

Prediction of robustly large molecular second-order nonlinear optical properties of terpyridine-substituted hexamolybdates: Structural modelling towards a rational entry to NLO materials

Muhammad Ramzan Saeed Ashraf Janjua^{a,1}, Wei Guan^a, Likai Yan^a, Zhong-Min Su^{a,*}, Muhammad Ali^b, Iftikhar Hussain Bukhari^b

^a Institute of Functional Material Chemistry and Key Laboratory of Polyoxometalate Science of Ministry of Education, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, PR China

^b Department of Chemistry, University of Sargodha, Sargodha 40100, Islamic Republic of Pakistan

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ABSTRACT

We have explored an innovative, versatile, and novel molecular hybrid containing polyoxometalate (POM) cluster linked with terpyridine ligand via π -bridged donor–acceptor (D–A) configuration. The dipole polarizabilities, density of states, and second-order nonlinear optical (NLO) properties of terpyridine-substituted hexamolybdates have been investigated by using time-dependent density functional response theory (TDDFT). This class of organic–inorganic hybrid compounds possesses a robustly large molecular second-order NLO response, especially $[\text{Mo}_6\text{O}_{18}(\text{N}_4\text{C}_{25}\text{H}_{16}\text{I}_2)]^{2-}$ (system **5**) and $[\text{Mo}_6\text{O}_{17}(\text{N}_4\text{C}_{25}\text{H}_{16}(\text{CN})_2)(\text{N}_4\text{C}_{25}\text{H}_{16}(\text{CN})_2)]^{2-}$ (system **10**) with the static second-order polarizability (β_{vec}) computed to be 1209.25×10^{-30} esu and 1622.67×10^{-30} esu respectively. Thus, these systems have the possibility to be excellent second-order nonlinear optical materials. Analysis of the major contributions to the β_{vec} value suggests that the charge transfer (CT) from POM-cluster to terpyridine ligand (D–A) along the z-axis plays the key role in the NLO response, POM-cluster (hexamolybdates) acts as a donor (D) whereas terpyridine ligand acts as an acceptor (A) in all the studied systems. The computed β_{vec} values increase by the incorporation of electron acceptors (halogen = F, Cl, Br and I) at the terminus of terpyridine ligand. Furthermore, substitution of trifluoromethoxy ($-\text{OCF}_3$), trifluoromethyl ($-\text{CF}_3$), and cyanide ($-\text{CN}$) at the end of terpyridine ligand respectively enhances the optical nonlinearity. Orbital analysis shows that the degree of CT between POM and terpyridine segment was increased in 2D and organometallic/POM hybrid systems. The present investigation provides important and thought provoking insight into the robustly large NLO properties of terpyridine-substituted hexamolybdates.

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1. Introduction

Polyoxometalate (POM) chemistry has progressed dramatically during the past two decades, and various new structural types with fascinating topological beauty and important electronic, optical, and catalytic properties have been explored [1–4]. Along with this rapid progress made on these inorganic metal–oxygen cluster anions, studies on organic and polymeric conjugated materials have also exploded and flourished [5–8]. Although they are vastly different in molecular structures, POMs and organic conjugated molecules are both electrically active materials with similar electrical and optical properties such as photochromism, electro-

chromism, and conductivity. The underlying mechanisms of these properties are, however, different for the two types of materials, with $d\pi$ electrons responsible for the inorganic clusters, and delocalized π electrons responsible for the organic counterpart. While both areas have been enjoying significant success, there has been little success in bringing these two types of materials together through covalent bonds [9,10]. Not only will such hybrid materials combine the advantages of organic materials, such as ease in processing and structural fine tuning, with those of inorganic clusters, but the close interaction of organic delocalized π electrons with the cluster d electrons may bring striking synergistic effects. Such materials with their unique structures are extremely interesting not only to synthetic chemists and materials scientists, but also to theoreticians and experimentalists.

Numerous classes of molecules have been investigated as novel molecular NLO materials during the last few decades. These molecules can be placed into three generic classes of NLO materials: inorganic salts, organic materials, and organometallic materials.

* Corresponding author.

E-mail addresses: dr_janjua2010@yahoo.com (M.R.S.A. Janjua), zmsu@nenu.edu.cn (Z.-M. Su).

¹ Tel.: +86 431 85099108/+92 300/321 6604948; fax: +86 431 85684009.

Each class possesses its own complement of favorable and unfavorable attributes for NLO application [11]. The NLO response of organic compounds often surpasses those of purely inorganic materials [12–14] although organic materials show several drawbacks which reduce the implications of such materials. For example, they usually have very poor thermal stability and (in poled host-guest systems) they may undergo a facile relaxation to a random orientation [15]. The limitations identified above have propelled much research into the NLO properties of various alternative materials, among which organometallic compounds are of particular interest because of their potential to integrate the benefits of both organic and inorganic materials [16–23]. The study of organometallic compounds with NLO properties has opened new horizons in this field. Moreover, the search for new molecular materials with large NLO response is in progress. Recently, our group has made much progress in POM-based organic–inorganic hybrid materials [24–27]. POMs have been found to be extremely versatile inorganic building blocks for constructing functionally active materials, and POM-based organic–inorganic hybrid compounds are the combination of POM anions with organic ligands. The molecular nature of these two types of materials offers the opportunity to generate covalently bonded molecular hybrids where the interplay between metal d electrons and organic delocalized π electrons can be explored at the molecular level. However, polyoxomolybdate cluster is considered to be an excellent electron acceptor which had been proven to be a donor as well by the pioneering work of Janjua et al. [27]. Therefore, POM-based organic hybrid material in which a terpyridine ligand covalently linked to a hexamolybdate cluster was reported by Xu et al. [28]. This hybrid molecule is a focal point of our current research work.

In this report, hexamolybdates-to-organoimido charge transfer was a vital determinant to increase the NLO response. And it is very absorbing that in our all studied systems the electron accepting property of POM-cluster has been changed as it acts as a donor and terpyridine ligand acts as an acceptor (D–bridge–A) via charge-transport property of π -conjugated bridge which has also established the identity of POM as a donor as well in a rigorous way. This behavior of POM as a donor is other way round from previously studied systems [24]. Thus, in the present work, we have designed different kinds of systems by incorporation of multiple electron acceptors; we performed DFT calculations on terpyridine derivatives of hexamolybdates to predict their first hyperpolarizabilities. The effect on second-order polarizability is investigated by introducing halogen atoms (F, Cl, Br and I) and some other strong electron acceptor groups ($-\text{OCF}_3$, $-\text{CF}_3$ and $-\text{CN}$) at the terminus of terpyridine ligand which established a strong donor–bridge–acceptor configuration (D–bridge–A). Furthermore, optical nonlinearity has been robustly improved by investigating 2D and D–D–bridge–A terpyridine-substituted hexamolybdates. The structure–property relationship with terpyridine derivatives of POMs will be helpful in designing the new NLO materials where motive is not only to bring different structural units together but also in the prospect of developing useful means to pursue high-performance nonlinear optical materials.

2. Computational details

The DFT calculations were carried out using the ADF2008.01 suite of programs [29]. The zero-order regular approximation (ZORA) was adopted in all the calculations to account for the scalar relativistic effects [30]. The generalized-gradient approximation (GGA) was employed in the geometry optimizations by using the Becke [31] and Perdew [32] (BP86) exchange–correlation (XC) functional. For the calculations, we made use of the standard ADF TZP basis set, which is triple- ζ plus polarization STO basis set. Triple- ζ plus polarization basis sets were used to describe the

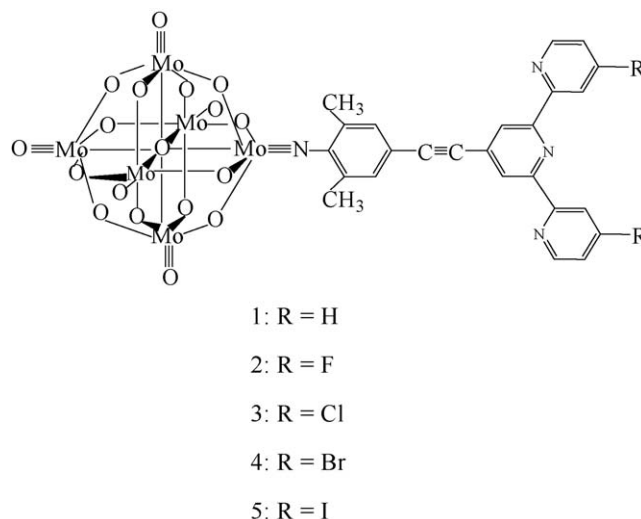


Fig. 1. Calculation models for systems 1–5.

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. The cores (C, N, O, F: 1s; Cl: 2p; Br: 3p; I: 4p; Fe: 2p) were kept frozen. In calculations of the polarizability, second-order polarizability and excitation property, the RESPONSE and EXCITATION modules [33] 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 the response properties [34]. The reliability of LB94 potential to calculate polarizabilities and hyperpolarizabilities has already been proven and well-documented [35–37]. 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 [38] was used to calculate density of states (DOS). The functional and basis set choices for our studied inorganic–organic hybrid compounds were based on the research work which has already been reported [39].

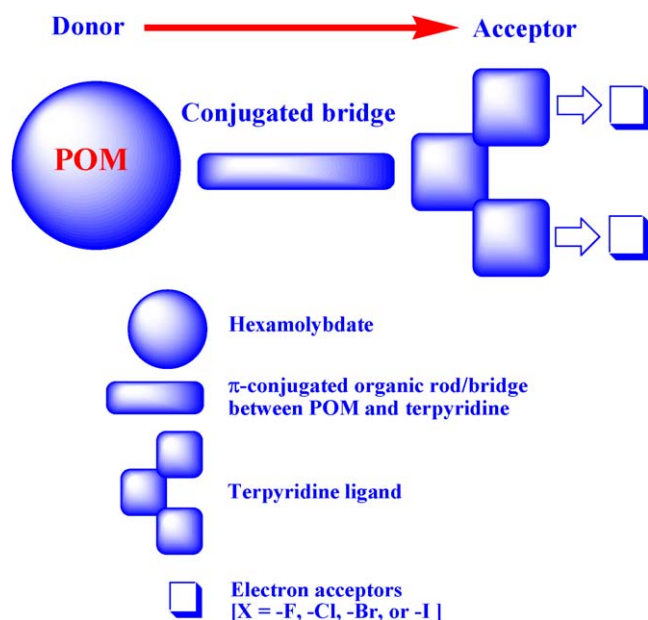
3. Molecular structures

The geometrical optimization of all systems (1–5) under symmetry constraint C_{2v} was carried out, whereas initial geometric data were obtained from the crystal data [28]. Their structures are sketched in Fig. 1 and the optimized bond distances in Table 1, which are in reasonable agreement with reported experimental data. The agreement between experimental and calculated metrical parameters of system 1 gives us confidence that the present study is consequential for this research work. As far as Scheme 1 is concerned, it shows the hypothetical calculation models with sketch map of various D–bridge–A configurations of studied systems.

Table 1
Bond lengths (Å) and angles ($^\circ$) calculated by DFT for systems 1–5.

Metrical parameters	1	2	3	4	5
C1–N1	1.344 (1.375) ^a	1.342	1.341	1.340	1.340
Mo1–N1	1.820 (1.747)	1.822	1.823	1.822	1.823
Mo1–O1	2.222 (2.213)	2.222	2.222	2.221	2.221
C1–N1–Mo1	180 (175.83)	180	180	180	180

^a Experimental values in parentheses are from Ref. [28].



Scheme 1. Hypothetical calculation models with sketch map of various D–A configurations of POMs.

4. Results and discussion

4.1. Static second-order NLO properties

In order to have better understanding about second-order NLO response (β), the knowledge of dipole polarizability is also important. The average polarizability, $\langle\alpha\rangle$ is defined as

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (1)$$

There are three components of dipole polarizability α_{xx} , α_{yy} and α_{zz} respectively. There exists a C_{2v} symmetry in our studied systems and the α_{zz} component has the largest value as compared to the α_{xx} and α_{yy} components and the property of the studied compounds (1–5) is predominantly evaluated by the z-direction transition (Fig. 1). The mathematical formulation of dipole polarizability along z-direction is defined in the following equation:

$$\alpha_{zz} \propto \frac{(M_z^{ge})^2}{E_{ge}} \quad (2)$$

According to Eq. (2), we know that the α value is directly proportional to the square of transition moment, and is inversely proportional to the transition energy. As a result, the system with least transition energy will have a larger α value. The excitation energies (E), transition moments (M_z^{ge}), and corresponding dominant molecular orbital (MO) transitions of systems 1–5 are provided in Table 3. The computed M_z^{ge} values of systems 1–5 are increasing as follows: $1 < 2 < 3 < 4 < 5$; the average polarizability, $\langle\alpha\rangle$ is in the following order: system $5 > 4 > 3 > 2 > 1$ as shown in Table 2. The TDDFT results show that the electron transition of system 1 mainly arises from POM-cluster (HOMO) to terpyridine ligand (LUMO + 6) and (HOMO – 4) to (LUMO + 6) along the z-direction, and this character of charge transfer similarly occurs on system 2 (HOMO to LUMO + 6) and (HOMO – 4 to LUMO + 6); system 3 (HOMO to LUMO + 6) and (HOMO – 4 to LUMO + 6); system 4 (HOMO to LUMO + 6) and (HOMO – 4 to LUMO + 6); system 5 (HOMO to LUMO + 8) and (HOMO – 4 to LUMO + 8). The molecular orbitals involved in the dominant electron transitions in

Table 2

The computed dipole polarizabilities (1×10^{-24} esu) for systems 1–5.

System	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
1	105.73	65.22	285.01	151.98
2	105.75	65.14	305.70	158.86
3	107.95	66.95	321.51	165.47
4	109.53	68.43	330.16	169.37
5	110.40	68.46	337.58	172.16

systems 1–5 are shown in Figs. 2 and 3. The crucial electronic transition of system 5 is more interesting as it originates from POM (HOMO) to terpyridine segment (LUMO + 8). The molecular orbitals involved in the dominant electron transitions in system 5 are shown in Fig. 3. Under the C_{2v} symmetry constraints, electronic transitions from the ground state to the singlet A_1 (z-direction) excited states are electric dipole allowed for our studied systems. For present calculated systems (1–5), the dominant electron transitions have the A_1 symmetry (see Table 3).

The contribution of different orbitals towards the electronic transitions has been modified by small changes at molecular level whereas the dominant electron transitions for the studied compounds have the same A_1 symmetry. Therefore, the major charge transfer arises from POM-cluster to terpyridine segment along the z-axis. These behaviors disclose that the terpyridine ligand acts as an acceptor and POM-cluster acts as a donor, which is entirely opposite to the character of charge transfer of arylimido hexamolybdates derivatives [24]. In system 1 POM is acting as a donor while terpyridine is behaving as an acceptor through its π -conjugated organic bridge/rod, composed of imido metal–nitrogen ($\text{Mo}\equiv\text{N}$) linkage and $\text{C}\equiv\text{C}$ triple bond amid aromatic ring between POM-cluster and terpyridine ligand (see Figs. 1 and 2). The charge transfer in systems 2–5 is also from POM towards electron acceptor groups via conjugated bridge indicating that terpyridine ligand acts as an acceptor and POM as a donor via conjugated bridge. In our systems (1–5) conjugation of π -electrons on terpyridine rings has been enhanced with the presence of $\text{C}\equiv\text{C}$ triple bond, $\text{C}-\text{C}$ π -bond along with $\text{Mo}-\text{N}$ π -bond is delocalized with the conjugation of central aromatic ring along with terpyridine rings. Thus, π -conjugation is extended and the delocalization is further improved from system 1 to system 5 by introducing different electron acceptors (halogen atoms = F, Cl, Br and I). This extended conjugation leads to smaller transition energy and larger oscillator strength which increases the degree of charge transfer. Therefore, large β_{vec} value has been generated in system 5 in contrast to system 1. In frontier molecular orbitals of systems 1–5, POM-cluster can modify the occupied molecular orbitals and extend its conjugation of π -electrons to the terpyridine segment as shown in Figs. 2 and 3 which results in charge transfer (CT) from POM-cluster to terpyridine segment.

In our designed and studied compounds the direction of dipole moment is along z-axis, β_{vec} can be defined as

$$\beta = \sum_i \frac{\mu_i \beta_i}{|\mu|} \quad i = x, y, z \quad (3)$$

$$\text{where } \beta_i = \left(\frac{3}{5}\right) \sum_{j-x,y,z} \beta_{ijj}$$

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 its individual components of systems 1–5 are shown in Table 4. There are seven components of

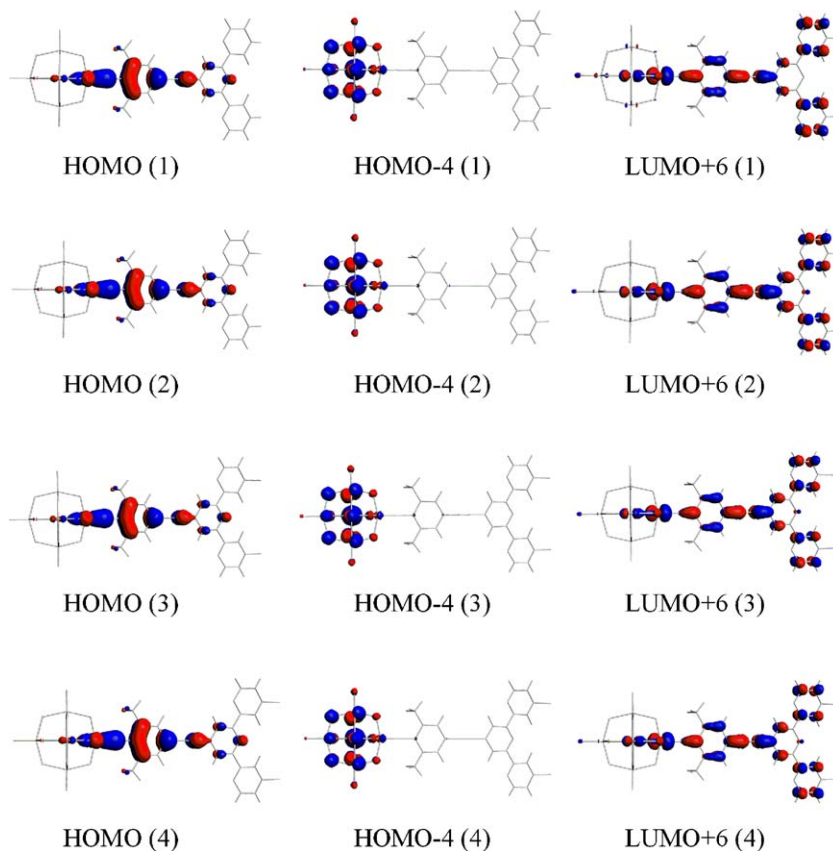


Fig. 2. The frontier molecular orbitals of systems 1–4 involved in the dominant electron transitions.

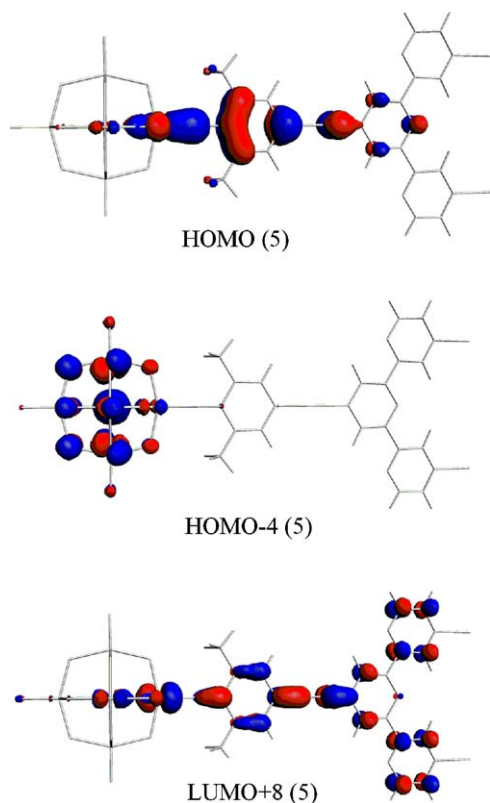


Fig. 3. The frontier molecular orbitals of system 5 involved in the dominant electron transitions.

the second-order polarizability owing to the C_{2v} symmetry. As we have discussed above in the dipole polarizability, the β_{zzz} component has the largest value. Hence, the major contribution to the second-order polarizability is the β_{zzz} component and the major charge transfer is also along the z-direction. As shown in Table 4 that all systems have large second-order polarizability coefficients compared to previously studied imido-substituted hexamolybdates by Yan et al. [24,25]. They computed β values in the range of 8.13×10^{-30} esu to 355.78×10^{-30} esu for typical POM-based inorganic–organic hybrid compounds with conventional D–A configuration [24]. Whereas in this study the POM-cluster linked to pendant terpyridine units through bridging group generates more efficient D–A compounds with significantly large second-order polarizability coefficients. Several other POM-based inorganic–organic hybrids with D–A/D– π –A configurations have been reported and maximum values of second-order NLO response were calculated to be 559.27×10^{-30} esu and 210.21×10^{-30} esu by Zhuang et al. [39a] and Janjua et al. [39b] respectively. This indicates that all the current studied systems have an excellent second-order NLO response. Due to charge transfer along z-axis in our studied systems the computed β_{vec} values of these systems show that the NLO response is as follows: system $5 > 4 > 3 > 2 > 1$. β_{zzz} component of system 1 has the lowest value while the β_{zzz} component of system 5 has the highest value as it exhibits the largest β_{vec} among systems 1–5. In short, electron withdrawing nature or electron accepting ability of terpyridine ligand has been considerably enhanced by introducing different electron acceptors (F, Cl, Br and I) respectively at the endmost of terpyridine segment which not only strengthened the D–bridge–A configuration but also leads to robustly large NLO response of terpyridine-substituted hexamolybdates. The halogen atoms have

Table 3Excitation energy (E , a.u.), oscillator strengths (f), transition moment (M_z^{ge} , a.u.)^a, symmetry (S), and corresponding dominant MO transitions of systems **1–5**.

System	Excitation energy	f	M_z^{ge}	S	MO transition
1	0.087	0.8245	3.773	A_1	HOMO \rightarrow LUMO + 6 (71%) HOMO \rightarrow 4 \rightarrow LUMO + 6 (10%)
2	0.084	0.8009	3.774	A_1	HOMO \rightarrow LUMO + 6 (68%) HOMO \rightarrow 4 \rightarrow LUMO + 6 (18%)
3	0.084	0.8660	3.920	A_1	HOMO \rightarrow LUMO + 6 (71%) HOMO \rightarrow 4 \rightarrow LUMO + 6 (16%)
4	0.084	0.8834	3.956	A_1	HOMO \rightarrow LUMO + 6 (71%) HOMO \rightarrow 4 \rightarrow LUMO + 6 (15%)
5	0.085	0.9358	4.064	A_1	HOMO \rightarrow LUMO + 8 (72%) HOMO \rightarrow 4 \rightarrow LUMO + 8 (13%)

^a $M_x^{ne} = M_y^{ne} = 0$.**Table 4**The computed static second-order polarizabilities and their individual components (1×10^{-30} esu) for systems **1–5**.

System	β_{zzz}	β_{yyz}	β_{xxz}	β_{yzy}	β_{zyy}	β_{xzx}	β_{zxx}	β_{vec}
1	−1444.800	−1.879	−30.727	−1.879	−1.879	−30.727	−30.727	886.550
2	−1805.300	−1.858	−56.130	−1.858	−1.858	−56.130	−56.130	1118.102
3	−1888.200	−1.642	−56.719	−1.642	−1.642	−56.719	−56.719	1168.041
4	−1946.800	−2.143	−58.870	−2.143	−2.143	−58.870	−58.870	1204.761
5	−1958.000	−1.783	−55.383	−1.783	−1.783	−55.383	−55.383	1209.254

tuned NLO response of system **1** as shown in systems **2–5** by strengthening accepting ability of terpyridine ligand.

However, the β_{vec} value of system **5** is one and half times larger than system **1** and the substitution effect on NLO response is in following manner: $I > Br > Cl > F$. All systems (**1–5**) are operating through D–bridge–A configuration. The β_{vec} value of terpyridine-substituted hexamolybdate has been enhanced by incorporation of the halogen atoms at the end of terpyridine ligand. NLO response has been significantly amplified by substitution of iodine as shown in system **5** that is why β_{vec} value has been increased from 886.55×10^{-30} esu (system **1**) to 1209.25×10^{-30} esu (system **5**). The system **5** has maximal NLO response among all five systems as accepting ability of terpyridine segment has been enhanced by incorporating iodine at the terminal positions of terpyridine ligand which further supports our idea that substitution of strong electron acceptor (iodine) at the end of terpyridine ligand is more important to enhance the optical nonlinearity. The system **5** is a model of excellence with regard to the systems **1–4** as it shows highest NLO response among all studied systems (**1–5**) by establishing D–bridge–A relationship in a compact manner which validates our idea that POM is acting as a donor and terpyridine ligand as an acceptor in our all studied systems. The degree of charge transfer and synergistic effect between POM-cluster (D) and terpyridine segment (A) have been substantially enhanced by introducing different electron acceptors (F, Cl, Br and I) respectively at the terminus of terpyridine ligand. The NLO properties of our studied systems have been improved greatly through the conjugation path and the choice of acceptors. Particularly, for our studied organic–inorganic hybrid materials, their NLO properties have been galvanized through the introduction of different electron acceptors, this incorporation of acceptor atoms is helpful to enhance the degree of charge transfer by decreasing the excited energy which leads to striking increase in the first hyperpolarizability as it is salient in system **5** where β_{vec} value computed to be 1209.25×10^{-30} esu.

Oudar and Chemla [40] have formulated a simple link between molecular hyperpolarizability and electronic transition in low-lying crucial excited states. On the basis of the complex sum-over-states (SOS) expression the paradigm two-level model can be

defined as under:

$$\beta \propto \frac{\Delta\mu_{ge} \cdot f_{os}}{\Delta E_{ge}^3} \quad (4)$$

where $\Delta\mu_{ge}$ is the dipole moment between the ground state (g) and the excited state (e), f_{os} is the oscillator strength, and ΔE_{ge} is the transition energy. These factors ($\Delta\mu_{ge}$, f_{os} , and ΔE_{ge}) are closely related with each other and governed by choice/strength of donor/acceptor along with conjugated bridge. The most favorable combination of these factors can provide larger β value. On the basis of above model we have designed different functionalized terpyridine derivatives of hexamolybdate systems by introducing different acceptors at the end of terpyridine ligand. Therefore, for any non-centrosymmetric molecule, the low transition energy (<1 a.u.) is the decisive factor for the large β . Hence, for the studied compounds, the low excitation energy and strong oscillator strength are the commanding factors in the β value. As the Table 3 illustrates, the values of excitation energy are related to the

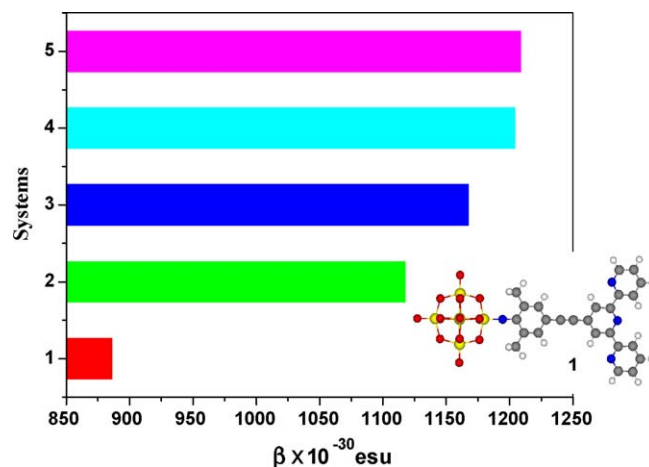


Fig. 4. Horizontal bars showing the incremental increase in β value from system **1** to system **5**.

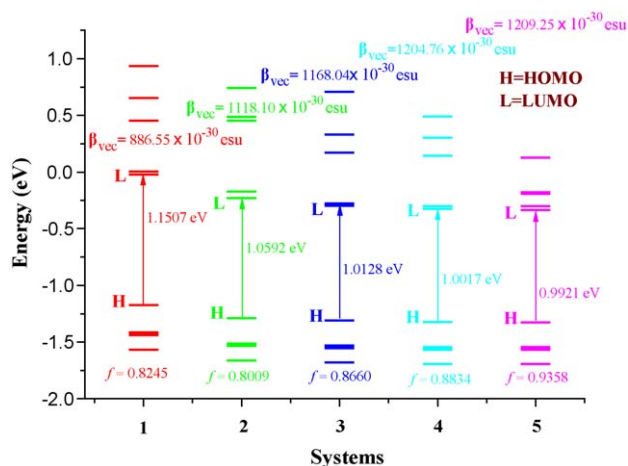
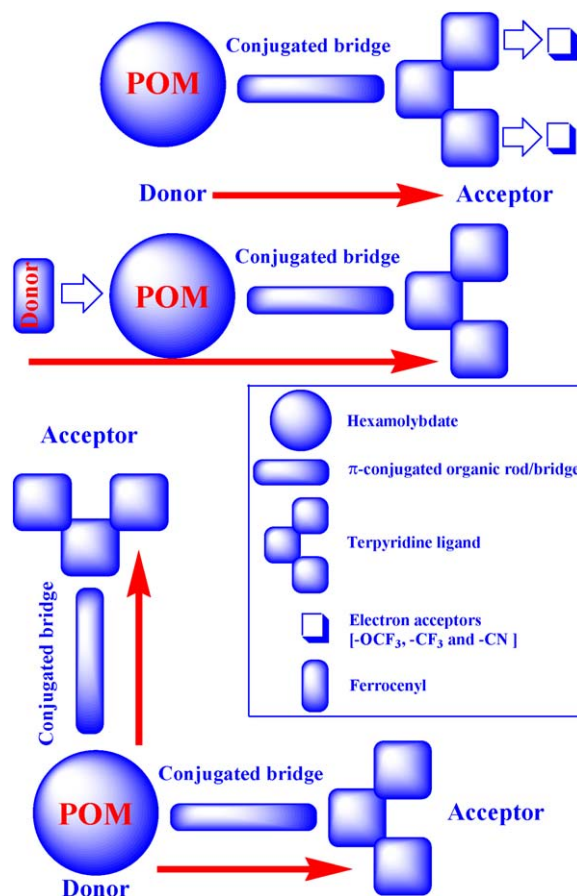


Fig. 5. Molecular orbital diagram, oscillator strength (f), and arrows indicate HOMO–LUMO energy gaps of systems 1–5.

structural character of the studied compounds. However, the values of excitation energy are almost same for systems 2–4 as follows: system 2 \approx 3 \approx 4 \approx 5 $<$ 1. The excitation energy of system 1 is 0.087 a.u., whereas it is smaller for systems 2–5 (0.084 a.u.). The red shift of the absorption band attributes the substitution of different electron acceptors (F, Cl, Br and I) respectively. From Eq. (4), this behavior significantly enhances β_{vec} value. Vividly, the excitation energy will tend to make dominant contribution to the β_{vec} values of the studied compounds. As we have already demonstrated that the β value is directly proportional to oscillator strength and inversely proportional to the transition energy. The low excitation energy and strong oscillator strengths are the authoritative factors to assign β value as it has been observed in



Scheme 2. Hypothetical calculation models with sketch map of various D–A and 2D configurations of POMs.

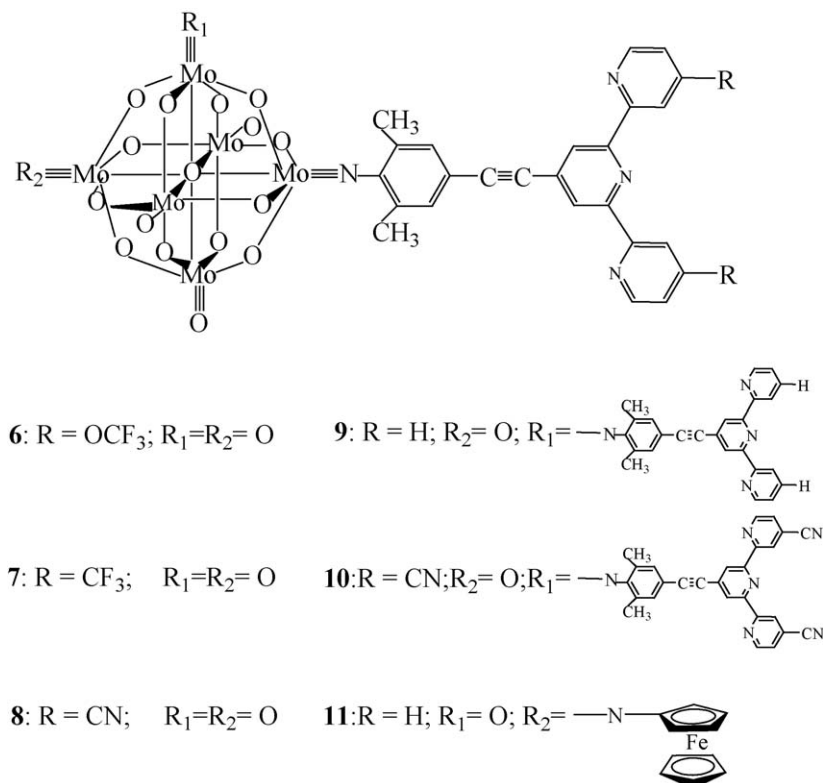


Fig. 6. Calculation models for systems 6–11.

Table 5

Excitation energy (E , a.u.), oscillator strength (f), transition moment (M_z^{ge} , a.u.), symmetry (S), the β_{zzz} components, computed static second-order polarizabilities (1×10^{-30} esu), and corresponding dominant MO transitions of systems **6–11**.

System	E	f	S	M_z^{ge}	β_{zzz}	β_{vec}	MO transition
6 (–OCF ₃)	0.084	0.7674	A_1	3.702	2066.000	1289.952	HOMO → LUMO + 6 (66%) HOMO – 4 → LUMO + 6 (23%)
7 (–CF ₃)	0.083	0.7256	A_1	3.630	2098.700	1315.008	HOMO → LUMO + 6 (63%) HOMO – 4 → LUMO + 6 (24%)
8 (–CN)	0.082	0.7668	A_1	3.744	2208.900	1393.027	HOMO → LUMO + 6 (65%) HOMO – 4 → LUMO + 6 (23%)
Two-dimensional POM-based organic hybrids							
9 (2D)	0.056	0.2549	A_1	2.623	654.400	1048.896	HOMO → LUMO + 1 (23%) HOMO – 1 → LUMO (23%) HOMO – 1 → LUMO + 2 (20%) HOMO → LUMO + 3 (17%)
10 (2D)	0.050	0.3619	A_1	3.290	1029.300	1622.678	HOMO – 1 → LUMO + 4 (46%) HOMO → LUMO + 5 (42%)
D–D–bridge–A organometallic/POM-based organic hybrids							
11 (DDA)	0.051	0.2840	A	2.894	2459.900	1499.990	HOMO – 3 → LUMO + 1 (59%) HOMO – 4 → LUMO + 1 (28%) HOMO – 3 → LUMO + 2 (8%)

systems **1–5** that low-lying transition energy along with strong oscillator strength are decisive/conclusive factors to determine NLO response as shown in Table 3. However, the oscillator strength f_{ge} for systems **1–5** are 0.8245, 0.8009, 0.8660, 0.8834, and 0.9358 respectively. The value of excitation energy of systems **2–5** are almost same and less than system **1**, while oscillator strength of systems **2–5** are increasing in following sequence: **2** < **3** < **4** < **5** in accordance with the increase of β value. In a word, oscillator strength is an authoritative factor towards β value while comparing systems **2–5**. Anyhow, low-lying excitation energy of systems **2–5** compared to system **1** is a decisive factor towards large β values. So, low-lying excitation energy is a key factor as it has power to assign NLO response in comparing systems (**2–5**) and **1**. Therefore, in these systems oscillator strength is a principal factor for increasing β_{vec} value.

Briefly, the large β_{vec} values come from the strong oscillator strength and small transition energy as shown in Table 3. So, the NLO response of systems **1–5** is as follows: system **5** > **4** > **3** > **2** > **1** (see Fig. 4) and it is obvious that the system **5** is offering maximum β value by establishing strong electronic communication through D–bridge–A configuration/relationship. It is also clear that substitution of acceptor has a majestic influence on the second-order NLO property in our studied systems. From these results, it can be concluded that incorporation of an electron acceptors (halogen atoms) at the terminal position of the terpyridine ligand is helpful to enhance the β value. In systems **1–5**, another important factor is lengthening via $C\equiv C$. Thus, the π -conjugation is extended and the delocalization is improved and introduction of acceptor (withdrawing groups: F, Cl, Br and I respectively) in systems **2–5** enhances β_{vec} value and more extended conjugation generally leads to a smaller energy difference between the ground and charge transfer excited states which accordingly enhances the degree of charge transfer. Therefore, the larger β_{vec} values are generated, as electron transition originates from POM-cluster to organic segment along the z-axis. It is said that the low-lying HOMO–LUMO energy gap might enhance NLO response. Generally, HOMO–LUMO energy gap is decreased by introduction of electron withdrawing groups (F, Cl, Br and I) as it occurred in systems **2–5**. As far as the HOMO–LUMO energy gaps of systems **1–5** are concerned it can be seen in Fig. 5 that the HOMO–LUMO energy gaps are decreasing as under: system **1** > **2** > **3** > **4** > **5** and NLO response is increasing accordingly: **1** < **2** < **3** < **4** < **5**. It means system **5** has least energy gap giving rise to maximal NLO response among all studied compounds as demonstrated in Fig. 5.

In addition, the total density of states (DOS) of systems **1–5** have also been included in supporting information (see Fig. S1) to easily and vividly observe the varieties of the HOMOs, LUMOs, and energy gaps. The investigated systems are particularly interesting for the nonlinear optical properties, appropriately operating by the substitution of different acceptors. Due to appropriate changes of the systems, one can also vary the NLO properties. Thus one requires reliable information about band structure which could be gathered from DOS diagram. The density of states (DOS) calculation has been carried out by using GaussSum, [38] it used to convolute density of states spectra from the molecular orbital data for systems **1–5**. The density of states in a band could be very large for some materials, it may not be uniform. It approaches zero at the band boundaries, and is generally highest near the middle of a band as it is corresponding in our studied systems (see Fig. S1).

On the basis of the special character of charge transfer and the large β_{zzz} value of systems **1–5**, we were driven to probe into the followings: the role of different but powerful electron withdrawing groups at the terminus of terpyridine ligand, the effect of two-dimensional configurations, and the influence of another strong donating group on POM-cluster in influencing the NLO response. In order to satisfy above queries we have also studied systems **6–8** (D–bridge–A), **9** and **10** (2D), and **11** (D–D–bridge–A) as shown in Fig. 6 and Scheme 2. The systems **6–10** investigated here show C_{2v} symmetry while symmetry axes are along the z-axis for systems **6–8**, and the bisector of the y- and z-axes for **9** and **10** respectively. Whereas the system **11** has no symmetry at all. Moreover, the charge transfer in system **6** arises from (HOMO → LUMO + 6) and (HOMO – 4 → LUMO + 6), system **7** (HOMO → LUMO + 6) and (HOMO – 4 → LUMO + 6), and this character of charge transfer similarly occurs on system **8** (HOMO → LUMO + 6) and (HOMO – 4 → LUMO + 6). The molecular orbitals involved in the dominant electron transitions in systems **6–8** are clarified in Fig. 7. The calculated β_{vec} values of systems **6–8** are 1289.95×10^{-30} esu, 1315.00×10^{-30} esu, and 1393.02×10^{-30} esu respectively. For these systems, the main contribution of β_{vec} is in the z-direction, and β_{zzz} components have larger values than those of other tensors. This point is in accord with the direction of the charge transfer (see Fig. 7) and values of β_{zzz} components are in following order; system **6** < **7** < **8** and transition energy is decreasing as follows: **6** > **7** > **8** (see Table 5). Theoretically, we have constructed and investigated systems **9** and **10** with two-dimensional (2D) characteristics as shown in Figs. 8 and 9 respectively. The quantum mechanical designing of 2D system is based on experimental work [41]. The system **10** is a masterpiece of 2D structural configuration by

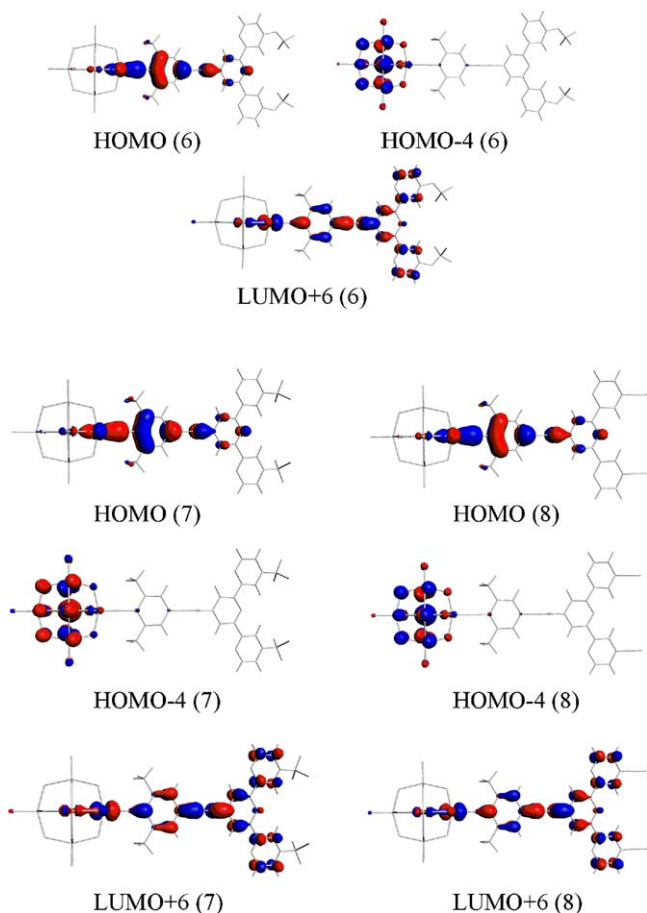


Fig. 7. The frontier molecular orbitals of systems **6–8** involved in the dominant electron transitions.

showing the outstanding and maximal NLO response among all the studied systems (**1–11**), whereas the static second-order polarizability (β_{vec}) is distinctly enhanced in 2D compounds. The β_{vec} values of 2D systems **9** (1048.89×10^{-30} esu) and **10** (1622.67×10^{-30} esu) are comparatively larger than their parental systems **1** and **8** respectively. With regard to transparency/efficiency trade-off systems **9** and **10** are superior to systems **1** and **8** because a major drawback of conventional 1D NLO materials is the so-called nonlinearity/transparency trade-off. We are further studying the NLO properties of 2D and 3D POM-based organic hybrids by DFT method.

After investigating, behavior of POM-cluster as a donor and terpyridine ligand as an acceptor in systems **1–10**, it was interesting to deal with the enhancement of donating ability of POM-cluster. In system **11**, we have incorporated ferrocenyl donor at the outer side of POM and the choice of introducing ferrocenyl ligand as a strong donor was also based on previous experimental work [9]. In system **11**, donating ability of POM has been reasonably enhanced and the β_{vec} value computed to be 1499.99×10^{-30} esu, which is the result of the existence of charge-transfer transition from POM-cluster and ferrocenyl donor to terpyridine segment along the z-direction leading to robustly large NLO response as shown in Fig. 10 and Table 5. The system **11** has reinforced our idea and conclusion as well that POM is acting as a donor leading to robustly large NLO response in this class of organic–inorganic hybrid composites, displaying a new path to experimentalists for synthesis of such kind of versatile, innovative, novel, and high-performance nonlinear optical materials which

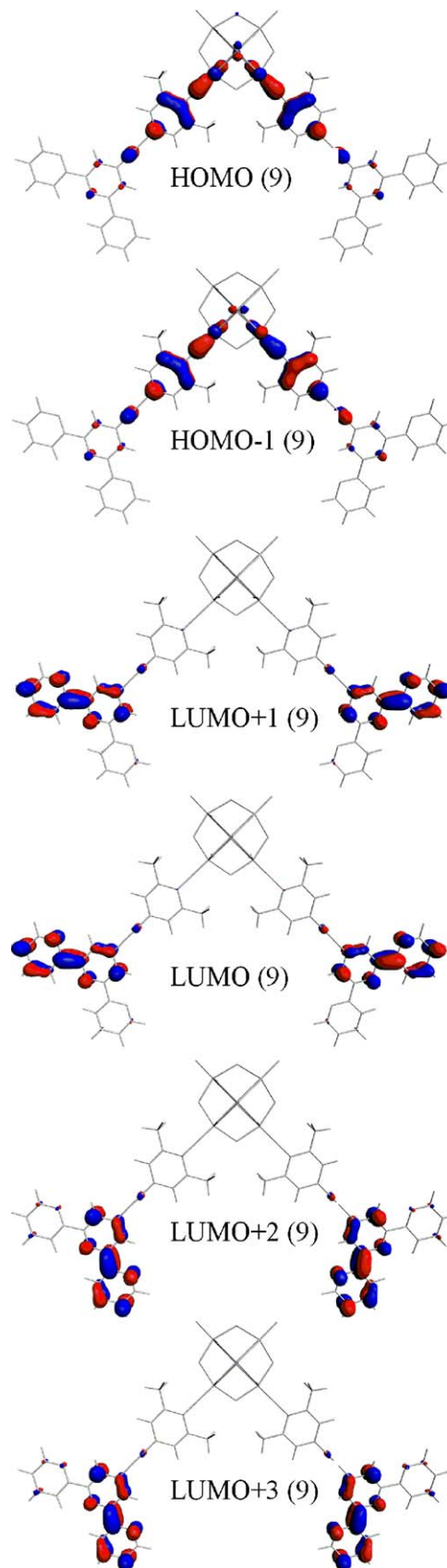


Fig. 8. The frontier molecular orbitals of system **9** involved in the dominant electron transitions.

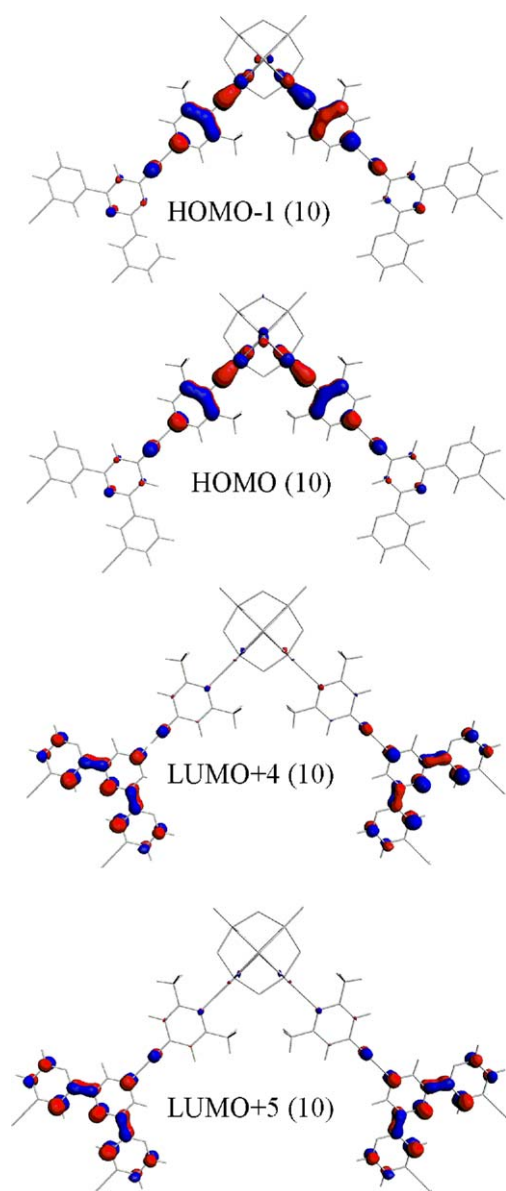


Fig. 9. The frontier molecular orbitals of system **10** involved in the dominant electron transitions.

might be a valuable entry to the field of functional material chemistry.

The present investigation gives novel physical insight into the NLO properties of terpyridine-substituted hexamolybdates and strives to reveal the origin of the remarkably large NLO properties of this family of hybrid compounds, which are interesting and appealing in design and synthesis of new promising NLO material. The study of the substituent effects as mentioned in this article and previously reported [42] research as well may shed light on improving the NLO properties. However, for our studied systems, the incorporation of an electron acceptor (Halogen atoms) leads to large β value, 2D systems prominently increase NLO response due to two-dimensional charge transfer while introduction of an electron donor (ferrocenyl ligand) at the outer side of POM-cluster enhances donating ability of POM leading to outstanding β values. These POM-based organic–inorganic hybrid compounds can become an excellent kind of material in the second-order NLO field. The electron acceptor atoms in the terpyridine segment enhance the first hyperpolarizability in our studied systems as POM acts as a donor and terpyridine ligand acts as an acceptor.

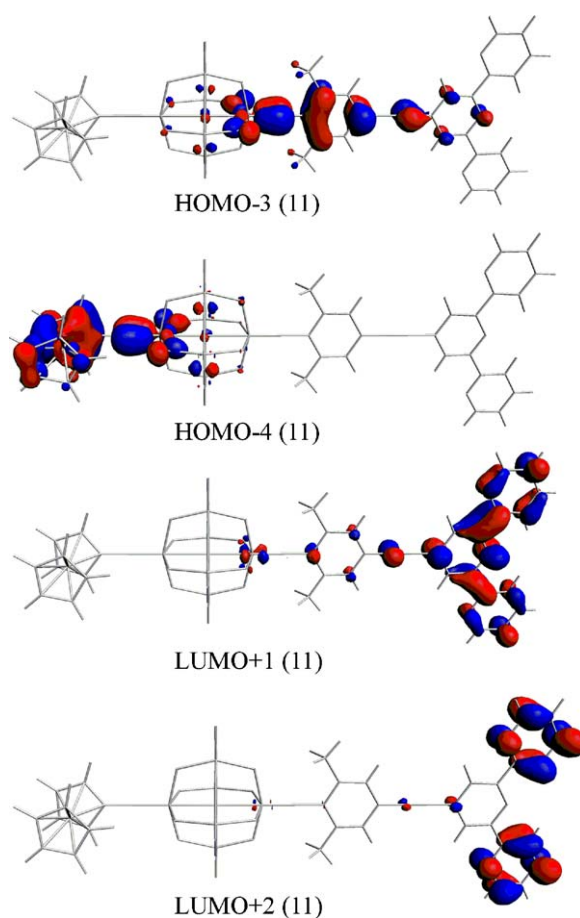


Fig. 10. The frontier molecular orbitals of system **11** involved in the dominant electron transitions.

To wrap up our discussion, the general approach for designing NLO materials with large molecular first-order hyperpolarizabilities (β values) – that might be appropriate for the eventual development of processable optoelectronic materials and devices – has involved coupling both an electron donor (D) and acceptor (A) to an organic framework that provides moderately strong electronic coupling between D and A. While a finite amount of D–A coupling is prerequisite for a significant first hyperpolarizability, the coupling mediated by the organic bridging must not be so strong as to remove the electronic asymmetry provided by the donor and acceptor groups. It is obvious in our research work (see Fig. 11) that electronic asymmetry between donor (POM-cluster)

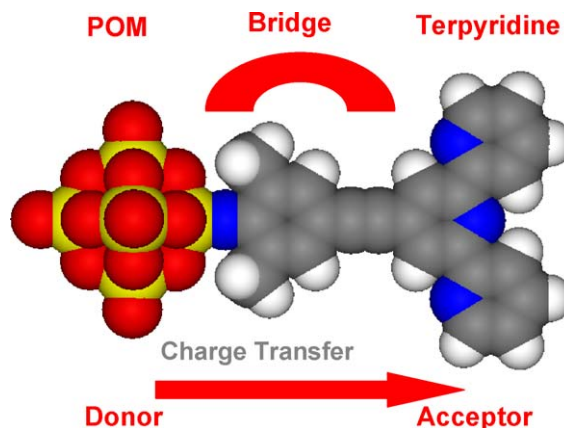


Fig. 11. D–A coupling via organic bridging in POMs.

and acceptor (terpyridine ligand) has been improved by different ways in our all studied systems (**1–11**), whereas imido metal–nitrogen (Mo≡N) linkage and C≡C triple bond amid aromatic ring act as a π -conjugated rod/bridge between POM and terpyridine ligand.

5. Conclusions

In the conclusion we have successfully predicted high-performance NLO materials as the first hybrid in which a POM-cluster and terpyridine ligand are linked by a π -conjugated bridge/rod where motivation lies not only to bring different structural units together but also in the prospect of generating new functional materials with refined nonlinear optical response by following ways: (a) by incorporation of different electron acceptor groups at the terminus of terpyridine ligand as in systems **1–8**. (b) By providing two-dimensional (2D) charge transfer as in systems **9** and **10**. (c) By launching another strong donor in order to enhance the donating ability of POM-cluster as in system **11**.

The terpyridine substituted hexamolybdates are found to possess strikingly large and robust static second-order polarizability. The optical excitation analysis in terms of frontier MOs shows that the charge transfer from POM-cluster to terpyridine ligand via π -conjugated bridge plays the key role in the NLO response. In systems **1–11** (except **9** and **10** as they are 2D) CT from POM to the terpyridine segment along z-axis is a vital determinant for the NLO response. According to the two-state model, the low excitation energy and strong oscillator strength are the commanding factors to assign the large β value. In the framework of this quantum mechanical study, we can jump at the following conclusions: (1) importantly notable are the robust molecular first hyperpolarizabilities exhibited by electronically asymmetric, donor–acceptor (D–A) versions of this new structural motif, exemplified by system **1**. (2) The structure–property relationship indicates that there are numerous ways to enhance the NLO response of this class of compounds. Interestingly, in our all studied systems POM-cluster is acting as a donor while terpyridine ligand as an acceptor through π -conjugated bridge. (3) The second-order NLO response could be enhanced by incorporation of the halogen atoms at the terminus of terpyridine segment, this introduction of electron acceptors (halogens X = F, Cl, Br and I) at the end of terpyridine ligand leads to larger β values by establishing strong D–bridge–A configuration. The influence on NLO response by halogens is as follows: I > Br > Cl > F. (4) The second-order NLO response of terpyridine-substituted hexamolybdates could further be improved by incorporation of $-\text{OCF}_3$, $-\text{CF}_3$ and CN at the terminal position of terpyridine ligand influencing NLO response as under: CN > OCF_3 > CF_3 . (5) The systems with 2D characteristics are found to possess appealingly large β value due to two-dimensional CT which is helpful to improve the nonlinearity/transparency trade-off. The systems **9** and **10** are registering more β values in contrast to their parental systems **1** and **8** respectively. (6) In system **11** metal to ligand (terpyridine) charge transfer (MLCT) transitions, originating from the iron in ferrocene and POM-cluster, are primarily responsible for large NLO response leading to D–D–bridge–A configuration. (7) These POM-based organic–inorganic molecules can become an excellent kind of materials in the second-order NLO field. The present calculations on terpyridine derivatives of hexamolybdates provide the theoretical framework in which the charge transfer and NLO properties might be understood. The POM-to-terpyridine ligand charge transfer may be responsible for the NLO properties of this kind of compounds. This work exhibits the tunable NLO behavior of terpyridine-substituted hexamolybdates and may provide new ways for the experimentalists to design high-performance NLO materials. This rational quantum mechanical

approach of designing various systems can be extended to the preparation and development of other hybrids by the researchers of experimental work.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jmgm.2010.01.011.

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