Nonlinear Optical and Two-Photon Absorption Properties of 1,3,5-Tricyano-2,4,6-tris(styryl)benzene-Containing Octupolar Oligomers

Bong Rae Cho,*[a] Ming Jun Piao,[a] Kyung Hwa Son,[a] Sang Hae Lee,[a] Soo Jung Yoon,[a] Seung-Joon Jeon,[a] and Minhaeng Cho[b]

Abstract: Octupolar oligomers containing 2–12 molecules of 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives have been synthesized and their nonlinear optical and two-photon absorption (TPA) properties were determined. The $\beta(0)$ values are in the range of $(85-1219) \times 10^{-30}$ esu and increase monotonically with the increasing number of the octupolar units within the molecule. The two-photon-induced fluorescence excitation spectra are quite similar to the single-photon absorption spectra except that the wavelength is doubled, indicating that the one- and two-photon allowed excited states are the same. The peak TPA cross-section values (δ_{max}) measured with nanosecond pulses by the two-photon-induced fluorescence method are in the range $(3010-62930) \times 10^{-50}$ cm^4 s photon^{-1}. The δ_{max} increases as the number of the octupolar units in the molecules increases. A linear relationship is observed between δ_{max} and β, and this $\delta-\beta$ relationship serves as a useful design strategy for the synthesis of novel octupolar oligomers and polymers with large TPA and β.

Keywords: fluorescence · nonlinear optics · octupole · polymers · two-photon absorption ·

Introduction

Organic nonlinear optical (NLO) materials have been extensively investigated for possible application in optical and opto-electronic devices. The useful NLO chromophores for such application must have large molecular hyperpolarizability, crystallize into a noncentrosymmetric structure to exhibit efficient bulk nonlinear optical activity, and possess optimum physical properties acceptable for device fabrication.[1, 2] Much effort has been focused on the synthesis of the donor–acceptor dipoles with such properties. One of the most important accomplishments in this endeavor is the emergence of polymer-based electro-optic devices with huge bandwidth acceptance and low modulation voltage.[1b] A fundamentally different approach to the NLO materials is to use octupolar molecules as alternative NLO chromophores. Theoretical studies predicted, and experimental results have confirmed that the β value of two-dimensional octupoles increases gradually with the extent of charge transfer.[3] Moreover, 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives spontaneously assembled into noncentrosymmetric crystals, which exhibited significant SHG with no sign of relaxation for a prolonged period of time.[4] This result provides a new design strategy for the synthesis of NLO materials with significant bulk nonlinearity, which may ultimately lead to the electro-optic devices without electric poling.

Another optical nonlinearity under intensive research is the two-photon absorption (TPA) process, which is the imaginary part of the third-order molecular susceptibility. Materials with large TPA cross-sections have been found to be useful for a variety of applications such as three-dimensional optical storage,[5–7] two-photon fluorescence excitation microscopy,[8–12] two-photon optical power limiting,[13–15] two-photon upconverted lasing,[16, 17] and photodynamic therapy.[18] The most frequently investigated structural motifs for efficient TPA chromophore are donor–bridge–acceptor (D–π–A) and donor–bridge–donor (D–π–D).[19–22] Such derivatives of fluorene,[19] triphenylamine,[20] dithienothiophene,[21] bis(styryl)benzene,[22] dihydrophenanthrene,[23] and dendrimers[24] have been synthesized and their structure-property relationships have been investigated. The results of these studies revealed that the increases of the donor strength and the conjugation length resulted in the increased TPA cross-

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[a] Prof. B. R. Cho, Dr. M. J. Piao, Dr. K. H. Son, S. H. Lee, S. J. Yoon, Prof. S.-J. Jeon
Molecular Opto-Electronics Laboratory
Department of Chemistry and Center for Electro- and Photo-Responsive Molecules, Korea University
1-Anamdong, Seoul 136-701(Korea)
Fax: (+82) 2-3290-3121
E-mail: chobr@korea.ac.kr

[b] Prof. M. Cho
Department of Chemistry and Center for Multidimensional Spectroscopy
Korea University, Seoul 136-701 (Korea)

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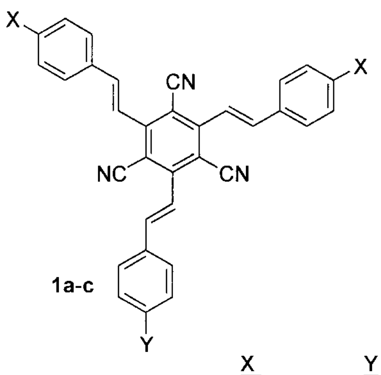
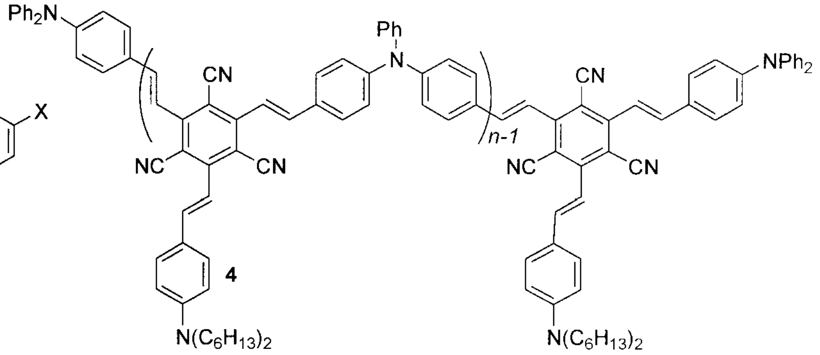
section.[25] Very recently, we reported that the 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives not only show large first hyperpolarizability, but exhibit efficient two-photon absorption property.[26] A linear relationship between these two nonlinear optical properties of this series of compounds were confirmed experimentally with additional supporting evidence from semiempirical calculations.

For practical application of such materials it is useful to incorporate the NLO chromophore into a polymer.[27] An ideal approach for this goal would be to design the polymer structure in such a way as to allow maximum utilization of monomeric NLO properties. In the case of polymers containing dipolar NLO chromophores, both decrease and enhancement of the monomeric optical nonlinearity have been reported.[28] Nevertheless, there is only one report regarding the nonlinear optical properties of octupolar polymers.[29] Furthermore, although the third-order optical nonlinearity of an octupolar oligomer containing the 2,4,6-tris(5′-alkylthio-2,2′-bithienyl-5-yl)-1,3,5-triazine moiety has been studied, no report regarding the two-photon absorption properties of octupolar polymers exists.[30] In this work we have synthesized octupolar oligomers containing 2–12 units of 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives. The second-order nonlinear optical and two-photon absorption properties of these molecules have been determined. In this paper, we present the β, spectral properties, and the TPA cross-sections of the octupolar molecules **1**–**6**. The structure-NLO property relationship of these molecules is established.



1a-c

	X	Y
1a	$NHex_2$	N(Me)EtOH
1b	N(Me)EtOH	$NHex_2$
1c	NPh_2	$NHex_2$



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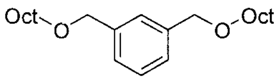

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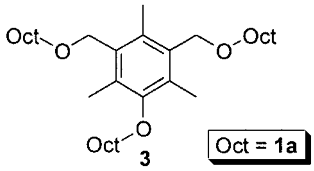

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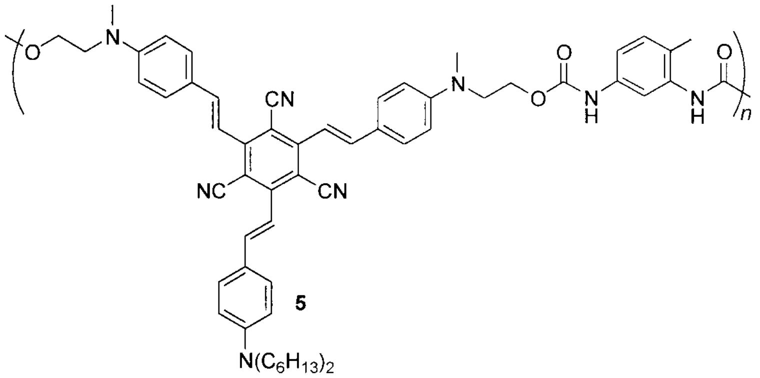
Oct = **1a**



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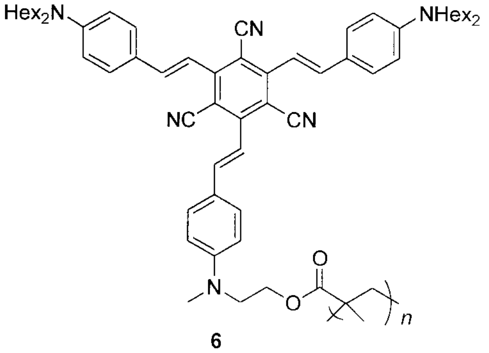

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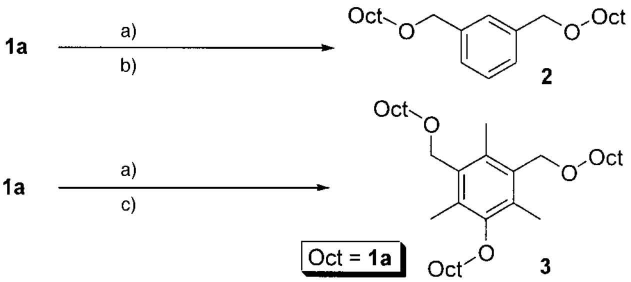
Results and Discussion

Synthesis: The octupolar molecules that we have synthesized are 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives (**1a**–**c**), in which three stilbene moieties are incorporated within a single molecule. All of the compounds were synthesized either by the Horner–Wittig reaction between 1,3,5-tricyano-2,4,6-tris(diethoxyphosphorylmethyl)benzene (**A**) and one equivalent of a substituted benzaldehyde to afford **B**, followed by a second olefination using two equivalents of another benzaldehyde, or by a similar procedure involving **C** (Scheme 1). The yields of the products based on the starting material **A** were 31–64%. The formation of the products was confirmed by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. Characteristic resonances of the vinylic protons at 7.1–7.8 ppm with large *trans* coupling constants ($J = 16$ Hz) were evident in the ^{1}H NMR spectra.

Compounds **2** and **3** were obtained by the reaction of α,α'-dibromo-*m*-xylene and 1,3,5-tris(bromomethyl)mesitylene with **1a** in the presence of NaH in THF (Scheme 2). The ^{1}H and ^{13}C NMR spectra of **2** and **3** were nearly identical to **1a**, indicating that they have symmetrical structures in solution.

Oligomer **4** was synthesized in two steps (Scheme 3). The intermediate **D** was prepared by the reaction between **B** and *N,N*-bis(*p*-formylphenyl)aniline under Horner–Wittig reaction conditions. When the reaction was almost complete, a small amount of **B** was added to the reaction mixture to convert the end groups to phosphonates. Excess *N*-(*p*-formylphenyl)-*N*-phenylaniline was then allowed to react with **D** to produce **4**. The product was characterized by IR and ^{1}H NMR spectroscopic analyses. An absorption attributable to the C≡N stretching vibration at 2221 cm^{-1} was clearly evident in the FTIR spectrum. The ^{1}H NMR spectrum had doublets at $\delta = 7.6$–7.8 ppm with coupling constants of 16 Hz, indicating the presence of *trans* double bonds. Multiplets were also present at $\delta = 3.32$, 1.63, 1.32, and 0.91 ppm that could be assigned to the methylene and methyl protons of the *n*-hexyl groups.

Reaction of **1b** with tolylene-2,4-diisocyanate produced polymer **5** in 75% yield (Scheme 4). The FTIR spectrum revealed characteristic N–H, C≡N, C=O, and C–O stretching vibrations at 3372, 2214, 1726, and 1175 cm^{-1}, respectively. ^{1}H NMR spectrum was similar to **1b**, except that all of the peaks appeared as multiplets.



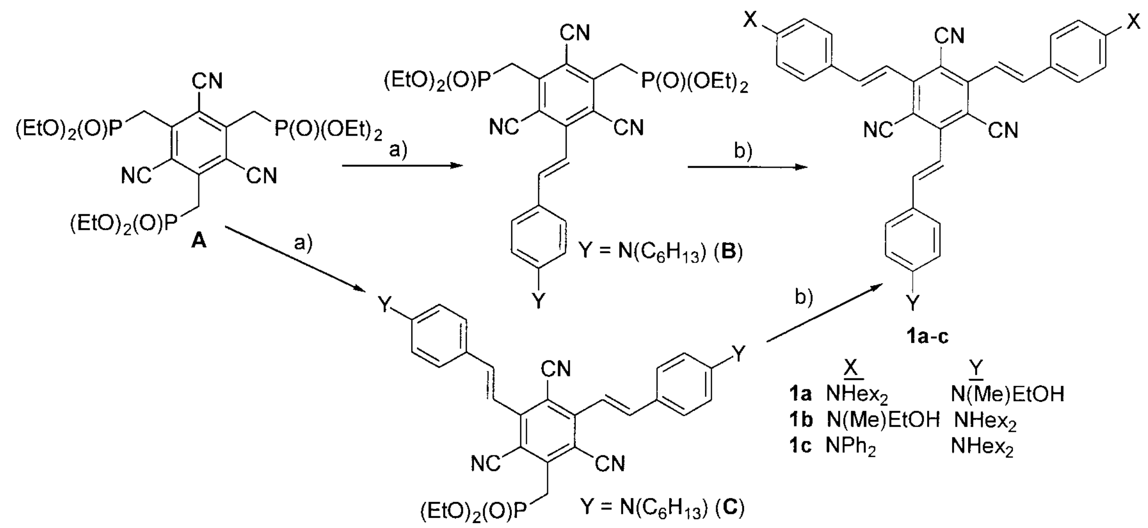
Scheme 2. Reaction conditions. a) NaH/THF, RT, 30 min; b) 1,3-(BrCH$_2$)$_2$Ph, 40 °C, 48 h; c) 1,3,5-(BrCH$_2$)$_3$PhMe$_3$, 40 °C, 48 h.

Synthesis of octupolar polymer **6** is summarized in Scheme 5. Reaction of **1a** with methacryloyl chloride produced the monomer **E**, which was polymerized under typical free radical polymerization conditions (Scheme 5).

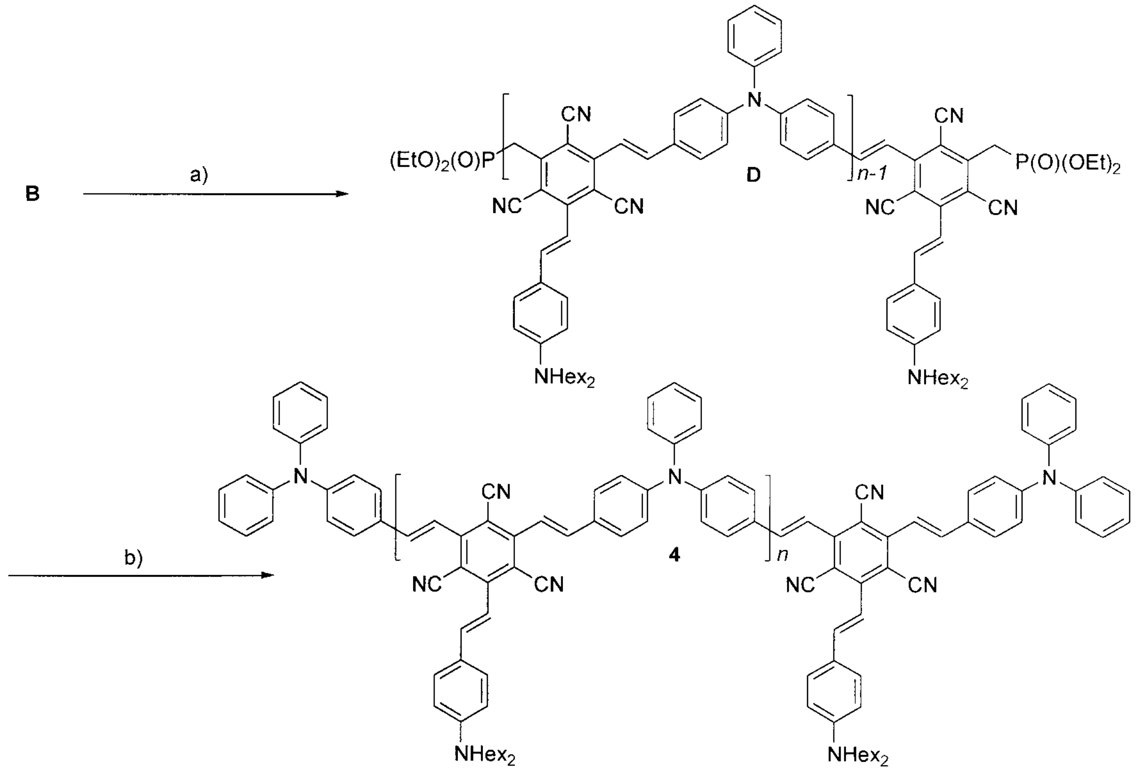
The FTIR spectrum of this compound displayed the C=O and C–O stretching vibrations at 1719 and 1182 cm^{-1}, respectively, in addition to the C≡N stretching vibration at 2214 cm^{-1}. The ^{1}H NMR spectrum was similar to **E** except that the vinylic C–H bond resonances were absent and all of the peaks were broadened.

The molecular weight and polydispersity of these oligomers were determined relative to a polystyrene standard with a GPC by using THF as the eluent. The M_w, M_n, and PDI of the polymers are summarized in Table 1. These oligomers have rather small molecular weights and contain 5–12 octupolar units within a molecule. The PDI ranges from 1.44 to 1.95. The highest molecular weight polymer was obtained by the free radical polymerization.

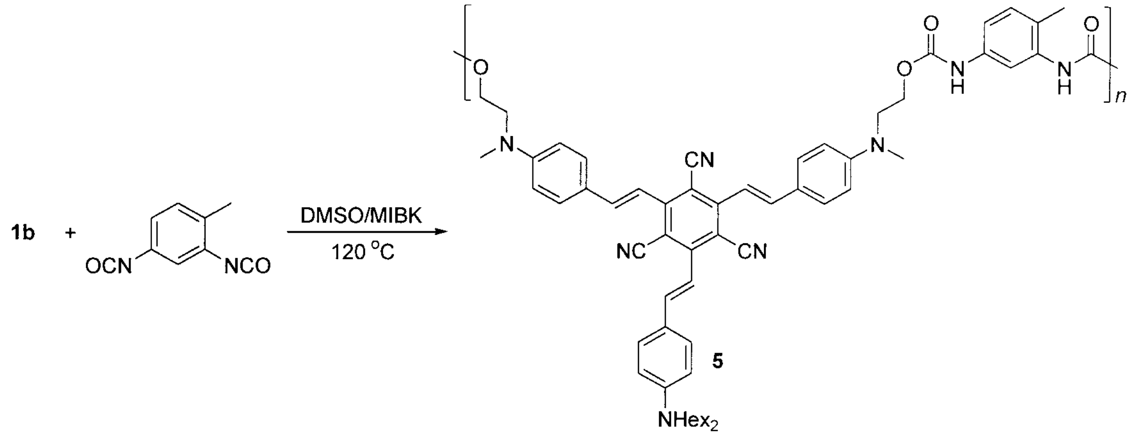
Nonlinear optical and two-photon absorption properties: The one-photon absorption spectra of **1**–**6** in CHCl$_3$ solution are depicted in Figure 1. They commonly exhibit two peaks at 305–320 and 485–505 nm, indicating that there are at least two one-photon allowed excited states in the experimental



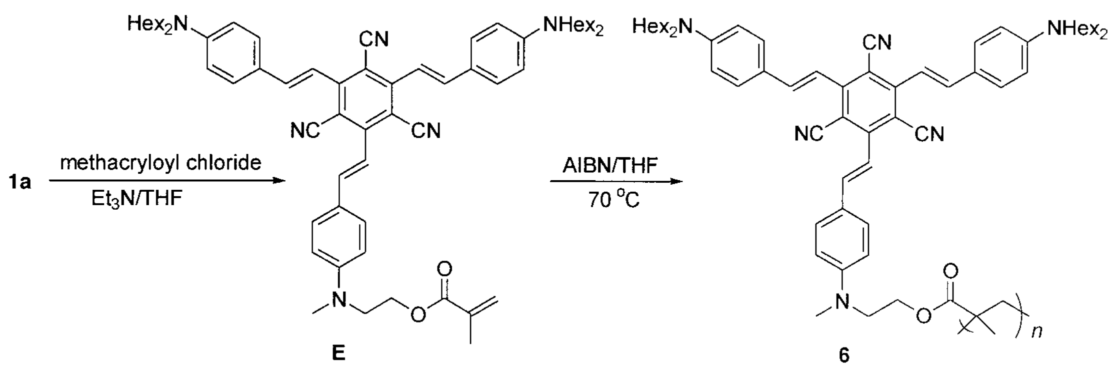
Scheme 1. Reaction conditions. a) 1) LDA/THF; 2) ArCHO, −78–0 °C, 2 h; b) 1) LDA/THF; 2) ArCHO/THF, −78 °C–RT, 12 h, Bu$_4$N$^+$F$^-$.



Scheme 3. Reaction conditions. a) 1) LDA/THF, −78 °C, 1 h; 2) $PhN(C_6H_4CHO)_2$, −78 °C–RT, 8 h; 3) **B**, RT, 4 h; b) 1) LDA/THF, −78 °C, 1 h; 2) p-$Ph_2NC_6H_4CHO$, −78 °C–RT, 8 h.



Scheme 4. Synthesis of polymer **5**.



Scheme 5. Synthesis of polymer **6** by free radical polymerization of **E**.

Table 1. Molecular weights of octupolar oligomers.

Polymer	M_w	M_n	PDI[a]	n[b]
4	8166	4181	1.95	5.38(4.28)[c]
5	8472	5870	1.44	6.09
6	17730	11803	1.50	12.2

[a] Polydispersity index. [b] Number of the repeating units in the oligomer except where otherwise noted. [c] M_n/M_W (**1c**).

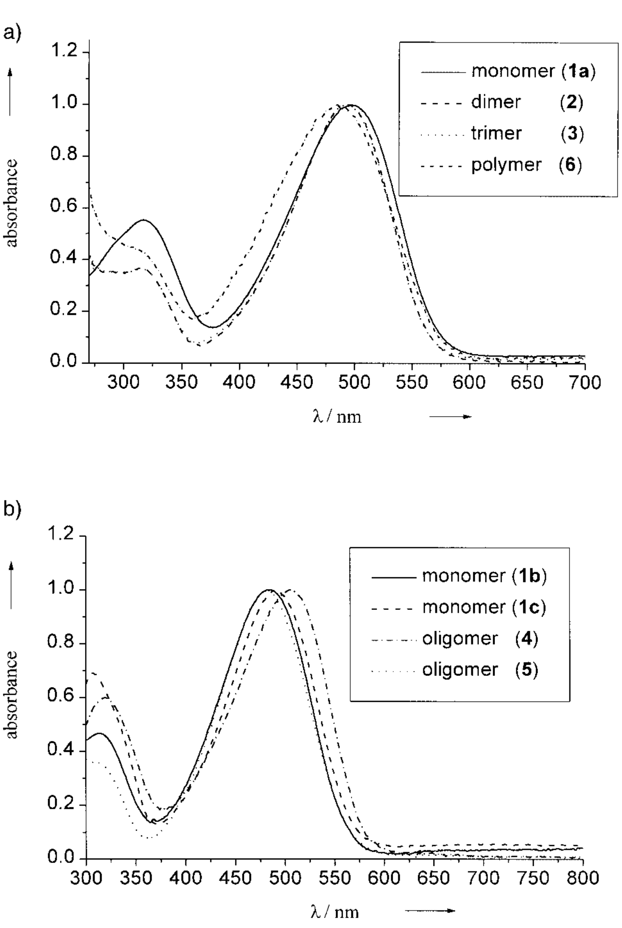


Figure 1. Absorption spectra of **1**–**6**.

frequency range. It is noted that the shapes and λ_{max} values of the absorption and the NMR spectra of three compounds, **1a** (monomer), **2** (dimer), and **3** (trimer), are nearly identical. This means that the electronic structures of each octupolar unit in **2** and **3** are almost similar to the monomeric octupolar molecule **1**.

On the other hand, the oligomers show a slightly different behavior. As the number of the repeating units increases in compounds **5** and **6**, the shapes of the spectra change systematically, that is, the NMR peaks of **5** become broad in comparison to those of **1**. Also, the UV/Vis spectrum of compound **6** is blue-shifted relative to those of **1a**, **2**, and **3**, and the NMR peaks of **6** are significantly broader than those of **1a**. By noting that only two carbon atoms separate the repeating octupolar units in **6**, the rotation of the pendant chromophores seems to be restricted and causes such effects.[31] Similar observations were also reported for other NLO polymers.[28, 29] A slight bathochromic shift in the λ_{max} of **4** is apparently due to the extended conjugation. However, interestingly, the molar extinction coefficients of the octupolar oligomers **4**–**6** are linearly proportional to the number of octupolar units. These results suggest that the octupolar units in **4**–**6** behave more or less independently within the oligomers.

The fluorescence spectra of **1**–**6** are displayed in Figure 2. Immediately, it is recognized that the fluorescence photon is emitted from the lowest excited state. Also, the shapes and peak positions of the fluorescence spectra of **2**, **3**, and **5** are essentially the same as **1a** and **1b**, respectively. On the other hand, λ^{fl}_{max} of **6** shows a slight bathochromic shift relative to **1a**, **2**, and **3**, probably as a result of the minor inter-chromophore interactions. Even though all of the compounds show large Stokes shifts of 3390–4220 cm^{-1}, the magnitude of the Stokes shift of each oligomer (**2**–**5**) is nearly the same as those of the monomeric octupole **1** except for **6**. The results are summarized in Table 2.

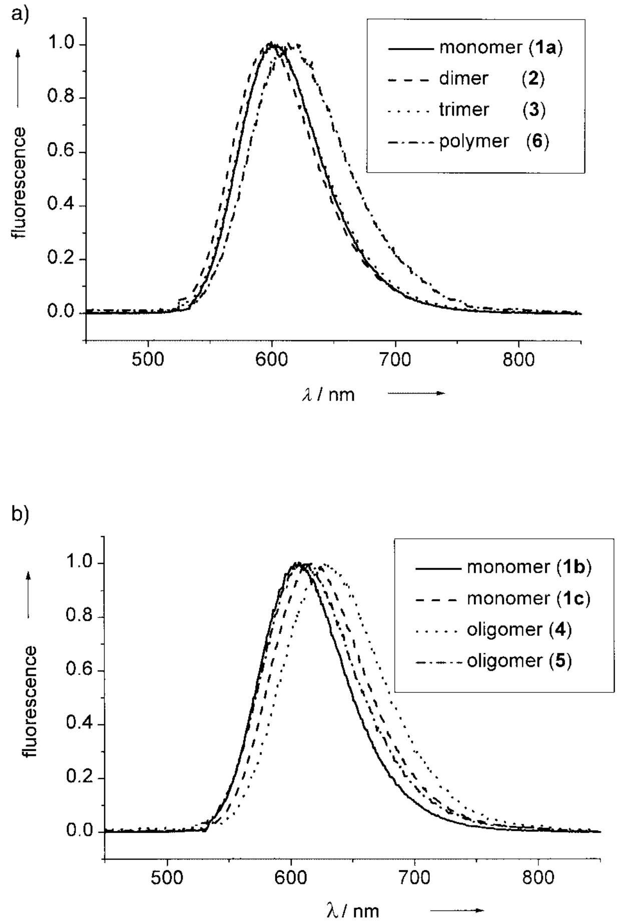


Figure 2. Steady-state fluorescence spectra of **1**–**6**.

Next, the nonlinear optical properties (β) of octupolar oligomers will be discussed. Over the years, the most notorious obstacles in utilizing the HRS method to measure the first hyperpolarizability were: 1) the re-absorption of the second-harmonic light by the chromophore, and 2) the additive contribution from two-photon-induced fluorescence to the HRS signal.[28b, 32–35] To ensure that these complications

Table 2. Absorption and fluorescence maxima and Stock shift of 1,3,5-tricyano-2,4,6-tris(vinyl)benzene derivatives.

	1a	**1b**	**1c**	**2**	**3**	**4**	**5**	**6**
$\lambda_{max}^{(1)}$	498	485	490	495	495	505	488	487
$(10^{-3}\,\varepsilon)$[a]	(75)	(74)	(67)	(164)	(249)	(363)	(420)	(895)
λ_{max}^{fl}[b]	599	604	617	597	601	630	610	613
$10^3\Delta\tilde{\nu}$[c]	3.39	4.06	4.20	3.45	3.56	3.93	4.10	4.22

[a] λ_{max} and the molar extinction coefficient of the one-photon absorption spectra in nm.[b] λ_{max} of the fluorescence spectra in nm.[c] Stokes shift in cm^{-1}.

did not hamper the measured β values, we carefully examined the UV and fluorescence spectra of all the compounds. We confirmed that none of the compounds absorbed light with a wavelength of 780 nm and fluoresces at 780 nm (Figure 1 and Figure 2). Also, the spectral purity of the detected signal was confirmed by using different filters.[3f, 32] Thus, the detected scattering signal at the wavelength of 780 nm is purely the HRS field. Furthermore, the fact that the shapes of the one- and two-photon-induced fluorescence spectra are nearly identical, and the measured HRS signal is quadratically dependent on the incident field intensity (see Figure 3) provide convincing evidence that the measured signal solely represents the HRS signal.

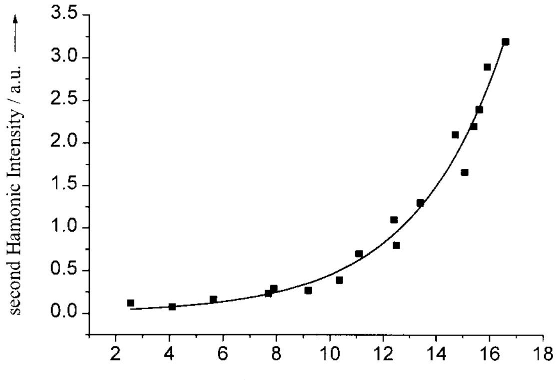


Figure 3. The quadratic dependence of the HRS signal ($I_{2\omega}$) on laser intensity (I_ω) for **6**.

$I_{2\omega}$(solution)/$I_{2\omega}$(solvent) versus N_c of compounds **1**–**6** are plotted in Figure 4. In the low concentration region, they all are linear (as expected from Equation (2), see Experimental Section) and the fitting results are summarized in Table 3. Also included are $f_\beta = \beta(0)/n$, in which n is the number of octupolar units in **2**–**6**. Although the $\beta(0)$ values of **1a** and **1b** are similar to each other because of their structural similarity, $\beta(0)$ of **1c** is larger than those of **1a** and **1b** due to the electron-donating group NPh$_2$. This effect of the NPh$_2$ group, enhancing the nonlinear optical properties, has previously been ascribed to a larger degree of charge transfer between the ground and excited states.[26a, 36]

As emphasized earlier, the main goal of the work reported herein is to elucidate the effects of polymerization on the HRS intensity of the octupolar molecules. Note that the HRS of NLO chromophores in solution is related to the fluctuations of molecular orientation and local density. Therefore, it is expected that the HRS intensity of the NLO chromophore should decrease in the polymeric environment because the corresponding fluctuation amplitude would be decreased.[28b] Indeed, significant reduction of the monomeric β was observed in semi-rigid NLO polymers such as helical poly(-isocyanide)s with azo dyes,[28a] polynorbonenes with pendant chromophores,[28c] and ruthenium-tris(bipyridyl)polyimide chromophores.[29] In strong contrast, $\beta(0)$ of the octupolar oligomer **6** increases *linearly* with respect to the number of

Table 3. Nonlinear optical and two-photon absorption properties of octupolar compounds.

Compound	$\lambda_{max}^{(1)}$[a]	$\lambda_{max}^{(2)}$[b]	β[c,d]	$\beta(0)$[e,f]	f_β[g]	Φ[h]	δ_{max}[i]	f_δ[j]
1a	498	990	171	91	1.0	0.101	3215	1.0
1b	485	990	152	85	1.0	0.0844	3010	1.0
1c	490	990	239	129	1.0	0.0841	5395	1.0
2	495	990	346	186	1.0	0.0826	7945	1.2
3	495	990	590	317	1.2	0.0632	8200	0.85
4	505	990	1298	506	0.90	0.0214	62930	2.7
5	488	800	1203	481	0.93	0.0371	24890	1.4
6	487	800	2213	1219	1.1	0.0175	50020	1.3

[a] λ_{max} of the one-photon absorption spectra in nm. [b] λ_{max} of the two-photon-induced fluorescence excitation spectra in nm. [c] First hyperpolarizability measured at 1560 nm. [d] The unit is 10^{-30} esu. [e] Corrected at $\lambda \rightarrow \infty$ using a three-level model.[3b] [f] $\beta(0)$ determined for 4-cyano-4′-methoxystilbene is 10×10^{-30} esu.[4] [g] $\beta(0)$ per octupolar unit. [h] Quantum yield. [i] The peak two-photon absorptivity in 10^{-50} cm^4 s photon^{-1}. [j] δ_{max}^{abs} per octupolar unit.

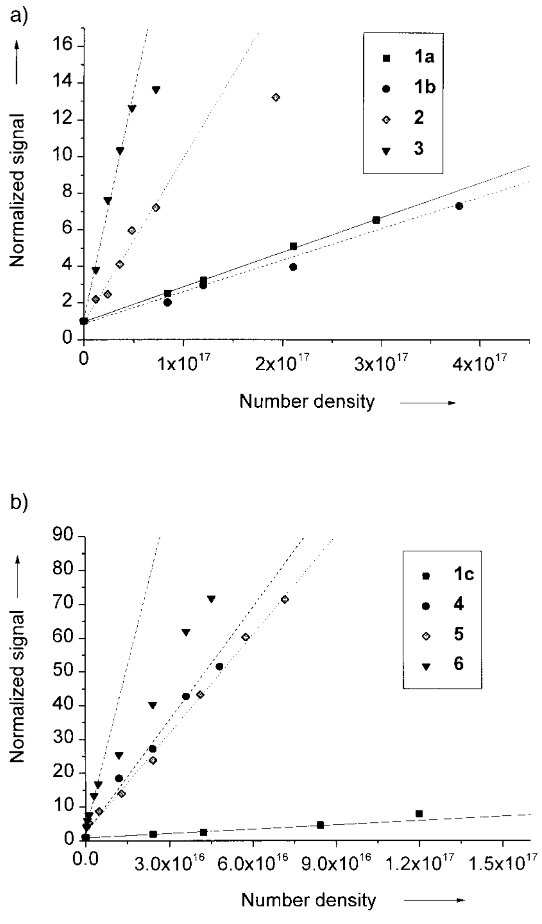


Figure 4. Plots of HRS intensity versus number density of the octupoles.

octupolar units and reaches a maximum value of 1219×10^{-30} esu (Table 3). Division of the $\beta(0)$ values by the number of octupolar units in **2**–**6** yields $f_\beta = 0.90-1.2$; this indicates that nearly 100% of the octupolar $\beta(0)$ contributes to the first hyperpolarizability of the oligomers. This retention of monomeric $\beta(0)$ observed in **4**–**6** may be attributed to the lack of the fluctuation effect. Because there are only four octupolar units within the molecule **4**, and 6–12 octupoles are connected by the flexible linkers in **5** and **6**, the fluctuation behavior of **4**–**6** is not expected to be very much different from the free octupole, and hence there is little difference in HRS intensity. Note that the inter-chromophore interaction observed for **6** is not strong enough to cause significant influence on β. Recently, Wang reported nearly identical β values for the disperse red 19 and its flexible polymer.[28b] The retention of β seems to be a general phenomenon in a flexible NLO polymer. Also, in dendrimers containing a dipolar azobenzene chromophore in a noncentrosymmetric environment and an octupolar ruthenium complex in which the chromophores are ordered in a semirigid, optimized acentric organization, either enhancement or retention of the monomeric β was observed to result in a coherent second-harmonic emission at the supramolecular level.[28c, 29] These results seem to indicate that β of the NLO chromophore will be significantly reduced upon polymerization if the structure of the resulting polymer is rigid, whereas it could be retained in a flexible polymer in which the fluctuation of chromophore orientation and density is not very much different from the free dye, and in dendrimers in which optimized acentric ordering of the chromophore is possible.

Although the nonlinear optical properties of octupolar oligomers and polymers have received much attention recently, the two-photon absorption properties of octupolar molecules have not. The two-photon-induced fluorescence (TPF) excitation spectra for **1**–**6** are given in Figure 5. The TPF spectra of **1a**–**c** are quite similar to the single-photon absorption spectra shown in Figure 1, except that the wavelength is doubled, $\lambda^{(1)}_{\max} = \lambda^{(2)}_{\max}/2$. Unlike the quadrupolar molecule with an inversion center, this result shows that one- and two-photon allowed states of these octupolar compounds are identical. As the number of octupolar molecule unit increases, that is, in compounds **2**–**6**, another strong TPF peak around 800 nm appears, indicating that these compounds have additional two-photon allowed electronic excited states. The intensity of this peak increases as the number of octupolar units in the oligomers increases and it becomes the strongest peak in the spectra of **5** and **6**. The wavelengths of the single- and two-photon absorption maxima ($\lambda^{(1)}_{\max}$ and $\lambda^{(2)}_{\max}$), $\beta(0)$, and the maximum values of the two-photon absorption cross-section ($\delta_{\max}$) are summarized in Table 3.

On the basis of the experimental results, we find that as the number of octupolar unit increases, the TPA cross-section increases, and the $\lambda^{(2)}_{\max}$ shifts to 800 nm. This trend turns out to be very important for practical applications. Most of the TPF microscopy uses a visible beam with a wavelength of 800 nm. Therefore, the development of TPA dyes in this wavelength region has been a primary target over the last decade. In this respect, we believe that a novel strategy for synthesizing TPA dyes with octupolar molecules and oligomers has been presented in this paper. The $\delta_{\max}$ value increases monotonically as the number of octupolar units increases. The f_δ ($= \delta_{\max}/n$) value is in the range 0.85–1.4, indicating that the $\delta_{\max}$ of the individual octupolar units fully contributes to the TPA cross-section of the oligomers. However, compound **4** provides an interesting exception to this trend. The TPA cross-section of **4** is much larger than that expected from the molecular weight as indicated by $f_\delta = 2.7$. This is to some extent unexpected because the monomeric contribution to first hyperpolarizability of **4** (f_β) is 0.9. This disparity is not clear at this moment. Nevertheless, to the best of our knowledge, $\delta_{\max} = 62\,930$ GM determined for **4** is the largest TPA cross-section reported in the literature.[19–22]

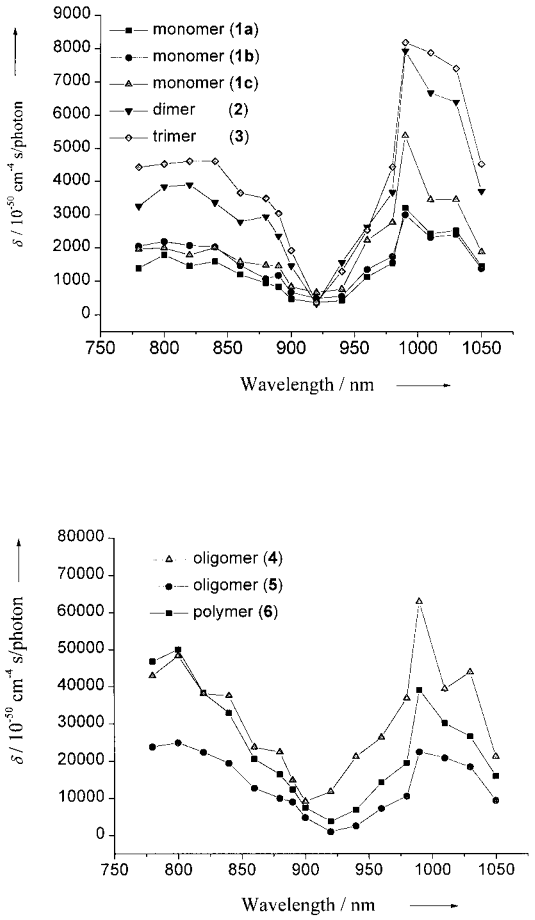


Figure 5. Two-photon-induced fluorescence excitation spectra of **1**–**6**.

Recently, by using the simple four-state valence-bond 3-charge-transfer model, it was theoretically predicted that β and δ are linearly correlated with each other for octupolar molecules. This relationship was confirmed by the ab initio calculations and the experiments for a few series of octupolar molecules.[4, 26] However, the previous investigation was limited to a series of octupolar molecules with the same conjugation linkers. The plots of $\delta_{\max}$ versus $\beta(0)$ for **1**–**6** are depicted in Figure 6, and we found that the two quantities are indeed almost linearly proportional to each other. Thus, the linear relationship seems to be valid even for a wide range of oligomers and polymers consisting of octupolar molecule units. Again, this result provides a useful design strategy for

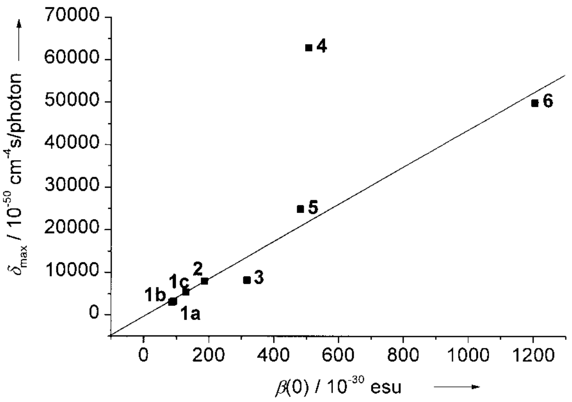


Figure 6. Plot of δ_{max} versus $\beta(0)$.

the synthesis of the octupolar polymers with large β and TPA cross-section.

In summary, octupolar oligomers containing 1,3,5-tricyano-2,4,6-tris(styryl)benzene derivatives show unprecedentedly large β and δ_{max}.

Conclusion

Herein, the first hyperpolarizabilities and TPA properties of various octupolar oligomers have been systematically investigated. Overall, the effects of increasing the number of octupolar units in the oligomers on the absorption, fluorescence, first hyperpolarizability, and TPA cross-section were studied in detail. The TPA excitation spectra indicated a gradual shift of $\lambda^{(2)}_{max}$ from 990 to 800 nm with the number of the octupolar units in the oligomers. A linear relationship between the first hyperpolarizability and TPA cross-section of the octupolar oligomers **1**–**6** was found experimentally. We have obtained octupolar oligomers with very large first hyperpolarizabilities and TPA cross-sections by using appropriate spacers connecting the octupolar units. This result provides a promising direction for the further development of novel octupolar polymers with such properties.

Experimental Section

General methods: *p*-Dihexylaminobenzaldehyde, *p*-(*N*-hydroxypiperidyl)-benzaldehyde, and (*N*-hydroxyethyl-*N*-methyl)aminobenzaldehyde were available from a previous study.[4] The hydroxyl group of the benzaldehyde derivatives was protected with *tert*-butyldimethylsilyl (TBDMS) chloride by a known method.[37] *N*-(*p*-Formylphenyl)-*N*-phenylaniline and *N*,*N*-(*p*-formylphenyl)aniline were synthesized by the reaction between triphenylamine and $POCl_3$ in DMF as reported in the literature.[38] The molecular weights and polydispersity of polymers were determined by means of GPC by using a Waters 600E GPC equipped with a Waters 410 differential refractometer. GPC columns (Styragel HR 1, 2, 3, 4, and 5) were calibrated relative to a polystyrene standard, and THF was used as the eluent.

1,3,5-Tricyano-2,4-bis[(diethoxyphosphoryl)methyl]-6-(*p*-dihexylaminostyryl)benzene (B): Lithium diisopropylamide (LDA) (1.0 mL, 1.4 mmol) was added dropwise to a stirred solution of 1,3,5-tricyano-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene (**A**) (2.5 g, 4.1 mmol) in anhydrous THF (50 mL) at −78 °C under nitrogen. The mixture was stirred for 30 min and *p*-dihexylaminobenzaldehyde (0.4 g, 1.4 mmol) in THF (5.0 mL) was added dropwise over a period of 10 min. After the mixture had been stirred for 10 min at −78 °C, the reaction temperature was allowed to rise to 0 °C, and stirring was continued for 2 h. Water (1 mL) was added to this mixture, and the solvent was evaporated. The crude product was taken up in CH_2Cl_2 (200 mL) and the organic layer was washed several times with water. The solvent was evaporated, and the product was purified by column chromatography with ethyl acetate as the eluent to give the title compound (1.8 g, 59 % yield). M.p. 153–154 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.81$ (d, $J = 16.4$ Hz, 1 H), 7.50 (d, $J = 8.3$ Hz, 2 H), 7.18 (d, $J = 16.4$ Hz, 1 H), 6.63 (d, $J = 8.3$ Hz, 2 H), 4.24 (q, $J = 6.9$ Hz, 8 H), 3.73 (d, $J = 23.1$ Hz, 4 H), 3.32 (t, $J = 7.2$ Hz, 4 H), 1.60 (m, 4 H), 1.33 (m, 24 H), 0.91 ppm (t, $J = 7.2$ Hz, 6 H); IR (KBr): $\tilde{\nu} = 2231$ cm^{-1} (C≡N).

1,3,5-Tricyano-2-[(diethoxyphosphoryl)methyl]-4,6-bis(*p*-dihexylaminostyryl)benzene (C): Synthesized from **A** and two equivalents of *p*-dihexylaminobenzaldehyde by the procedure described for **B** to give the title compound in 53 % yield. M.p. 83–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.80$ (d, $J = 16.5$ Hz, 2 H), 7.51 (d, $J = 9.0$ Hz, 4 H), 7.18 (d, $J = 16.5$ Hz, 2 H), 6.63 (d, $J = 9.0$ Hz, 4 H), 4.24 (q, $J = 7.2$ Hz, 4 H), 3.74 (d, $J = 23.1$, 2 H), 3.32 (t, $J = 7.8$ Hz, 8 H), 1.59 (m, 8 H), 1.34 (m, 30 H), 0.91 ppm (t, $J = 6.6$ Hz, 12 H); IR (KBr): $\tilde{\nu} = 2215$ cm^{-1} (C≡N).

1,3,5-Tricyano-2,4-bis(*p*-dihexylaminostyryl)-6-{[(*N*-hydroxyethyl-*N*-methyl)amino]styryl}benzene (1a): Synthesized from **C** and one equivalent of {*N*-[2-(*O*-TBDMS)ethyl]-*N*-methyl}aminobenzaldehyde by the procedure described for **B**, followed by the deprotection of the TBDMS group with Bu_4NF to give the title compound in 59 % yield. M.p. 151–153 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 15.9$ Hz, 2 H), 7.72 (d, $J = 16.5$ Hz, 1 H), 7.54 (d, $J = 8.7$ Hz, 2 H), 7.52 (d, $J = 8.7$ Hz, 4 H), 7.22 (d, $J = 16.5$ Hz, 1 H), 7.20 (d, $J = 15.9$ Hz, 2 H), 6.78 (d, $J = 8.7$ Hz, 2 H), 6.63 (d, $J = 8.7$ Hz, 4 H), 3.87 (t, $J = 5.1$ Hz, 2 H), 3.59 (t, $J = 5.1$ Hz, 2 H), 3.32 (t, $J = 7.2$ Hz, 8 H), 3.08 (s, 3 H), 1.58 (m, 8 H), 1.33 (m, 24 H), 0.91 ppm (t, $J = 6.6$ Hz, 12 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.80$, 149.50, 149.28, 149.20, 142.01, 141.57, 129.70, 129.44, 123.64, 122.16, 116.76, 116.58, 115.44, 112.06, 111.35, 105.65, 105.43, 60.21, 54.66, 51.10, 39.07, 31.74, 27.31, 26.84, 22.75, 14.15 ppm; IR (KBr): $\tilde{\nu} = 3423$ (OH), 2215 cm^{-1} (CN); elemental analysis calcd (%) for $C_{60}H_{78}N_6O$: C 80.13, H 8.74, N 9.35; found: C 80.13, H 8.63, N 9.42.

1,3,5-Tricyano-2-(*p*-dihexylaminostyryl)-4,6-bis{[(*N*-hydroxyethyl-*N*-methyl)amino]styryl}benzene (1b): Synthesized from **B** and two equivalents of {*N*-[2-(*O*-TBDMS)ethyl]-*N*-methyl}aminobenzaldehyde by the procedure described for **B**, followed by the deprotection of the TBDMS group with Bu_4NF to give the title compound[37] in 79 % yield. M.p. 213–215 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.77$ (d, $J = 15.3$ Hz, 1 H), 7.73 (d, $J = 16.1$ Hz, 2 H), 7.53 (d, $J = 8.4$ Hz, 4 H), 7.51 (d, $J = 8.1$ Hz, 2 H), 7.22 (d, $J = 16.1$ Hz, 2 H), 7.20 (d, $J = 15.3$ Hz, 1 H), 6.77 (d, $J = 8.4$ Hz, 4 H), 6.64 (d, $J = 8.1$ Hz, 2 H), 3.86 (t, $J = 5.1$ Hz, 4 H), 3.58 (t, $J = 5.1$ Hz, 4 H), 3.32 (t, $J = 7.4$ Hz, 4 H), 3.08 (s, 6 H), 1.61 (m, 4 H), 1.33 (m, 12 H), 0.91 ppm (t, $J = 6.6$ Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.82$, 149.51, 149.25, 149.15, 142.11, 141.66, 129.74, 129.48, 123.52, 122.08, 116.69, 116.43, 115.30, 112.03, 111.32, 105.72, 105.49, 60.19, 54.63, 51.10, 39.09, 31.74, 27.30, 26.84, 22.76, 14.16 ppm; IR (KBr): $\tilde{\nu} = 3423$ (OH), 2215 cm^{-1} (C≡N); elemental analysis calcd (%) for $C_{51}H_{60}N_6O_2$: C 77.63, H 7.66, N 10.65; found: C 77.60, H 7.72, N 10.83.

1,3,5-Tricyano-2-(*p*-dihexylaminostyryl)-4,6-bis(diphenylaminostyryl)benzene (1c): Synthesized from **B** and two equivalents of *p*-diphenylaminobenzaldehyde by the procedure described for **B** to afford the title compound in 45 % yield. M.p. 83–84 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.82$ (d, $J = 15.9$ Hz, 1 H), 7.67 (d, $J = 15.9$ Hz, 2 H), 7.52 (d, $J = 8.7$ Hz, 2 H), 7.49 (d, $J = 8.7$ Hz, 4 H), 7.30 (m, 8 H), 7.27 (d, $J = 15.9$ Hz, 2 H), 7.16 (d, $J = 15.9$ Hz, 1 H), 7.13 (m, 12 H), 7.05 (d, $J = 8.7$ Hz, 4 H), 6.63 (d, $J = 8.7$ Hz, 2 H), 3.32 (t, $J = 7.8$ Hz, 4 H), 1.60 (m, 4 H), 1.33 (m, 12 H), 0.91 ppm (t, $J = 6.6$ Hz, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 149.73$, 149.60, 149.15, 149.08, 146.79, 142.60, 141.32, 129.91, 129.34, 128.88, 128.33, 125.16, 123.80, 121.97, 118.75, 116.35, 114.94, 111.39, 106.78, 106.20, 51.13, 31.75, 27.32, 26.85, 22.76, 14.16 ppm; IR (KBr): $\tilde{\nu} = 2215$ cm^{-1} (C≡N); elemental analysis calcd (%) for $C_{69}H_{64}N_8$: C 84.80, H 6.60, N 8.60; found: C 84.87, H 6.71, N 8.60.

Octupolar dimer 2: A solution of **1a** (0.15 g, 0.17 mmol) in THF (2 mL) was added dropwise to a stirred suspension of oil-free sodium hydride (0.033 g, 0.82 mmol) in THF (2 mL), and stirring was continued for 30 min. α,α'-Dibromo-*m*-xylene (0.025 g, 0.09 mmol) in THF (1 mL) was added to this solution, and the mixture was heated for 48 h at 40 °C. The reaction mixture was filtered, evaporated, and the product was purified by column chromatography with ethyl acetate/hexane (1:3) as eluent to afford the title compound (0.045 g, 28% yield). M.p. 126–128°C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.75$ (d, $J = 15.9$ Hz, 4H), 7.74 (d, $J = 15.9$ Hz, 2H), 7.51 (d, $J = 8.7$ Hz, 12H), 7.21 (m, 4H), 7.19 (d, $J = 15.9$ Hz, 2H), 7.18 (d, $J = 15.9$ Hz, 4H), 6.69 (d, $J = 8.7$ Hz, 4H), 6.62 (d, $J = 8.7$ Hz, 8H), 4.50 (s, 4H), 3.65 (m, 8H), 3.31 (t, 16H, $J = 7.2$ Hz), 3.05 (s, 6H), 1.60 (m, 16H), 1.32 (m, 48H), 0.91 ppm (t, $J = 6.6$ Hz, 24H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 150.38$, 149.47, 149.21, 149.16, 141.94, 141.73, 138.19, 129.69, 129.48, 128.40, 126.66, 126.43, 123.12, 122.19, 116.77, 116.21, 115.49, 111.72, 111.34, 105.54, 105.38, 67.59, 52.18, 51.11, 39.20, 31.73, 29.76, 27.31, 26.84, 22.75, 14.15 ppm; IR (KBr): $\tilde{\nu} = 2215$ cm^{-1} (C≡N); elemental analysis calcd (%) for $C_{128}H_{162}N_{12}O_2$: C 80.88, H 8.59, N 8.84; found: C 80.77, H 8.68, N 8.27.

Octupolar trimer 3: Synthesized according to the procedure described for **2** except that **1a** (0.15 g, 0.17 mmol), NaH (0.03 g, 0.82 mmol), and tris(bromomethyl)mesitylene (0.02 g, 0.02 mmol)[39] were used to give the title compound (0.05 g, 32% yield). M.p. 113–116°C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.75$ (d, $J = 15.9$ Hz, 9H), 7.53 (d, $J = 8.7$ Hz, 6H), 7.50 (d, $J = 8.7$ Hz, 12H), 7.20 (d, $J = 15.9$ Hz, 3H), 7.16 (d, $J = 15.9$ Hz, 6H), 6.67 (d, $J = 8.7$ Hz, 6H), 6.61 (d, $J = 8.7$ Hz, 12H), 4.54 (s, 6H), 3.71 (t, $J = 4.8$ Hz, 6H), 3.60 (t, $J = 4.8$ Hz, 6H), 3.30 (t, $J = 7.2$ Hz, 24H), 3.02 (s, 9H), 2.37 (s, 9H), 1.60 (m, 24H), 1.32 (m, 72H), 0.91 ppm (t, $J = 6.6$ Hz, 36H); ^{13}C NMR (75 MHz, CDCl$_3$): $\delta = 150.26$, 149.42, 149.14, 141.85, 141.73, 137.95, 132.42, 129.66, 129.49, 123.06, 122.17, 116.80, 116.17, 115.48, 111.65, 111.30, 105.47, 105.31, 68.054, 67.64, 52.24, 51.08, 39.28, 31.73, 29.75, 27.30, 26.83, 22.74, 14.15 ppm; IR (KBr): $\tilde{\nu} = 2213$ cm^{-1} (CN); elemental analysis calcd (%) for $C_{192}H_{246}N_{18}O_3$: C 80.80, H 8.69, N 8.83; found: C 80.88, H 8.66, N 8.06.

Oligomer 4: LDA (1.4 mL, 2.1 mmol) was added dropwise to a stirred solution of **B** (0.5 g, 0.7 mmol) in anhydrous THF (10 mL) at −78°C under nitrogen, and stirring was continued for 1 h. *N,N*-Bis-(4-formylphenyl)aniline (0.21 g, 0.7 mmol) in THF (5 mL) was added dropwise to this solution. The mixture was stirred for 10 min at −78°C, the reaction temperature was allowed to rise to room temperature, and stirring was continued overnight. The mixture was cooled to 0°C, a small amount of **B** (25 mg, 0.03 mmol) in THF (2 mL) was added, and the reaction was continued for 4 h at room temperature. *N*-(4-Formylphenyl)-*N*-phenylaniline (19 mg, 0.07 mmol) in THF (2 mL) was added at 0°C, and the mixture was stirred overnight at room temperature. The reaction was quenched with water, and the mixture was poured into methanol. The deep red solid that precipitated was washed several times with methanol and dried under vacuum overnight to afford the title compound (0.40 g, 77% yield). $M_w = 4200$; PDI = 1.95; m.p. >280°C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.84$ (d, $J = 15.9$ Hz, 1H), 7.68 (d, $J = 16.5$ Hz, 2H), 7.54 (m, 6H), 7.33 (m, 3H), 7.16 (m, 6H), 6.64 (d, $J = 8.1$ Hz, 2H), 3.32 (s, 4H), 1.63 (m, 4H), 1.32 (m, 12H), 0.91 ppm (m, 6H); IR (KBr): $\tilde{\nu} = 2214$ cm^{-1} (C≡N).

Polymer 5: Compound **1b** (1.7 g, 2.2 mmol), tolylene-2,4-diisocyanate (0.4 g, 2.2 mmol), and DMSO/methyl isobutyl ketone (MIBK) (3 mL, 1:1) were added to a three-neck flask equipped with a mechanical stirrer and a condenser under nitrogen. The mixture was stirred at 70°C until all of the reactants were dissolved, and heated for 3 h at 120°C. The reaction mixture was then cooled to room temperature and poured into a large amount of water. The crude product was dissolved in a small amount of CH$_2$Cl$_2$ and precipitated by adding ethyl acetate. The product was filtered and dried in vacuo to afford the title compound (1.6 g, 75% yield). M_w 8500; PDI 1.44; m.p. 194–200°C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.68$ (m, 3H), 7.45 (m, 6H), 7.06 (m, 4H), 6.60 (m, 8H), 4.28 (m, 2H), 3.54 (m, 8H), 3.28 (m, 4H), 2.96 (m, 6H), 2.05 (m, 3H), 1.60 (m, 4H), 1.32 (m, 12H), 2.10 ppm (m, 6H); IR (KBr): $\tilde{\nu} = 3372$ (N−H), 2214 (C≡N), 1726 (C=O), 1175 cm^{-1} (C−O).

Monomer E: Methacryloyl chloride (110 mg, 1.1 mmol) was added dropwise to a stirred solution of **1a** (0.77 g, 0.86 mmol) and Et$_3$N (0.25 g, 2.5 mmol) in anhydrous THF (10 mL), and stirring was continued for 1 h at 0°C under nitrogen. The solvent was evaporated and the crude product was taken up in CH$_2$Cl$_2$. The product was isolated by the usual workup procedure and purified by column chromatography with ethyl acetate/hexane (1:5) as eluent to afford the title compound (0.41 g, 50% yield) as a red oil. ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.77$ (d, $J = 16.2$ Hz, 2H), 7.73 (d, $J = 15.9$ Hz, 1H), 7.53 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 9$ Hz, 4H), 7.21 (d, $J = 15.9$ Hz, 1H), 7.19 (d, $J = 16.2$ Hz, 2H), 6.74 (d, $J = 8.4$ Hz, 2H), 6.63 (d, $J = 9$ Hz, 4H), 6.06 (s, 1H), 5.56 (s, 1H), 4.34 (t, $J = 5.7$ Hz, 2H), 3.71 (t, $J = 5.7$ Hz, 2H), 3.31 (t, $J = 7.8$ Hz, 8H), 3.06 (s, 3H), 1.92(s, 3H), 1.60 (m, 8H), 1.32 (m, 24H), 0.91 (t, $J = 6.3$ Hz, 12H); ^{13}C NMR (300 MHz, CDCl$_3$): $\delta = 167.04$, 150.14, 149.48, 148.23, 148.18, 141.98, 141.57, 135.75, 129.68, 129.44, 125.93, 123.62, 122.15, 116.72, 116.59, 115.42, 111.83, 111.33, 105.66, 105.42, 61.72, 51.08, 50.77, 38.74, 31.72, 27.30, 26.82, 22.73, 18.38, 14.13 ppm; elemental analysis calcd (%) for $C_{64}H_{82}N_6O_2$: C 79.46, H 8.54, N 8.69; found: C 79.59, H 8.94, N 8.31.

Polymer 6: Compound **E** (0.22 g, 0.23 mmol), 2,2′-azobisisobutronitrile (AIBN; 5 mg, 0.03 mmol), and anhydrous THF (1 mL) were introduced into a pressure tube under nitrogen. The pressure tube was sealed and heated for 24 h at 70°C. The mixture was cooled to room temperature and poured into methanol. The product that precipitated was filtered, washed with methanol, and dried under vacuum to afford the title compound (0.12 g, 55% yield). $M_w = 17730$; PDI = 1.50; m.p. 136–142°C; ^{1}H NMR (300 MHz, CDCl$_3$): $\delta = 7.67$ (m, 3H), 7.37 (m, 6H), 6.67 (m, 3H), 6.53 (m, 6H), 3.99 (m, 2H), 3.48 (m, 2H), 3.24 (m, 8H), 2.94 (m, 3H), 1.55 (m, 8H), 1.26 (m, 26H), 0.87 ppm (m, 15H); IR (KBr): $\tilde{\nu} = 2216$ (C≡N), 1726 (C=O), 1181 cm^{-1} (C−O).

Single-photon absorption, one- and two-photon fluorescence spectra: Absorption spectra were measured with a HP-8453 UV/Vis system, and the one-photon fluorescence spectra were obtained with an Aminco Bowman Series 2 luminescence spectrometer. The excitation wavelength for the emission spectra of **1**–**5** and **6** were 531 and 558 nm, respectively.

The two-photon-induced fluorescence spectra were obtained by exciting the solution containing the octupolar molecules with the nanosecond laser pulses as described below. The fluorescence quantum yield was determined by the literature method using rhodamine B as the reference.[40]

Hyper-Rayleigh scattering determination of first hyperpolarizabilty (*β*): The β values of the octupoles were measured at 1560 nm by the hyper-Rayleigh scattering (HRS) method as described in elsewhere.[32] To avoid complications due to multiphoton excitation, the excitation wavelength was shifted to 1560 nm with the OPO laser (Continuum Surelite OPO, 5 ns pulses), which was pumped by the 355 nm third-harmonic of a Nd:YAG laser (Continuum SL-II-10, Q-switched, 10 Hz).[33] The spectral purity of the detected signal was checked by using different filters as described in the literature.[3f, 32]

The chromophores were dissolved in CHCl$_3$ at a concentration of $(0.10–6.6)\times 10^{-7}$ M. The HRS intensities of the solvent and the CHCl$_3$ solutions of the chromophores were collected under the same conditions. The HRS intensity of each solution was plotted against the number density of the chromophores. The HRS intensity of a very dilute NLO solution is given by Equation (1) in which N_s and N_c represent the concentration of solvent and

$$I_{2\omega}(\text{solution}) = K(N_s\langle\beta_s^2\rangle + N_c\langle\beta_c^2\rangle)I_\omega^2 \qquad (1)$$

chromophore, respectively; $\langle\beta^2\rangle$ is the orientationally-averaged β; I_ω and $I_{2\omega}$ are the intensities of incident and scattered second-harmonic radiation; and K is a proportionality constant depending upon the scattering geometry and the solvent environment of the chromophore.[32–35]

Equation (1) can be rewritten as Equation (2).

$$I_{2\omega}(\text{solution})/I_{2\omega}(\text{solvent}) = 1 + N_c\langle\beta_c^2\rangle/N_s\langle\beta_s^2\rangle \qquad (2)$$

Equation (2) indicates that the slope of the line, that is, $I_{2\omega}$(solution)/$I_{2\omega}$(solvent) versus N_c, corresponds to the ratio, $\langle\beta_c^2\rangle/\langle\beta_s^2\rangle$, so that β_c can be experimentally estimated once the reference value ($\langle\beta_s^2\rangle$) is known.

Two-photon absorption cross-section (δ) measurement: The two-photon absorption cross-section of the octupolar compounds has been measured with the two-photon-induced fluorescence method by using the nanosecond laser pulses as described before.[22b, 26a, 41] The same aforementioned OPO laser was used as the excitation source.

Samples were dissolved in CHCl$_3$ at concentrations of $(0.60–2.5)\times 10^{-6}$ M, and the two-photon-induced fluorescence intensity was measured. The plot of the fluorescence intensity against the sample concentration was a straight line at low concentration but showed a downward curve at higher concentration, probably as a result of the concentration quenching. The highest concentration in the linear region was used for the measurement, that is, **1a**–**c** (1.50×10^{-6} M), **2** and **3** (2.50×10^{-6} M), **4** (1.75×10^{-6} M), **5** (8.00×10^{-7} M), **6** (6.00×10^{-7} M). The TPA cross-sections were measured at 800–1050 nm using rhodamine B in MeOH (1.00×10^{-4} M) as the reference. The intensities of the two-photon-induced fluorescence spectra of the reference and sample emitted at the same excitation wavelength were determined. The TPA cross-section, measured by using the two-photon-induced fluorescence measurement technique, can be measured by using Equation (3), in which the subscripts *s* and *r* stand for the sample and reference molecules, respectively.[22b]

$$\delta = \frac{S_s \Phi_\mathrm{r} \phi_\mathrm{r} \mathrm{c}_\mathrm{r}}{S_r \Phi_\mathrm{s} \phi_\mathrm{s} \mathrm{c}_\mathrm{s}} \delta_r \qquad (3)$$

The intensity of the signal collected by a PMT detector was denoted as S. Φ is the fluorescence quantum yield. ϕ is the overall fluorescence collection efficiency of the experimental apparatus. The number density of the molecules in solution was denoted as c. δ_γ is the TPA cross-section of the reference molecule.

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