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Impact of Diradical/Ionic Character on Third-Order Nonlinear Optical Property in Asymmetric Phenalenyl Dimers

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The dissociation behavior of the asymmetric hetero-phenalenyl dimers is theoretically investigated from the viewpoint of the open-shell singlet third-order nonlinear optical (NLO) systems. It is found that the second hyperpolarizability γ of all the investigated phenalenyl dimers exhibit bell-shape behavior with maximum at the intermediate dissociation region, and that the γ value of the most effective asymmetric dimer reaches about 20 times the maximum of the original phenalenyl dimer. This behavior is clarified by the new definition of diradical/ionic characters, identifying that the significant enhancement of γ occurs in the intermediate ionic region as well as in the intermediate diradical region. The present result extends the concept of diradical character based design of NLO molecules toward ionic closed-shell region in a realistic molecular framework, and demonstrates the intermediate ionic systems as a new target in the NLO molecules with open-shell molecular frameworks.

Organic molecules with large third-order nonlinear optical (NLO) properties have attracted much attention because of their future applications in optoelectronics.[1,2] Although these organic NLO systems exhibit some superiorities compared to the inorganic materials such as fast-response property, tailorability and low cost, their relatively small optical nonlinearities prevents us from the realization of the organic NLO materials. In order to overcome this drawback, several guidelines for the further enhancement of NLO properties have been presented for the organic molecules.[2] One of such guidelines focuses on the open-shell singlet character.[1e,f,3] It was theoretically predicted that the intermediate open-shell singlet molecules exhibit gigantic enhancement of the second hyperpolarizability γ, which is a microscopic measure of the third-order NLO properties.[3] On the basis of this guideline, several open-shell singlet NLO molecules have been designed and investigated from both the theoretical and experimental points of view. Especially, recent successes in the synthesis of the very stable open-shell singlet molecules kindle the development of this field, and future applications of these systems in the device engineering field are expected.[4]

In 2013, the correlation between the open-shell singlet nature and the γ value has been theoretically extended to the asymmetric systems by applying the asymmetric two-electron and two-orbital minimal model.[5a] The result shows that the introduction of the asymmetricity into the open-shell singlet molecular framework could cause a gigantic enhancement of the NLO properties compared to the symmetric counterparts. Until now, however, the explorations of the realistic open-shell singlet NLO molecules have been limited to the symmetric molecules, and only a few studies have been carried out on the asymmetric open-shell systems.[5b–d] Recently, we have investigated the boron or nitrogen analogues of Chichibabin's hydrocarbons and have found that the asymmetric analogues have various charge transfer character in the closed-shall electronic structures, resulting in the large variations of γ.[5d] These results suggest that the modification of the charge transfer character in the potentially open-shell singlet molecular framework could lead to the gigantic enhancement of γ value, but the detailed relationship between γ and the electronic structure has not been clarified yet because of the lack of the model asymmetric open-shell singlet systems with suitable variables, which can describe the electronic structures with a wide range of diradical/ionic character in the potentially open-shell singlet molecular framework.

In this study, we investigate the dissociation behaviors of the hetero-phenalenyl dimers as a realistic model of the asymmetric open-shell singlet molecules. The dimer model is suitable for the detailed discussion of the γ values in the realistic asymmetric open-shell molecular framework since the interaction between monomers can be smoothly controlled by the intermolecular distance and the combination of the phenalenyl monomers.[6] Such asymmetric phenalenyl dimers have been investigated by focusing on the interaction energies, stable conformations and the second-order NLO properties in the stable distance.[6b–d] But these studies did not deal with

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neither the third-order NLO properties nor the dissociation behavior. Geometry optimization is carried out for each monomer in the neutral states using the UB3LYP/6-311G* method. The eclipse-type dimer model is constructed so that the optimized monomers are placed in a face-to-face manner with each fixed intermolecular distance. Note that the anti-type dimer is also tested for [Phn-B, Phn-N] system and the similar results are obtained as well as [Phn-C, Phn-C] system in the previous study[6a] (Figure S11 and S12). The dimerization energy of each eclipse-type dimer is calculated using the UB3LYP–D/6-31+G* and UM05-2X/6-31+G* methods and the most stable stacking distance is located between 3.2 to 3.6 Å for all the eclipse-type dimers (Figure S10 and Table S2). For each distance, the ground state electronic structure is characterized by the new definition of the diradical/ionic characters y^{new}, which was defined in the previous paper and enables us to access the clarification of the ionic region as well as the diradical region of the open-shell molecular frameworks.[7] The y^{new} value quantifies the balance between the diradical-like or ionic-like natures in the set of localized orbital basis, and takes a fractional value between 1 (pure diradical) and –1 (pure ionic), where 0 corresponds to the non-correlated limit. The y^{new} value is given by[7]

$$y^{\mathrm{new}}=\begin{cases} 2\left(\left|C_{a\bar{b}}\right|^2+\left|C_{\bar{a}b}\right|^2\right)-1 & \left(\left|C_{a\bar{b}}\right|^2+\left|C_{\bar{a}b}\right|^2\geq 0.5\right) \\ 1-2\left(\left|C_{a\bar{a}}\right|^2+\left|C_{b\bar{b}}\right|^2\right) & \left(\left|C_{a\bar{b}}\right|^2+\left|C_{\bar{a}b}\right|^2<0.5\right) \end{cases} \tag{1}$$

where C_{ij} represents the configuration interaction (CI) coefficient of the determinants in the localized orbitals basis. It should be noted that the present definition can quantify the open-shell singlet nature with its positive value and takes a negative value when the ionic character is larger than the diradical character. Therefore, the present definition covers all the electronic structure from purely ionic to purely diradical region and is useful for the present purpose. The set of C_{ij} values are calculated using the complete active space CI (CAS-CI) method with two-electron and two-orbital active space together with 6-31G* basis set (see Supporting Information for further details). The estimation of the third-order NLO property is carried out by the dominant component of the static second hyperpolarizability tensor parallel to the intermolecular direction calculated using the long-range corrected (LC) UBLYP/6-31+G* method, which was confirmed to be sufficient for the estimation of the second hyperpolarizability in the dissociation of the original phenalenyl dimer.[6a, 8]

At the first stage, we focus on the dissociation behaviors of the three phenalenyl dimers, original symmetric [Phn-C, Phn-C], and two asymmetric [Phn-B, Phn-C]$^-$ and [Phn-B, Phn-N] (Figure 1). The constituting monomers exhibit variations in the vertical ionization energy of radical state (Table S1). Such variations induce an asymmetric electronic structure in the dimer configurations depending on the difference of ionic potentials, that is, no difference for [Phn-C, Phn-C], large difference for [Phn-B, Phn-N] and intermediate between them for [Phn-B, Phn-C]$^-$, which determines the dissociation behaviors. The variations of y^{new} values clearly show the dissociation behavior of these systems (Figure 2). Both the symmetric [Phn-C, Phn-C] and asymmetric [Phn-B, Phn-C]$^-$ systems exhibit increasing the y^{new} value in the positive region, which corresponds to the homolytic dissociation attaining two radicals at the extreme, though the asymmetric one exhibits a relatively smaller y^{new} value because of the larger ionic configuration. On the other hand, [Phn-B, Phn-N] system shows completely different dissociation behavior that the y^{new} decreases along with the intermolecular distance R, attaining ionic limit. Considering them together with the fact that all the systems exhibit small positive y^{new} values showing the covalent interaction at the very small R region, we can illustrate the dissociation behavior of these phenalenyl dimers (Scheme 1). This tendency is also validated by the dissociation behavior of the Hirshfeld charge difference $\Delta\rho$ between the monomers, where only the [Phn-B, Phn-N] dimer shows the increase of $\Delta\rho$ reaching 2 at dissociation limit though the others reaches to 0 (Figure S5).[7]

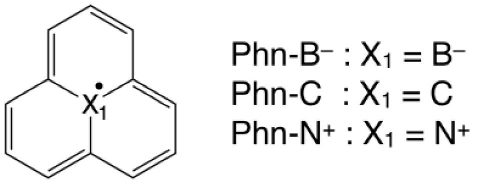


Figure 1. Three model phenalenyl radicals Phn-B$^-$, Phn-C and Phn-N$^+$.

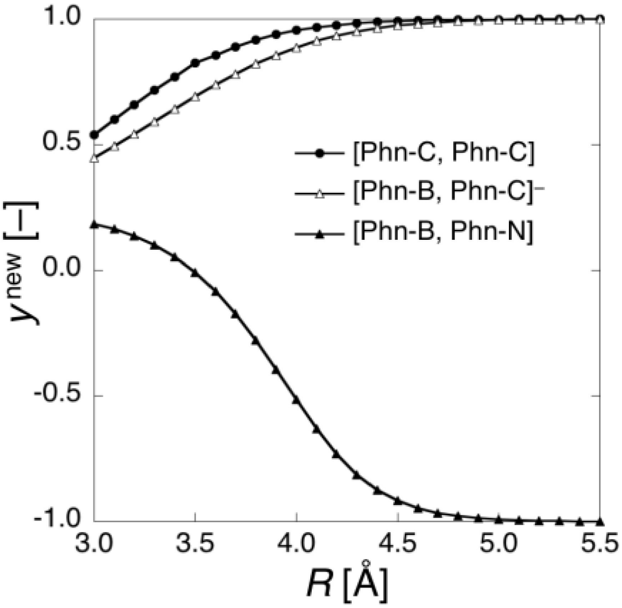
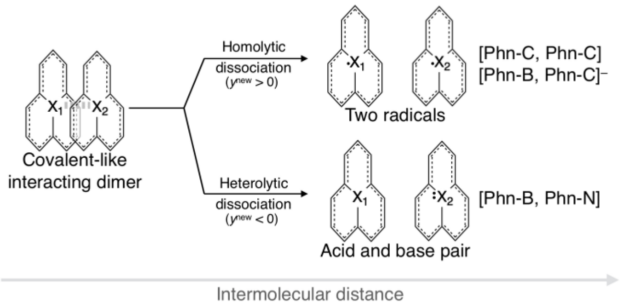


Figure 2. Dissociation behavior of y^{new} along intermolecular distance R.

The variations of the ground state electronic structure have a strong impact on the static second hyperpolarizability of



Scheme 1. Schematic picture of dissociation behavior of three phenalenyl dimers.

these dimers. It is found that all the phenalenyl dimers exhibit bell-shape dependence of γ as a function of y^{new}, resulting in the maximum γ value at the intermediate dissociation region (Figure 3). This y^{new}-dependence of γ clearly demonstrates the significant enhancement of γ value in the intermediate ionic electronic structure as well as the diradical one. In fact, the y^{new} values, at which the maximum γ is obtained, are all intermediate values (0.600 for [Phn-C, Phn-C], 0.691 for [Phn-B, Phn-C]$^{-}$ and –0.731 for [Phn-B, Phn-N]). Since the absolute value of y^{new} gets decrease when the difference of the ionic potential gets larger, the intermediate y^{new} value could be achieved in relatively larger R value (Figure S4). Furthermore, it should be noted that the maximum γ values of the asymmetric systems are about 6 times that of the symmetric [Phn-C, Phn-C] dimer (17.9×10^{4} a.u. for [Phn-C, Phn-C], 109×10^{4} a.u. for [Phn-B, Phn-C]$^{-}$ and 110×10^{4} a.u. for [Phn-B, Phn-N]). These results show that the NLO properties of the asymmetric phenalenyl dimers could surpass those of the original [Phn-C, Phn-C] dimers especially at larger intermolecular distance region.

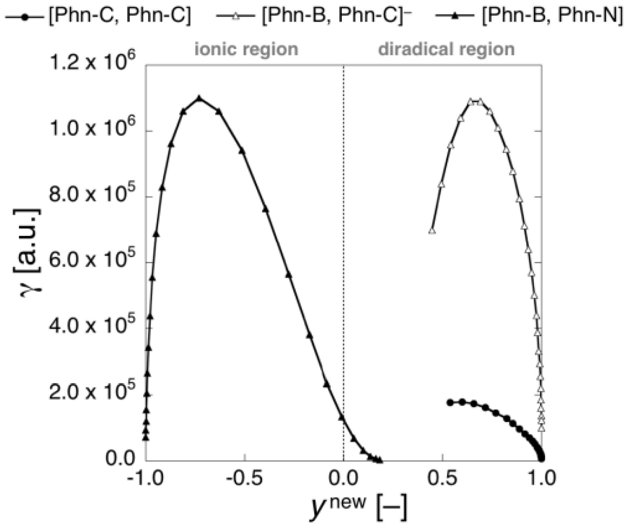


Figure 3. Dissociation behavior of γ value along with y^{new} value.

At the final stage, we design the asymmetric phenalenyl dimers in the ionic region with larger γ values based on the result of asymmetric two-site and two-electron model.[5a] From the theoretical model, it is expected that the decrease of the asymmetric electronic distribution of the ionic ground systems would lead to further enhancement of the γ values in the large dissociation region. In order to achieve this, we replace phenalenyl framework of Phn-B^{-} monomer with triazaphenalenyl framework (TAP-B^{-}) to decrease the electron donor nature of Phn-B^{-} monomer (Figure S9).[6b] The ionization energy ΔE_{rad} in the radical state of TAP-B^{-} is, in fact, increases about 0.7 eV from that of Phn-B^{-} monomer (2.17 for Phn-B^{-} radical and 2.86 for TAP-B^{-} radical). This variation would lead to the decrease of asymmetric distribution realizing the relatively smaller asymmetric electronic distribution. In fact, the absolute value of y^{new} and the electronic Hirshfeld charge difference $\Delta\rho$ decreases while keeping the similar dissociation trend (Figure S4 and S5). This result validates our prediction that [TAP-B, Phn-N] system exhibits heterolytic dissociation behavior with smaller asymmetric electronic structure than [Phn-B, Phn-N]. The γ value of [TAP-B, Phn-N] also follows our prediction that the maximum γ value attains 350×10^{4} a.u. at y^{new} of –0.833 and R of 4.5 Å (Figure S7 and S8). This maximum γ value is about 3 times as large as those of the other asymmetric system (about 20 times as large as that of original symmetric system). Not only TAP framework, mono- and di-azaphenalenyl frameworks (MAP and DAP) are also applied instead of phenalenyl framework of Phn-B^{-} molecules, and it is found that the increase in the number of the nitrogen atoms smoothly decreases the asymmetric electronic distribution and increases the maximum γ value (Figure S4–S9). These results further demonstrate the impact of the modification of the asymmetric electronic structure in the ionic ground state molecules on the NLO properties.

In the present communication, we have firstly clarified the dissociation behavior of the asymmetric hetero-phenalenyl dimers from the viewpoint of NLO properties. The bell-shape dependence of the second hyperpolarizability has been observed for all the phenalenyl dimers though the dissociation pattern (heterolytic or homolytic) depends on the difference between the ionic potentials of constituting monomers. The characterization of the dissociation pattern using the new definition of diradical/ionic character shows that the enhancement of the γ value in the intermediate diradical character region turns out to be comparable to that in the intermediate ionic character region, which is expressed as a negatively-intermediate value of y^{new}. This finding of the significant enhancement in the intermediate ionic character region would be related to the large enhancement of γ value in the intermediate charge separation state of asymmetric polyenes.[9] But the overall discussion was carried out mainly on the bond-length alternation and resonance structure basis, while the two-electron and two-orbital picture or diradical region has not been investigated before. In this regard, the present finding extends the diradical-character-based design guidelines for NLO molecules toward the ionic region, and then contributes to constructing more comprehensive design guidelines in a wide range of diradical/ionic region of the NLO molecules.

Although the studied asymmetric phenalenyl-derivative dimer systems with intermediate ionic character might not be realizable in the usual aggregate systems due to the large intermonomer distances, the similar electronic structure could be realizable using the rigid linkers as demonstrated experimentally in a biphenyl-bridged imidazole dimer.[10] In other realistic molecular frameworks, such intermediate ionic states are presumably achieved in weak Lewis acid and base pair dimer like frustrated Lewis pair series [11] or in π-conjugated molecules with intramolecular intermediate charge transfer character within the molecules. [5d] Furthermore, the effects of surrounding medium will be interesting and important for realizing realistic NLO systems due to their impact on the ionic and diradical characters.[12] The investigation of open-shell character and NLO responses of such realistic compounds as well as of the surroundings effects are now in progress in our laboratory.

Supporting Information Summary Paragraph

Calculation details, chemical structures of aza-substituted phenalenyl systems, potential energy curves of dimers, comparison with anti-type dimers and Cartesian coordinates of the optimized structures are given in the supporting information section.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: Diradical Character · Intermolecular Interaction · Open-Shell Singlet · Phenalenyl Dimer · Third-Order Nonlinear Optical Properties

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