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Size scaling of intramolecular charge transfer driven optical properties of substituted polyenes and polyynes

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The origin of dramatic variation in optical polarizabilities of push–pull conjugated chains with respect to the conjugation length is discussed. *Ab initio* calculations of intramolecular charge transfer (ICT)-driven dipole moment (μ_{CT}), polarizability (α_{CT}), and first hyperpolarizability (β_{CT}) show that the values of $\alpha_{\mathrm{CT}}/\mu_{\mathrm{CT}}$ and $\beta_{\mathrm{CT}}/\mu_{\mathrm{CT}}$ change linearly and quadratically with respect to the conjugation length, respectively. The maximum ICT-driven coherence sizes of α_{CT} and β_{CT} are consistent with the time-dependent densities to the first ($\rho^{(1)}$) and second ($\rho^{(2)}$) orders of the electric field obtained from the collective electronic oscillators method. [DOI: 10.1063/1.1607917]

I. INTRODUCTION

There has been considerable interest in using organic materials for nonlinear optical (NLO) devices, functioning as second-harmonic generators, frequency converters, and electro-optical modulators. Organic compounds containing an electron-donating (D) and accepting (A) group interacting through an extended π-conjugated bridge, show high NLO response with large second-order electric susceptibilities.[1–6] There are two issues of primary interest in the design of highly nonlinear optical materials: the dependence of NLO properties on donor and acceptor strengths, and the scaling of NLO properties with size.

Electronic structure calculations have made an important contribution to the understanding of electronic polarization underlying the molecular NLO processes[7] and the underlying structure–property relationships.[8,9] NLO properties have been investigated for many types of donors, acceptors, and bridge systems such as quinones, polyenes, polyynes, stilbenes, thiophenes, etc. In particular, since π-conjugated systems linking a donor (D) and acceptor (A) show a large NLO response, a number of theoretical studies have been reported.[1,2] Another family of NLO chromophores (σ-bonded donor–acceptor systems) has also been investigated.[10–13] Most NLO compounds involve intramolecular charge transfer (ICT) upon excitation with light. One of the parameters widely used to explain the relation between ICT and donor or acceptor strength is bond length alternation defined as the difference between average single-bond length (C–C) and averaged double-bond length (C═C) of the bridge.[8] Recently, we proposed another parameter composed of electronegativity and polarizability to account for the magnitude of ICT in push–pull π-conjugated systems for different bridge systems.[14]

A number of studies have focused on the structural changes induced by ICT. The rate of CT through insulating molecular spacers has been reported to depend strongly on the nature of chemical bonding of spacer. Sachs *et al.*[15] measured the rate of interfacial CT between a gold electrode and a ferrocene group covalently connected to gold by π-conjugated spacer and a trans alkane spacer. The presence of both donor and acceptor at opposite ends of the bridge results in an additional contribution due to ICT. For a donor–bridge–acceptor system, the ICT is influenced by the bridge as well as the substituents.[1] Several groups have investigated the scaling of polarizability (α) and second hyperpolarizability (γ) with size.[16–30]

In the case of polyacetylene with N repeating chains where $N \leqslant 10$, the value of α_{zz}/N tends to level off, while γ_{zz}/N shows no such trend.[18] On the other hand, from the study through $N = 31$, Kirtman reported the convergence behavior of longitudinal polarizability and second hyperpolarizability of polyacetylene.[30] For long chains, however, the polarizability per repeating unit (α/N) becomes saturated and size-independent,[20–30] indicating that the α shows the extensive property. The variation of optical polarizabilities

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with path length is often described by the scaling law $\sim N^b$. In the cases of odd order responses (α and γ), the exponent b varies considerably for short lengths ($1<b<2$ for α, and $2<b<8$ for γ, depending on the system and model).[31]

Few studies were focused on the size dependence of the first hyperpolarizability (β) in oligomeric or polymeric chains. Dulcic *et al.*[17] observed the second nonlinear optical properties of conjugated hydrocarbons with the increasing donor–acceptor distance for a given donor–acceptor pair, and obtained the empirical form $\mu\cdot\beta = CN^{2.1}$, where μ is the dipole moment, N is the number of conjugated carbon–carbon double (or triple) bonds, and the prefactor C is characteristic to each donor–acceptor pair. The values of β for polymethineimine[32] and polyaniline[33] chains were obtained at empirical and semiempirical levels. Existing experimental and theoretical studies have not established the precise scaling law of β. Different functional forms have been employed to fit the chain length dependence of optical polarizabilities (α, β, and γ) and to obtain their asymptotic limits.[25,34]

The size scaling of polarizabilities for donor/acceptor-substituted polyenes has been analyzed by Tretiak *et al.*,[35] using two-dimensional correlation plots representing the changes in charge and bond-order distributions induced by the optical field. The value of β was found to originate from the localized regions at the donor/acceptor ends and be saturated to a constant value for large polyenes. The size dependence of the frequency-dependent NLO properties in polyenes has been investigated by Hasan *et al.* at frequencies below the first resonance.[36] These size scaling forms were often suggested empirically. On the other hand, the understanding of the size scaling is not clear due to the complex origin of the optical properties with both mesomeric and ICT effects. Therefore, in this article we study the ICT-driven dipole moment (μ_{CT}), polarizability (α_{CT}), and first hyperpolarizability (β_{CT}) in push–pull polyenes and polyynes, and investigate their size scaling.

II. NUMERICAL SIMULATIONS

It has been experimentally established that the value of γ geometrically increases with respect to the number of conjugated repeating units (N) between the donor and the acceptor. The saturation of α/N was predicted to be around $n=9$,[18] and that of γ/n, around $n=15-20$[37] for polyenes. Values of γ were measured using the electric field induced second-harmonic generation (EFISH) and the third harmonic generation (THG) experimental techniques for α,ω-disubstituted polyenes with various donor and acceptor end groups.[38] The sharp increase in γ values with the increasing conjugation length was modeled with $\gamma = kN^a$, where the exponent a was dependent on the substituents. The dependence of γ values on conjugation length was studied by EFISH for a series of triblock copolymers containing polyenic chains with N of up to 16.[39,40] The saturation behavior of γ/N was first observed in model polyenic oligomers for chain length up to $N=240$.[41] The size dependence of γ was investigated for polyene-like molecules with very long conjugation length (N up to 1100).[42]

Like the γ value, it is also experimentally observed that the value of β increases with increasing conjugation length.[43,44] For example, Barzoukas *et al.* measured the second-order nonlinear optical properties for push–pull polyene molecules with aldehyde as an acceptor and dimethylaniline or benzodithia as a donor in solution by EFISH.[45] Although they could not observe a saturation behavior, they observed the evolution of $\mu\cdot\beta$ proportional to $N^{2.1}$. The variation of β was studied for push–pull polyenes and carotenoids, and a steeper increase of β was observed when the end groups are weaker electron donors and acceptors. This suggests a possible saturation of the donor–acceptor interaction for a long conjugation length, and indicates that the choice of donor and acceptor end groups is not so crucial for very long polyenic chains.[46]

Since there are extensive theoretical and experimental studies on chain length dependence of molecular nonlinear optical properties, there should be some linkage between theoretical results and experimental data. The experimental values are often obtained at a given wavelength, and sometimes other research groups carry out equivalent experiments at different wavelengths for the same molecular systems, while a coupled-perturbed Hartree–Fock calculations (finite-field methods) give the static values. For example, in equivalent EFISH measurements on phenyl based polyenes with $n=1-5$, the $\mu\cdot\beta$ was shown to be proportional to $N^{3.0}$ by Huijts and Hesselink,[47] while $N^{2.1}$ by Dulcic *et al.*[17] Since the experimentally measured hyperpolarizabilities can be significantly affected by dispersive enhancement, the static values are often reported, for comparison, with the measured data divided by the relevant dispersion factor.[48] The dispersion factor is obtained using two-level model which takes into account only predominant charge transfer process.[44,49] Thus, for systematic investigation, the static hyperpolarizabilities were often reported along with the original experimental data. Furthermore, the estimated $\gamma(0)$ using such dispersion factor showed the same saturation behavior as $\gamma(3\omega)$[42] by THG and $\gamma(2\omega)$[46] by EFISH.

In particular, we are interested in qualitative analysis of optical properties depending on chain length. Thus, we have investigated the static optical properties based on *ab initio* Hartree–Fock (HF) calculations. To investigate the size dependence of optical polarizabilities, we have studied several families of polyenes ($\mathrm{D-(C{=}C)}_N\mathrm{-A}$, $1\leq N\leq 12$) and polyynes ($\mathrm{D-(C{\equiv}C)}_N\mathrm{-A}$, $1\leq N\leq 13$) with D/A=H/H, $\mathrm{NH_2/H}$, $\mathrm{H/NO_2}$, and $\mathrm{NH_2/NO_2}$. We fully optimized the geometries and obtained optical polarizabilities at the HF level of calculations with double-zeta basis sets, using the GAUSSIAN 98 suite of programs.[50] The correlation effect should be considered to obtain correct values of hyperpolarizabilities, however, in linear polyenes, it was stressed that the HF deficiency has no influence on the description of the (hyper)polarizabilities since $2A_g$ state has small transition dipole moments with other states and does not play any significant role in the nonlinear optical response of linear polyenes.[48,51,52] In addition, the different basis sets give the same chain length dependencies, though the absolute values are slightly different.[48]

To analyze our results we defined the optical properties due to ICT as the difference between the actual and superposition values:

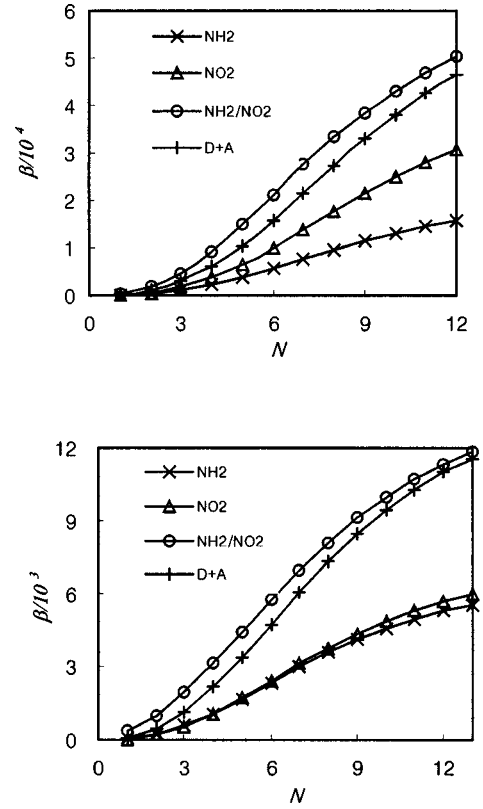

FIG. 1. Path length dependencies of β for polyenes (top) and polyynes (bottom) with both donor and acceptor (NH_2/NO_2), a donor (NH_2), or an acceptor (NO_2), and that of the additive sum of a donor and an acceptor (D+A).

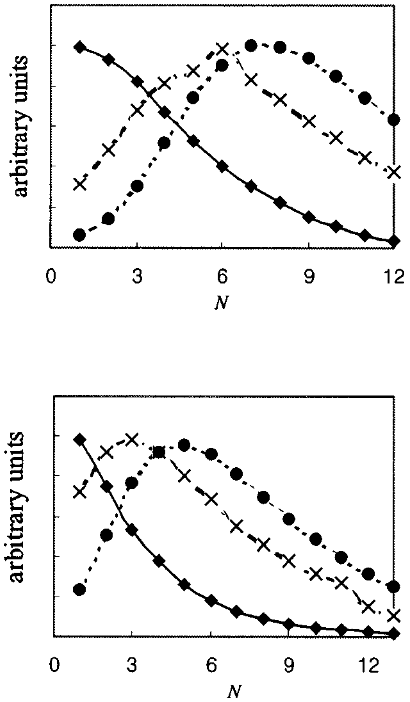

FIG. 2. Path length dependencies of ICT-driven μ_{CT} (◆), α_{CT} (×), and β_{CT} (●) for polyenes (top) and polyynes (bottom). The curves were fitted to $N^m \exp(-aN)$.

$$\mu_{\mathrm{CT}}=\mu_{\mathrm{DA}}+\mu_{\mathrm{H}}-\mu_{\mathrm{D}}-\mu_{\mathrm{A}},$$

$$\alpha_{\mathrm{CT}}=\alpha_{\mathrm{DA}}+\alpha_{\mathrm{H}}-\alpha_{\mathrm{D}}-\alpha_{\mathrm{A}},$$

$$\beta_{\mathrm{CT}}=\beta_{\mathrm{DA}}+\beta_{\mathrm{H}}-\beta_{\mathrm{D}}-\beta_{\mathrm{A}},$$

where the subscripts DA, D, A, and H refer to the systems with NH_2/NO_2, NH_2/H, H/NO_2, and H/H as D/A pairs. To obtain the coherence size, we used the collective electronic oscillator technique, which was successfully used for π-conjugated oligomers and through-space charge-transfer molecular systems.[53]

Figure 1 shows the first hyperpolarizabilities of polyenes and polyynes for DA; D, A, and D+A (sum for A and D). The first hyperpolarizabilities for (H) are zero due to the inversion symmetry. The difference between $\beta_{(\mathrm{DA})}$ and $\beta_{(\mathrm{D+A})}$ provides a good measure for ICT. The first hyperpolarizability does reflect the ICT much more profoundly compared with the polarizability and second hyperpolarizability, where the contributions of backbone polarization affect is also significant. It should be noted from Fig. 1 that the first hyperpolarizability for DA (β_{DA}) is larger than for D+A ($\beta_{\mathrm{D+A}}\equiv\beta_{\mathrm{D}}+\beta_{\mathrm{A}}$), and their difference (β_{CT}) increases as the size increases from zero, and it reaches a maximum at a certain size, and then it decreases to be zero. The β_{CT} value decreases at shorter size for polyynes than for the polyenes.

The ICT-driven dipole moments of polyynes decrease sharply with chain length (N) but less so for polyenes. The μ_{CT}, α_{CT}, and β_{CT} shown in Fig. 2 can be represented well with the functional form $N^m \exp(-aN)$, which has a maximum at $N=m/a$. The fitted exponent value a is 0.38 for both polyenes and polyynes and the power values m of μ_{CT}, α_{CT}, and β_{CT} are 0.5, 1.8, and 2.7, respectively, for polyenes, and 0.2, 1.1, and 1.9, for polyynes.

The length dependence of μ_{CT} for polyenes is very different from that for polyynes. For diatomic molecules, the ICT-driven dipole moment can be written as $\mu_{\mathrm{CT}}=Q^{\mathrm{eff}}R_{\mathrm{DA}}$, where R_{DA} is the distance between donor and acceptor, and Q^{eff} is the effective charge transfer which depends on R_{DA}. The size dependence of Q^{eff} in polyenes is different from that in polyynes. From the fitting of our *ab initio* results, we note that Q^{eff} scales as $\exp(-aN)$ for polyenes and $\exp(-aN)/N$ for polyynes; hence μ_{CT} scales as $[N\exp(-aN)]$ for polyenes and $\exp(-aN)$ for polyynes. This may be rationalized by considering the effective (screened) charge as a function of donor/acceptor separation. In general, the screened effective charge at a distance d from a point charge decreases exponentially with distance. From the Poisson equation, the screened effective charges in one-, two-, and three-dimensional systems show the distance-scaling $\exp(-ad)$, $\exp(-ad)/d$, and $\exp(-ad)/d^2$, respectively. In polyenes, the π electron moves along essentially a one-dimensional path from the donor to acceptor (with small two-dimensional diversions), while in polyynes, it dissipates along the two-dimensional cylindrical surface. We thus expect length scaling of the form μ_{CT} $N^{1-\delta}\exp(-aN)$ (polyenes) and $N^{\varepsilon}\exp(-aN)$ (polyynes), where δ and ε are small positive parameters (less than 0.5). The fitted curves are indeed $N^{0.5}\exp(-aN)$ and $N^{0.2}\exp(-aN)$, respectively. Furthermore, we have recently demonstrated that polyenes offer more effective pathways for charge transfer than polyynes.[54]

We thus expect the value of m for μ_{CT} in polyenes to be larger than that in polyynes.

Using the functional form of μ_{CT},

$$\begin{aligned}\mu_{\mathrm{CT}} &= R^m \exp(-aR)\\ &= C_1(R)\exp(-aR), \qquad (1)\end{aligned}$$

we obtain

$$\begin{aligned}\alpha_{\mathrm{CT}} &= \partial\mu_{\mathrm{CT}}/\partial E\\ &= (\partial R/\partial E)(R^{m-1} - aR^m)\exp(-aR)\\ &= C_2(R)\exp(-aR), \qquad (2)\\ \beta_{\mathrm{CT}} &= \partial\alpha_{\mathrm{CT}}/\partial E\\ &= (\partial R/\partial E)\{a^2R^m - (m+1)aR^{m-1} + (m-1)R^{m-2}\}\\ &\quad \times \exp(-aR)\\ &= C_3(R)\exp(-aR), \qquad (3)\end{aligned}$$

where E is the applied electric field. To simplify the forms of α_{CT} and β_{CT}, we have investigated the dependence of $(\partial R/\partial E)$ on chain length $R = Na$, where a is the length of repeating unit in $H_2N-(C{\equiv}C)_N-NO_2$. The external electric field can be consistently applied for each N along the molecular axis. From the geometry optimization for each N in the presence of applied electric field, we find that $(\partial R/\partial E)$ varies logarithmically with chain length $[1.87\ln(N) + 1.75]$. The α, β, and γ components are calculated analytically via electric field derivatives of the HF self-consistent-field total energy,

$$\begin{aligned}V &= V^0 - \mu_i^0 E_i - 1/2\alpha_{ij}^0 E_i E_j - 1/6\beta_{ijk}^0 E_i E_j E_k\\ &\quad - 1/24\gamma_{ijkl}^0 E_i E_j E_k E_l - \cdots,\\ \mu_i^0 &= (\partial V/\partial E_i) = (\partial V/\partial R)\times(\partial R/\partial E_i),\end{aligned}$$

where the subscripts, which identify the tensor components, are summed over the Cartesian axes; V^0 is the unperturbed total energy; E_i is the component of the field in the i direction; μ^0 is the permanent dipole moment; α^0, β^0, and γ^0 are the static polarizability, first, and second hyperpolarizabilities. Thus, the physical meaning of $(\partial R/\partial E)$ can be understood as the change of the equilibrium bond length with respect to the applied electric field, or the dipole moment per relaxation force.

Using the functional form of $(\partial R/\partial E)$, and m/a values of polyenes and polyynes, we display the variation of the coefficients, $C_2(N)$ and $C_3(N)$ with the chain length in Fig. 3. They show power law scaling (N^m). The bridge size dependencies of C_2 for polyenes and polyynes are $N^{1.8}$ and $N^{1.1}$, respectively, while C_3 varies as $N^{2.7}$ and $N^{1.9}$. C_1 of polyenes and polyynes show the power law behavior of $N^{0.5}$ and $N^{0.2}$, respectively, and their C_3/C_1 show that of $N^{2.2}$ and $N^{1.7}$, respectively. C_3/C_1 corresponds to γ/α. Thus, our results are in good agreement with the experimental scaling of α and γ with length for conjugated polyenes ($\alpha \sim N^3$ and $\gamma \sim N^5$).[55] It should be noted that our results apply for large chains, while the effective conjugation length may depend on the basis set and the level of theory.

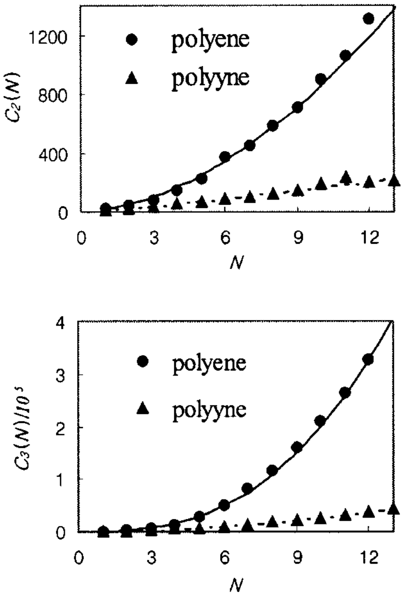

FIG. 3. Path length dependencies of $C_2(N)$ (top) and $C_3(N)$ (bottom) for polyenes and polyynes. From the fitting, we have $C_2(N) = N^{1.8}$ and $N^{1.1}$ for polyenes and polyynes, respectively, and $C_3(N) = N^{2.7}$ and $N^{1.9}$, respectively.

Figure 4 depicts the time-dependent densities to first $[\rho^{(1)}]$ and second $[\rho^{(2)}]$ order in the external electric field of $NH_2-(HC{=}CH)_{13}-NO_2$ computed using the collective electronic oscillator (CEO) method. The characteristic coherence length $L_\rho^{(k)}$ of the kth order density matrix response may be defined as the inverse participation ratio:[56] $L_\rho^{(k)} = [(\Sigma|\rho_{mn}|)^2]/[N_0\Sigma|\rho_{mn}|^2]$, where N_0 is the number of atoms and ρ_{mn} are the density matrix elements. Since α and β are directly dependent on $\rho^{(1)}$ and $\rho^{(2)}$, respectively, $L_\rho^{(1)}$ and $L_\rho^{(2)}$ depend on the characteristic chain lengths to give maximum values of α_{CT} and β_{CT}, respectively. It is evident from our results that the saturation of α_{CT} and β_{CT} takes place at much smaller chain lengths than α and β which are saturated at very large chain lengths. Therefore, it is suffi-

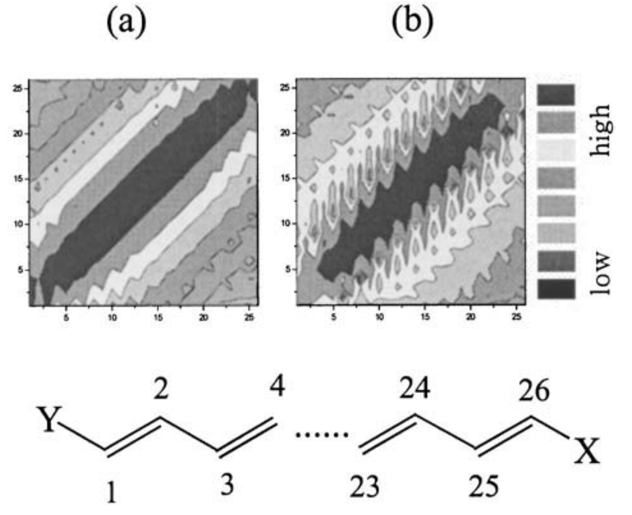

FIG. 4. Contour plots of the (a) first- and (b) second-order density matrices of $X-(HC{=}CH)_{13}-Y$ with $X/Y{=}NH_2/NO_2$. The axes label the atomic numbering depicted in the molecule.

cient to investigate the saturation of α_{CT} and β_{CT} for short polyenes (such as $N \approx 10$), and so the size scaling can be studied at much higher levels of theory with sufficient accuracy. We obtained the following values (7.3, 6.3), (8.1, 7.3), (8.5, 7.9), and (13.9, 14.2) for $(L_\rho^{(1)}, L_\rho^{(2)})$ for H/H, $\mathrm{NH_2}$/H, H/$\mathrm{NO_2}$, and $\mathrm{NH_2}$/$\mathrm{NO_2}$, respectively, which gives for the ICT-driven quantity of $L_\rho^{(1),\mathrm{CT}} = 4.6$ and $L_\rho^{(2),\mathrm{CT}} = 5.3$. These ICT-driven coherence lengths (in number of carbon–carbon chains) are consistent with the maximum α_{CT} and β_{CT} (which are 4.9 and 7.3, respectively).

III. CONCLUSION

We have elucidated the mechanism for the size scaling of α_{CT} and β_{CT}. The new measures suggested here vanish for large chain lengths, in contrast to the asymptotic values of α and β for large chains, which are large and difficult to estimate. By extracting the ICT components from μ, α, and β, we pinpoint how the NLO properties change with the chain length of substituted polyenes and polyynes. The variations of μ_{CT}, α_{CT}, and β_{CT} have been investigated in terms of molecular size, resulting in a simple formula for μ_{CT}, α_{CT}, and β_{CT} which is given by the product of the power law (N^m) and exponentially decaying function $[\exp(-aN)]$. In polyenes and polyynes, the exponential decays are similar, but the scaling exponents m are very different. The exponentially decaying behavior is related to charge screening. The parametrized function is found to be in good agreement with the previous experimental results. We have also obtained the coherence lengths for polyenes from the CEO method, and found that the ICT-driven coherence length is consistent with the ICT-driven polarizability and first hyperpolarizability. This study provides clear insight into the characteristic chain length for the maximum NLO properties for the first time, which is crucial for the rational design of novel highly efficient NLO materials. The functional forms proposed here will be further studied in different other systems in the future.

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