



Theoretical study on the second hyperpolarizabilities of one-dimensional heteronuclear transition-metal–metal bonded systems: Metal alignment effects



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ABSTRACT

We investigate the diradical character (γ) dependences of the second hyperpolarizabilities (γ) in one-dimensional heterotetranuclear metal–metal bonded systems composed of Cr(II) and/or Mo(II) with various alignments using the spin-unrestricted coupled-cluster method. These species are found to exhibit a bell-shape variation of γ for γ as well as dominant $d\sigma$ -electron contribution to the maximum γ (γ_{\max}), which are also observed in other metal chain systems. The ratios of the γ_{\max} between these systems are shown to attain about 3.5 at the maximum due to the charge distribution. This result indicates that the γ values can be efficiently controlled by the metal alignment.

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1. Introduction

Recently, open-shell singlet molecules have attracted much attention from theoretical and experimental researchers due to their unique electronic structures [1–4] and physico-chemical properties including highly active nonlinear optical (NLO) properties [5–7] and efficient singlet fission [8,9]. Especially, for open-shell singlet NLO systems, it has been revealed that the intermediate diradical character γ causes the enhancement of the second hyperpolarizability γ , which is referred to as ‘ γ – γ correlation’ [5–7] and a lot of experimental investigations have been conducted for various organic compounds [10–19]. As an exploration for a new class of open-shell singlet systems, we examined transition-metal–metal multiple bonded systems and found that open-shell nature appears depending on the bond length [20]. Also, the open-shell nature in such metal–metal bonded systems is found to be controlled by modification of the ligands [21,22]. Then, we have investigated naked dimetal models and found that these systems could be novel candidates for NLO materials with intermediate diradical characters [23]. Furthermore, we have revealed that the metal–metal bonded systems with axial or equatorial ligands also show large γ values in the intermediate diradical character region [24,25].

From the ‘ γ – γ correlation’, it is found that a large effective diradical distance leads to the enhancement of γ [6]. In the

previous Letter [26], building open-shell singlet one-dimensional (1D) multiradical systems, referred to as ‘1D multiradicalization’, has been proposed to realize both the large effective diradical distance and intermediate diradical character. Polynuclear transition metal complexes with appropriate metal–metal multiple bonds are proposed as examples of the open-shell singlet 1D systems with intermediate interaction between these radical electrons [27]. These multinuclear 1D metal chain systems can be realized by using the appropriate ligands [28–31]. On the other hand, the appropriate asymmetry (asymmetric electron distribution), which is related to the difference of the ionization potentials of metals, was found to cause extremely large enhancement of γ [32], the feature of which is in qualitative agreement with the previous results on the asymmetric diradical model system [33].

Then, we speculate that the combination of these two effects, 1D multiradicalization and asymmetry, leads to a synergetic effect on the enhancement of γ in 1D metal chain systems. Indeed, 1D metal chain systems involving heterometals have been experimentally reported [34–37], and measurements of γ values have been conducted in several systems [38,39]. Although heteronuclear 1D systems have a variety of metal alignments, the metal alignment effects on the open-shell nature and γ values have not been clarified. In this study, therefore, we investigate the dependences of open-shell character and γ on the metal atom alignments and the system size in order to build a novel molecular design guideline for highly efficient NLO systems based on open-shell singlet metal-atom chains.

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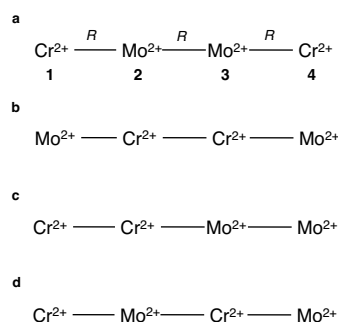


Figure 1. Structures of model systems **a–d**, where R represents the metal–metal bond length. Atom number is also shown in **a**.

2. Model systems and calculation methods

We investigate four tetranuclear model systems **a–d** composed of Cr(II) and/or Mo(II) with different alignments and identical bond lengths (R) (Figure 1). The difference in the ionization potentials between Cr(II) and Mo(II) is expected to cause different charge distributions in these model systems [32]. For comparison, homo/hetero-dinuclear and homotetranuclear models composed of Cr(II) and/or Mo(II) atoms are also examined. To realize a wide range of the open-shell characters, we consider the bond length extension from 2.0 to 4.0 Å, the range of which includes the typical experimental bond lengths of Cr(II)₂, 2.0–2.6 Å, and of Mo(II)₂, 2.0–2.4 Å [40]. The orbital interactions between the valence d atomic orbitals lead to four $d\sigma$, $d\pi$, $d\pi'$, $d\delta$ and $d\delta'$ orbitals (totally 20 orbitals), where the $d\pi'$ orbital is rotated from the $d\pi$ orbitals by 90° around the bond axis (z -axis) and the $d\delta'$ orbital is also rotated from the $d\delta$ orbital by 45° around the bond axis. The 16 d -electrons formally occupy the lowest two orbitals of each $d\sigma$, $d\pi$, $d\pi'$ and $d\delta$ symmetry. In the spin-unrestricted, i.e., broken-symmetry, single-determinant formalism, the highest two natural orbitals (NOs) of each symmetry possess fractional occupation numbers smaller than 1, and this electron configuration leads to the four radical nature for each $d\sigma$, $d\pi$, $d\pi'$, and $d\delta$ orbital in the tetranuclear systems, resulting in a quadruple four radical nature for the whole system.

The diradical characters y_i can be defined by the occupation number of the lowest unoccupied natural orbitals (LUNO) + i ($n_{\text{LUNO}+i}$, where $i = 0, 1, \dots$) for each orbital symmetry. In this study, we calculate the y_i values using the spin-unrestricted coupled-cluster with singles and doubles (UCCSD) method, which is known to provide reliable open-shell nature and hyperpolarizabilities of these species [23]. The y_i value ranges from 0 to 1, which indicate the closed-shell and pure open-shell states, respectively, and is related to the effective bond order: the larger the diradical characters, the smaller the effective bond order [41]. In the tetranuclear systems, the diradical characters for the different dX orbitals [$y_i(dX)$, where $X = \sigma, \pi$ and δ ($i = 0, 1$)] are evaluated from the occupation numbers of the corresponding dX bonding and anti-bonding NO pairs.

All calculations were conducted with the effective core potential (ECP) of the Stuttgart group with corresponding valence basis set (SDD) for Cr [42]. For Mo, the SDD basis set [43] is supplemented with an additional set of f polarization functions [44] (referred to as ‘SDD(f)’ in this Letter). This is required to get a balanced basis sets because, contrary to Cr, the SDD basis set for Mo does not include f polarization functions. These basis sets were found to be sufficient for obtaining quantitative γ values of transition metal–metal bonded systems at the spin-unrestricted coupled-cluster with singles and doubles (UCCSD) and that with perturbative triples (UCCSD(T)) levels of approximation [23].

The static longitudinal γ_{zzzz} (simply referred to as γ , hereafter) values were calculated at the UCCSD level of approximation using the finite-field (FF) approach [45], which consists in the fourth-order differentiation of the energy with respect to the applied electric field. The power series expansion convention (called B convention [46]) was selected for the definition of the γ . A tight convergence threshold of 10^{-10} a.u. was used on the energy to obtain precise γ values. In order to investigate the spatial contributions of electrons to γ , we apply the γ density analysis [47,48]. At the UCCSD level, γ is then partitioned into the contributions of the dX electrons [$\gamma(dX)$], calculated from the corresponding $\gamma(dX)$ density [$d^{\text{dX}(3)}(\mathbf{r})$] [47,48]:

$$\gamma(dX) = -\frac{1}{3!} \int z d^{\text{dX}(3)}(\mathbf{r}) d\mathbf{r}, \quad (1)$$

where $d^{\text{dX}(3)}(\mathbf{r})$ is the third-order electric field derivative of the electron density, referred to as $\gamma(dX)$ density [47,48], of the bonding (dX) and anti-bonding (dX^*) NO pair and it reads

$$d^{\text{dX}(3)}(\mathbf{r}) = \frac{\partial}{\partial F^3} \left\{ n_{dX} \varphi_{dX}^*(\mathbf{r}) \varphi_{dX}(\mathbf{r}) + n_{dX^*} \varphi_{dX^*}^*(\mathbf{r}) \varphi_{dX^*}(\mathbf{r}) \right\} \Bigg|_{F=0}. \quad (2)$$

Here, $\varphi_{dX}(\mathbf{r})$ and n_{dX} represent the dX NO and its occupation number, respectively. All these calculations were performed using the GAUSSIAN 09 program package [49].

3. Results and discussion

3.1. Alignment effect on the diradical characters

Before investigating the metal alignment effects on the diradical characters in heteronuclear transition-metal clusters, we briefly explain our previous results on the structure–property relationships of various 1D transition-metal clusters. Homodinuclear systems show (i) that the diradical characters of each orbital symmetry satisfy $y(d\sigma) < y(d\pi) < y(d\delta)$ in the whole atomic distance region, which is explained by the difference in the orbital overlaps, (ii) that the γ values indicate bell-shape dependences on the diradical character, and (iii) that $d\sigma$ electrons give primary contributions to γ , which attains a maximum at an intermediate $y(d\sigma)$ value [23]. From the results of longer 1D homo transition-metal chain systems, we found that the γ per dimer unit, which shows the same y – γ correlation, significantly increases with the chain length [27]. Furthermore, in heterodinuclear systems, it has been revealed that the significant enhancement of γ is observed in the case of appropriate asymmetry, which is induced by an appropriate combination of different metals based on their ionization potential differences [32].

From the above results, we speculate that the bond length (R) dependences of the open-shell character are changed by the metal atom alignment. We introduce the average open-shell character [$y^{\text{odd}}(dX)$] of dX orbital contributions $y_i(dX)$ ($i = 0, 1$), defined by

$$y^{\text{odd}}(dX) = \frac{y_0(dX) + y_1(dX)}{2}. \quad (3)$$

The R dependences of the open-shell characters [$y^{\text{odd}}(dX)$] for $R = 2.0$ – 4.0 Å indicate the relative amplitude relationships at each R : $y^{\text{odd}}(d\delta) > y^{\text{odd}}(d\pi) > y^{\text{odd}}(d\sigma)$ (see Figure 1S in Supplementary data). This tendency is the same as that in our previous studies on the transition-metal systems with metal–metal multiple bonds [23]. The alignment dependence of the open-shell characters is found to be the largest in the $d\sigma$ orbitals, e.g., the $y^{\text{odd}}(d\sigma)$ shows the order for $R = 2.0$ – 2.5 Å: Cr(II)Mo(II)Mo(II)Cr(II) (**a**) > Cr(II)Cr(II)Mo(II)Mo(II) (**c**) > Cr(II)Mo(II)Cr(II)Mo(II) (**d**) > Mo(II)Cr(II)Cr(II)Mo(II) (**b**). Such larger differences in $y^{\text{odd}}(d\sigma)$ than in $y^{\text{odd}}(d\pi)$ and $y^{\text{odd}}(d\delta)$ are

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