

Prediction of Second-Order Optical Nonlinearity of Trisorganotin-Substituted β -Keggin Polyoxotungstate

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The dipole polarizabilities, second-order polarizabilities, and origin of second-order nonlinear optical (NLO) properties of trisorganotin-substituted β -Keggin polyoxotungstate $[XW_9O_{37}(SnR)_3]^{(11-n)-}$ ($X = P, Si, Ge, R = Ph; X = Si, R = PhNO_2, PhC\equiv CPh$) have been investigated by using time-dependent density functional response theory. This class of organic–inorganic hybrid complexes possesses a remarkably large molecular second-order NLO response, especially for $[SiW_9O_{37}(SnPhC\equiv CPh)_3]^{7-}$ (system 5) with the static second-order polarizability (β_{vec}) computed to be 1569.66×10^{-30} esu. Thus, these complexes 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 from the heteropolyanion to the organic segment along the z-axis plays the key role in the NLO response of $[XW_9O_{37}(SnR)_3]^{(11-n)-}$. The computed β_{vec} values increase as a heavy central heteroatom changes in the order $Ge > Si > P$. Furthermore, nitro substitution on the aryl segment and the lengthening of organostannic π -conjugation are more important in enhancing the optical nonlinearity, especially for the latter factor. The present investigation provides important insight into the origin of the NLO properties of trisorganotin-substituted heteropolyoxotungstate.

Introduction

Polyoxometalates (POMs) have been found to be extremely versatile inorganic building blocks for constructing functionally active materials.¹ The covalent attachment of organic or organometallic groups to the POMs via linkages constitute an extremely interesting class of organic–inorganic hybrid polyoxoanions, which not only combine the advantages of organic materials so as to realize the so-called “value-added properties” but also contribute to exploring the possible synergistic effects. It is noteworthy that such hybrid materials have been continuously and rapidly growing because of their potential applications in catalysis, medicine, magnetism, optics, conductivity, etc.^{2,3} The POM-based

hybrids containing organometallic moieties have especially received much attention. Since the first organometallic-substituted heteropolyanion, $[PW_{11}O_{39}(TiCp)]^{4-}$, was reported in 1978,⁴ a fairly large number of POM-based organometallic hybrid materials have been synthesized and characterized in solution and in solid state.² Organotin derivatives of polyoxoanions are particularly attractive in these complexes because of the stability of the tin–carbon bond and size compatibility of WO_4^{4-} and SnR_3^{3+} moieties.^{5d} Furthermore, covalent character in the Sn–C bond is compatible with physiological conditions which allow us to envision applications of such complexes in medicine.⁶ The research groups of Pope, Liu, Knoth, and Kortz investigated the reactivity of trichlorostannanes $RSnCl_3$ with Keggin-type

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and Dawson-type lacunary polyanions.^{5–8} These reactions give several novel compounds (e.g., trisubstituted Keggin-type $[\text{SiW}_9\text{O}_{37}(\text{SnR})_3]^{7-}$, trisubstituted Dawson-type $[\text{P}_2\text{W}_{15}\text{O}_{59}(\text{SnR})_3]^{9-}$, and sandwich-type $[(\text{SnR})_3(\text{SiW}_9\text{O}_{34})_2]^{7-}$).

The NLO materials based on molecular compounds have continued to be of considerable current interest because they hold promise for potential applications in optical switching, telecommunications, optical computing, etc. With respect to the NLO properties of POM-based organic–inorganic hybrid complexes, Attansaio et al. have synthesized reversible photochromic materials, which consist of the combinations of Keggin anions or β - $[\text{Mo}_8\text{O}_{26}]^{4-}$ anion with quinolin-8-ol, the *N,N,N,N*-tetramethyl-*p*-phenylenediamine, and the tetraphenylporphyrinato Zn^{II} complex (ZnTPP).⁹ You et al. have investigated charge-transfer salts resulting from the combination of Lindqvist and α -Keggin-type anions with hemicyanine dyes.¹⁰ Others have made significant contributions as well.¹¹ However, the quite weak organic–inorganic interactions allowed in the solid state by this kind of charge transfer salts have prevented the occurrence of an effective electron transfer between the two components. To generate strong electronic communication, researchers are pursuing the synthesis of related compounds in which the organic molecule is covalently linked to the polyoxoanions.³ This class of organic–inorganic hybrid complexes may offer a greater scope for creation of multifunctional NLO materials by virtue of their low-energy, yet sometimes intense, electronic transitions. Recently, our attention has been given to the POM-based organic derivatives as potential NLO materials. We have investigated the second-order polarizabilities and origin of the NLO properties of organoimide hexamolybdates derivatives.¹² Organoimido-to-polyanion charge transfer may be responsible for the NLO properties, and the lengthening of organoimido π -conjugation or increasing organoimido polyanion is helpful for enhancing the β value. Then what is the origin of the second-order NLO properties of organometallic-substituted heteropolyanions? To explore the NLO properties of the type of hybrids, we turn our attention to trisorganotin-substituted derivatives of Keggin-type tungstate,^{5d} which is an interesting molecular material because of its significant advantage over structure–

design–flexibility, e.g., by variation in metal, oxidation state, ligand environment, geometry, etc.

Density functional theory (DFT) has proved very successful in predicting the properties of molecules and materials in the past decade, including NLO properties.¹³ Modeling of polyoxoanions has made progress.¹⁴ Recently, we have systematically investigated the properties of $[\text{X}_2\text{Mo}_5\text{O}_{23}]^{6-}$ ($\text{X} = \text{P}^{\text{V}}, \text{S}^{\text{VI}}, \text{As}^{\text{V}}, \text{Se}^{\text{VI}}$), $[\text{PTi}_2\text{W}_{10}\text{O}_{40}]^{7-}$, and $[\text{Mo}_6\text{O}_{17}\text{R}_2]^{2-}$ ($\text{R} = \text{organoimido}$) clusters by DFT, such as bonding character, redox properties, protonation, stability, and NLO properties.^{12,15} Theoretical studies would be helpful in the rationalization of the observed properties and in the design of novel POM-based hybrid materials with functional properties from the exploitation of the unique electronic and structural characteristics of these complexes. In this paper, we present time-dependent density functional theory (TD-DFT) calculations on the NLO properties of trisorganotin-substituted derivatives of Keggin-type polyoxometalates, which should be second-order NLO active because of the lack of centrosymmetry features (favorable charge-transfer ability). These POM-based organic–inorganic hybrid complexes may represent a promising family of the NLO materials.

Computational Details

The DFT calculations were carried out using the ADF2004.01 suite of programs.¹⁶ The zero-order regular approximation (ZORA) was adopted in all calculations to account for the scalar relativistic effects.¹⁷ The generalized-gradient approximation (GGA) was employed in geometry optimizations by using the Becke¹⁸ and Perdew¹⁹ (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. The cores (C, N, O: 1s; P, Si: 2p; Ge: 3p; Sn: 4p; W: 4d) were kept frozen. In calculations of the polarizability, second-order polarizability, and excitation properties, the RESPONSE and EXCITATION modules²⁰ implemented in the ADF program were used on the basis of the optimized geometries. The van Leeuwen–Baerends XC potential

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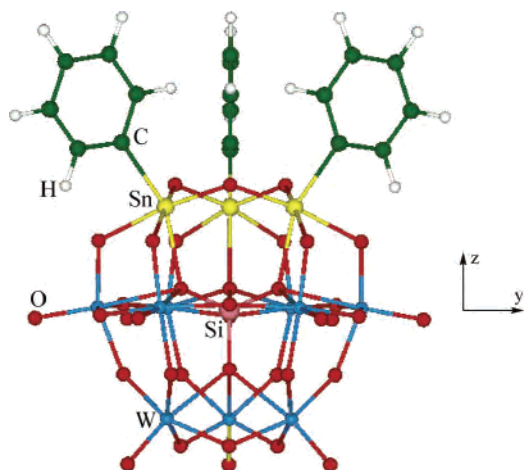


Figure 1. Structure and orientation of $[\beta\text{-SiW}_9\text{O}_{37}(\text{SnPh})_3]^{7-}$.

(LB94) was chosen for calculations of all the response properties.²¹ 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.

Molecular Structures. Herein, five trisorganotin-substituted β -Keggin tungstates $[\text{XW}_9\text{O}_{37}(\text{SnR})_3]^{(11-n)-}$ ($\text{X} = \text{P}, \text{Si}, \text{Ge}, \text{R} = \text{Ph}$; $\text{X} = \text{Si}, \text{R} = \text{PhNO}_2, \text{PhC}\equiv\text{CPh}$) were chosen for investigating the second-order NLO properties. All systems hold similar geometrical structures. The structure of heteropolyanion $[\beta\text{-SiW}_9\text{O}_{37}(\text{SnPh})_3]^{7-}$ is shown in Figure 1. The heteropolyanions $[\beta\text{-XW}_9\text{O}_{37}(\text{SnR})_3]^{(11-n)-}$, in which three corner-shared WO_6 octahedra of the β -Keggin anion are replaced by three RSnO_3 groups, retain the same β -structures as the starting trivacant species. The phenyl groups are oriented in such a way that virtual C_{3v} symmetry is maintained. The heteropolyanion $[\beta\text{-SiW}_9\text{O}_{37}(\text{SnPh})_3]^{7-}$ has been synthesized through an experiment,^{5d} whereas other systems were designed to understand the central heteroatom (X), electron-acceptor group, and the π -conjugation effects on the nonlinear optical response. $[\beta\text{-PW}_9\text{O}_{37}(\text{SnPh})_3]^{6-}$ (system 1), $[\beta\text{-SiW}_9\text{O}_{37}(\text{SnPh})_3]^{7-}$ (system 2), and $[\beta\text{-GeW}_9\text{O}_{37}(\text{SnPh})_3]^{4-}$ (system 3) are distinguished by the different central heteroatoms (X), whereas $[\beta\text{-SiW}_9\text{O}_{37}(\text{SnPhNO}_2)_3]^{7-}$ (system 4) and $[\beta\text{-SiW}_9\text{O}_{37}(\text{SnPhC}\equiv\text{CPh})_3]^{7-}$ (system 5) are derived from the substitution by the nitro groups as a conventional electron acceptor at the end of organostannic π -conjugation and the organotin segments lengthened via $\text{C}\equiv\text{C}$, respectively.

The geometries of all systems were optimized under C_{3v} symmetry constraints. The selected average optimized bond distances of $[\beta\text{-SiW}_9\text{O}_{37}(\text{SnPh})_3]^{7-}$ are given in Table 1. The average measurement obtained from previous reports in ref 5d is abbreviated as expt. Present calculations in bond lengths show good consistency with experimental measurements.

Results and Discussion

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

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

The computed dipole polarizability coefficients for systems

Table 1. Selected Average Optimized Bond Lengths (Å) in $[\beta\text{-SiW}_9\text{O}_{37}(\text{SnPh})_3]^{7-}$

	bond length	
	DFT	expt ^a
Si–O	1.66	1.66
Sn–C	2.26	2.06
Sn–O(Si)	2.32	2.28
Sn–O(Sn)	2.02	2.08
Sn–O(W)	2.18	2.07
W=O	1.77	1.74
W–O(Si)	2.44	2.42
W–O(Sn)	1.85	1.85
W–O(W)	1.96	1.93

^a See ref 5d.

Table 2. The Computed Dipole Polarizabilities (1×10^{-24} esu) for Systems 1–3

	α_{xx}	α_{yy}	α_{zz}	$\langle\alpha\rangle$
(1)	125.59	125.59	152.44	134.54
(2)	128.59	128.59	157.16	138.11
(3)	129.47	129.47	158.40	139.11

Table 3. Vertical Transition Wavelengths (λ_{gm} , nm), Transition Moment (M_z^{gm} , a.u.^a), and Corresponding Dominant MO Transitions of Systems 1–3

complex	λ_{gm}	M_z^{gm}	symmetry	MO transition
(1)	400	0.5540	A_1	HOMO-1 \rightarrow LUMO + 7 (94%)
(2)	489	0.5276	A_1	HOMO-3 \rightarrow LUMO + 2 (97%)
(3)	505	0.4714	A_1	HOMO-3 \rightarrow LUMO + 1 (97%)

^a $M_x^{\text{mg}} = M_y^{\text{mg}} = 0$.

1–3 are listed in Table 2. Because of the C_{3v} symmetry of the studied heteropolyanions, only the diagonal dipole polarizability tensors α_{ii} ($i = x, y, z$) are nonzero. Among the α_{ii} components, the α_{zz} component is the largest, whereas the α_{xx} and α_{yy} components are smaller. Hence, the property of the studied complexes is dominantly determined by the z -direction transition (Figure 1). All the dipole polarizability tensor components increase as a heavy central heteroatom changes in the order $\text{Ge} > \text{Si} > \text{P}$.

The expression of dipole polarizability (z -direction) is described in the following

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

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, the system with a strong electronic absorption peak and low transition energy will have a larger α value. Transition wavelengths (λ_{gm}), transition moment (M_z^{gm}), and corresponding dominant molecular orbital (MO) transitions of systems 1–3 are provided in Table 3. Transition moments for systems 1–3 are comparable each other, whereas the λ_{gm} values increase as a heavy central heteroatom changes in the order $\text{Ge} > \text{Si} > \text{P}$. Thus, the transition energy mainly determines the α value of the studied systems.

Under the C_{3v} symmetry constraints, electronic transitions from the ground state to the singlet A_1 (z -direction) and E (x -direction) excited states are electric-dipole allowed. For present studied complexes, the dominant electron transitions

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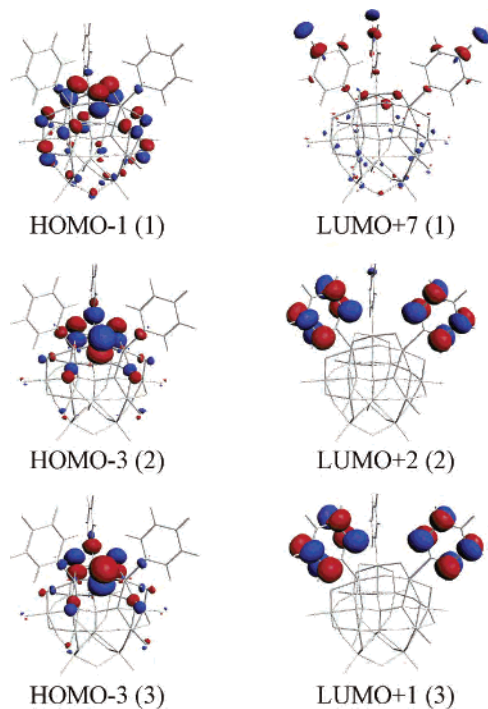


Figure 2. Molecular orbitals of systems 1–3 involved in the dominant electron transitions.

have A_1 symmetry. (Table 3) According to the TDDFT calculations, the electron transition of system 1 mainly arises from the heteropolyanion cluster (HOMO – 1) to the aryl segment (LUMO + 7) along the z -direction, and this character of charge transfer similarly occurs on system 2 (HOMO – 3 to LUMO + 2) and system 3 (HOMO – 3 to LUMO + 1). The molecular orbitals involved in the dominant electron transitions in systems 1–3 are shown in Figure 2. It can be seen that the occupied orbitals involved in the electronic transitions mainly delocalize over the p orbitals of bridge oxygen linked to two tins, whereas the unoccupied orbitals are π orbitals located on the aryl segment. Although the changes in molecular structures modify the contribution of different orbitals to the electronic transitions, the dominant electron transitions for the studied complexes have the same A_1 symmetry; that is, the major charge transfer originates from the heteropolyanion cluster to the aryl segment along the z -axis. These behaviors indicate that the aryl segment acts as the acceptor and the heteropolyanion cluster as the donor, which is different from the character of charge transfer for arylimido hexamolybdates derivatives.¹²

Static Second-Order Polarizability. The second-order polarizability is related to second-harmonic generation (SHG). For these heteropolyanions with their dipole moment along the z -axis, β_{vec} is given by

$$\beta_{\text{vec}} = \frac{1}{3} \sum_{i=x,y,z} (\beta_{zii} + \beta_{izi} + \beta_{iiz}) \quad (3)$$

The static second-order polarizability (β_{vec}) is called 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 in systems 1–3 are shown in Table

Table 4. Computed Static Second-Order Polarizabilities and Their Individual Components^a (1×10^{-30} esu) for Systems 1–3

	1	2	3
β_{zzz}	19.09	42.92	47.37
β_{yyz}	6.56	14.68	16.25
β_{yyx}	3.80	8.72	9.29
β_{vec}	19.33	43.36	47.92

$$^a \beta_{\text{yyz}} = \beta_{\text{xxz}} = \beta_{\text{yzy}} = \beta_{\text{zyy}} = \beta_{\text{zxx}} = \beta_{\text{zxx}}; \beta_{\text{yyx}} = \beta_{\text{xyy}} = \beta_{\text{xyy}} = -\beta_{\text{xxx}}.$$

4. There are 11 nonzero components of the second-order polarizability because of the C_{3v} symmetry, but only the three tensor components are independent, because $\beta_{\text{yyz}} = \beta_{\text{xxz}} = \beta_{\text{yzy}} = \beta_{\text{zyy}} = \beta_{\text{zxx}} = \beta_{\text{zxx}}$ and $\beta_{\text{yyx}} = \beta_{\text{xyy}} = \beta_{\text{xyy}} = -\beta_{\text{xxx}}$. As in the discussion of 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 along the z -direction. (Figure 2) As shown in Table 4, it can be seen that all systems have larger second-order polarizability coefficients. For example, the computed β_{vec} value of system 2 is about 450 times larger than the average second-order polarizability of the organic urea molecule²² and 10 times larger than measured value for highly π -delocalized phenyliminomethyl ferrocene complex.²³ This indicates that all the studied complexes in Table 4 have an excellent second-order NLO response. The computed β_{vec} values of all systems show that the NLO response is the following: system 3 > system 2 > system 1. In systems 1–3, the molecular composition is identical except for the central heteroatom (X). However, the β_{vec} values of systems 2 and 3 are twice as large as that of system 1.

To shed further light on the origin of second-order NLO properties of the studied complexes, the elucidation of the structure–property relationship is necessary. How does it cause the variations in the computed β_{vec} values? The two-state model that linked between β and a low-lying charge-transfer transition has been established from the complex sum-over-states (SOS) expression.²⁴ For the static case, the following model expression is employed to estimate β_{CT}

$$\beta_{\text{CT}} \propto \frac{\Delta\mu_{\text{gm}} f_{\text{gm}}}{E_{\text{gm}}^3} \quad (4)$$

where f_{gm} , E_{gm} , and $\Delta\mu_{\text{gm}}$ are the oscillator strength, the transition energy, and the difference of the dipole moment between the ground state (g) and the m th 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. Hence, for the studied complexes, the low excitation energy is the decisive factor in the β value.

As can be found from Table 3, the λ_{gm} values are related to the structural character of the studied complexes. The

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computed M_z^{gm} values are comparable; however, the λ_{gm} values increase monotonically from systems 1 to 3. The λ_{gm} value of system 1 is only 400 nm, whereas it is larger for system 3 (505 nm). The bathochromic shift of the absorption band attributes the substitution of a heavy central heteroatom (Ge > Si > P). From eq 4, we can see this behavior significantly enhances the β_{vec} value. Clearly, the excitation energy will tend to make a dominant contribution to the β_{vec} values of the studied complexes. From these results, it can be concluded that the substitution of a heavy central heteroatom (Ge > Si > P) is helpful in enhancing the β value.

On the basis of the special character of charge transfer and the large β_{zzz} value of systems 1–3, we were inspired to probe into the role of electron-acceptor group and π -conjugation in influencing the NLO response (systems 4 and 5). Present DFT calculations predict the β_{vec} values of systems 4 and 5 to be 618.01×10^{-30} and 1569.66×10^{-30} esu, respectively. It is noticeable that system 4 has the same geometrical character as *p*-nitroaniline. It forms a dipolar molecule that contains an electron-donor group connected to an electron acceptor via a π -conjugated bridge, in which π -conjugation commonly provides a pathway for the redistribution of electrons under the influence of an electric field.²⁵ In *p*-nitroaniline, the charge transfer occurs between the nitril and the benzene. Under the laser frequency of $\omega = 0.65$ eV, the β value of *p*-nitroaniline is 9.2×10^{-30} esu in the experiment²⁶ and 11.28×10^{-30} esu in the present DFT calculations, whereas the β value of *p*-nitroaniline is computed to be 8.9×10^{-30} esu at the static electronic field. The computed β_{vec} value of system 4 is about 70 times larger than the static second-order polarizability of *p*-nitroaniline. In system 5, the organotin units are lengthened via C \equiv C; thus, the π -conjugation is extended and the delocalization is improved. More extended conjugation generally leads to a smaller energy difference between the ground and charge-

transfer excited states; accordingly, this enhances the degree of charge transfer. Therefore, the larger β_{vec} values are generated, as electron transition originates from the heteropolyanion cluster to the organic segment along the *z*-axis.

Conclusions

Trisorganotin-substituted β -Keggin tungstate [XW₉O₃₇-(SnR)₃]⁽¹¹⁻ⁿ⁾⁻ (X = P, Si, Ge, R = Ph; X = Si, R = PhNO₂, PhC \equiv CPh) compounds are found to possess remarkably large static second-order polarizabilities. The optical excitation analysis in terms of frontier MOs shows that the charge transfer from the heteropolyanion cluster to the organic segment along the *z*-axis plays the key role in the NLO response. According to the two-state model, the low excitation energy is the decisive factor in the large β value. Complexes with a longer wavelength transition have a higher computed β value. The structure–property relationship indicates that there are three ways to enhance the NLO response of this class of organic–inorganic hybrid complexes. First, the heteropolyanions with a heavy central heteroatom (Ge > Si > P) have a larger nonlinearity. Second, for our studied systems, the incorporation of an electron acceptor (the nitro group) leads to a larger β value at the end of the π -conjugated bridge. Third, the lengthening of organostannic π -conjugation is helpful in enhancing the optical nonlinearity. Among these factors, the last one is most important in increasing the optical nonlinearity. Therefore, these POM-based organic–inorganic hybrid complexes can become an excellent kind of material in the second-order NLO field.

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