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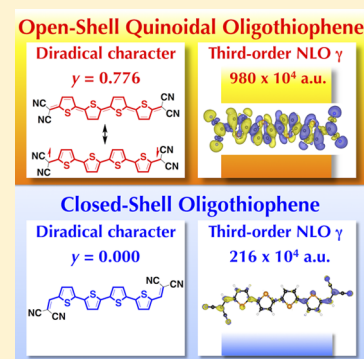
Theoretical Study on the Electronic Structure and Third-Order Nonlinear Optical Properties of Open-Shell Quinoidal Oligothiophenes

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S Supporting Information

ABSTRACT: The chain-length dependences of geometric and electronic structures and third-order nonlinear optical (NLO) properties of open-shell quinoidal oligothiophenes (QTs) are investigated from the viewpoint of diradical character (γ) using the broken-symmetry density functional theory method. The results are compared with those of closed-shell oligothiophenes. The bond-length alternation and the nucleus-independent chemical shift values are evaluated to clarify the chain-length dependence of aromaticities of the terminal and middle thiophene rings in the oligomer chain, which is closely related to the variation in the diradical character through the quinoidal/aromatic resonance structure. The γ values of these QTs ranging from monomer to hexamer are found to have a wide variety of γ values [0 (closed-shell state) $\leq \gamma \leq 1$ (pure diradical state)]. The γ values per unit of the open-shell QTs having intermediate γ are found to be significantly enhanced as compared to those of the closed-shell counterparts. The feature of γ dependence of γ in open-shell QTs is found to be in good agreement with so-called “ γ - γ correlation”, which has been proposed on the basis of the simple two-site diradical model using the valence configuration interaction method. These results reveal the relationships among the terminal substituent group, molecular structure and size, and diradical character, which contribute to building design guidelines for highly efficient third-order NLO materials based on the open-shell one-dimensional oligomers.



1. INTRODUCTION

Quinoidal oligothiophenes (QTs), which were first synthesized as the acceptor analogues of 7,7,8,8-tetracyanoquinodimethane (TCNQ),^{1–3} are known as one-dimensional thiophene oligomers having quinoidal nature of their geometric and electronic structures.^{1–12} They are expected to have a relatively small energy gap between the highest occupied and the lowest unoccupied molecular orbitals (HOMO and LUMO, respectively) compared with the usual aromatic thiophene oligomers owing to the quinoidal nature of their electronic structure, and thus, they have attracted a great deal of attention as ambipolar carrier transport materials for the organic field-effect transistor (OFET),^{6,7} as well as photonic and electro-optical materials.^{4,5,8,9} To investigate the electronic structures and physicochemical properties as well as to realize such applications, several synthetic strategies such as the increase in the number of thiophene units (n) have been proposed. Recently, Takahashi and co-workers designed a new family of QTs, where each thiophene unit is fused with a bis-(butoxymethyl)cyclopentane ring, and succeeded in synthesizing QTs, where $n = 1–6$.⁵ This has brought further progress in the synthesis of QT-based oligomer systems and detailed understanding of their electronic structures. Several spectroscopic techniques such as Raman, UV–vis, and ESR experiments as well as theoretical calculations^{4–12} revealed that the

electronic structures of QTs are described by the resonance structures shown in Figure 1a.^{11,12} To sum up, (i) the singlet ground (S_0) state is described by the resonance between the closed-shell quinoidal and the open-shell diradical (aromatic) forms, (ii) for small n , the S_0 state is mainly described by the quinoidal form, but the contribution of the diradical form increases with the increase of n , and (iii) the energy gap between S_0 and T_1 (purely diradical triplet) states decreases with the increase of n , and for large n , the S_0 and T_1 states are in the thermal equilibrium state at a given temperature T . These indicate the singlet diradical nature of QTs, i.e., the open-shell nature in the S_0 state. Such unique chain-length dependence of the electronic structure of the open-shell S_0 state in QTs is expected to lead to unique physicochemical properties, in particular optical response properties. Indeed, linear and nonlinear optical (NLO) spectroscopic experiments have suggested that QTs are also promising as NLO materials.^{4,8,13} However, the detailed mechanism and fundamental understanding of the chain-length dependence of optical response properties of QTs in relation to the open-shell (diradical) nature of the S_0 state have not been clarified yet though the

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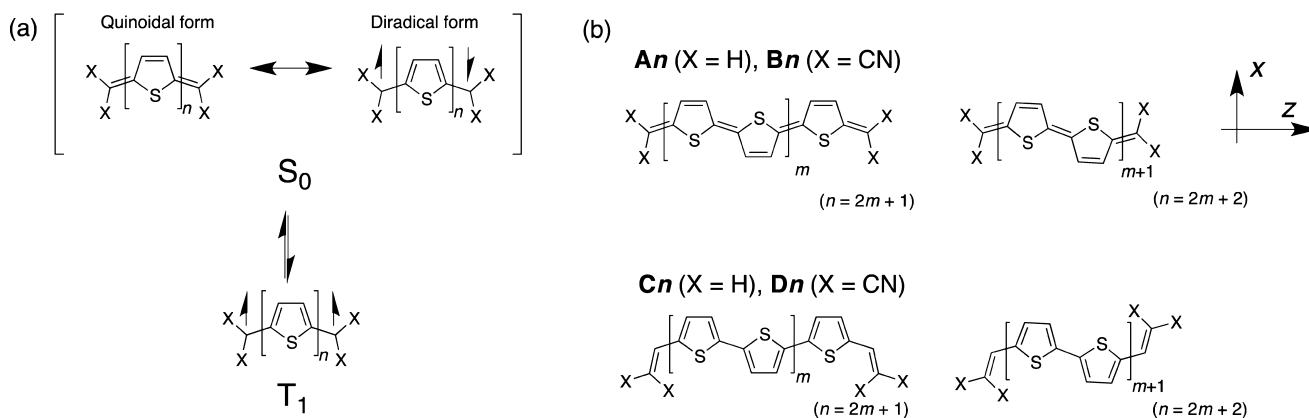


Figure 1. Molecular structures of S_0 and T_1 states of QTs (a) and calculated models (b): open-shell systems A_n ($X = H$) and B_n ($X = CN$) and closed-shell systems C_n ($X = H$) and D_n ($X = CN$) for $n = 1-6$ ($m = 0, 1$, and 2). Coordinate axes are also shown.

open-shell nature is found to govern the excited-state energies and properties as well as the relative stability of each spin state.^{14–17} Thus, one of the objectives of this study is to establish a fundamental understanding of the relationship between the geometric/electronic structures and the NLO properties of QTs on the basis of the diradical nature in the S_0 state, which is expected to deepen the understanding of open-shell singlet systems and to extend applications of QTs in material sciences.

The diradical nature in the S_0 state can be quantitatively described by the diradical character, y , which is theoretically defined as twice the weight of the bond-breaking double excitation configuration in the S_0 state wave function.^{18,19} y takes a value from 0 (closed-shell) to 1 (pure diradical), where the intermediate y ($0 < y < 1$) indicates the diradical-like (diradicaloid) state. Another chemical interpretation of y is that $1 - y$ represents the effective bond order.¹⁹ Since the instability of a chemical bond is expected to be closely related to the electronic responses of chemical species to the external chemical and physical perturbations, we have theoretically investigated the relationship between y and the optical response properties, i.e., excitation energies and properties, of open-shell singlet molecules.^{14–16,20–24} On the basis of the valence configuration interaction (VCI) analysis using the simplest two-site diradical model, we have derived analytic expressions of excitation energies and transition dipole moments between the S_0 and low-lying excited states in terms of y .^{15,16} Accordingly, we have found a novel electronic structure–NLO property relationship for the second hyperpolarizability γ (the third-order NLO property at the molecular level): the γ value of the system having intermediate y is predicted to be larger than those of closed-shell ($y \approx 0$) and pure diradical ($y \approx 1$) systems of similar size.^{14–16,20,21} This structure–property relationship has been substantiated by several high-precision quantum chemical calculations of several model^{14,15,20,21,24} and real^{22,23,25} diradical compounds. Subsequently, several experimental studies on the real open-shell singlet molecules having intermediate y , e.g., diphenalenyl diradical compounds,²⁶ zethrene derivatives,²⁷ and bis(acrydine) dimer,²⁸ have evidenced the validity of our structure–property relationship, referred to as “ y – γ correlation”. These studies have paved the way for the diradical-character-based design of novel NLO materials.^{29,30} At the present stage, further explorations of novel open-shell singlet molecules other than polycyclic hydrocarbons,^{29,30} e.g., one-dimensional oligomers involving hetero-

atoms, are strongly expected for the extension of the field of open-shell NLO materials. In this regard, practical design guidelines for open-shell singlet systems with variable diradical character are desired. Fortunately, such guidelines can be constructed on the basis of the resonance structure, which is a very familiar concept for most chemists: if we can illustrate both the closed-shell (Kekulé) and open-shell (diradical) forms as the possible resonance structures, the system has the potential of exhibiting diradical character. Furthermore, the diradical character is expected to increase when the open-shell form is relatively stabilized in the resonance structures, which results in the increase of the contribution of the open-shell form. From this point of view, QTs are expected to be not only suitable for the reference materials for further systematic verification of y – γ correlation in real systems involving heteroatoms, but also promising constituents of novel open-shell NLO materials, since the number of thiophene rings is directly related to the contribution of the open-shell form, i.e., diradical character (see Figure 1). In this study, we thus investigate the relationships among the chain length n , diradical character y , and second hyperpolarizability γ of QTs (systems A_n and B_n in Figure 1b) by broken-symmetry density functional theory (BS-DFT) calculations. We compare these results with those of a different family of oligothiophenes (systems C_n and D_n in Figure 1b), which are regarded as closed-shell aromatic systems. The substituent effects at the terminal functional group (X) are also examined by changing $X = H$ and CN . On the basis of these results, we present practical design guidelines for NLO active open-shell one-dimensional oligomers having different diradical nature.

2. THEORETICAL METHODS

Geometry optimizations were performed at the (U)B3LYP level of approximation using the 6-311G* valence triple- ζ basis set. No symmetry constraints were imposed during the optimizations. After that, frequency analysis calculations were performed to obtain the global minimum structure. The UB3LYP-optimized geometries of open-shell systems are reported to be in good agreement with the experimental results of X-ray analysis.^{16,28} Within the calculation of static γ , we set the coordinate axis so that the linear line going through the carbon atoms at both ends linked with the terminal thiophene rings lies on or is parallel to the z -axis (see Figure S1 in the Supporting Information).

The diradical character y is defined by the occupation numbers (n_L) of the lowest unoccupied natural orbital (LUNO) obtained by diagonalizing the one-particle density matrix.^{31,32}

$$y \equiv n_L \quad (1)$$

where y takes a value from 0 (closed shell) to 1 (pure diradical). The original diradical character is defined as 2 times the weight of the double-excitation configuration in the ground-state wave function based on the multiconfigurational self-consistent-field (MC-SCF) theory,^{18,19} but the y values are formally expressed by eq 1 in the spin-unrestricted single-determinant schemes. The open-shell character of a molecule can be described by the spatial distribution of the odd-electron densities $D_{\text{LUNO}}^{\text{odd}}(\mathbf{r})$ and $D_{\text{HONO}}^{\text{odd}}(\mathbf{r})$, where HONO = highest occupied natural orbital. According to ref 32, we obtain

$$D_y^{\text{odd}}(\mathbf{r}) = D_{\text{HONO}}(\mathbf{r}) + D_{\text{LUNO}}(\mathbf{r}) \quad (2)$$

where each of the contributions is defined as³¹

$$D_k^{\text{odd}}(\mathbf{r}) = \min(2 - n_k, n_k) \phi_k^*(\mathbf{r}) \phi_k(\mathbf{r}) \quad (3)$$

The term $\min(2 - n_k, n_k)$ can be regarded as the probability of the electron being unpaired in the k th NO $\phi_k(\mathbf{r})$. In the case of $n_{\text{HONO}} + n_{\text{LUNO}} = 2$, which is satisfied exactly in single-determinant schemes and approximately in general, the diradical character reads³²

$$y = \frac{1}{2} \text{tr}[D_y^{\text{odd}}(\mathbf{r})] \quad (4)$$

highlighting that the spatial distribution of y is described by the odd-electron densities.

Previous experimental and theoretical studies on the structural parameters and vibrational frequencies revealed that the chain-length dependence of the open-shell character of QTs is closely related to the aromatic/quinoidal characteristics of thiophene rings.¹¹ To further confirm the relationship, we evaluate the nucleus-independent chemical shift (NICS) aromaticity for each ring.^{33–35} The NICS aromaticity is defined as the opposite of the isotropic magnetic shielding constant, i.e., $\text{NICS} = -1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$,³³ so that a negatively large NICS value corresponds to more aromatic characteristics of a ring. In this study, we evaluate the NICS values at the position of 1.0 Å above the center of mass of each thiophene ring, namely, the NICS(1 Å) value, which has been reported to be one of the good measures of the aromaticity originating in the delocalization of π -electrons.³⁵ The correlation between the NICS(1 Å) aromaticity and y has been discussed in our previous study for one-dimensional open-shell polycyclic aromatic and antiaromatic hydrocarbons.³⁶

The static γ value was calculated by the finite-field (FF) approach.³⁷ In the FF approach, the z -axis component of the static second hyperpolarizability tensor, γ_{zzzz} , in B -convention is calculated using the fourth-order numerical differentiation formula

$$\gamma_{zzzz} = \frac{1}{36(F^z)^4} \{E(3F^z) - 12E(2F^z) + 39E(F^z) - 56E(0) + 39E(-F^z) - 12E(-2F^z) + E(-3F^z)\} \quad (5)$$

where $E(F^z)$ represents the total energy of a system in an electric field with an amplitude of F^z (z -axis component of the field). The convergence on the total energy was fixed to 10^{-10}

au. In the present calculations, such a convergence criterion is found to give the numerical accuracy of γ values within $\sim 1\%$ relative error. y and γ were calculated by using the long-range-corrected UBLYP (LC-UBLYP) functional³⁸ with the 6-31G*+p basis set. The exponents of diffuse p functions on C (0.0523), N (0.0582), and S (0.0402) atoms were determined by the even-tempered method. The range separating parameter μ of the LC-BLYP functional is set to 0.33 bohr^{-1} since it has been found to semiquantitatively reproduce γ of open-shell molecules calculated by the strongly correlated spin-unrestricted coupled cluster method including single and double excitations as well as a perturbative treatment of the triple excitations [UCCSD(T)].²⁵ Although the broken-symmetry DFT calculations, in principle, suffer from spin-contamination effects, the LC-UBLYP results of y and γ of open-shell singlet systems have been reported to be in nice agreement with the correlated ab initio results where spin contaminations are negligible [such as the UCCSD(T) results] or effectively removed [such as the spin-flip CI results].²⁵ The LC-(U)BLYP exchange-correlation functional is also reliable for the evaluation of the (hyper)polarizabilities of large-size π -conjugated molecules as demonstrated in recent investigations on the size dependences of the polarizability and the second hyperpolarizability in polyacetylenes, polydiacetylenes, and hydrogen chains as compared to other conventional functionals such as B3LYP.^{39,40} The magnetic shielding tensor calculations for the NICS(1 Å) values were performed at the LC-(U)BLYP/6-31G*+p level of approximation using the gauge-invariant atomic orbital (GIAO) method.³⁴ These calculations were performed using the Gaussian 09 program package.⁴¹

3. RESULTS AND DISCUSSION

3.1. Chain-Length Dependences of Geometric Parameters, Aromaticity, And Diradical Character. Bond-length alternation (BLA) patterns of QTs in the S_0 and T_1 states have already been discussed well in previous studies by using the spin-restricted and -unrestricted DFT methods associated with the characterization of their UV-vis, IR, and Raman spectra to establish the electronic structure shown in Figure 1.^{6,11} We here further examine the correlation among the geometric parameters (i.e., planarity and bond length alternation) and electronic structures (i.e., aromaticity and diradical character) of QTs. The planarity of QTs is expected to closely correlate with the contributions of quinoidal/diradical resonance forms, because the quinoidal form gives the double-bond contribution to the linker C–C bonds. For systems **An** and **Bn**, all the optimized geometries are found to be planar with the highest possible symmetry (C_{2h} for odd n and C_{2v} for even n) except for $n = 6$. From the results of frequency analysis, the lowest frequency corresponding to the out-of-plane mode decreases with the increase of n and then, at $n = 6$, slightly nonplanar arched (almost C_2) structures are obtained [the lowest frequencies (cm^{-1}) are 104.28 (**A1**), 54.71 (**A2**), 29.84 (**A3**), 19.69 (**A4**), 12.73 (**A5**), and 5.93 (**A6**) for **An** and 52.85 (**B1**), 28.23 (**B2**), 17.64 (**B3**), 11.68 (**B4**), 8.60 (**B5**), and 5.28 (**B6**) for **Bn**]. In the previous work by Ortiz and co-workers,¹¹ a planar C_{2h} structure was obtained for **B6** at the UB3LYP/6-31G** level of approximation. The difference in the results is considered to originate in the choice of the basis set; i.e., we have employed a more flexible valence triple- ζ basis set. On the other hand, for systems **Cn** and **Dn**, all the optimized geometries are obtained as nonplanar bent structures except

for $n = 1$, because the aromatic resonance form is dominant in systems **Cn** and **Dn**.

Figure 2 shows the calculation results for C–C bond lengths, where we numbered each C–C bond starting from the terminal

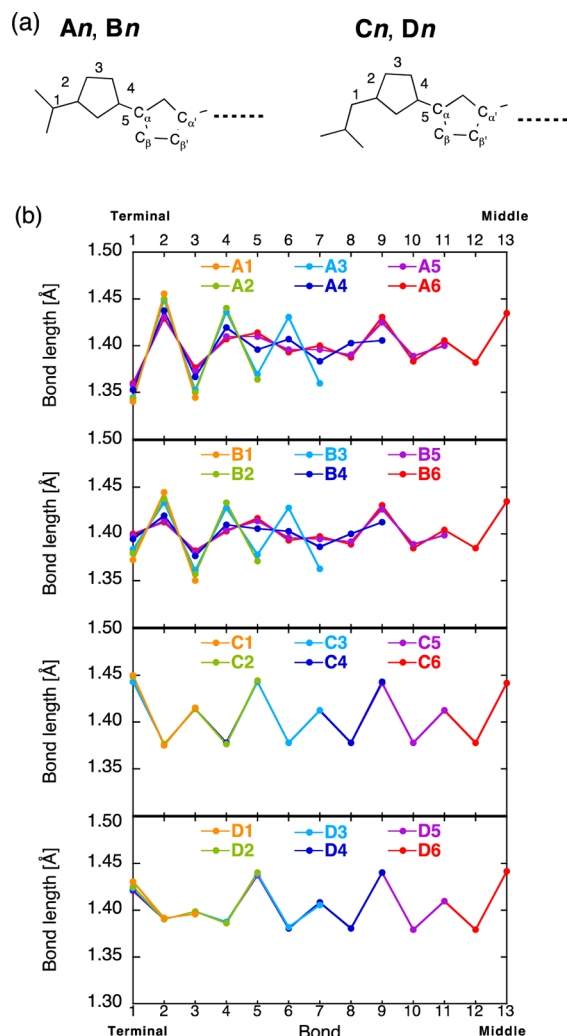


Figure 2. Numbering of each C–C bond (a) and the variations in the bond lengths for **An–Dn** (b) calculated at the (U)B3LYP/6-311G* level of approximation.

of the chain to the middle (see Figure 2a). Bonds 1, 5, 9, and 13 correspond to the linker $C_{\alpha}-C_{\alpha'}$ bonds. The lengths of the terminal C–C bonds are found to lie around 1.34–1.36 Å for systems **An** and 1.37–1.40 Å for systems **Bn**. For $n \leq 3$, all the $C_{\alpha}-C_{\beta}$ ($C_{\alpha'}-C_{\beta'}$) bonds (i.e., 2, 4, and 6) are longer than the nearest-neighbor $C_{\alpha}-C_{\alpha'}$ (i.e., 1 and 5) and $C_{\beta}-C_{\beta'}$ (i.e., 3 and 7) bonds, which indicates that all the thiophene rings in the chain possess the quinoidal feature for these systems. In such a case, the open-shell character in the S_0 state is expected to be small. However, the BLA patterns for **An** and **Bn** are found to change for systems with $n \geq 4$. Although these QTs with longer chain length also exhibit the quinoidal feature in the terminal ring, the oscillatory behavior of BLA tends to disappear in the rings next to the terminal ones. For $n \geq 5$, the BLA patterns in the middle rings were perfectly inverted as compared with those in the terminal rings; i.e., an aromatic feature of BLA begins to appear in the middle region. From the resonance structure given in Figure 1, the open-shell character is expected

to be considerable for $n \geq 5$. Judging from these results, the effect of an introduction of terminal $-CX_2$ groups that tend to prefer the quinoidal structure is considered to efficiently reach the second-neighboring thiophene ring. On the other hand, the lengths of the terminal C–C bonds are found to be around 1.45 Å for systems **Cn** and 1.42–1.43 Å for systems **Dn**, which are much longer than those of **An** and **Bn**. In sharp contrast to the results for **An** and **Bn**, the chain-length dependences of the BLA patterns for **Cn** and **Dn** were negligible. As expected from their resonance structures, these BLA patterns of **Cn** and **Dn** indicate an aromatic feature of each thiophene ring.

The chain-length dependence of the aromaticity of each thiophene ring can be illustrated more clearly by evaluating the BLA and NICS(1 Å) values at each ring. Here, the BLA value of a ring is defined as the bond length of $C_{\beta}-C_{\beta'}$ subtracted by the average lengths of $C_{\alpha}-C_{\beta}$ and $C_{\alpha'}-C_{\beta'}$ bonds (see Figure 2a), which is the same definition as in the previous study.¹¹ Parts a and b of Figure 3 show the chain-length dependences of the BLA values calculated for the terminal and middle rings, respectively. Note that, for $n \leq 2$, the terminal and middle rings are identical to each other. For both the terminal and middle rings of systems **An** and **Bn**, the BLA values are found to be negative for small n and then to increase with the increase of n . The BLA values of the terminal rings are found to remain negative for all n , while those of the middle rings turn out to be positive for $n \geq 5$. On the other hand, the BLA values for systems **Cn** and **Dn** are found to always be positive and to be almost independent of n . For $n = 6$, the BLA values at the middle rings for systems **An** and **Bn** are found to be very similar to those for **Cn** and **Dn**, which indicates recovery of aromatic character in the middle regions of QTs having a longer chain length. Furthermore, an introduction of acceptor groups is found to reduce the absolute value of BLA in the terminal rings.

Parts c and d of Figure 3 show the NICS(1 Å) values calculated at 1.0 Å above the centers of the terminal and middle thiophene rings, respectively. As the reference value, the NICS(1 Å) value for an isolated thiophene molecule was calculated to be -10.04 ppm at the same level of approximation. The chain-length dependences of NICS(1 Å) values show a tendency very similar to that of the chain-length dependences of the BLA values. For systems **An** and **Bn**, the NICS(1 Å) values on both the terminal and middle rings are found to increase negatively with the increase of n . As seen from this figure, the NICS(1 Å) values tend to converge to a value at $n = 6$ (-6.59 ppm for **A6** and -6.81 ppm for **B6**). However, the NICS(1 Å) values in the terminal rings (-4.57 ppm for **A6** and -5.62 ppm for **B6**) are found to be smaller negative values compared with those of **C6** (-7.26 ppm) and **D6** (-7.91 ppm). Such relatively slower decreasing ratios of the NICS(1 Å) values in the terminal ring for **An** and **Bn** are predicted to originate in the direct influence of terminal $-CX_2$ groups. The NICS(1 Å) values of systems **Cn** and **Dn** are found to always be negatively large and to be almost unchanged with respect to n . However, these values are not shown to reach the value of an isolated thiophene owing to the effects of terminal functional groups and oligomerization. These chain-length dependences of the aromaticities are in nice agreement with the previous results of the BLA value of QTs except for **B6**, where the planarities of the optimized geometries are different from each other.¹¹

Figure 4a shows the chain-length dependences of diradical characters y for the calculated systems (see also Table 1). The calculated y values of all the monomer systems ($n = 1$) are

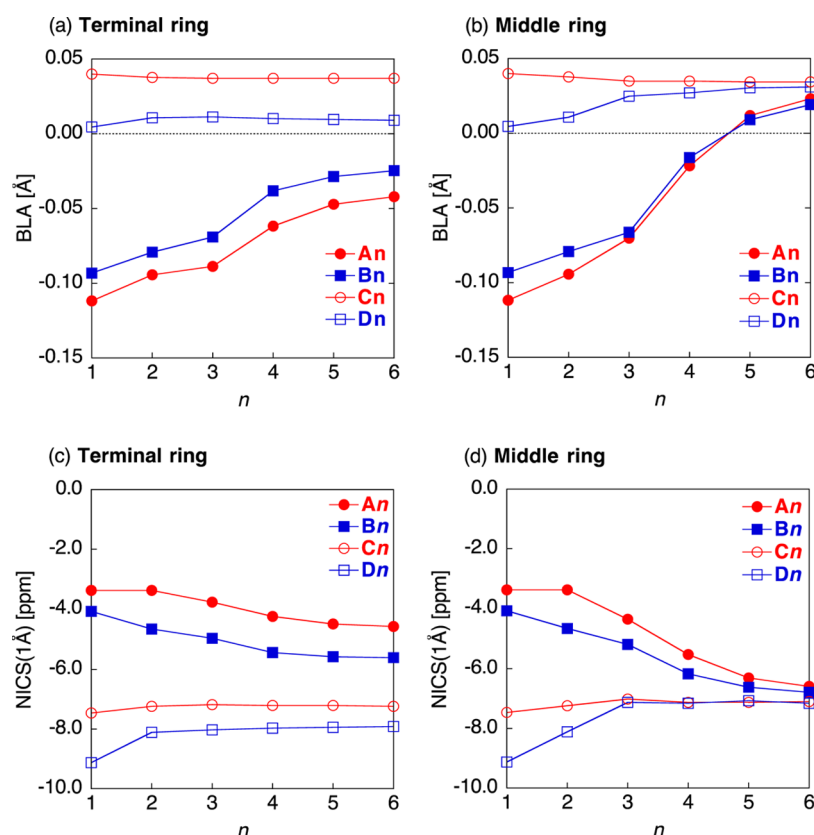


Figure 3. Bond-length alternation (BLA) values of the terminal ring (a) and the middle ring (b) calculated at the (U)B3LYP/6-311G* level of approximation and the NICS(1 Å) values of the terminal ring (c) and the middle ring (d) calculated at the LC-(U)BLYP/6-31G*+p level of approximation.

found to be 0, which indicates the closed-shell state. As expected, the y values of systems **An** and **Bn** are found to gradually increase with the increase of n ; i.e., these QTs with larger n are regarded as open-shell singlet species. For $n = 6$, these values are shown to be close to 1 ($y = 0.964$ for **A6** and 0.967 for **B6**), which indicates almost the pure diradical state. Consequently, these QTs ranging from monomer to hexamer show a variety of y values, the feature of which is suited for verifying the y - γ correlation in real systems. From the comparison of the results of **Bn** with those of **An**, an introduction of the acceptor ($-\text{CN}$) groups is found to increase the y values, since the electron-withdrawing nature of the acceptor groups contributes to the stabilization of the diradical form in the resonance structure. For both systems, the occupation number of LUNO + 1 (n_{L+1}) is found to be small ($n_{L+1} < 0.1$), which indicates that these QTs have negligible tetraradical nature; i.e., these systems are regarded as diradicaloids. On the other hand, the y values of systems **Cn** and **Dn** are found to remain 0 for all considered n , which indicates that these systems have a closed-shell electronic structure as expected from their resonance structures.

Figure 4b shows the spatial distributions of HONO and LUNO with their occupation numbers (n_{H} and n_{L}) for systems **Bn** and **Dn** with even numbers of n . The doubly occupied HONOs of all the closed-shell systems **Dn** are found to have aromatic (benzenoid) features, which is in good agreement with the results from the geometric parameters and NICS aromaticities. In contrast, the distributions of these NOs for open-shell systems **Bn** are found to depend strongly on the number of units (n). The HONO of **B2** ($n_{\text{H}} = 1.821$) shows the

quinoidal topology in its distribution, while the LUNO ($n_{\text{L}} = 0.179$) has the aromatic topology. With the increase of n , the quinoidal feature in the HONO tends to disappear gradually. Actually, the HONO ($n_{\text{H}} = 1.224$) of **B4** has both the quinoidal and aromatic topologies, while the LUNO ($n_{\text{L}} = 0.776$) has the aromatic topology. For system **B6**, the spatial distributions of the HONO ($n_{\text{H}} = 1.033$) and LUNO ($n_{\text{L}} = 0.967$) are found to be almost the same, except for their relative phases, and to be delocalized over the terminal dicyanomethylene groups and the terminal thiophene rings. The open-shell nature of electron density distribution can also be characterized by the odd-electron density distribution,³² which represents the spatial distribution of unpaired electrons concerning y . Figure 4c represents the odd-electron density distributions of systems **Bn** and **Dn**. As seen from this figure, the amplitudes of odd-electron densities are found to increase with the increase of n . The odd-electron densities for the open-shell systems **B4** and **B6** are found to be delocalized over the dicyanomethylene groups and the terminal thiophene rings. This feature suggests that there are contributions of other resonance forms which have unpaired electrons in the terminal thiophene rings. In summary, we found that there are quantitative relationships among the geometric parameters, the BLA and NICS aromaticities of each thiophene ring, and the diradical character (y) of open-shell QTs.

3.2. Chain-Length Dependence of the Second Hyperpolarizability per Unit (γ/n). Figure 5a shows the variations in the second hyperpolarizability per thiophene ring, γ/n , for these compounds as a function of n (see also Table 2). For all the calculated systems, the γ/n values are found to increase with

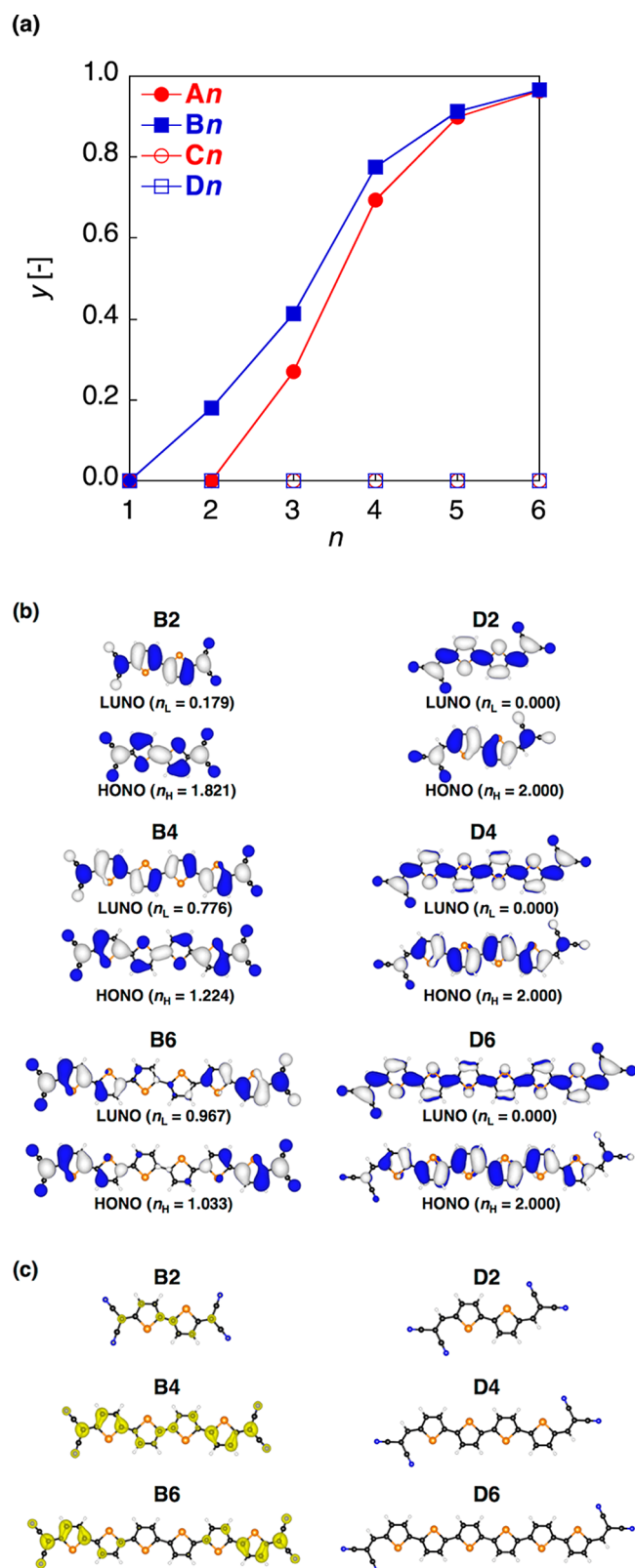


Figure 4. Chain-length (n) dependences of the diradical characters (γ) for systems An , Bn , Cn , and Dn (a), spatial distributions of HONO and LUNO with corresponding occupation numbers n_H and n_L of Bn and Dn for $n = 2, 4$, and 6 (b), and odd-electron density distributions obtained from the HONO–LUNO pair of Bn and Dn for $n = 2, 4$, and 6 (c).

Table 1. Diradical Character γ of All the Systems Calculated at the LC-UBLYP/6-31G*+ p Level of Approximation Using the Fully Optimized Geometries

n	γ			
	An	Bn	Cn	Dn
1	0.000	0.000	0.000	0.000
2	0.000	0.179	0.000	0.000
3	0.271	0.413	0.000	0.000
4	0.695	0.776	0.000	0.000
5	0.898	0.913	0.000	0.000
6	0.964	0.967	0.000	0.000

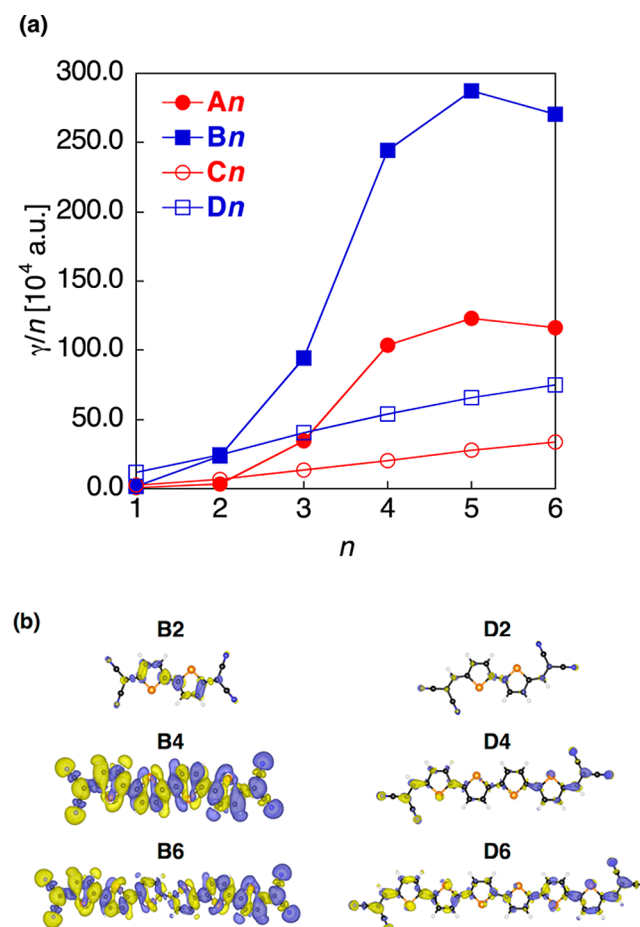


Figure 5. Size dependences of the second hyperpolarizability γ per unit (γ/n) of systems An and Bn (a) and γ density distribution for systems Bn and Dn for $n = 2, 4$, and 6 (b). Yellow and blue meshes represent positive and negative γ densities with contour values of ± 2000 a.u.

the increase of n , but their increasing behaviors are very different from each other. In the region of $n = 1$ – 6 , the γ/n values of closed-shell oligomers Cn and Dn are found to increase moderately with respect to n , while those of QTs An and Bn increase rapidly around the region of $n = 2$ – 4 , with intermediate γ values, attain the maximum at $n = 5$, and then decrease. A similar tendency of γ/n is observed in the polycyclic dicyclopenta-fused oligoacenes with antiaromatic open-shell electronic structures.³⁶ It is found that the increase ratios of γ/n (open-shell QTs vs closed-shell oligomers), i.e., $r_{AC}(n) = [\gamma/n(An)]/[\gamma/n(Cn)]$ and $r_{BD}(n) = [\gamma/n(Bn)]/[\gamma/n(Dn)]$, also increase with the increase of n , take the maximum at $n = 4$

Table 2. Second Hyperpolarizability γ per Unit (γ/n) of All the Systems Calculated at the LC-UBLYP/6-31G*+ p Level of Approximation Using the Fully Optimized Geometries

n	γ/n (10^4 au)			
	An	Bn	Cn	Dn
1	0.665	1.72	2.84	12.2
2	3.22	23.4	7.14	24.5
3	34.3	94.7	13.1	40.3
4	104	245	20.4	54.2
5	123	287	27.8	65.9
6	116	270	34.1	75.4

$[r_{AC}(4) = 5.10$ and $r_{BD}(4) = 4.52]$, and then decrease (see Table 3); i.e., the γ/n value is found to be significantly

Table 3. Increase Ratios of Second Hyperpolarizability $r_{AC}(n) = [\gamma/n(\text{An})]/[\gamma/n(\text{Cn})]$, $r_{BD}(n) = [\gamma/n(\text{Bn})]/[\gamma/n(\text{Dn})]$, $r_{BA}(n) = [\gamma/n(\text{Bn})]/[\gamma/n(\text{An})]$, and $r_{DC}(n) = [\gamma/n(\text{Dn})]/[\gamma/n(\text{Cn})]$ of all the Systems Calculated at the LC-UBLYP/6-31G*+ p Level of Approximation Using the Fully Optimized Geometries

n	$r_{AC}(n)$	$r_{BD}(n)$	$r_{BA}(n)$	$r_{DC}(n)$
1	0.23	0.14	2.59	4.30
2	0.45	0.96	7.27	3.43
3	2.62	2.35	2.76	3.08
4	5.10	4.52	2.36	2.66
5	4.42	4.36	2.33	2.37
6	3.40	3.58	2.33	2.21

enhanced in the QTs having intermediate γ . Increase ratios of γ/n ($X = \text{CN}$ vs $X = \text{H}$), i.e., $r_{BA}(n) = [\gamma/n(\text{Bn})]/[\gamma/n(\text{An})]$ and $r_{DC}(n) = [\gamma/n(\text{Dn})]/[\gamma/n(\text{Cn})]$, are also examined to clarify the effect of terminal acceptor groups on the γ/n value (see Table 3). After $n = 3$, where the open-shell character of **An** emerges at the present level of approximation, the behavior of $r_{BA}(n)$ for the open-shell systems as a function of n is found to be similar to that of $r_{DC}(n)$ for the closed-shell systems [$r_{BA}(3) = 2.76$ and $r_{DC}(3) = 3.08$]: these increase ratios gradually decrease with the increase of n and tend to converge to a value [$r_{BA}(6) = 2.33$ and $r_{DC}(6) = 2.21$] for $n \leq 6$. At $n = 2$, a significant increase ratio of $r_{BA}(2) = 7.27$ is obtained for open-shell systems; however, this is considered to be caused by the overestimation of the γ value in the small γ region ($\gamma < 0.2$) for **B2** ($\gamma = 0.179$) calculated using the LC-UBLYP functional (with the range separating parameter of 0.33 bohr^{-1}).²⁵ As seen from this result, for small n , the effect of terminal acceptor groups reaches over the entire region of the system, giving significant enhancement of γ/n , while for systems with a long chain length, the effect of terminal acceptor groups is predicted to be limited within the terminal regions near the acceptor groups, giving a relatively small increase ratio of γ/n . As a result, the introduction of acceptor groups, which has been known as an effective strategy to enhance γ of closed-shell systems, is also found to be an effective strategy in the open-shell QTs, where a further enhancement of γ is expected relative to that of closed-shell systems in the relatively small chain-length region due to the intermediate diradical character. The origin of these unique size dependences of γ/n for open-shell QTs is further analyzed in the next subsection on the basis of the VCI two-site diradical model.¹⁵

As already explained, all the optimized geometries of **An** and **Bn** are found to be planar with the highest possible symmetry (C_{2h} for odd n and C_{2v} for even n) except for $n = 6$. Since the closed-shell systems **Cn** and **Dn** are found to have nonplanar structures for $n \geq 2$, one may be interested in the effect of the reduction of planarity on the resulting γ/n values. We therefore perform geometry optimizations of all systems under the constraint of highest possible symmetries (C_{2h} for odd n and C_{2v} for even n). Note that these optimized structures for **A6**, **B6**, **Cn**, and **Dn** for $n \geq 2$ are found to have one or more imaginary frequency mode(s). In Tables S1 and S2 (Supporting Information), we summarize the results of γ and γ/n . From Table S1, the γ values of these open-shell systems having C_{2h} symmetry were almost unchanged at $n = 6$. Systems **Cn** and **Dn** were closed-shell regardless of the symmetry constraint. For **Cn** and **Dn**, the γ/n values of planar structures are found to be slightly larger than those of nonplanar structures. However, both the values are much smaller than those of open-shell systems **An** and **Bn**. We therefore conclude that a significant enhancement of γ of open-shell QTs around $n = 4$ is attributed mainly to the intermediate diradical nature of these systems.

To discuss the spatial contributions of electrons to γ , we examined the γ density analysis.⁴² From the expansion of the charge density function $\rho(\mathbf{r}, \mathbf{F})$ and of the dipole moment in a power series of applied electronic field \mathbf{F} , γ can be expressed by⁴²

$$\gamma_{zzzz} = \frac{1}{3!} \int r^z \rho_{zzz}^{(3)}(\mathbf{r}) d\mathbf{r} \quad (6)$$

where

$$\rho_{zzz}^{(3)}(\mathbf{r}) = \left. \frac{\partial^3 \rho(\mathbf{r}, \mathbf{F})}{\partial F^z \partial F^z \partial F^z} \right|_{F=0} \quad (7)$$

Here, r^z represents the z -axis component of the electron coordinate. This third-order derivative of the electron density with respect to the applied electric fields, $\rho_{zzz}^{(3)}(\mathbf{r})$, is referred to as the γ density.⁴² The γ density map represents the relative phase and magnitude of change in the third-order charge densities between two spatial points with positive and negative γ densities. The relationship between γ and its density $\rho_{zzz}^{(3)}(\mathbf{r})$ is explained by considering a simple example: a pair of localized γ densities with positive and negative values. The sign of the contribution to γ is positive when the direction from positive to negative γ density coincides with the positive direction of the coordinate axis. The sign becomes negative in the opposite case. Moreover, the magnitude of the contribution associated with this pair of γ densities is proportional to the distance between them. Since the positive and negative γ densities correspond to the increase and decrease of field-induced third-order charge densities, respectively, we can understand the spatial contributions of third-order polarization from the γ density map. In Figure 5b, we compare the γ density maps between systems **Bn** and **Dn** with even numbers of n . For open-shell system **B4** having intermediate γ (0.776), the positive and negative γ densities are found to alternately appear in the middle region of the oligomer, both contributions to γ of which cancel each other out in the middle region. However, large positive and negative γ densities are also found to be distributed over the functional groups at both ends and the terminal thiophene rings. These positive and negative contributions are well separated to the left- and right-hand sides, resulting in the significant field-induced third-order polarization effects in

system **B4** having intermediate y . For system **B6** in the almost pure diradical state ($y = 0.967$), the amplitudes of positive and negative γ densities in the middle region are found to be small, while those in the terminal region remain large. Spatial distributions of γ densities with such large amplitudes are found to correlate well with those of odd-electron densities³² (see Figure 4c). On the other hand, the γ density amplitudes of closed-shell systems **Dn** are found to be very small as compared to those of open-shell systems **Bn** in the entire region, indicating smaller field-induced polarization effects in this system. Actually, as shown in Figure 4c, systems **Dn** have closed-shell electronic structures with no odd-electron density distributions. From these results, the significant third-order NLO response observed in the open-shell system **B4** having intermediate y is predicted to originate in the response of odd electrons.

3.3. Discussion of y – γ Correlation in QTs Based on the VCI Analysis. In most cases, the γ per unit (γ/n) value is considered to be a good measure for the chain-length dependence of γ of one-dimensional oligomer systems. However, the γ/n values of almost pure diradical systems **A6** ($y = 0.964$, $\gamma/n = 116 \times 10^4$ au) and **B6** ($y = 0.967$, $\gamma/n = 270 \times 10^4$ au) are shown to be slightly larger than those of intermediate diradical systems **A4** ($y = 0.695$, $\gamma/n = 104 \times 10^4$ au) and **B4** ($y = 0.776$, $\gamma/n = 245 \times 10^4$ au); these results seem to disagree with the y – γ correlation. On the basis of the sum-over-states expression, it is known that the γ of a symmetric system depends on the fourth power of the transition dipole moment, which is strongly correlated to the molecular size, while it inversely depends on the third power of the excitation energy. Therefore, γ/n as a function of n may not give a clear understanding of the y dependence of third-order NLO properties of open-shell one-dimensional systems. According to the VCI results based on the two-site diradical model, the γ of the symmetric open-shell system is expressed by the following equation:^{15,16,43}

$$\gamma = f(y, r_K) (R^4/U^3) \quad (8)$$

where

$$f(y, r_K) = \frac{8(1-y)^4}{\{1 + \sqrt{1 - (1-y)^2}\}^2 \{1 - 2r_K + 1/\sqrt{1 - (1-y)^2}\}^3} + \frac{4(1-y)^2}{\{1 - 2r_K + 1/\sqrt{1 - (1-y)^2}\}^2 \{1/\sqrt{1 - (1-y)^2}\}^3} \quad (9)$$

Here, R , U , and r_K are the effective diradical distance, effective Coulomb repulsion, and 2 times the direct exchange integral divided by U defined using the localized natural orbitals (LNOs). $f(y, r_K)$ is the dimensionless function of y and r_K . From this equation, γ is composed of the R^4/U^3 contributions and the diradical-character-dependent dimensionless function $f(y, r_K)$. To further clarify the diradical character dependence of the third-order NLO property of QTs, we also investigate the size and diradical character dependences of the γ value divided by R^4/U^3 of open-shell systems **An** and **Bn**. Here, R was approximately evaluated from the one-electron transition dipole moment between the HONO [$\phi_H(\mathbf{r})$] and LUNO [$\phi_L(\mathbf{r})$] obtained by the (BS-)DFT calculations as $R = |2\mu_{HL}| = |2\int \phi_H(\mathbf{r})\mathbf{r}\phi_L(\mathbf{r}) d\mathbf{r}|$. Here, we estimated U by the direct exchange integral in these NOs, $U = 2K_{HL} = 2\int \phi_H^*(\mathbf{r}_1)$

$\phi_L(\mathbf{r}_1)(1/r_{12})\phi_L^*(\mathbf{r}_2)\phi_H(\mathbf{r}_2) d\mathbf{r}$, though these NOs are obtained by using the LC-(U)BLYP exchange correlation functionals. These calculations are performed using Gaussian 09⁴¹ and GAMESS⁴⁴ program packages. Figure 6a shows the

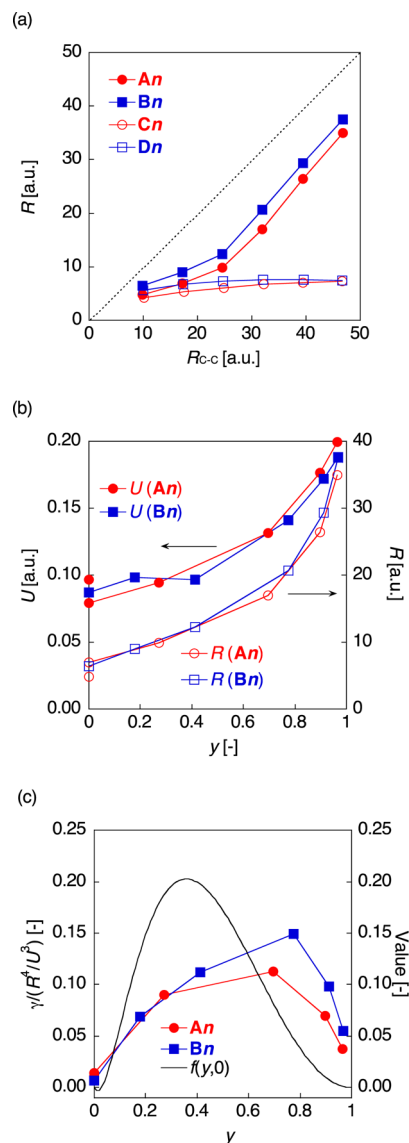


Figure 6. Distance between the carbon atoms of the terminal $-CX_2$ groups, R_{C-C} , vs effective diradical distance R (a), effective Coulomb repulsion U and effective diradical distance R as a function of y (b), and diradical character dependence of dimensionless $\gamma \equiv \gamma/(R^4/U^3)$ of systems **An** and **Bn** as well as the dimensionless function $f(y, 0)$ defined by eq 9 as a function of y (c).

comparison of the calculated effective diradical distance (R) with the molecular size represented by the distance between the carbon atoms of the terminal $-CX_2$ groups (R_{C-C}). For closed-shell systems **Cn** and **Dn**, the R values are shown to be almost unchanged though the actual molecular sizes increase. In sharp contrast, the R values of open-shell systems **An** and **Bn** are found to increase with the increase of their molecular sizes, which indicates the variation in diradical character. We here focus on the open-shell systems **An** and **Bn** for qualitative verification of the y – γ correlation. Figure 6b shows the variations in U and R as a function of y . Both U and R are found to increase with the increase of n and y ; however, R is shown to

increase rapidly for $y > 0.8$. This is considered to originate in the localization of unpaired electrons in such a y region. It is found that there are small differences of U and R between **A n** ($X = H$) and **B n** ($X = CN$). Figure 6c shows the results of dimensionless γ as a function of y along with the results of $f(y, r_K)$ with $r_K = 0$ defined by eq 9 (all the results are summarized in Tables S3 and S4, Supporting Information). Both systems show the bell-shaped behavior, which qualitatively agrees with the analytic result of $f(y, 0)$ derived on the basis of the two-site diradical model,¹⁵ except for the peak position shifts to the larger y region. The maximum value of the dimensionless γ is obtained at $n = 4$ for both systems ($y = 0.695$ for **A4** and $y = 0.776$ for **B4**). In comparison between the results of **B n** and those of **A n** , the effect of the introduction of terminal acceptor groups on the dimensionless γ is found to appear more remarkably in the intermediate and large y regions. Therefore, the y – γ correlation is found to hold for these one-dimensional QTs. These results indicate that the diradical character dependence of the third-order NLO properties of open-shell QTs is qualitatively described well by the VCI two-site diradical model.¹⁵

4. CONCLUDING REMARKS

In summary, we have theoretically investigated the relationship between the chain length n and the molecular third-order NLO property γ of open-shell QTs in terms of the diradical character y . The optimized geometries of QTs are found to be planar except for $n = 6$ by using the UB3LYP method with the 6-311G* basis set of valence triple- ζ quality. The BLA and NICS(1 Å) values are found to give similar tendencies for the aromaticities of the terminal and middle rings. It turns out that the y values of open-shell QTs increase with the increase of n and reach 1 at $n = 6$, indicating that the systems with a long chain length have almost pure diradical nature in the S_0 state. The introduction of the terminal acceptor groups are found to contribute to the stabilization of the diradical form in the resonance structure, which results in the increase of y at a given n . Compared with the closed-shell oligothiophenes, the γ/n values of open-shell QTs having intermediate y are found to be significantly enhanced, which is found to be in good agreement with the y – γ correlation obtained in our previous studies by using the VCI-based analysis. The present results are expected not only to stimulate both theoreticians' and experimentalists' interests in working on organic synthesis and the relationships between molecular structures and magnetic/optical properties of one-dimensional open-shell oligomers, but also to have an impact on the molecular design of functional materials based on the diradical character, e.g., diradical-character-based design for efficient singlet fission.^{43,46} Furthermore, in real molecular systems, the open-shell electronic structures of the QTs are speculated to be strongly affected by the planarity of the systems, which may be reduced by the introduction of several groups to increase the solubility of QTs. In such situations, a lack of planarity may occur for QTs with $n < 6$. Introduction of substituent groups, such as bis(butoxymethyl)cyclopentane, at the β -positions of each thiophene ring may cause additional distortion in the solution phase, which will result in the variation of diradical character as well as of vibrational and optical spectra. These substituent and environmental effects will be considered in our future study by using, e.g., quantum mechanics/molecular mechanics (QM/MM) simulations. To further substantiate the theoretically predicted y – γ correlation in real systems, theoretical prediction and characterization of

experimental electronic and vibrational spectra of real open-shell QTs are very important. Investigations toward these directions for real open-shell quinoidal oligothiophenes are now in progress in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

All the molecular geometries of calculated systems, computational details, and summary of the VCI analysis for the y – γ correlation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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