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LETTER

Origin of the Enhancement of the Second Hyperpolarizabilities in Open-Shell Singlet Transition-Metal Systems with Metal–Metal Multiple Bonds

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S *Supporting Information*

ABSTRACT: Using the spin-unrestricted coupled-cluster method, we explore the origin of the second hyperpolarizabilities (γ) of singlet dichromium(II) and dimolybdenum(II) model systems with various bond lengths as a function of the diradical characters of the $d\sigma$, $d\pi$, and $d\delta$ orbitals. Both systems exhibit enhanced γ values in the intermediate diradical character region, but by using a partitioning scheme, the $d\sigma$ electrons are shown to play the essential role in contrast with the π-electrons of conventional organic π-conjugated systems. Then, in the equilibrium bond length region, the γ values are still governed by $d\sigma$ electrons in the dichromium(II) system, although by $d\delta/d\pi$ electrons in the dimolybdenum(II) system.

SECTION: Molecular Structure, Quantum Chemistry, General Theory

Second Hyperpolarizability

$\gamma(d\delta) = -2$ au

$Cr^{II} \equiv Cr^{II}$
← 2.2 Å →
$\gamma = 743$ au

$2\gamma(d\pi) = 82$ au

$\gamma(d\sigma) = 681$ au
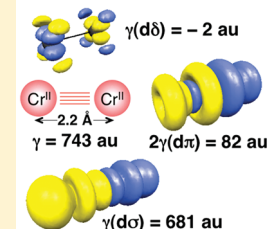
In previous studies,[1−7] we have theoretically proposed open-shell singlet organic molecules as a novel class of nonlinear optical (NLO) systems and have revealed that singlet diradical systems with intermediate diradical characters tend to exhibit larger second hyperpolarizabilities γ (the third-order NLO properties on the molecular scale) than pure diradical and closed-shell systems with similar size of π-conjugation. The mechanism of this structure−property relationship has been unraveled by resorting to summation-over-states (SOS) expressions of the static γ and of the two-photon absorption cross section.[1,2] This relationship has also been verified by ab initio molecular orbital (MO) and density functional theory (DFT) studies on several model and real molecular systems including p-quinodimethane model,[3] diphenalenyl diradical systems,[4] π-conjugated molecules involving imidazole rings,[5] graphene nanoflakes,[6] and also square planar Ni complexes.[7] These theoretical predictions have been confirmed by two-photon absorption measurements on s-indaceno[1,2,3-cd;5,6,7-c'd']diphenalene[8] and by third-harmonic generation spectrum of 1,4-bis-(4,5-diphenylimidazole-2-ylidene)-cyclohexa-2,5-diene.[9]

In transition-metal complexes, d−d orbital interactions often lead to multiple bonds of $d\sigma$, $d\pi$, and $d\delta$ characters. These multiple bonds exhibit diradical characters as shown by Nishino et al.[10] from spin-unrestricted Hartree−Fock (UHF) and DFT calculations of the occupation numbers of the $d\sigma$, $d\pi$, and $d\delta$ natural orbitals (NOs) in the naked dichromium(II) model system. Moreover, the effective bond orders (EBOs) of such complexes are predicted to be generally smaller than their formal bond orders; for example, the $[Cr_2(O_2CCH_3)_4]$ dichromium(II) complex has a formal bond order of 4, but its EBO is 1.99.[11]

These results indicate characteristic weak metal−metal bonds and the possible emergence of singlet multiradical character. Therefore, transition-metal complexes with multiple metal−metal bonds also appear as promising systems for their third-order NLO properties, which constitutes the topic of this Letter, where the γ values of two kinds of open-shell singlet metal−metal bonded systems are investigated to clarify the origin of γ from the viewpoint of the multiple diradical characters of $d\sigma$, $d\pi$, and $d\delta$ orbitals. The direct metal−metal bond contributions to the NLO properties have not been investigated, except in a few theoretical and experimental studies on, for example, the (hyper)polarizabilities of the copper dimer[12] and the first hyperpolarizabilities (β) of dirhenium complexes[13] and penta-nuclear transition metal clusters,[14] none of which having addressed the relationship between the open-shell character of metal−metal bond and the NLO properties.

We examine the naked dichromium(II) $[Cr(II)−Cr(II)]$ model because dichromium(II) complexes with $Cr(II)−Cr(II)$ bonds are typical metal−metal multiply bonded open-shell singlet systems with intermediate and strong electron correlations at equilibrium bond lengths.[10] The naked dimolybdenum-(II) $[Mo(II)−Mo(II)]$ model can be regarded as a nearly closed-shell reference system at equilibrium bond length. Their comparison was therefore carried out as a function of the metal−metal bond length. Both systems possess one $d\sigma$, two equivalent $d\pi$, and one $d\delta$ bonds due to $d^4−d^4$ interactions but, because of different
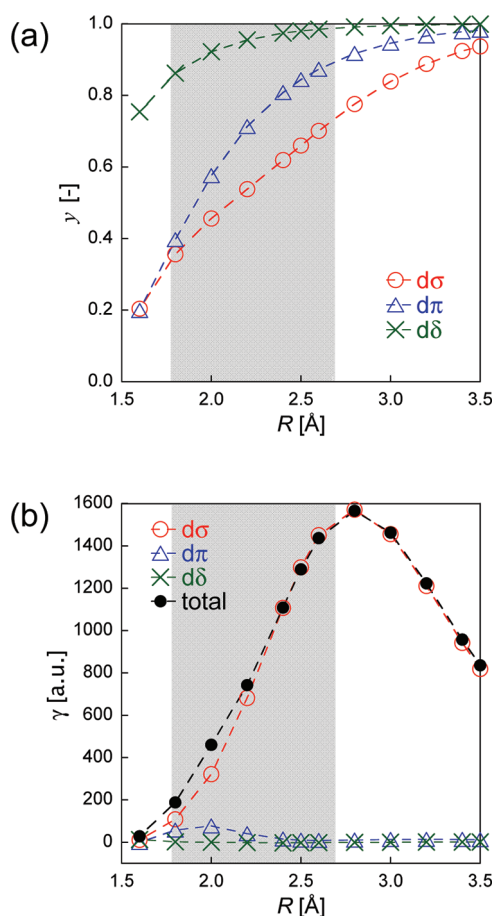
Figure 1. Effects of the bond length (R) on the UHF diradical character (y) (a) and on the UCCSD longitudinal second hyperpolarizability (γ) (total) (b) of Cr(II)−Cr(II) as well as on their $d\sigma$, $d\pi$, and $d\delta$ orbital contributions. Note that $\gamma(d\pi)$ indicates one of the two equivalent $d\pi$ orbital contributions to γ. The gray-colored region represents the equilibrium bond length range (1.77−2.69 Å)[21,22] of real dichromium-(II) complexes.

d−orbital overlaps, each of the $d\sigma$, $d\pi$, and $d\delta$ orbitals displays a different diradical character for a given bond length.
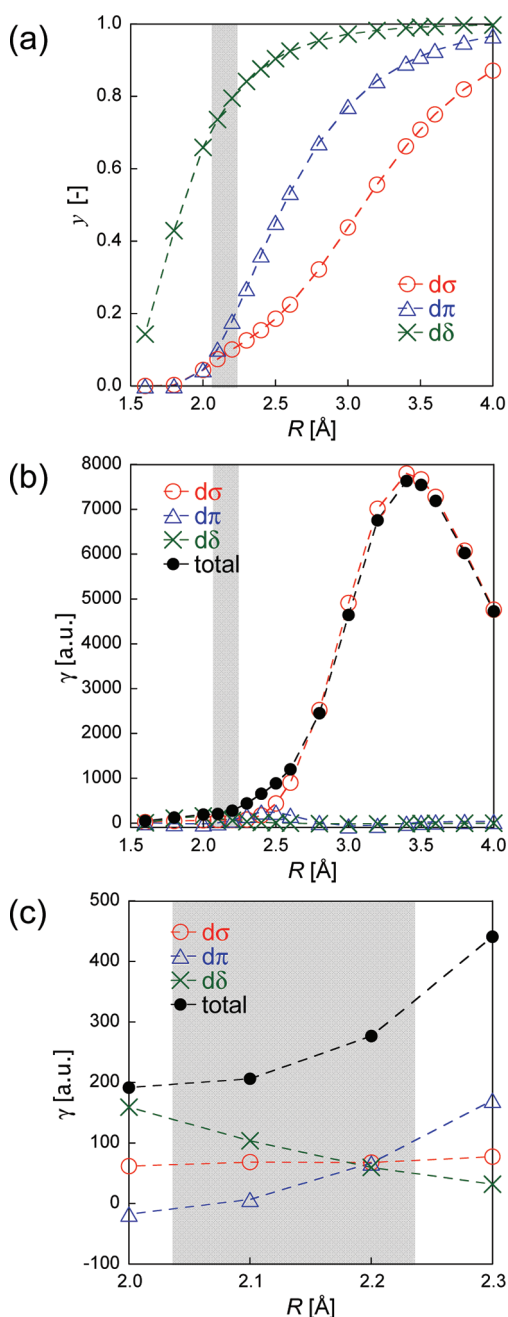
The diradical characters of the orbitals [$y(dX)$, where $X = \sigma, \pi, \delta$] were estimated from the occupation numbers of the UHF NOs, corrected from spin-contamination using an approximate spin-projection scheme.[15] The SDD basis set[16] was employed for Cr, whereas for Mo, the SDD basis set[17] was supplemented with an additional f polarization function ($\zeta_f = 1.0430$)[18] (referred to as "SDD(f)" in this Letter). This is required for a balanced treatment because contrary to Cr the SDD basis set for Mo does not contain f polarization function. We focused on the dominant longitudinal component γ_{zzzz} ($\equiv \gamma$) along the bond axis because the spin polarization occurs in this direction. The γ values were calculated by the finite-field (FF) approach[19] at the UCCSD level of approximation. (See the Supporting Information for details of calculation methods.) All calculations were performed using the Gaussian 09 program package.[20]

The relationship between the bond length (R) and the diradical characters [$y(dX)$] for Cr(II)−Cr(II) is shown in Figure 1a. For $R = 1.6$−3.5 Å, the diradical character of the $d\delta$ orbital is always larger than those of the $d\sigma$ and $d\pi$ orbitals. Then, the $d\pi$ orbital shows a larger diradical character than the $d\sigma$ orbital

at any bond length except for 1.6 Å ($y(d\sigma) = 0.204$ and $y(d\pi) = 0.199$). Because singlet dichromium(II) complexes can display Cr−Cr quadruple bonds with bond lengths ranging from 1.773[21] to 2.688 Å[22] depending on the ligands, the diradical characters of the $d\sigma$ and $d\pi$ orbitals can be tuned by choosing appropriate ligands, although the $d\delta$ orbital keeps a large diradical character. The bond length dependence of γ is displayed in Figure 1b, where the bond length range of real singlet dichromium(II) complexes is highlighted in gray. It is found that the total γ increases, attains a maximum ($\gamma = 1570$ au) at $R = 2.8$ Å, and then decreases with R. The γ value at $R = 2.8$ Å is about eight times as large as that ($\gamma = 188$ au) at $R = 1.8$ Å. Although many studies on metal−metal multiply bonded complexes have focused on the complexes with short metal−metal bonds from the challenging viewpoint of creating multiple bonds,[23] the present results predict that the complexes with fairly long metal−metal bonds exhibit larger third-order NLO properties than those with short bond lengths. This is an advantage of metal−metal bonded complexes for the design of highly efficient NLO systems.

To clarify the origin of the bond length dependence of γ, we examine the total γ values and the d−d interaction contributions partitioned into those of the dX electrons ($\gamma(dX)$, where $X = \sigma, \pi, \delta$) (see Supporting Information for the partitioning method) (Figure 1b). Note that there is a small difference between the total γ and the $\gamma(d\sigma) + 2\gamma(d\pi) + \gamma(d\delta)$ sum. It originates from the contribution of the nearly closed-shell inner-shell electrons, which is negligible as compared with the total γ in the inter-mediate diradical character region. (See Tables 2S and 3S in Supporting Information.) Provided $R \geq 1.8$ Å, $\gamma(d\sigma)$ is the dominant contribution, whereas $\gamma(d\pi)$ and $\gamma(d\delta)$ are small or almost negligible at $R \geq 2.4$ Å. It is also found that $\gamma(d\sigma)$ increases, attains a maximum [$\gamma_{max}(d\sigma) = 1570$ au at $R = 2.8$ Å, where $y(d\sigma) = 0.776$], and then decreases with R and $y(d\sigma)$. The $\gamma(d\pi)$ value is also enhanced in the intermediate $y(d\pi)$ region [$\gamma_{max}(d\pi) = 77$ au at $R = 2.0$ Å, where $y(d\pi) = 0.576$]. Judging from the bond length dependence of $\gamma(d\delta)$ as well as of $y(d\delta)$ (see Table 2S of the Supporting Information), the maximum $\gamma(d\delta)$ contribution should show up for a bond length smaller than 1.6 Å. These results indicate that the usual diradical character dependence of the π-electron contribution to γ of π-conjugated organic molecules is generalized to those of the σ- and δ-electron contributions to γ.

The bond length dependences of $y(dX)$ for Mo(II)−Mo(II) (Figure 2a) display for $R \geq 2.0$ Å the same amplitude ordering as in the case of Cr(II)−Cr(II), that is, $y(d\sigma) < y(d\pi) < y(d\delta)$, but, for a given R, the diradical characters of Mo(II)−Mo(II) are smaller than those of Cr(II)−Cr(II) because of the larger d−d interactions due to the larger d atomic orbital in Mo than in Cr. The equilibrium bond lengths of real dimolybdenum(II) complexes range from 2.037 to 2.239 Å[24] and, in that case, the $d\delta$ orbital presents an intermediate diradical character [$y(d\delta) = \sim0.7$ to ~0.8], whereas the $d\sigma$ and $d\pi$ orbitals have small diradical characters [$y(d\sigma) = \sim0.05$−0.1, $y(d\pi) = \sim0.05$−0.2]. Then, Figure 2b shows the bond length dependences of γ and $\gamma(dX)$. Although Mo(II)−Mo(II) exhibit a larger γ_{max} value (7630 au) than Cr(II)−Cr(II), such value will not be achieved because the corresponding bond length (3.4 Å) is well outside the range of equilibrium bond lengths. Similar to Cr(II)−Cr(II), enhancements of $\gamma(dX)$ are observed in the intermediate $y(dX)$ region for $d\sigma$, $d\pi$, and $d\delta$ orbitals: $\gamma_{max}(d\sigma) = 7800$ au at $R = 3.4$ Å [$y(d\sigma) = 0.662$], $\gamma_{max}(d\pi) = 246$ au at $R = 2.4$ Å [$y(d\pi) = 0.362$], and $\gamma_{max}(d\delta) = 159$ au at $R = 2.0$ Å [$y(d\delta) = 0.659$].

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Figure 2. Effects of the bond length (R) on the UHF diradical character (y) (a) and on the UCCSD second hyperpolarizability (γ) (total) (b,c) of Mo(II)−Mo(II) as well as on their dσ, dπ, and dδ orbital contributions. Note that γ(dπ) indicates one of the two equivalent dπ orbital contributions to γ. The gray-colored region represents the equilibrium bond length range (2.04 to 2.24 Å)[24] of real dimolybdenum(II) complexes.

From Figure 2c highlighting the bond length dependences of γ and γ(dX) in the equilibrium bond length region ($R = 2.0−2.3$ Å), it appears that dδ electrons provide the dominant contribution to γ for $R = 2.0$ to 2.1 Å but decrease with R, whereas the sum of the two equivalent dπ contributions increases with R and attains the half of total γ value at 2.2 Å. In contrast, the dσ contribution is not dominant and does not significantly vary in this bond length region. As a result, unlike for dichromium(II), the γ values of real

dimolybdenum(II) complexes with relatively short equilibrium metal−metal bond lengths are primarily described by dπ and dδ electrons.

Although γ(dσ), γ(dπ), and γ(dδ) attain a maximum in the intermediate y region, their maximum values are very different. This result can be rationalized by comparing the bond lengths [R_{max}(dX)] giving the maximum γ(dX) values. Indeed, for a symmetric two-site diradical system (A$^{\bullet}$− B$^{\bullet}$) using a basis of two localized natural orbitals, the SOS γ expression is given as a function of the diradical character y, a direct exchange integral (K_{ab}), the difference between the onsite and inter-site Coulomb integrals (U), and the effective diradical distance (R_{BA}), which is approximately regarded as the distance between A and B[1]

$$\gamma = f(y, r_k)\frac{R_{BA}^4}{U^3} \tag{1}$$

where $r_k \equiv 2K_{ab}/U$. Usually, r_k is close to zero, and $f(y,0)$ is maximum in the intermediate y region, which is the origin of the γ enhancement for singlet diradical systems. γ is thus also strongly affected by R_{BA}: the longer the bond length, the larger the γ value, but this is not the unique tuning parameter. Indeed, because γ(dX) corresponds to the third-order response of the two-site diradical system with bonding and antibonding dX orbitals, γ_{max}(dX) also depends on R_{max}(dX), the bond length presenting an intermediate overlap between the d orbitals, and the difference among γ_{max}(dσ), γ_{max}(dπ), and γ_{max}(dδ) comes from that among R_{max}(dσ), R_{max}(dπ), and R_{max}(dδ). Moreover, the R_{max}(dσ) > R_{max}(dπ) > R_{max}(dδ) ordering can be understood by the fact that (i) the lobes of the d$_{z^2}$ orbitals, which form the dσ orbitals, are oriented along the bond axis, (ii) those of d$_{xz}$ and d$_{yz}$ orbitals, which are the origin of the dπ orbitals, form an angle of 45° with the bond axis, and (iii) those of d$_{xy}$ orbitals, which build the dδ orbitals, are perpendicular to the bond axis. As a consequence, by combining the effects of both the bond length and of the diradical character, one obtains the following ordering at equilibrium distances: γ(dσ) > γ(dπ) > γ(dδ).

In this Letter, we have theoretically clarified the origin of the γ values in singlet dichromium(II) and dimolybdenum(II) systems by analyzing the diradical characters of their dσ, dπ, and dδ orbitals. The dichromium(II) system exhibits a maximum γ value around the bond length of 2.8 Å that primarily originates from the dσ electrons because of the intermediate diradical character of the dσ orbital. For the dimolybdenum(II) system, although a similar γ(dσ) exaltation might occur for 3.0 to 4.0 Å bond lengths corresponding to intermediate diradical characters, the real bond lengths (2.037 to 2.239 Å) are much shorter so that dπ and dδ electrons give the major contribution to γ. Therefore, real singlet dichromium(II) and dimolybdenum(II) complexes are "σ-dominant" and "π-dominant"/"δ-dominant" third-order NLO systems, respectively. These results on transition-metal complexes with metal−metal multiple bonds contrast with previous works on "π-dominant" third-order NLO systems based on π-conjugated organic molecules but also highlight for the first time the existence of both a novel class of "σ-dominant" third-order NLO systems as well as of very unique "δ-dominant" third-order NLO systems. Finally, these results will also serve as guidelines to elaborate metal−metal multiply bonded complexes involving ligands, where the latter are expected to tune the diradical characters as well as to bring their own, although small, contributions to γ.

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■ ASSOCIATED CONTENT

ⓢ Supporting Information. Details of calculation methods of the diradical character y and second hyperpolarizability γ as well as of the partition procedure of γ into each orbital, for example, $d\sigma$, $d\pi$, and $d\delta$ contribution. y, γ, and $\gamma(dX)$ values at each bond length of $Cr(II)-Cr(II)$ and $Mo(II)-Mo(II)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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