First Hyperpolarizabilities of 1,3,5-Tricyanobenzene Derivatives: Origin of Larger $\beta$ Values for the Octupoles than for the Dipoles


A series of donor–acceptor substituted stilbene and diphenylacetylene derivatives and their octupolar analogues have been synthesized and the linear and nonlinear optical properties ($\beta$) studied by both experiments and theoretical calculation. The $\lambda_{\text{max}}$ of the dipoles increases with the conjugation length and is always larger when the C=C bond is used, instead of the C≡C bond, as the conjugation bridge. Although the $\lambda_{\text{max}}$ values of the octupoles show no clear trend, they are much larger than those of the dipoles. The $\beta(0)$ values of the dipoles increase with conjugation length and as the conjugation bridge is changed from the C≡C to C=C bond. This increase is accompanied by an increase in either $\lambda_{\text{max}}$ or the oscillator strength. Similarly, the $\beta(0)$ values of the octupoles increase with the conjugation length and with a change in the donor in the order: NEt$_2$ < N(i-amy)Ph < NPh$_2$. Moreover, $\beta_{\text{max}}/\beta_{\text{max}}$ ratios are in the range of 1.6–3.9 and decrease with the conjugation length. $\beta$ values calculated by the finite-field and sum-over-states methods are in good agreement with the experimental data. Also, there is a parallel relationship between the calculated $\beta$ values and bond length alternation (BLA). From these results, the origin of the larger $\beta$ values for octupoles than for dipoles is assessed.

Introduction

There is much interest in the development of organic nonlinear optical (NLO) materials for possible applications in electrooptic devices. The most intensively studied NLO chromophores are donor–acceptor substituted dipolar molecules.[1] While such studies have led to a detailed understanding of the relationship between the chromophore structure and the NLO properties, it has become apparent that the dipoles have certain limitations. One such problem is the difficulty associated with aligning the dipoles non-centrosymmetrically in the solid state to achieve a maximum bulk effect.

More recently, octupolar molecules with three-fold symmetry have been developed as alternative NLO chromophores.[2–6] An advantage of such molecules in comparison to the more conventional dipolar molecules is the fact that the second-harmonic response of octupoles does not depend on the polarization of the incident light because it is more isotropic than that of the dipolar NLO molecules.[2c] Also, the two-dimensional octupoles favor the formation of non-centrosymmetric crystals, which is important for practical applications.[3] Moreover, there is a design strategy for the synthesis of octupoles with large first hyperpolarizabilities.[7] According to the VB-3CT model, the $\beta$ value of two-dimensional octupoles increases gradually with the extent of charge transfer. Hence, the $\beta$ values of such molecules could be significantly enhanced by simultaneously increasing the donor–acceptor strength, the charge-transfer ability of the conjugation bridge, and the conjugation length. Accordingly, various derivatives of subphthalocyanine, truxene, 1,3,5-tris[p-styryl]phenyl]benzene, 1,3,5-tricyano-2,4,6-tris-(ethyl)benzene, 1,3,5-tris(ethynyl)-2,4,6-triazine, triphenylamine, and hexa-substituted donor–acceptor benzene derivatives have been synthesized and their structure–property relationship investigated.[2–4] Recently, we reported that 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives and their dendrimers show modest to very large first hyperpolarizabilities.[4c,5] The most interesting result from this study is that 1,3,5-tricyano-2,4,6-tris(p-diethylaminostyryl)benzene produces a non-centrosymmetric crystal, which exhibits one of the largest second-harmonic generations (SHG) known in the literature.[5b] Moreover, octupolar molecules showed modest to large enhancement in the first hyperpolarizability compared to dipolar molecules.[14,4f] However, the origin of this enhancement has not been clearly established.

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Supporting information for this article is available on the WWW under http://www.chemphyschem.org or from the author.
Here, we have synthesized a series of donor–acceptor substituted dipolar compounds (A, B) and their octupolar analogues (C, D) and studied the linear and nonlinear optical properties by experiments and theoretical calculations. The effects of conjugation bridge, conjugation length, donor, and molecular symmetry on the linear and nonlinear optical properties of A–D have been studied. From these results, the origin of the larger $\beta$ values for the octupoles than for the dipoles is assessed.

**Results and Discussion**

**Synthesis**

Compounds A1a, A3a, C1a, C3a, and C3c were available from a previous study. Synthesis of A2a, B2a, and B3a is summarized in Scheme 2. All dipolar compounds were synthesized from 1–3 by using Sonogashira coupling and the Horner–Wittig reaction.

The octupolar molecules C2a and C2c were synthesized by the Horner–Wittig reaction between 1,3,5-tricyano-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene and appropriate benzaldehyde derivatives, as reported. Synthesis of D1a–c and D2a–c is shown in Scheme 3. All compounds were prepared by the Sonogashira coupling between 1,3,5-tribromo-2,4,6-tricyanobenzene (3) or 1,3,5-tricyano-2,4,6-tris(p-iodophenylethynyl)benzene (4) and substituted phenylacetylenes.[7] The structures of the new compounds were unambiguously confirmed by $^1$H and $^{13}$C NMR spectroscopy, IR spectroscopy, and elemental analysis. D1a was previously synthesized by a similar procedure starting from 1,3,5-trichloro-2,4,6-tricyanobenzene.[3e] Although one of the C-13 NMR peaks was reported to be missing, the $^1$H NMR spectrum, the UV spectrum, and the melting point are consistent with our results.

**Structures of A–D**

We performed geometry optimizations for the dipolar compounds (A, B) and their octupolar analogues (C, D) with ab initio molecular-orbital theory at the RHF/6-31G level using the Gaussian98 program.[8] Vibrational frequency calculations were executed to verify the identity of each stationary point as a minimum at the same level. The torsion angles of A1a–A3a and C1a–C3a are summarized in Table 1. The corresponding data for B1–3a and D1–3a are summarized in Table S1 of the Supporting Information.

The torsion angles between the phenyl groups linked by the C–C bonds ($\phi_3$, $\phi_6$) are in the range 33–40°, indicating that they are significantly distorted by the steric effect. For comparison, the calculated $\phi_3$ value of 36.1° for C1a is significantly larger than that of 26.7° observed in the crystal.[5b] This indicates that the molecule is more planar in the crystal where the stacking interaction is important.

The $\phi_1$ value decreases from 160° to 135° from A1a–A3a to C1a–C3a. This is because the C–C bonds are located between the two CN groups in the latter,
which increases the steric effect. When the steric effects are similar, the torsion angles are also similar. Note that the absolute values of $\phi_1$ and $\phi_2$ for A1a–A3a are similar to $\phi_2$ of C1a–C3a and $\phi_4$ and $\phi_5$ of B3a and C3a (Tables 1 and S1). Furthermore, C1a has $C_1$ symmetry. As the conjugation length is increased to C2a and C3a, the structures are more distorted and the $C_1$ symmetry is broken. In contrast, the phenyl groups linked to the C=C bond are nearly coplanar regardless of the molecular symmetry (A2a, B1a–B3a, C2a, and D1a–D2c) (Tables 1 and S1). Also, the D3 symmetry of D1a is maintained in D2a.

**Absorption Spectra**

Figure 1 shows that the $\lambda_{\text{max}}$ values of A1a and A2a are nearly the same, whereas that of A3a is red-shifted by 24 nm (1472 cm$^{-1}$) from A2a (Table 2). This indicates a more efficient intramolecular charge transfer (ICT) in A3a than in A2a, and that the C=C bond is a more effective conjugation bridge than the C=C bond. Consistently, the $\lambda_{\text{max}}$ value of B1a is blue-shifted from A1a by 18 nm (1190 cm$^{-1}$). In addition, the $\lambda_{\text{max}}$ values of B1a and B2a are almost the same, and that of B3a is red-shifted by 26 nm (1668 cm$^{-1}$) compared to B2a (Table 2). Interestingly, the $\lambda_{\text{max}}$ value of B3a is red-shifted by 16 nm (1000 cm$^{-1}$) from A2a, even though the donor/acceptor and the conjugation bridge are the same (Table 2). This may be due to the fact that the C=C bond is more electron-deficient than C=C and enhances the acceptor strength of B3a while reducing the donor strength of A2a. However, the larger $\lambda_{\text{max}}$ value of A3a compared to B3a suggests that this effect is not as important as the nature of the conjugation bridge.

A similar result is observed for the octupolar molecules (Figure 2). $\lambda_{\text{max}}$ of C2a is blue-shifted from that of C1a by 35 nm (1632 cm$^{-1}$), despite the extended conjugation. When the second conjugation bridge is changed from C=C (C2a) to the more efficient C=C bond (C3a), the shorter-wavelength band decreases and $\lambda_{\text{max}}$ increases (Figure 2).

As observed for B1a and B2a, $\lambda_{\text{max}}$ of D1a and D2a are the same, indicating that the factors affecting $\lambda_{\text{max}}$ are more or less the same regardless of the molecular symmetry for the ethynyl derivatives (Figures 1 and 2). Also, the shorter-wavelength bands in D1a and D2a are nearly identical to the charge-transfer (CT) bands of p-diethylaminophenylethynylacetylene (1') and 4-(p-diethylaminophenylethynyl)phenylethynylacetylene (2), indicating that they are due to the localized absorption (Figure S2).

The octupoles show large bathochromic shifts ranging from 54 to 104 nm (3089 to 5655 cm$^{-1}$) from their dipolar analogues (Table 3). This indicates that these octupoles are not just three molecules of dipoles arranged in a symmetrical way but the extension of the latter sharing the central phenyl group, so that an efficient $\pi$-orbital overlap is possible to enhance the ICT. Moreover, the $\lambda_{\text{max}}$ values of D1a and D2a are red-shifted by more than 100 nm (5474 cm$^{-1}$) from their dipolar analogues, whereas C1a, C2a, and C3a show smaller red shifts. This is as expected because the more planar the molecule is, the more effective the $\pi$-orbital delocalization will be.

**First Hyperpolarizabilities of Dipolar Molecules**

The $\beta$ values were measured at 1064 nm by the hyper-Rayleigh scattering (HRS) method. To determine the $\beta$ values accurately, the pure HRS signal was obtained by subtracting the two-photon-excited fluorescence (TPF) from the total signal intensity, followed by the correction for the self-absorption. In all cases, an average of 200 signals was used for the calculation (see the Experimental Section for details).

Table 2 shows that the $\beta(0)$ values of A1a–A3a are in the range: (49–150) $\times 10^{-30}$ esu. They increase with the conjugation length and as the conjugation bridge is changed from C=C to C=C, that is, A1a < A2a < A3a. Note that the increase is accompanied either by a larger oscillator strength (A1a < A2a) or by a larger $\lambda_{\text{max}}$ (A2a < A3a), as predicted by the two-level model.

<table>
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<th>Compd.</th>
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<th>$\phi_2$</th>
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<th>$\phi_5$</th>
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$[a]$ $\phi_1$–$\phi_6$ are the torsion angles between the cyanophenyl group (Ph1) and C2a, the structures are more distorted while reducing the donor strength of C1a, that is, $\lambda_{\text{max}}$ increases from 18 nm (1190 cm$^{-1}$) from A1a by 18 nm (1190 cm$^{-1}$). In addition, the $\lambda_{\text{max}}$ values of B1a and B2a are almost the same, and that of B3a is red-shifted by 26 nm (1668 cm$^{-1}$) compared to B2a (Table 2). Interestingly, the $\lambda_{\text{max}}$ value of B3a is red-shifted by 16 nm (1000 cm$^{-1}$) from A2a, even though the donor/acceptor and the conjugation bridge are the same (Table 2). This may be due to the fact that the C=C bond is more electron-deficient than C=C and enhances the acceptor strength of B3a while reducing the donor strength of A2a. However, the larger $\lambda_{\text{max}}$ value of A3a compared to B3a suggests that this effect is not as important as the nature of the conjugation bridge.

Figure 1. Molar absorptivity spectra for A1a–A3a and B1a–B3a.
Hyperpolarizabilities of Tricyanobenzene Derivatives

Table 2. Linear and nonlinear optical properties of A–B in THF.

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<th>Entry</th>
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<th>$\lambda_{\text{max}}$ [nm]</th>
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<th>$\beta^|_{0}$ [10$^{-30}$ esu]</th>
<th>$\beta^{\perp}_{0}$ [10$^{-30}$ esu]</th>
<th>$\beta^{\perp\perp}_{0}$ [10$^{-30}$ esu]</th>
<th>BLA$^{(h)}$</th>
<th>$\sqrt{&lt;\beta^{\perp\perp}_{0}&gt;^2}$</th>
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<td>351</td>
<td>123</td>
<td>297</td>
<td>--0.23350</td>
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[a] Absorbance maximum. [b] Molar extinction coefficient. [c] Oscillator strength estimated by the relationship: $f = 4.319 \times 10^{-4} \frac{\text{molL}^{-1}\text{cm}^{-1}}{\text{L}^{-1}\text{mol}^{-1}}$. [d] Determined at 1064 nm. [e] Estimated uncertainty: ±15%. [f] Corrected at $\lambda = \infty$ using a two-level model.[i] Calculated from the relationship: $\langle \beta^\perp \rangle = 8(6/35)\beta_0^{\perp\perp}$ for 1D chromophores.[j] Bond length alternation of the conjugation bridge nearest to the cyanophenyl group. [k] Calculated by using the finite-field method.[k] Estimated by assuming that the experimental ratio of $\beta_{\perp\perp}$ for A1a and B1a is the same as the calculated value.

Table 3. Linear and nonlinear optical properties of octupolar molecules.

<table>
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<tr>
<th>Entry</th>
<th>Cmpd.</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$10^{-4} \chi(0)$ [molL$^{-1}$cm$^{-1}$]</th>
<th>$\beta^|_{0}$ [10$^{-30}$ esu]</th>
<th>$\beta^{\perp}_{0}$ [10$^{-30}$ esu]</th>
<th>$\beta^{\perp\perp}_{0}$ [10$^{-30}$ esu]</th>
<th>BLA$^{(h)}$</th>
<th>$\sqrt{&lt;\beta^{\perp\perp}_{0}&gt;^2}$</th>
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[a–e],[h] See Table 2 for the footnotes. [i] Corrected at $\lambda = \infty$ using a three-level model. [j] Calculated from the relationship: $\langle \beta^\perp \rangle = 8(6/35)\beta_0^{\perp\perp}$ for 1D chromophores. [k] Calculated using the finite-field method unless otherwise noted. [l] The numbers in the parenthesis are calculated by the sum-over-states method ($\beta_{\text{SOSS}}^{\perp\perp}$).

Figure 2. Molar absorptivity spectra for C1a–C3a, D1a, and D2a.

(see below).[11] A similar result is observed for B1a–B3a, that is, B2a<B3a, although the experimental value of $\beta$ for B1a is not available because the measurement was hampered by the two-photon-excited fluorescence. Here again, $\lambda_{\text{max}}$ increases by the same order and the oscillator strength is larger for B2a than for B1a (Table 2). Interestingly, the $\beta(0)$ values for A1a–A3a and B1a–B3a are not very much different, probably because the $\lambda_{\text{max}}$ values and the oscillator strength are similar for the two series of compounds.

First Hyperpolarizabilities of Octupolar Molecules

The first hyperpolarizability of a $D_3$ symmetric molecule can be expressed by the three-level model [Eq. (1)], where $\mu_{10}$ is the transition moment between the ground and degenerate first excited CT state, $\mu_{12}$ is the transition moment connecting the degenerate excited states, $\omega_{10}$ is the CT energy and $\omega$ is the energy of the incident laser light (Figure 3).[21] The equation is identical to that of the two-level model of molecular nonlinearity for the dipoles if $\mu_{12}$ is substituted by $(\mu_1 - \mu_2)$, where $\mu_1$ and $\mu_2$ are the dipole moments in the ground and in the first excited CT state, respectively.[21]

$$\beta_{\text{yy}} = \frac{1}{2} \mu^2 (\mu_{12}/\mu_{10})^2 (\omega^2 - 4\omega^2) / (\omega_{10}^2 - \omega^2)$$

The $\beta(0)$ values of C1a–C3a gradually increase from 252×10$^{-30}$ esu to 348×10$^{-30}$ esu in the order: C1a<C2a<C3a (Table 3). For the change from C1a to C2a, $\lambda_{\text{max}}$ is blue-shifted...
The β values have also been calculated by the sum-over-states (SOS) method (\( \beta_{\text{SOS}} \)). The \( \beta_{\text{SOS}} \) can be expressed by using Equation (2):

\[
\beta = \frac{1}{\hbar} \sum_{n} \frac{1}{\omega_{n}^2} \frac{M_{n}^2 M_{n}^b}{(\omega_{n} - \omega_{1}) (\omega_{n} - \omega_{2})}
\]

where \( g \) refers to the ground state and \( n \) and \( s \) are various excited states with \( \omega_{n} = \omega_{s} - \omega_{1} \). \( M_{n} \) is the transition dipole matrix element between \( |g\rangle \) and \( |n\rangle \), and \( s \) denotes the transition (if \( n = s \)) or the permanent dipole moment (if \( n \neq s \)) of the excited state. This equation is essentially the same as Equation (1), except that more excited states are included.

Table 3 shows that there is parallel increase in \( \beta_{\text{SOS}} \) and BLA for both series of octupoles (C1–C3 and D1–D2). Hence, the gradual increase in the calculated \( \beta_{\text{SOS}} \) with the octupolar structure variation can be attributed to a smaller CT energy, a larger transition dipole matrix element between the ground and excited states, and a larger transition or permanent dipole moment of the excited state [Equation (2)]. Moreover, \( \beta_{\text{SOS}} \) is almost linearly proportional to the experimental value \( \beta(0) \) (Table 3). In contrast, there is no relationship between BLA and \( \lambda_{\text{max}} \) probably because the calculation has been conducted in the gas phase, and spectral data are obtained in tetrahedrofuran (THF) solution. Nevertheless, because the \( \lambda_{\text{max}} \) values and the oscillator strengths of the octupoles are scattered, the gradual increase in \( \beta(0) \) with the conjugation length can, at least in part, be attributed to the transition or permanent dipole moment of the excited state.

Origin of the Larger \( \beta(0) \) Values for the Octupoles than for the Dipoles

Comparison of the \( \beta(0) \) values reveals that octupoles show much larger first hyperpolarizabilities than dipoles. According to tensor addition calculations, the \( \beta_{\text{SOS}} \) - \( \beta_{\text{Py}} \) value of a D1 symmetric molecule is 3/4 of the \( \beta_{\text{SOS}} \) value of its dipolar analog if subchromophore interactions are negligible. In case of triarylmethane derivatives, the \( \beta_{\text{SOS}}(\text{dipole})/\beta_{\text{SOS}}(\text{octupole}) \) ratios of 0.94–1.0 have been reported. For comparison, the corresponding ratios for C1a, C2a, C3a, D1a, and D2a calculated by using the relationships \( \beta_{\text{SOS}}(\text{octupole}) \) ratios of 0.94–1.0 have been reported. For comparison, the corresponding ratios for C1a, C2a, C3a, D1a, and D2a calculated by using the relationships \( \beta_{\text{SOS}}(\text{dipole})/\beta_{\text{SOS}}(\text{octupole}) \) ratios of 0.94–1.0 have been reported.

As seen in Tables 2 and 3, \( \lambda_{\text{max}} \) is red-shifted by 83 nm (4336 cm\(^{-1}\)) and the oscillator strength increases by a factor of 2.7 from A1a to C1a. Although it is not possible to compare the values of \( \mu_{12} \) of C1a and of \( \mu_{12} \) of A1a with existing data, the large ratio of \( \beta_{\text{Py}}/\beta_{\text{SOS}} = 3.5 \) calculated for C1a can be attributed to the smaller CT energy and the larger transition moment between the ground and excited states [Equation (1)]. Similar changes in \( \lambda_{\text{max}} \) (104 nm (5655 cm\(^{-1}\))) and the oscillator strength (2.7-fold) are observed from B1a to D1a, which therefore leads to a similar ratio of 3.9. As stated above, the large bathochromic shifts in the \( \lambda_{\text{max}} \) of the octupoles in comparison to the dipoles has been ascribed to the efficient π-or-
bital overlap between the three dipolar units sharing the central phenyl group. Because the transition moment is expected to increase with ICT, the origin of large $\beta_{pD}/\beta_{zz}$ ratios can be attributed to the efficient $\pi$-orbital overlap. Consistently, the calculated BLA and $\beta$ are larger for the octupoles than for the dipoles, probably for the same reason (Tables 2 and 3). In addition, the ratio decreases in the order: $C1a > C2a > C3a$, indicating that this effect becomes less important as the conjugation length increases. Interestingly, the $\beta_{pD}/\beta_{zz}$ ratios calculated by the finite field method show a similar trend, although the absolute magnitudes are much smaller.

Conclusions

We have studied linear and nonlinear optical properties of a variety of newly synthesized dipolar and octupolar molecules. The $\beta(0)$ values of dipoles increase with conjugation length and as the conjugation bridge is changed from $C \equiv C$ to $C=C$ bond. The $\beta(0)$ values of the octupoles also increase with the conjugation length, but are relatively insensitive to the nature of the conjugation bridge. Except for $D2a-c$, $\beta(0)$ increases as the donor is changed in the order: $\text{NET}_2 < \text{N-(amylyl)Ph} < \text{NPh}_2$. Moreover, $\beta$ values calculated by the finite-field and SOS methods show similar trends with the experimental data. Furthermore, $\beta_{pD}/\beta_{zz}$ ratios are in the range: 1.6–3.9 and decreases with the conjugation length. The origin of the larger $\beta$ values for octupoles than for dipoles has been attributed to the efficient $\pi$-orbital overlap between the three dipolar units sharing the central phenyl group. Furthermore, this result suggests an interesting possibility that $\beta$ values of octupoles can be significantly enhanced in comparison to dipoles, if they are designed to have maximum $\pi$-orbital delocalization to enhance the ICT. Secondly, the shorter the conjugation length, the larger the value of $\beta_{pD}/\beta_{zz}$. Thirdly, the use of an $N$-Ph substituent in the donor should be a plus.

Experimental Section

Measurement of the First Hyperpolarizability by Hyper-Rayleigh Scattering Method: The $\beta$ values were measured at 1064 nm by hyper-Rayleigh Scattering (HRS) method using an Nd:YAG laser (Continuum Powerlite II 8000, 10 Hz, 9.3-ns pulse width).[8–10] Solutions of increasing concentrations ($c=5 \times 10^{-12}–2 \times 10^{-10}$ molecules mL$^{-1}$) of A–D in THF were cleaned through 0.2-µm Millipore filters to remove microscopic particles. The emitted photons from the sample cuvette were collected at the right angle and collimated to the monochromator by two lenses, while changing the wavelength in 0.1-nm increments to obtain the HRS and two-photon fluorescence spectra. As shown in Figure 4, all of the chromophores emitted a sharp HRS signal at 532 nm along with the broad two-photon fluorescence (TPF) when excited by 1064-nm laser photons. To determine the $\beta$ values accurately, the total HRS and TPF intensity was measured by averaging 200 laser pulses in the range: 528–536 nm. The fluorescence intensity was subtracted from the total signal intensity to obtain the pure HRS signal (Figure 4, inset).[10a] The octupoles also have absorption bands at 532 nm (Figures 1, 2, 51, and S2). The HRS intensity was further corrected for self-absorption by using Equation (3):[10b]

$$I_{\text{HRS}}(\text{obs}) = I_{\text{HRS}}(\text{true})e^{-\alpha l}$$

where $I_{\text{HRS}}(\text{obs})$ and $I_{\text{HRS}}(\text{true})$ are the intensity of the second-harmonic light detected after absorption and that actually generated, respectively, $\alpha = 1000 \ln(10)/N_0$ where $N_0$ is Avogadro’s number and $l$ is the path length of the scattering cell, and $N$ is the number density of the chromophore.[10c] The corrected HRS intensities were plotted against the number density ($N$) of chromophores in Figure 4. The $\beta$ values of the chromophores were calculated using $p$-nitroaniline ($\beta_{\text{ct}} = 21.4 \times 10^{-30}$ esu) as the external reference.[10c] According to the external-reference method, $\beta$ can be calculated by using Equation (4):

$$\beta = \beta_{\text{ct}} \sqrt{m/m_a}$$

where $\beta$, $\beta_{\text{ct}}$ and $m_a$ are the chromophore and standard effective molecular hyperpolarizabilities, respectively, and $m$ and $m_a$ are the slopes of the plots in Figure 4 for the chromophores and the standard, respectively. The estimated uncertainty for this measurement is ±15%.

Theoretical Calculations: All calculations, for geometry optimization and configuration interaction, were performed using the Gaussian 98 software package.[11] We performed the geometry optimizations for dipolar compounds (A, B) and their octupole analogues (C, D) with ab initio molecular orbital theory at the RHF/6-31G level using the Gaussian 98 program.[11] Vibrational frequency calculations were executed to verify the identity of each stationary point as a minimum at the same level. The first hyperpolarizabilities of $A1a$–$D2c$ have been calculated by the finite-field method with the HF/6-31G Hamiltonian.[10] To make direct comparisons of the HF/6-31G-calculated $\beta (<\beta_{\text{exp}}>)$ with the experimental values, the following depolarization ratios were applied.[10] For dipolar compounds, the orientationally averaged quantity, $<\beta_{\text{exp}}> = <\beta_{\text{exp}}><\sqrt{6}/15$, where $\beta_{\text{exp}}$ is the $\langle zz \rangle$ tensor element with the molecular $z$ axis being one of the rotation axes, was obtained. For octupolar compounds, $<\beta_{\text{exp}}^2> = <\beta_{\text{exp}}^2><\sqrt{6}/21$ was obtained for comparison where $\beta_{\text{exp}}$ is the $\langle yy \rangle$ tensor element with the molecular $y$ axis representing the largest hyperpolarizability.
The SOS calculation was performed by using configuration interaction (CI) with single excited configurations (SCI) only. This level of theory has been generally accepted to be adequate for computing first hyperpolarizability. The summations over excited states used in the SOS expressions generated from CI calculations are in general infinite. In practice, one usually truncates these sums after apparent convergence has been reached. It is generally accepted that the first hyperpolarizability $\beta$ converges rapidly with the number of lower excited states.\textsuperscript{14}\textsuperscript{14} In this SOS calculation, the lowest CI energy states were included.

Supporting Information for this article is available. This information includes synthesis of dipolar and octupolar molecules, representative torsion angles in the optimized (6-31G) structures of B1a–B3a and D1a–D2c, molar absorptivity spectra for C2c, C3c, D1b, D2b, and D2c, and normalized absorption spectra for D1a, $p$-diethyldiaminophenylethynylphenylacetylene (1), D2a, and 4-($p$-diethyldiaminophenylethynyl)-phenylacetylene (2).

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Keywords: dipoles · donor–acceptor systems · hyperpolarizability · octupoles · structure–property relationships


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