. This factor becomes relevant and important especially if the conjugating pathway is made up of aromatic rings. The lower the aromatic delocalization energy barrier, the higher the first hyperpolarizability should be. Simple five-membered heteroaromatics such as thiophene (29 kcal/mol) possess lower delocalization energy[37] relative to benzene (36 kcal/mol) and, therefore, is expected to be more effective than benzene in promoting charge transfer on the acceptor end, thus increasing the β value. As pointed out earlier, the magnitude of β is determined not only by the nature of the heterocyclic ring but also by its location. In donor−acceptor-substituted NLO molecules, π conjugation commonly provides a pathway for the redistribution of electrons under the influence of an electric field. In some cases, the nature of π conjugation can alter the electron-donating and -accepting ability of the substituents. For example, if any of the segments within the π-conjugation pathway possesses electron-releasing or -withdrawing characteristics, the overall electron-donating or -accepting ability of the substituents, and thereby the effective charge transfer and molecular nonlinearity, will be affected. These effects depend not only on the nature of the conjugating segments but also on their location in the molecular framework. Last but not least, thiophene, being the electron-deficient five-membered heteroaromatic ring studied here, assists the nitro group in **1a**, resulting in a more pronounced electron-withdrawing effect, whereas in **2a**, it counteracts the electron-donating effect of the hexamolybdates, resulting in a decrease in the β value. Thiophene, being the least electron-rich heteroaromatic ring studied here, and the observed trends in **1a** and **2a** may be attributed mainly to its lower delocalization energy with respect to benzene.

Similarly, the trends can be seen from the calculated data (Table 3) obtained for fully heteroaromatic stilbenes (system **3**, series **3a**−**3i**; Figure 3). Thus, the increase or decrease of the molecular nonlinear activity in these systems depends on the nature as well as the location of the heteroaromatic ring. Of all of the nine combinations studied in this series, system **3c** with pyrrole and thiophene on the acceptor and donor ends, respectively, is predicted to be the most active one. When both rings contain the same heteroatoms as in structures **3a**, **3e**, and **3i**, the computed values show differing trends. However, the variations in β in these molecules are relatively small. The same type of ring present on either side of the molecule evidently induces conflicting responses.

Nevertheless, in systems **4** and **5**, one of the rings is pyrrole (on the donor side in **4** and the acceptor side in **5**), while the other ring has two heteroatoms (e.g., thiazole, oxazole, and imidazole). Substantially higher β values are noted for system **5** in which the diheteroatom ring is present on the donor end. These systems also show the largest resonance enhancements in all of the systems considered here. Thiazole is found to be more effective than imidazole, which, in turn, is more effective than oxazole. In contrast, compounds **4**, where the same two heteroatom rings are present on the acceptor end, show reduced β values, with the least active one being the oxazole-derived system **4b**. Thus, the calculated β values predict that the molecular NLO activity of POM-based, nitro-substituted stilbenes can be fine-tuned by replacement with heteroaromatic rings. The magnitude of enhancement or reduction is prominent, with rings containing two heteroatoms or one heteroatom. In addition to the nature of the ring system, the β values are also dependent on their position in the molecular framework. In POM (polyanion) with a single phenyl ring, the charge transfer originated from organoimido to polyanion (LUMO concentrates on POM) and is responsible for the NLO properties of single-ring-substituted hexamolybdates.[17a] However, the charge transfer became the other way around when the double phenyl rings were introduced because the polyanion to organoimido (LUMO concentrates on the organic unit) charge transfer was responsible in this case.[18a] Interestingly, a reversal in the role of the hexamolybdate (POM) fragment from electron acceptor to electron donor had also been observed where single-ring to double-ring lengthening of π conjugation leads to a change of the charge-transfer direction.[31] Moreover, on the basis of the NLO response and direction-tunable charge transfer for organoimido-substituted hexamolybdates, at certain conjugated chain length, the polyanion acts as a donor, whereas organoimido acts as an acceptor.[31] Thus, the β value could be enhanced efficiently when an acceptor is introduced along the charge-transfer direction, whereas the opposite trend is observed when a donor is introduced.[18a,31]

The computed β values of the studied series of systems **1**−**5** show that the highest NLO responses among all of the studied series of systems are in following order: systems **1c** > **1a** > **1b** > **2a** > **5a** > **5c** > **5b** > **3c**. However, in our studied systems, the accepting ability of end heteraromatic rings has been enhanced by the incorporation of an electron-withdrawing group ($-NO_2$), which is helpful in increasing the optical nonlinearity in such types of inorganic−organic hybrid compounds based on heteroaromatic imido-substituted hexamolybdates. In system **1**, the presence of pyrrole, thiophene, and furan with the acceptor group and the benzene ring with the donor group (hexamolybdates) enhances the withdrawing ability of heteroaromatic rings, as a result of β values computed as 339.00×10^{-30} esu (**1c**), 318.47×10^{-30} esu (**1a**), and 282.72×10^{-30} esu (**1b**), respectively. System **1** offers a maximal NLO response among all of the studied systems, and it also indicates that POM is acting as a donor in all of the studied systems.

For the discussion of the second-order polarizability (β), examining the physical mechanism concerning determination of the dipole polarizability (α) is also important. The average polarizability, $\langle\alpha\rangle$, is given by

$$\Big\langle \alpha > = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \tag{1}$$

The computed dipole polarizabilities for systems **1**−**5** are listed in the Supporting Information (Table S1). Hence, the property of the studied systems **1**−**5** is dominantly determined by the x or y-direction transition. For example, the expression of dipole polarizability (x direction) is described in the following equation:

$$\alpha_{xx} \propto \frac{(M_x^{\mathrm{gm}})^2}{E_{\mathrm{gm}}} \tag{2}$$

According to eq 2, we can know that the α value is directly proportional to the square of the transition moment and is inversely proportional to the transition energy. As a result, in general, the system with a strong electronic absorption peak will have a larger α value. Transition energies (E), transition moments ($M_x^{\mathrm{gm}}/M_y^{\mathrm{gm}}$), and corresponding dominant MO transitions of systems **1**−**5** are provided in Tables 2 and 3. To throw further light on the origin of the second-order NLO properties of the studied series of systems, the demonstration of the structure−property relationship is also important. How does it cause variations in the computed β_{vec} values? From the complex sum-overstates (SOS) expression, a two-state model linked between β and a low-lying charge-transfer transition has been established.[38] For the static case, the following model expression is employed to estimate β_{CT}:

$$\beta_{\mathrm{CT}} \propto \frac{\Delta\mu_{\mathrm{gm}} f_{\mathrm{gm}}}{E_{\mathrm{gm}}{}^3} \tag{3}$$

where f_{gm}, E_{gm}, and $\Delta\mu_{\mathrm{gm}}$ are the oscillator strength, transition energy, and difference of the dipole moment between the ground state (g) and the mth excited state (m), respectively. In the two-state model expression, the second-order polarizability caused by charge transfer, β_{CT}, is proportional to the optical intensity and is inversely proportional to the cube of the transition energy. Therefore, for any noncentrosymmetric molecule, the low transition energy is the decisive factor for the large β. However, all of the studied series of systems possess almost identical conjugation bridges, which is why they would not have much difference in $\Delta\mu$, whereas the values of the ground-state dipole moment (μ) have been included in the Supporting Information (Table S1). However, a few equations have also been mentioned in the literature to evaluate the first hyperpolarizabilities, as shown in expressions (4)−(6).

$$\beta_{\text{vec}} = (\sum_i \beta_i^2)^{1/2} \tag{4}$$

$$\beta_i = \beta_{iii} + 1/3 \sum_{j\neq i} (\beta_{ijj} + 2\beta_{jji}) \tag{5}$$

$$\beta_{\text{two state}} = \frac{3e^2}{2\hbar^3} \frac{\omega_{\text{ge}} f_{\text{ge}} \Delta\mu_{\text{ge}}}{[\omega_{\text{ge}}{}^2 - \omega^2][\omega_{\text{ge}}{}^2 - 4\omega^2]} \tag{6}$$

While the degree of charge transfer and synergistic effects between POM (D) and heteroaromatic rings have been strongly enhanced by the introduction of different aromatic rings by different ways, particularly through the increased strength of the electron acceptor at the end of aromatic rings. Therefore, the larger β values are generated because electron transition originates from the POM cluster to heteroaromatic rings. In this way, a large class of donor−acceptor-substituted molecules with heterocyclic rings has been examined for their molecular NLO response.

5. CONCLUSIONS

It has been demonstrated that heteroaromatic imido-substituted hexamolybdates with large β values can be designed by taking the appropriate combination of heteraromatic rings. The NLO response depends strongly not only on the nature but also on the location of the heterocyclic ring. For example, a pyrrole ring at the acceptor end is very effective in enhancing β. At the donor end, this ring leads to a lower β value than the corresponding derivative, as shown in system **4**. Two furan rings cause smaller changes, as shown in system **3e**. Thiophene leads to larger β values more effectively at the acceptor end (system **1a**) compared to the donor end (system **2a**). Molecules with the largest β values have to be designed appropriately. Among the systems considered, the highest β values have been computed for systems in which pyrrole is at the acceptor end, as shown in system **1c** and **5a**−**5c**.

The first hyperpolarizabilities of (heteroaromatic) imido-substituted 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) (Heteroaromatic stilbene) hexamolybdates have considerably large first hyperpolarizabilities ranging from 32.84 × 10^{-30} to 339.00 × 10^{-30} esu. The polyanion acts as an electron donor, and the heteroaromatics act as an electron acceptor. The double aromatic rings in (heteroaromatics) hexamolybdates can prompt the conjugation between the d-electron system of hexamolybdates and the p−π electron of heteroaromatic stilbenes. (2) The presence of pyrrole, thiophene, and furan with an acceptor group ($-NO_2$) and a benzene ring with a donor group (hexamolybdates) has exhibited an excellent second-order NLO response, as shown by system **1**. (3) The presence of a benzene ring with an acceptor group ($-NO_2$) and thiophene with a donor group (hexamolybdates) has shown another way to increase the second-order NLO response, as shown by system **2a**. (4) The presence of a pyrrole ring with an acceptor group ($-NO_2$) and thiazole, imidazole, and oxazole with a donor group (hexamolybdates) is also a new class of entrants in NLO materials, as shown by system **5**. This work exhibits the tunable NLO behavior of (heteroaromatic stilbene) hexamolybdates and may provide a new means for experimentalists to design high-performance NLO materials.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cartesian coordinates, dipole moments and polarizabilites, and frontier MOs. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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