

# Theoretical predication of third-order optical nonlinearities of $[Al_4MA_4]^{n-}$ ( $n = 0-2$ , $M = Ti, V$ and $Cr$ ) clusters

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**Abstract** We investigate the nonlinear third-order polarizabilities of novel sandwichlike clusters  $[Al_4MA_4]^{n-}$  ( $n = 0-2$ ,  $M = Ti, V$  and  $Cr$ ). The calculations have been performed by employing time-dependent density functional theory combined with sum-over-states method. The results show that these complexes possess remarkably large third-order static polarizability, and change of a metal centre has a great influence on the third-order nonlinear optical properties. The calculated third-order polarizability follows:  $[Al_4CrAl_4] > [Al_4VAl_4]^- > [Al_4TiAl_4]^{2-}$ . Analysis of the main contributions to the third-order polarizability suggests that charge transfer ( $Al_4^{2-} \rightarrow M$ ) along the  $z$ -axis direction plays a key role in the nonlinear optical response.

**Keywords** Sandwich complexes · Nonlinear optics · Charge transfer · Aluminum · Density functional theory

## 1 Introduction

The recently synthesized  $Al_4^{2-}$  aromatic square ring [1] has gained much attention [2]. The unexpected large resonance energy of  $Al_4^{2-}$  has been attributed to the multiple-fold aromaticity [3–8] and later experimentally confirmed by Berndt [9, 10]. Multiple-fold aromaticity applies to molecules that possess more than one independent delocalized bonding

system, these aromatic rings are easily polarized which possibly lead to large polarization response. These  $Al_4^{2-}$  clusters (such as  $Al_4M_4$  and their anions  $Al_4M_4$ ,  $M =$  alkali metals) are recently reported to have large optical coefficients due to their ionic character, contrary to conventional  $\pi$ -conjugated systems [11].

Nonlinear optical processes are being increasingly exploited in a variety of optoelectronic and photonic applications. Three generic classes of NLO material exist: inorganic salts, semiconductors and organic compounds. Each class possesses its own complement of favorable and unfavorable attributes for NLO application [12]. Inorganic salts possess a large transparency range, are robust, are available as large single crystals, and suffer very low optical losses, but the purely electronic NLO effects are often accompanied by those arising from lattice distortions; response times are slow; synchronization of the phase of the interacting optical fields is not easy to satisfy [13]. Semiconductors possess NLO effects originating from saturable absorption [14]. Their third-order NLO responses are amongst the largest known [15], but NLO processes based on such resonant interactions may be relatively slow. The organic materials are of major interest because of their relatively low cost, ease of fabrication and integration into devices, tailorability which allows one to fine tune the chemical structure and properties for a given nonlinear optical process, high laser damage thresholds, low dielectric constants, fast nonlinear optical response times, and off-resonance nonlinear optical susceptibilities comparable to or exceeding those of ferroelectric inorganic crystals [16]. Organic materials have several disadvantages: low energy transitions in the UV–vis region enhance the NLO efficiency, but result in a trade-off between nonlinear efficiency and optical transparency, they may have low thermal stability and (in poled guest–host systems) they may undergo a facile relaxation to random orientation [13]. It is believed that metal

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clusters may possess the combined advantages of both organic polymers and inorganic semiconductors. With the gaining popularity of various ab initio level methods, there has been a tremendous impetus in investigating the structure and electronic properties of both homogeneous and heterogeneous small clusters in recent years [17–20].

One interesting feature is the possibility that  $\text{Al}_4^{2-}$  could be incorporated into sandwich complexes [21]. More recently, Mercero et al. [22] reported that the early transition metals can also form stable novel sandwich complexes with the  $\text{Al}_4^{2-}$  ring through the computational method. We anticipate that these complexes offer some interesting new opportunities to third-order nonlinear optical materials.

In this paper, our goal is to shed light on the nature and origin of third-order nonlinear optical properties of  $[\text{Al}_4\text{MAl}_4]^{n-}$  ( $n=0-2$ ,  $M=\text{Ti}$ ,  $\text{V}$  and  $\text{Cr}$ ), using the TDDFT-SOS method, and elucidate the influence of different metal centre on NLO properties from the micromechanism.

## 2 Computational details

The B3LYP functional [23], as implemented in Gaussian 03 [24], with the standard 6-311+G\* basis set was employed for the geometry optimizations with the  $D_{4d}$  symmetry. The charge decomposition analysis (CDA) [25,26] was performed to quantify the charge donor–acceptor interactions between the center metal and  $\text{Al}_4^{2-}$  rings. In the CDA method, the (canonical, natural, or Kohn–Sham) molecular orbitals of the complex are expressed in terms of the MOs of appropriately chosen fragments. We carried out single-point energy calculations of complexes  $[\text{Al}_4\text{MAl}_4]^{n-}$  and the fragments of metal centre (1) and two  $\text{Al}_4^{2-}$  (2) of complexes  $[\text{Al}_4\text{MAl}_4]^{n-}$  in the optimized geometry of complexes using the B3LYP functional with the same basis sets. The CDA calculations were performed using the program AOMIX-CDA [27]. Time-dependent density functional theory (TDDFT) [28], is one of the most popular methods for the calculation of excitation energies in quantum chemistry due to its efficiency and accuracy. We employed the TDDFT model with the B3LYP method at the 6-311+G\* basis set to calculate the transition energies and oscillator strengths, respectively.

The static third-order polarizabilities were then calculated using the sum-over-states formula. The expression of static

third-order polarisabilities  $\gamma$  can be obtained by application of time-dependent perturbation theory to the interacting electromagnetic field and microscopic system, as described in the following [29]:

$$\gamma_{ijkl} = \frac{4\pi^2}{3\hbar^3} P(i, j, k, l; -\omega_\sigma, \omega_1, \omega_2, \omega_3) \times \sum_{m \neq g} \sum_{n \neq g} \sum_{p \neq g} \left[ \frac{(\mu_i)_{gm} (\bar{\mu}_j)_{mn} (\bar{\mu}_k)_{np} (\mu_l)_{pg}}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_2)(\omega_{pg} - \omega_3)} \right] - \sum_{m \neq g} \sum_{n \neq g} \left[ \frac{(\mu_i)_{gm} (\mu_j)_{mg} (\mu_k)_{gn} (\mu_l)_{ng}}{(\omega_{mg} - \omega_\sigma)(\omega_{ng} - \omega_2)(\omega_{ng} - \omega_3)} \right]$$

Here,  $(\mu_i)_{gm}$  is an electronic transition moment along the  $i$  axis of the Cartesian system, between the ground state and the excited state;  $(\bar{\mu}_j)_{ng}$  is the dipole difference equal to  $(\mu_j)_{mn} - (\mu_j)_{gg}$ ;  $\omega_{mg}$  is the transition energy;  $\omega_1$ ,  $\omega_2$  and  $\omega_3$  are the frequencies of the perturbation radiation fields, and  $\omega_\sigma = \omega_1 + \omega_2 + \omega_3$  is the polarization response frequency;  $P(i, j, k, l; -\omega_\sigma, \omega_1, \omega_2, \omega_3)$  indicates all permutations of  $\omega_1, \omega_2, \omega_3$  and  $\omega_\sigma$  along with associated indices  $i, j, k, l$ . When  $\omega_\sigma$  or  $\omega_1$  approaches to  $\omega_{mg}$ , the equation above will diverge. An average value  $\langle \gamma \rangle$  is obtained from the expression:

$$\langle \gamma \rangle = 1/5 [\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{xxzz} + \gamma_{yyzz})]$$

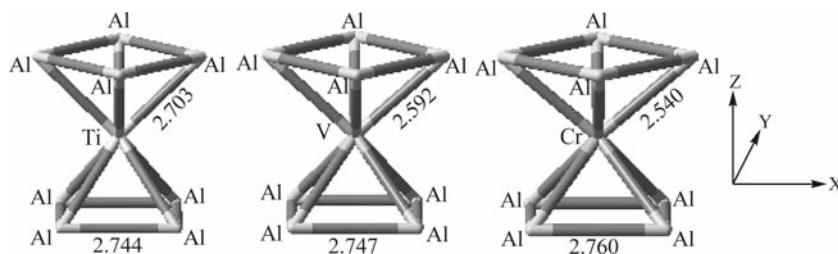
The transition energy, transition moments and dipole moments can be obtained from the calculated results on the basis of the TD model of Gaussian 03. Firstly, 100 excited states were calculated using TD model of Gaussian 03 for all compounds. Those physical values were then taken as input of the sum-over-states (SOS) formula to calculate the third-order polarizabilities. One-hundred excited states are enough according to the converge curves of sum-over-states (SOS) method (supporting information). Furthermore, the accuracy of the TDDFT-SOS method was proven by Cheng et al. [30,31] and our group [32–36].

## 3 Results and discussion

### 3.1 Electronic structures

These optimized geometry structures are shown in Fig. 1. The Al–Al bond length increases slightly from Ti to Cr, on

**Fig. 1** Optimized structures of complexes  $[\text{Al}_4\text{MAl}_4]^{n-}$  ( $n=0-2$ ,  $M=\text{Ti}$ ,  $\text{V}$  and  $\text{Cr}$ ). Bond lengths are given in Å



**Table 1** Net charge donation: CT ( $2 \rightarrow 1$ )–CT ( $1 \rightarrow 2$ ) and natural charge

Complexes	CT ( $2 \rightarrow 1$ ) – CT ( $1 \rightarrow 2$ )	Natural charge (M)	Natural charge (Al)
$[\text{Al}_4\text{TiAl}_4]^{2-}$	1.471	–3.546	0.193
$[\text{Al}_4\text{VAl}_4]^-$	3.051	–3.691	0.336
$[\text{Al}_4\text{CrAl}_4]$	4.635	–3.475	0.434

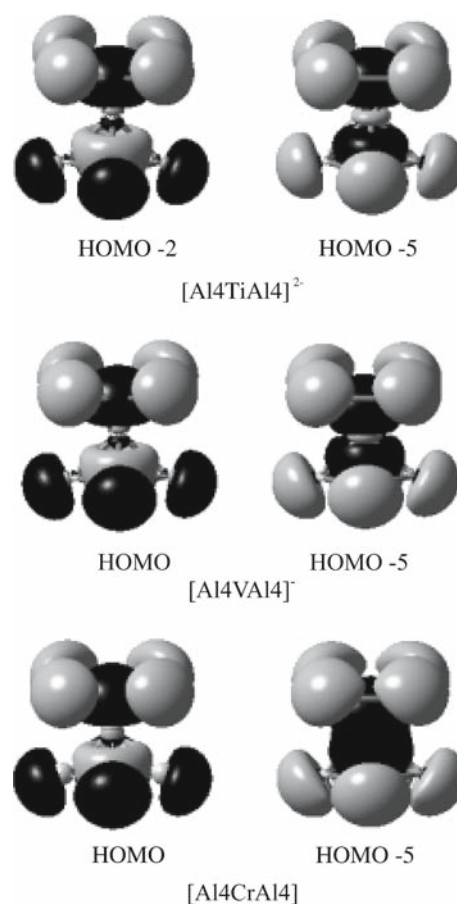
the contrary, the distance between the transition metal and the  $\text{Al}_4^{2-}$  rings decreases due to the Coulombic attraction between the charged moieties increases. The results of optimized geometry structures are in accordance with those of Mercero et al. [22] reported at the same level. The Al–Al bond length is 2.744, 2.747, 2.760 Å, in  $[\text{Al}_4\text{TiAl}_4]^{2-}$ ,  $[\text{Al}_4\text{VAl}_4]^-$  and  $[\text{Al}_4\text{CrAl}_4]$ , respectively.

The difference of charge donation between  $2 \rightarrow 1$  ( $\text{Al}_4^{2-}$ -to-M donation) and  $1 \rightarrow 2$  (M-to- $\text{Al}_4^{2-}$  back donation) in Table 1 is not equal to the net charge transfer between the metal centre and  $\text{Al}_4^{2-}$  ligands. This is related to the fact that, in CDA, the terms donation and back-donation correspond to an overall reorganization of electronic density, which includes the intra-fragment reorganization as well as charge transfer. The CDA results for the complexes are shown in Table 1. The calculated net charge donation (CT), CT ( $2 \rightarrow 1$ ) – CT ( $1 \rightarrow 2$ ), follows  $[\text{Al}_4\text{CrAl}_4] > [\text{Al}_4\text{VAl}_4]^- > [\text{Al}_4\text{TiAl}_4]^{2-}$ , which could have effect on photophysical properties.

The results of the CDA method suggest that the amount of donation from  $\text{Al}_4^{2-}$  to M is much larger than the amount of back donation from M to  $\text{Al}_4^{2-}$  fragments. The most important complex orbitals for the  $\text{Al}_4^{2-}$ –M interactions are listed in Table 2, and shown in Fig. 2. Electron donation between fragments includes both charge donation and electronic polarization contributions. There are two dominant orbitals that contribute to the  $\text{Al}_4^{2-} \rightarrow \text{M}$  donation in each complex, which correspond to the two  $\sigma$  tangential systems of the two tetra-aluminum rings. Furthermore, the CDA results for the complexes show that  $[\text{Al}_4\text{TiAl}_4]^{2-}$ ,  $[\text{Al}_4\text{VAl}_4]^-$  and  $[\text{Al}_4\text{CrAl}_4]$  can be considered to be donor–acceptor complexes, because the value for the residue  $\Delta$  is essentially zero [37].

**Table 2** Dominant orbital interactions of CT ( $2 \rightarrow 1$ )

Complexes	Orbital contribution	Total	$\Delta$	
$[\text{Al}_4\text{TiAl}_4]^{2-}$	HOMO-2	–0.337	–0.518	–0.011
	HOMO-5	–0.159		
$[\text{Al}_4\text{VAl}_4]^-$	HOMO 0	–0.326	–0.523	–0.010
	HOMO-5	–0.186		
$[\text{Al}_4\text{CrAl}_4]$	HOMO 0	–0.287	–0.520	–0.009
	HOMO-5	–0.245		

**Fig. 2** Dominant orbital interactions as revealed by the CDA

### 3.2 Electronic spectra

When the metal center is different, there is certain influence on structure of  $[\text{Al}_4\text{MAl}_4]^{n-}$  ( $n = 0 - 2$ ,  $\text{M} = \text{Ti}, \text{V}$  and  $\text{Cr}$ ). How does the different metal center affect the electronic transition? In order to find the effect, the electronic spectra of these complexes have also been calculated at the same level. In Table 3, we list the excitation wavelength values, oscillator strengths and major contribution obtained using the TDB3LYP with the B3LYP geometries. It is noted that oscillator strengths  $> 0.05$  are listed.

From the calculated spectra of these complexes, the following results can be found: (1) electronic transitions for these complexes can be assigned to metal-to-ligand charge transfer (MLCT) or ligand-to-metal charge transfer (LMCT) (Supporting information). From this point, when the metal centre is different, transition nature of molecule changed. (2) There is one wide intense absorption band around  $\sim 449.1$  nm in the absorption spectra of complex  $[\text{Al}_4\text{TiAl}_4]^{2-}$ . In the case of complex  $[\text{Al}_4\text{VAl}_4]^-$ , three absorption bands around  $\sim 601.5$ ,  $\sim 473.6$  and  $\sim 360.7$  nm, respectively, are observed in which the former two bands are comparatively

**Table 3** Calculated excitation wavelengths ( $\lambda$ , nm), oscillator strengths ( $f$ ) and corresponding dominant MO transitions of the optically allowed excited states

Complexes	$\lambda$	$f$	MO transitions
[Al <sub>4</sub> TiAl <sub>4</sub> ] <sup>2-</sup>	515.2	0.1886	H-5→L+4
	515.2	0.1886	H-5→L+3
	482.7	0.1196	H-2→L+10
	449.1	0.1131	H-6→L+3 H-1→L+16
	449.1	0.1131	H-6→L+4 H-0→L+16
	435.5	0.1148	H-2→L+11
	435.5	0.1148	H-2→L+12
	417	0.3105	H-6→L+2
[Al <sub>4</sub> VAL <sub>4</sub> ] <sup>-</sup>	601.5	0.1481	H-4→L+2 H-3→L+3 H-6→L+4 H-2→L+5
	473.6	0.0893	H-5→L+6
	473.6	0.0893	H-5→L+5
	432	0.1149	H-0→L+10
	366.2	0.1751	H-6→L+4
	360.7	0.2585	H-0→L+13 H-0→L+14
	360.7	0.2585	H-0→L+14 H-0→L+13
	714.2	0.0666	H-0→L+9 H-2→L+2 H-1→L+3 H-3→L+0
[Al <sub>4</sub> CrAl <sub>4</sub> ]	447.1	0.0934	H-5→L+4 H-5→L+5
	447.1	0.0934	H-5→L+5 H-5→L+4
	323.8	0.127	H-6→L+8
	309.4	0.1384	H-0→L+12

Assignment: H HOMO, L LUMO

weak. To complex [Al<sub>4</sub>CrAl<sub>4</sub>], there are also three absorption bands around ~714.2, ~447.1 and ~309.4 nm, respectively, and the former two bands are comparatively weak.

### 3.3 The third-order polarizabilities

The third-order static polarizability is termed the zero frequency second-order hyperpolarizability and is an estimate of the intrinsic molecular third-order polarizability in the absence of any resonance effect. The calculated individual components of the third-order polarizabilities are given in Table 4. It is found that the molecular third-order polarizabilities of these sandwich-like metal clusters are considerably larger than those of typical organometallic and organic compounds of similar sizes [38–40], and the order of the average

**Table 4** Calculated third-order static polarizabilities (10<sup>-36</sup> esu)

Complexes	$\gamma_{xxxx}$	$\gamma_{yyyy}$	$\gamma_{zzzz}$	$\gamma_{xxyy}$	$\gamma_{xxzz}$	$\gamma_{yyzz}$	$\langle\gamma\rangle$
[Al <sub>4</sub> TiAl <sub>4</sub> ] <sup>2-</sup>	-259	-259	-872	-86	-159	-159	-440
[Al <sub>4</sub> VAL <sub>4</sub> ] <sup>-</sup>	-375	-388	-3,181	-127	-376	-382	-1140
[Al <sub>4</sub> CrAl <sub>4</sub> ]	-1,474	-1,474	-21,690	-491	-2,091	-2,091	-6,800

values  $\langle\gamma\rangle$  are: [Al<sub>4</sub>CrAl<sub>4</sub>] > [Al<sub>4</sub>VAL<sub>4</sub>]<sup>-</sup> > [Al<sub>4</sub>TiAl<sub>4</sub>]<sup>2-</sup>. Among these components, the main contribution to  $\langle\gamma\rangle$  is  $\gamma_{zzzz}$ , which is the direction of the C<sub>4</sub> axis (z-direction).

As the discussion of CDA in part 1, the calculated net charge donation, CT(2→1)–CT(1→2), is in accordance with the  $\langle\gamma\rangle$  value of these three complexes, and the donation from Al<sub>4</sub><sup>2-</sup> to M (2→1) is dominant. This indicates that the charge transfer along the C<sub>4</sub> axis (z-axis) direction has significant influence on the third-order nonlinear optical response, and complexes with more net charge donation between fragments have the possibility of larger third-order nonlinear optical response.

To the SOS method, the third-order polarizability is governed by the product of the transition moments and the transition energy. Furthermore, theoretical study shows that the transition energy is a decisive factor in determining the third-order polarizability [41]. Thus, the electronic transition relative to the maximal absorption wavelength plays a key role in enhancing the third-order polarizabilities of complexes. In the case of the complexes we studied, although the oscillator strengths relative to the maximal absorption wavelength of complex [Al<sub>4</sub>TiAl<sub>4</sub>]<sup>2-</sup> are larger than those of complexes [Al<sub>4</sub>VAL<sub>4</sub>]<sup>-</sup> and [Al<sub>4</sub>CrAl<sub>4</sub>], the order of maximal absorption wavelength of the complexes is [Al<sub>4</sub>CrAl<sub>4</sub>] (714.2 nm) > [Al<sub>4</sub>VAL<sub>4</sub>]<sup>-</sup> (601.5 nm) > [Al<sub>4</sub>TiAl<sub>4</sub>]<sup>2-</sup> (515.2 nm). Therefore, the third-polarizability follows: [Al<sub>4</sub>CrAl<sub>4</sub>] > [Al<sub>4</sub>VAL<sub>4</sub>]<sup>-</sup> > [Al<sub>4</sub>TiAl<sub>4</sub>]<sup>2-</sup>. The major electronic transitions that contribute to the  $\gamma$  value of the complexes are those charge transfers from Al<sub>4</sub><sup>2-</sup> to M (2→1) (LMCT).

## 4 Conclusions

Our theoretical study shows that these sandwich-like metal clusters contained aromatic rings Al<sub>4</sub><sup>2-</sup> provide a new promising class of materials with high nonlinear optical properties. By comparing with the electronic structure of these three complexes, it is found that stronger net charge donation [CT(2→1)–CT(1→2)] is beneficial in enhancing the third-order nonlinear optical response. Furthermore, the optical excitation analysis in terms of frontier MOs shows that the CTs from the Al<sub>4</sub><sup>2-</sup> to M (2→1) make dominant contributions to the NLO effects. Thus, the calculated nonlinear third-order polarizability follows: [Al<sub>4</sub>CrAl<sub>4</sub>] > [Al<sub>4</sub>VAL<sub>4</sub>]<sup>-</sup> > [Al<sub>4</sub>TiAl<sub>4</sub>]<sup>2-</sup>. It is hoped that the results presented in this paper will provide new opportunities to design third-order nonlinear optical materials in experimental research.

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