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Novel azo octupoles with large first hyperpolarizabilities†

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Novel two-dimensional octupoles containing azo groups and their oligomers have been synthesized and their first hyperpolarizabilities were determined. The λ_{max} and $\beta(0)$ values of azo octupoles are nearly the same regardless of the nature of the bridge or the conjugation length. On the other hand, 1,3,5-tricyano-2,4,6-tris-[4-(*p*-diethylaminostyryl)styryl]benzene has a larger $\beta(0)$ value than the corresponding azo analogue probably due to the more efficient conjugation ability of C=C compared with the N=N bond. The $\beta(0)$/MW of the octupoles are larger than the corresponding dipoles, whereas those of the azo octupoles are comparable to the latter. Also, retention of monomeric $\beta(0)$ is observed in the octupolar oligomers.

Introduction

There is contemporary research interest in the synthesis of efficient nonlinear optical (NLO) materials with large first hyperpolarizabilities.[1] Among the most extensively investigated NLO chromophores are azobenzene derivatives.[2] They are relatively easy to synthesize and exhibit similar first hyperpolarizabilities to those of corresponding stilbene derivatives. Also, poled NLO polymers containing azobenzene moieties have been shown to exhibit significant electro-optic coefficients. On the other hand, the dipolar character of these molecules causes considerable drawbacks. Dipole–dipole interactions favor anti-parallel arrangements of the chromophores resulting in relaxation of the poled polymers and a subsequent cancellation of the nonlinear response of bulk materials. Moreover, the highly anisotropic structure of electro-optic materials containing polar rod-like molecules is not compatible with the polarization independent NLO response required for devices to be inserted in optical telecommunication systems.[3]

Recently, octupolar molecules with three-fold symmetry have been developed as an alternative NLO chromophore.[4] An advantage of such molecules in comparison to the dipolar molecules is that the second harmonic response of the octupoles does not depend on the polarization of the incident light because they are more isotropic than the dipolar NLO molecules.[4d] Secondly, there is a design strategy for the synthesis of octupoles with large first hyperpolarizabilities.[5] According to the VB-3CT model, the β values of two-dimensional octupoles increase gradually with the extent of charge transfer. Hence, the β values of such molecules could be significantly enhanced by simultaneously increasing the donor–acceptor strength, the π orbital energy, and the conjugation length. Thirdly, two-dimensional octupoles have been shown to be advantageous over dipolar systems with regard to the formation of noncentrosymmetric crystals.[6] Finally, electro-optic materials containing octupolar molecules are less likely to undergo relaxation due to the lack of a ground state dipole moment. Accordingly, various derivatives of subphthalocyanine, truxenone, 1,3,5-tris[(*p*-styryl)phenyl]benzene, 1,3,5-tricyano-2,4,6-tris(ethynyl)benzene, triphenylamine, 1,3,5-methoxy-2,4,6-tris(styryl)benzene, 1,3,5-trinitro-2,4,6-tris(styryl)benzene, 1,3,5-tricyano-2,4,6-tris(styryl)benzene have been synthesized and their structure–property relationships investigated.[6,7]

In view of the wide interest in dipolar azo compounds, it seems worthwhile to synthesize the corresponding octupolar molecules. It is expected that these molecules would exhibit similar first hyperpolarizabilities to those of corresponding octupoles containing C=C bonds. In addition, because the azo compounds could be arranged along the long axis by using optical and electrical alignment, it might be possible to utilize the azo group to align them non-centrosymmetrically in the bulk material to obtain significant second harmonic generation (SHG).[8] Furthermore, these molecules may find useful applications in optical devices, such as in optical memory, optical display, and optical switching, that utilize the photo-responsive azo group.[9]

In this work, we have synthesized a series of dipoles (**1d,e**), and two-dimensional octupoles and oligomers containing azo groups (**2b–d**, **P1**, and **P2**) and investigated their nonlinear optical properties (Chart 1). We were interested in learning the effects of (i) incorporating three units of dipolar molecules (**1a,d,e**) into the octupolar structure (**2a,d,e**), (ii) successively grafting azo groups at the periphery of **2a** (**2b–d**), (iii) changing the conjugation bridge from C=C to N=N (**2d,e**), and (iv) the molecular weight of the oligomers (**P1** and **P2**) on the linear and nonlinear optical properties. The results of these studies are reported here.

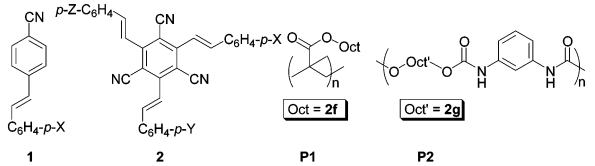

Chart 1 X = Y = Z = Et_2N (**a**); X = Y = Et_2N, Z = N=N–C_6H_4-*p*-NEt_2 (**b**); X = Y = N=N–C_6H_4-*p*-NEt_2, Z = NEt_2 (**c**); X = Y = Z = N=N–C_6H_4-*p*-NEt_2 (**d**); X = Y = Z = CH=CH–C_6H_4-*p*-$NHex_2$ (**e**); X = N=N–C_6H_4-*p*-$NHex_2$, Y = $NHex_2$, Z = –$CH_2CH_2NMe_2$ (**f**); X = N=N–C_6H_4-*p*-$NHex_2$, Y = Z = –$CH_2CH_2N(Me)$- (**g**)

†Electronic supplementary information (ESI) is available: molar absorptivity spectra of **1a,d,e**, **P1** and **P2** in THF and plots of $I_{2\omega}$ *vs.* number density for **1a,d,e** and **2a,c,e** in THF at 1064 nm. See http://www.rsc.org/suppdata/jm/b3/b300777d/

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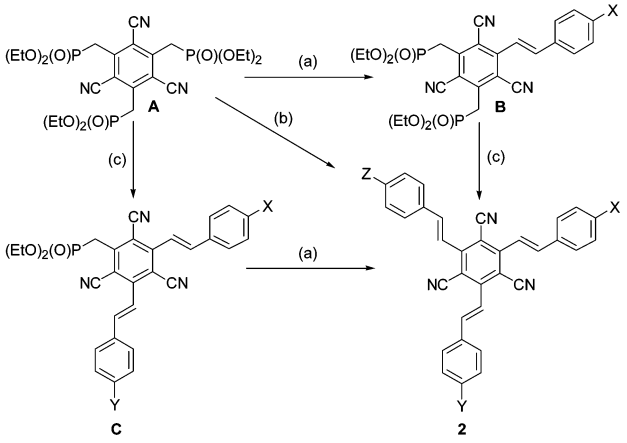
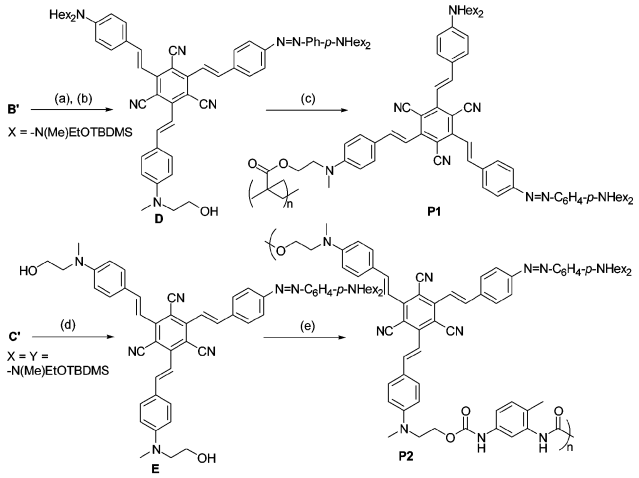


Scheme 1 *Reagents and conditions*: (a) i) LDA/THF/−78 °C; ii) ArCHO (1.2 equiv.), RT, 1 day, 65–92%. (b) i) LDA/THF/−78 °C; ii) ArCHO (3.2 equiv.), RT, 1 day, 65%. (c) i) LDA/THF/−78 °C; ii) ArCHO (1.8 equiv.), RT, 1 day, 68–92%.



Scheme 2 *Reagents and conditions*: (a) i) LDA/THF/−78 °C, 30 min; ii) $Hex_2NPhCHO$, RT, 1 day, 92%. (b) i) LDA/THF/−78 °C, 30 min; ii) $Hex_2NPhN{=}NPhCHO$, RT, 1 day, 92%; iii) KF/DMF, 82%. (c) i) $CH_2{=}C(Me)COCl/Et_3N$, 0 °C, 1 h, 50%; ii) AIBN/THF, 70 °C, 1 day, 55%; (d) i) LDA/THF/−78 °C, 30 min; ii) $Hex_2NPhN{=}NPhCHO$, RT, 1 day, 87%; iii) KF/DMF, 72%. (e) 2,4-$(NCO)_2$PhMe/DMSO/$MeCO^iBu$, 75%

Results and discussion

Synthesis

Dipolar molecules **1d,e** were synthesized by the Horner–Wittig reactions between 4-(diethoxyphosphorylmethyl)benzonitrile and 4-(*p*-diethylaminophenylazo)benzaldehyde or 4-(*p*-diethylaminostyryl)benzaldehyde as described in the Experimental section. Synthesis of octupolar molecules containing the azo groups (**2b–d**) was accomplished by the same methods by using 1,3,5-tricyano-2,4,6-tris[(diethoxyphosphoryl)methyl]benzene (**A**) and substituted benzaldehyde derivatives (Scheme 1). **A** was prepared by the bromination of 1,3,5-tricyanomesitylene followed by phosphorylation with $P(OEt)_3$.[6c] 4-(*p*-Diethylaminophenylazo)benzaldehyde was prepared by the DIBAL-H reduction of 4-(*p*-diethylaminophenylazo)benzonitrile, which was obtained by the coupling of the *p*-cyanobenzene diazonium ion with *N*,*N*-dialkylaniline. Condensation between **A** and *p*-diethylaminobenzaldehyde or 4-(*p*-diethylaminophenylazo)-benzaldehyde afforded the intermediates **B** and **C** in 65–92% yields. Compound **2d** was prepared in 65% yield by reacting **A** with an excess amount of 4-(*p*-diethylaminophenylazo)-benzaldehyde under the same conditions, whereas **2b,c** were synthesized from **B** or **C** and the appropriate benzaldehyde derivatives. The structures of **1d,e** and **2b–d** were unambiguously confirmed by ^1H, and ^{13}C NMR, IR, and elemental analysis.

To synthesize oligomer **P1**, **D** was prepared by successively reacting **B′** with *p*-dihexylaminobenzaldehyde and 4-(*p*-dihexylaminophenylazo)benzaldehyde (Scheme 2). Reaction of **D** with methacryloyl chloride produced a monomer, which was then polymerized under typical free radical polymerization conditions to afford **P1**. Oligomer **P2** was obtained in 75% yield from the reaction of tolylene-2,4-diisocyanate with **E**, which was synthesized by the reaction between **C′** and 4-(*p*-dihexylaminophenylazo)benzaldehyde. The molecular weight and polydispersity of these oligomers were determined relative to a polystyrene standard by GPC using THF as the eluent. The M_n of **P1** and **P2** are 3426 (PDI = 1.87) and 10253 (PDI = 1.47), respectively. These oligomers have rather small molecular weights and contain approximately 3 to 9 octupolar units within a molecule.

One-photon absorption spectra

Table 1 shows that λ_{max} of **1a**,**d**,**e** increases in the order **1a** < **1e** < **1d** (see Fig. S1 in the supplementary information†). The oscillator strengths, *f*, of **1a,d** are similar, whereas that of **1e** is significantly larger.

Fig. 1 shows the molar absorptivity spectra for **2a–e**. All of the molecules exhibit maximum absorption peaks near 485 nm, regardless of the nature of the bridge or the conjugation length. This indicates that the successive grafting of phenylazo or styryl groups at the periphery of **2a** does not significantly increase the charge transfer, probably because the structures of **2b–e** are distorted and so interrupt the effective conjugation. On the other hand, the higher energy band near 370 nm

Table 1 Linear and nonlinear optical properties of dipolar and octupolar molecules and their oligomers in THF

Entry	Compound	$\lambda_{max}{}^a$	ε^b	$\nu_{1/2}{}^c$	f^d	$\beta^{e,f,g}$	$\beta(0)^{f,g,h}$	$\beta_{yyy}{}^{f,i}$
1	**1a**	398	38 400	3730	0.62	130	49	118[j]
2	**1d**	464	30 700	4720	0.63	824	160	386[j]
3	**1e**	416	55 800	4580	1.1	457	150	362[j]
4	**2a**	481	103 000	3700	1.7	1730	252	408
5	**2b**	484	82 800	4080	1.5	1580	215	
6	**2c**	485	69 200	4560	1.4	1720	230	
7	**2d**	485	90 900	5070	2.0	1840	246	399
8	**2e**	480	102 000	5400	2.3	2350	348	564
9	**P1**	485	97 100[k]	4730[k]	2.0[k]	1320[k]	176[k]	
10	**P2**	474	89 800[k]	4900[k]	1.9[k]	1320[k]	218[k]	

[a]Absorbance maximum in nm. [b]Molar extinction coefficient in mol L^{-1} cm^{-1}. [c]Band width at half-height in THF. [d]Oscillator strength was estimated from the relationship: $f = 4.319 \times 10^{-9} \varepsilon \nu_{1/2}$. [e]Determined at 1064 nm. [f]10^{-30} esu. [g]Estimated uncertainty, ±15%. [h]Corrected at $\lambda \rightarrow \infty$ using a three-level model (see ref. 4*a*). [i]Calculated from the relationships $<\beta^2> = (6/35)\beta_{zzz}{}^2$ and $<\beta^2> = (8/21)\beta_{yyy}{}^2$ for 1D and D_3 chromophores, respectively (see ref.12) . [j]β_{zzz}. [k]The values are per octupolar unit in the oligomers.

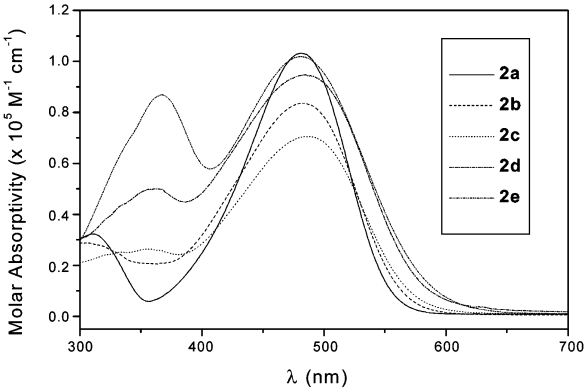


Fig. 1 Molar absorptivity spectra of **2a–e** in THF.

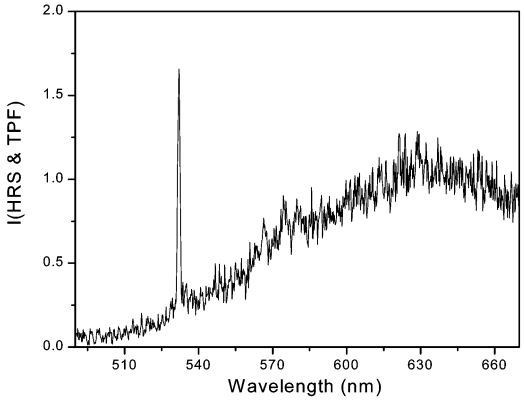


Fig. 2 HRS and two-photon fluorescence spectra of **2d** in THF excited by 1064 nm laser photons. The spectrum was averaged over 200 laser pulses at each wavelength while changing the wavelength in 0.1 nm increments.

monotonically increases as the chromophore structure is gradually changed from **2a** to **2e**, probably due to the absorption by the additional phenylazo or styryl groups. Note that the absorption spectra of **2d,e** are very similar except for the larger molar absorptivity of the latter. However, the width of the absorption peak, *i.e.*, $v_{1/2}$, becomes increasingly broader from **2a** to **2e**, probably because the number of conformers increases with molecular size (Table 1). Also, the oscillator strength calculated by the relationship $f = 4.319 \times 10^{-9} \varepsilon v_{1/2}$ increases in the order **2b,c** < **2a** < **2d** < **2e**. The absorption spectra of **P1** and **P2** are nearly the same as that of **2b** except for the slight bathochromic shift of the λ_{max} of the latter (Table 1 and Fig. S1). Similar blue shifts were observed in other polymers.[11b,16a,16b] Appreciable changes in the ε, $v_{1/2}$, and f values are noticable, indicating some interchromophore interactions within the oligomers.

Comparison of the spectral data reveals that the λ_{max} of **2a**,**d**,**e** are red shifted by 83, 21, and 64 nm, respectively, compared with **1a**,**d**,**e**, indicating that the charge transfer (CT) energy of the octupoles are significantly smaller than the corresponding dipoles (Table 1). This might be due to the fact that the former are not just three molecules of the latter arranged in a symmetrical way but are an extension of the latter by sharing a central phenyl group. Also, the oscillator strengths increase by 2.7-, 3.3-, and 2.2-fold by the same variation of the chromophore structure. It was previously reported that the ratio between the oscillator strengths of dipolar and octupolar molecules should be close to or smaller than 1 : 3, if there is no or significant interactions between the dipolar units. The observed ratios are in the range of 2–3, despite the significant interactions between the subchromophores. Hence the present results cannot be explained by the simple additivity rule. Noteworthy is the significantly smaller charge transfer energies and much larger oscillator strengths of the octupoles than the corresponding dipoles.

First hyperpolarizabilities (β) of 1, 2, P1, and P2

The β values were measured at 1064 nm by the hyper-Rayleigh scattering (HRS) method.[10,11] The HRS signal intensities from dilute solutions (6×10^{-6}–3×10^{-3} M) of **1**, **2**, **P1**, and **P2** in THF were collected at 532 nm and the β values were calculated by the external reference method using *p*-nitroaniline as the reference.[11c] The data reported were averaged over 200 pulses at each wavelength and the estimated uncertainty is $\pm 15\%$.

The HRS intensity of a very dilute NLO solution is given by eqn. (1),

$$I_{2\omega} = GI_{\omega}^2(N_s\beta_s^2 + N_c\beta_c^2) \quad (1)$$

where N_s and N_c are the number density of the solvent and chromophore, respectively, β_s and β_c are the effective molecular first hyperpolarizabilities of the solvent and chromophores, respectively, and G is a proportionality constant depending upon the scattering geometry and the solvent environment of the chromophore.

As shown in Figs. 2 and S2, 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. They also have absorption bands at 532 nm (Figs. 1 and S1). Therefore, corrections have been made for both TPF and absorption to obtain the intensity of the second-harmonic light actually generated.[11a,b]

To accurately determine the β values, the total HRS and TPF intensity was measured by averaging 200 laser pulses in the range of 528–536 nm. The fluorescence intensity was subtracted from the total signal intensity to obtain the pure HRS signal (Fig. 3b).[11a] The HRS intensity was further corrected for the absorption by using eqn. (2),

$$I_{2\omega}(\text{obs}) = I_{2\omega}(\text{true})e^{-\sigma lN} \quad (2)$$

where $I_{2\omega}$(obs) and $I_{2\omega}$(true) are the intensities of the second harmonic light detected after absorption and that actually generated, respectively, $\sigma = 1000\varepsilon ln(10)/N_A$, where N_A is Avogadro's number and ε is the molar absorptivity expressed in units of M^{-1} cm^{-1}, l is the path length of the scattering cell, and N is the number density of the chromophore.[11b]

In Fig. 3, the corrected HRS intensities *vs.* N_c of compounds

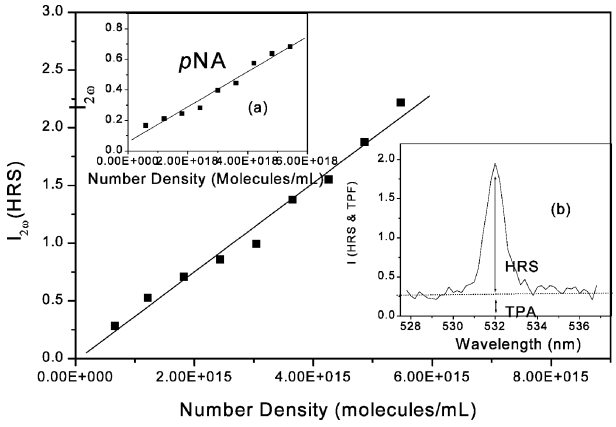


Fig. 3 Plot of $I_{2\omega}$ *vs.* number density for **2d** in THF at 1064 nm. The solid lines represent the linear squares fit through the experimental data. Insets: (a) the same plot for *p*-nitroaniline; (b) HRS and TPF spectrum of **2d** ($c = 4.25 \times 10^{15}$ molecules mL^{-1}) obtained by averaging 200 laser pulses in the range of 528–536 nm. The HRS intensity was obtained by subtracting the TPF intensity from the total signal intensity.

2d and *p*-nitroaniline are plotted. The corresponding plots for **1a,d,e** and **2a,c,e** are depicted in Fig. S2 in the supplementary information. †In the low concentration region, they are linear, as expected from eqn. (1). The β values of the chromophores were calculated using *p*-nitroaniline ($\beta_{st} = 21.4 \times 10^{-30}$ esu) as the external reference.[11c] According to the external reference method, β can be calculated by using eqn. (3),

$$\beta_c = \beta_{st} (m_c/m_{st})^{1/2} \quad (3)$$

where β_c and β_{st} are the effective molecular hyperpolarizabilities for the chromophore and standard, respectively, and m_c and m_{st} are the slopes of the plots in Fig. 3 for the chromophores and the standard, respectively. The calculated β values are summarized in Table 1.

The first hyperpolarizability of a D_3 symmetric molecule can be expressed by the three-level model (eqn. (4)),

$$\beta_{yyy} = \frac{1}{\hbar} \times \frac{\mu_{01}^2 \mu_{12}}{\omega_{01}^2} \times \frac{\omega_{01}^4}{(\omega_{01}^2 - 4\omega^2)(\omega_{01}^2 - \omega^2)} \quad (4)$$

where μ_{01} is the transition moment between the ground and degenerate first excited CT state, μ_{12} is the transition moment connecting these degenerate excited states, ω_{01} is the CT energy and ω is the energy of the incident laser light.[4a] The equation is identical to that of a two-level model of molecular nonlinearity for the dipoles if μ_{12} is substituted by $(\mu_2 - \mu_1)$, where μ_1 and μ_2 are the dipole moments in the ground and in the first excited CT state, respectively.[13]

Table 1 shows that the $\beta(0)$ value increases as the conjugation length increases from **1a** to **1d,e** and remains the same for **1d,e** (entries 1–3). When the chromophore structure is changed from **1a** to **1d**, λ_{max} increases by 66 nm without an appreciable change in the oscillator strength, which is proportional to the square of the transition moment (μ_{01}^2). Hence the 3-fold increase in $\beta(0)$ from **1a** to **1d** is primarily due to the smaller CT energy. A similar increase in $\beta(0)$ from **1a** to **1e** can be attributed to both a smaller CT energy and a larger oscillator strength. On the other hand, λ_{max} decreases but the oscillator strength increases by the change from **1d** to **1e**. Therefore, the nearly identical $\beta(0)$ values of **1d,e** indicate that these two opposing factors contribute to the $\beta(0)$ values to similar extents.

When the structure of the octupolar molecule is gradually changed from **2a** to **2d** by successively grafting phenylazo groups at the periphery of **2a**, $\beta(0)$ remains nearly the same (entries 4–7). However, a further change to **2e** results in a remarkable increase in $\beta(0)$ to 348×10^{-30} esu, which is comparable to the most efficient octupoles reported to date.‡ Hence, if other applications that utilize azo groups are excluded, azo octupoles **2b–d** are inferior to **2a** and **2e** in terms of $\beta(0)$/MW. Moreover, $\beta(0)$ of **2a** is 5-fold larger than **1a**, whereas those of **2d,e** are 1.5- and 2.3-fold larger than **1d,e**, indicating that the $\beta(0)$/MW value of **2a** is larger than **1a** but those of **2d,e** are inferior or comparable to **1d,e** (entries 1 & 4, 2 & 7, 3 & 8).

According to tensor addition calculations, the $\beta_{xxy} = -\beta_{yyy}$ value of a D_3 symmetric molecule is 3/4 of the β_{zzz} value of a dipolar analogue if subchromophore interactions are negligible.[4b] In the case of triarylamine derivatives, β_{zzz}(dipole):β_{yyy}(octupole) ratios of 0.94–1.0 have been reported.[7f,g] For comparison, the corresponding ratios for **2a,d,e** have been calculated by using the relationships $<\beta^2> = (6/35)\beta_{zzz}^2$ and $<\beta^2> = (8/21)\beta_{yyy}^2$ for 1D and D_3 chromophores, respectively.[12] The values are 3.5, 1.0, and 1.6 for **2a,d,e**, respectively. The values for **2a,e** are much larger than those for the triarylamine derivatives. Other groups and ourselves have previously reported similar enhancements of hyperpolarizability in octupolar molecules compared to their dipolar counterparts.[7c–h] However, in no case has such a large enhancement been observed. On the other hand, the ratio for **2a** is similar to those of the triphenylamine derivatives.

As can be seen in Table 1, λ_{max} increases by 83 nm and the oscillator strength increases by 2.7-fold as the chromophore structure is changed from **1a** to **2a**. Although it is not possible to compare μ_{12} of **2a** and $(\mu_2-\mu_1)$ of **1a** with existing data, the large ratio of $\beta_{yyy}/\beta_{zzz} = 3.5$ calculated for **2a** can be attributed to the smaller CT energy and larger transition moment of **2a** than **1a** (eqn. (4)). Similar but smaller changes in the λ_{max} ($\Delta\lambda_{max} = 64$ nm) and oscillator strength (2.1-fold) are observed on changing from **1e** to **2e**, hence a smaller ratio of 1.6 for **2e**. Since the oscillator strength increases by 3.2-fold from **1d** to **2d**; the smallest ratio of 1.0 for **2d** is probably due to the modest decrease in the CT energy ($\Delta\lambda_{max} = 21$ nm).

It is interesting to compare the β values of **2d,e**. The value of β for **2d** is significantly smaller than for **2e**, indicating that N=N is not as efficient a conjugation bridge as C=C in the octupolar molecules. Similarly, the first hyperpolarizabilities of ethylene and azo bridged donor–acceptor dipoles were found to be smaller than that of the C=C analogue.[14] Since the CT energy and ground state transition moment μ_{01} of **2d,e** are similar, this result indicates that the transition moment μ_{12} between the excited states of **2d** should be smaller than **2e**. A plausible explanation for this result might be that the azo group may reduce the amount of charge transfer from the donor to the acceptor, which would in turn decrease the state dipole moment difference along the individual arms to attenuate μ_{12} and β.

For practical applications, it is useful to graft the NLO molecules into a polymer. An ideal approach would be to design a polymer such that the monomeric NLO property is maximally utilized. However, considering that the HRS of a NLO chromophore is related to the fluctuations of molecular orientation and local density, a polymeric environment is expected to decrease the HRS intensity because the fluctuation would be inhibited.[11b] On the other hand, the monomeric β is significantly enhanced by vector addition in semi-rigid NLO polymers such as helical poly(isocyanides) with azo dyes.[15] Similar results were observed in polynorbonenes having pendant chromophores, dendrimers containing a dipolar azobenzene chromophore, and an octupolar ruthenium complex, in which the chromophores are ordered in a semi-rigid, optimized acentric organization, resulting in a coherent second harmonic emission at the supramolecular level.[16]

Fig. 4 shows that the slope of the plot of $I_{2\omega}$ *vs.* number density of the octupolar units for **2b** is somewhat larger than

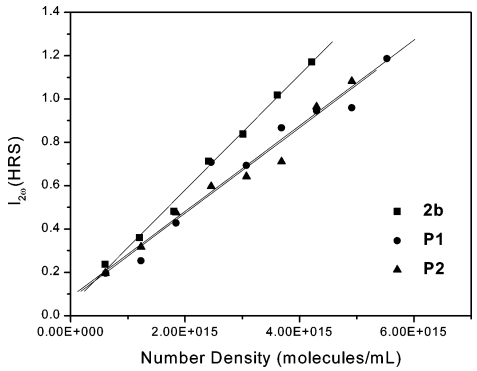


Fig. 4 Plots of $I_{2\omega}$ *vs.* number density for **2b**, **P1**, and **P2** in THF at 1064 nm. The solid lines represent the linear squares fit through the experimental data.

‡The most efficient octupoles are 1,3,5-trimethoxy-2,4,6-tris{*p*-[2-(3-dicyanomethylidene-5,5-dimethylcyclohex-1-enyl)vinyl]styryl}benzene ($\lambda_{max} = 319$ nm, $\beta(0) = 163 \times 10^{-30}$ esu),[7h] 4,4′-bis(dibutylamino-styryl)-2,2′-bipyridine Zn(II) complex ($\lambda_{max} = 466$ nm, $\beta(0) = 241 \times 10^{-30}$ esu),[4e] and 1,3,5-tris(methylsufonylbistyryl)benzene ($\lambda_{max} = 377$ nm, $\beta(0) = 510 \times 10^{-30}$ esu).[7b]

those for **P1** and **P2**. However, the calculated $\beta(0)$ values of these molecules are nearly the same within experimental error (Table 1, entries 5, 9 and 10). The retention of monomeric β noted in these oligomers can be attributed to the small change in the fluctuation. Because only 3–9 units of **2b** are connected by the flexible linkers in these oligomers, the fluctuation behavior of **P1** and **P2** is not expected to be very much different from **2b**, and hence there is little difference in HRS intensity. Recently, Wang and co-workers reported nearly identical β values for DR19 and its flexible polymer.[11b] We also reported similar results in octupolar oligomers.[7j] Hence, the retention of monomeric β seems to be a general phenomenon in flexible polymers.

In conclusion, we have synthesized novel octupolar NLO molecules and oligomers containing azo groups with large first hyperpolarizabilities. The octupoles exhibit much larger β values than the corresponding dipoles, probably due to smaller CT energies and larger oscillator strengths. On the other hand, azo octupole **2d** has a signifcantly smaller β than the C=C analogue **2e**, indicating that the N=N bond is not such an efficient conjugation bridge as the C=C bond in octupolar molecules. Finally, retention of monomeric β is observed in flexible polymers. These molecules may ultimately find useful applications as electro-optic materials.

Experimental section

Synthesis of octupolar molecules and oligomers (1, 2 P1, and P2)

Compounds **1a**, **2a**, and **2e** were available from a previous study.[6c] The syntheses of **1d**,**e**, **2b–d**, **P1**, and **P2** are described below.

Synthesis of 4-[4-(*p*-diethylaminophenylazo)styryl]benzonitrile (1d) and 4-[4-(*p*-diethylaminostyryl)styryl]benzonitrile (1e)

4-(Diethoxyphosphorylmethyl)benzonitrile. α-Bromo-*p*-toluonitrile (2.0 g, 3.5 mmol) was dissolved in 10 ml of triethyl phosphite. The mixture was heated at 160 °C for 2 hours. After cooling, the excess triethyl phosphite was evaporated under reduced pressure. The residue was dissolved in methylene chloride and washed with water. The product was purified by flash column chromatography using ethyl acetate as the eluent. Yield 2.1 g (85%);^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.62 (d, 2H, J = 9.0 Hz), 7.44 (d, 2H, J = 9.0 Hz), 4.05 (q, 4H, J = 7.5 Hz), 3.20 (d, 2H, J = 21.0 Hz), 1.26 (t, 6H, J = 6.0 Hz).

4-[4-(*p*-Diethylaminophenylazo)styryl]benzonitrile (1d). LDA (1.5 M in THF, 0.71 mL, 1.1 mmol) was added dropwise to a solution containing 4-(diethoxyphosphorylmethyl)benzonitrile (0.21 g, 0.87 mmol) in 10 mL of THF and stirred for 30 min at −78 °C. To this solution was added 4-(*p*-diethylaminophenylazo)benzaldehyde (0.20 g, 0.71 mmol) in 10 mL of THF and the reaction was allowed to proceed for 1 day at room temperature. The reaction was quenched with H_2O and the product was extracted with CH_2Cl_2 and purified by column chromatography using CH_2Cl_2 as the eluent. Yield 0.25 g (92%); mp 257 °C; IR (KBr, cm^{-1}) 2221 (CN);^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.87 (d, 2H, J = 9.0 Hz), 7.85 (d, 2H, J = 9.0 Hz), 7.65 (d, 2H, J = 9.0 Hz), 7.62 (d, 2H, J = 9.0 Hz), 7.59 (d, 2H, J = 9.0 Hz), 7.26 (d, 1H, J = 15.0 Hz), 7.13 (d, 1H, J = 15.0 Hz), 6.72 (d, 2H, J = 9.0 Hz), 3.46 (q, 4H, J = 6.5 Hz), 1.24 (t, 6H, J = 6.5 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 153.5, 150.5, 143.5, 142.0, 137.2, 132.7, 132.1, 127.8, 127.3, 127.1, 125.7, 122.9, 119.3, 111.2, 110.8, 45.0, 12.9. Anal. Calcd for $C_{25}H_{24}N_4$: C, 78.92; H, 6.36; N, 14.73. Found: C, 78.96; H, 6.52; N, 14.56%.

4-[4-(*p*-Diethylaminostyryl)styryl]benzonitrile (1e). Synthesized by the same procedure as described above for the synthesis of **1d** except that 4-(diethoxyphosphorylmethyl)-benzonitrile and 4-(*p*-diethylaminostyryl)benzaldehyde were used. Yield 53%; mp 271°C; IR (KBr, cm^{-1}) 2220 (CN);^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.64 (d, 2H, J = 9.0 Hz), 7.58 (d, 2H, J = 9.0 Hz), 7.49 (s, 4H), 7.40 (d, 2H, J = 9.0 Hz), 7.21 (d, 1H, J = 16.5 Hz), 7.09 (d, 1H, J = 16.5 Hz), 7.07 (d, 1H, J = 16.5Hz), 6.88 (d, 1H, J = 16.5 Hz), 6.86 (d, 2H, J = 9.0 Hz), 3.39 (q, 4H, J = 6.5 Hz), 1.19 (t, 6H, J = 6.5 Hz). Anal. Calcd for $C_{27}H_{26}N_2$: C, 85.68; H, 6.92; N, 7.40. Found: C, 85.65; H, 6.86; N, 7.28%.

Synthesis of azo octupoles (2b–d)

4-(*p*-Dialkylaminophenylazo)benzonitrile. A solution of $NaNO_2$ (0.97 g, 14 mmol) in HCl(aq) (1 M, 30 mL) was added dropwise to a solution containing 4-cyanoaniline (1.5 g, 14 mmol) in HCl(aq) (5 M, 30 mL) and stirred for 2 h at 0–5 °C. To this solution was added *N*,*N*-dialkylaniline (14 mmol) in HCl(aq) (1 M, 30 mL). A small amount of THF was added to dissolve all of the starting materials, if necessary. After stirring for 1 h, the pH was adjusted to 4–5 with AcONa. The solid product that precipitated was filtered and dried in air for 1 day.

*4-(*p*-Diethylaminophenylazo)benzonitrile.* Yield 76%; mp 114 °C; IR (KBr, cm^{-1}) 2219 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H, J = 9.0 Hz), 7.85 (d, 2H, J = 9.0 Hz), 7.74 (d, 2H, J = 8.9 Hz), 6.73 (d, 2H, J = 8.9 Hz), 3.47 (q, 4H, J = 7.2 Hz), 1.24 (t, 6H, J = 7.2 Hz).

*4-(*p*-Dihexylaminophenylazo)benzonitrile.* Yield 78% (oil); IR (KBr, cm^{-1}) 2223 (CN); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H, J = 8.7 Hz), 7.85 (d, 2H, J = 8.7 Hz), 7.72 (d, 2H, J = 9.0 Hz), 6.68 (d, 2H, J = 9.0 Hz), 3.37 (t, 4H, J = 7.8 Hz), 1.64 (m, 4H), 1.34 (m, 12H), 0.91 (t, 6H, J = 6.4 Hz).

4-(*p*-Dialkylaminophenylazo)benzaldehyde. A solution of DIBAL-H in hexane (1.0 M, 3.3 mL) was added dropwise to a solution of 4-(*p*-dialkylaminophenylazo)benzonitrile (1.7 mmol) in THF (10 mL) at −78 °C under nitrogen. The solution was warmed to ambient temperature and stirred for 3 h. The reaction was quenched by adding an aqueous solution of AcOH (10%, 10 mL) and the product was extracted with CH_2Cl_2 and purified by column chromatography using hexane–CH_2Cl_2 = 5 : 1 as the eluent.

*4-(*p*-Diethylaminophenylazo)benzaldehyde.* Yield 84%; mp 108 °C; IR (KBr, cm^{-1}) 1801 (C=O); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.97 (d, 2H, J = 8.4 Hz), 7.93 (d, 2H, J = 8.4 Hz), 7.89 (d, 2H, J = 9.0 Hz), 6.73 (d, 2H, J = 9.0 Hz), 3.47 (q, 4H, J = 7.2 Hz), 1.24 (t, 6H, J = 7.2 Hz).

*4-(*p*-Dihexylaminophenylazo)benzaldehyde.* Yield 76% (oil); IR (KBr, cm^{-1}) 1756 (C=O); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 10.0 (s, 1H), 7.97 (d, 2H, J = 8.4 Hz), 7.93 (d, 2H, J = 8.4 Hz), 7.88 (d, 2H, J = 9.0 Hz), 6.74 (d, 2H, J = 9.0 Hz), 3.37 (t, 4H, J = 7.8 Hz), 1.63 (m, 4H), 1.34 (m, 12H), 0.91 (t, 6H, J = 6.4 Hz).

1,3,5-Tricyano-2-(4-diethylaminostyryl)-4,6-bis(diethoxyphosphorylmethyl)benzene (B) and 1,3,5-tricyano-2,4-bis(4-diethylaminostyryl)-6-(diethoxyphosphorylmethyl)benzene (C). Intermediate B was synthesized by the same procedure as described above for the synthesis of **1d** except that **A** and 4-(*p*-diethylaminophenylazo)benzaldehyde were used in a ratio of 1 : 1.2 and the benzaldehyde derivative was added dropwise to the ylide solution over 30 minutes at −78 °C, and the

reaction was conducted at room temperature for 6 h. To synthesize **C**, the reactant ratio was increased to 1 : 1.8 and the benzaldehyde derivative was added rapidly to the ylide solution.

*1,3,5-Tricyano-2-[4-(*p*-diethylamino)styryl]-4,6-bis(diethoxyphosphorylmethyl)benzene (**B**).* Yield 65%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.81 (d, 1H, J = 16.2 Hz), 7.52 (d, 2H, J = 8.7 Hz), 7.18 (d, 1H, J = 16.2 Hz), 6.67 (d, 2H, J = 8.7 Hz), 4.23 (q, 8H, J = 7.2 Hz), 3.74 (d, 4H, J = 23.1 Hz), 3.41 (q, 4H, J = 7.1 Hz), 1.36 (t, 12H, J = 7.2 Hz), 1.19 (t, 6H, J = 7.1 Hz).

*1,3,5-Tricyano-2,4-bis[4-(*p*-diethylamino)styryl]-6-(diethoxyphosphorylmethyl)benzene (**C**).* Yield 78 %; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.81 (d, 2H, J = 16.2 Hz), 7.52 (d, 4H, J = 8.7 Hz), 7.18 (d, 2H, J = 16.2 Hz), 6.67 (d, 4H, J = 8.7 Hz), 4.23 (q, 4H, J = 7.2 Hz), 3.74 (d, 2H, J = 23.1 Hz), 3.41 (q, 8H, J = 7.1 Hz), 1.36 (t, 6H, J = 7.2 Hz), 1.19 (t, 12H, J = 7.1 Hz).

1,3,5-Tricyano-2,4,6-tris[4-(*p*-diethylaminophenylazo)styryl]-benzene (2d). LDA (1.5 M in THF, 3.4 mL, 5.1 mmol) was added dropwise to a solution containing **A** (0.76 g, 1.3 mmol) in 15 mL of THF and stirred for 30 min at −78 °C. To this solution was added 4-(*p*-diethylaminophenylazo)benzaldehyde (1.2 g, 4.1 mmol) in 20 mL of THF and the reaction was allowed to proceed for 1 day at room temperature. The reaction was quenched with H_2O and the product was extracted with ethyl acetate and purified by column chromatography using CH_2Cl_2 as the eluent. Yield 0.83 g (65%); mp 114–115 °C; IR (KBr, cm^{-1}) 2219 (CN); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.90 (d, 6H, J = 8.7 Hz), 7.88 (d, 6H, J = 8.7 Hz), 7.84 (d, 3H, J = 16.2 Hz), 7.76 (d, 6H, J = 8.4 Hz), 7.49 (d, 3H, J = 16.2 Hz), 6.74 (d, 6H, J = 8.4 Hz), 3.47 (q, 12H, J = 7.2 Hz), 1.24 (t, 18H, J = 7.2 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ154.2, 150.3, 148.5, 143.2, 141.7, 135.3, 128.6, 125.6, 122.7, 120.9, 115.7, 110.9, 108.5, 44.8, 12.8. Anal. Calcd for $C_{63}H_{60}N_{12}$: C, 76.80; H, 6.14; N, 17.06. Found: C, 76.94; H, 6.22; N, 16.84%.

1,3,5-Tricyano-2,4-bis(*p*-diethylaminostyryl)-6-[4-(*p*-diethylaminophenylazo)styryl]benzene (2b) and 1,3,5-tricyano-2-(*p*-diethylaminostyryl)-4,6-bis[4-(*p*-diethylaminophenylazo)styryl]benzene (2c). Synthesized by the same procedure as described for **2d** except that **B** or **C** was used in place of A.

*1,3,5-Tricyano-2,4-bis(*p*-diethylaminostyryl)-6-[4-(*p*-diethylaminophenylazo)styryl]benzene (**2b**).* Yield 89%; mp 168 °C; IR (KBr, cm^{-1}) 2208 (CN); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 4H, J = 8.7 Hz), 7.81 (d, 2H, J = 16.2 Hz), 7.76 (d, 1H, J = 16.2 Hz), 7.72 (d, 2H, J = 9.0 Hz), 7.54 (d, 4H, J = 8.7 Hz), 7.45 (d, 1H, J = 16.2 Hz), 7.22 (d, 2H, J = 16.2 Hz), 6.74 (d, 2H, J = 9.0 Hz), 6.69 (d, 2H, J = 8.7 Hz), 6.66 (d, 2H, J = 8.7 Hz), 3.44 (q, 8H, J = 7.2 Hz), 3.43 (q, 4H, J = 7.2 Hz), 1.22 (t, 12H, J = 7.2 Hz), 1.21 (t, 6H, J = 7.2 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ153.8, 150.2, 149.2, 148.7, 143.1, 142.2, 140.7, 135.7, 129.9, 128.4, 125.5, 122.6, 122.1, 122.1, 121.7, 116.5, 116.4, 115.1, 111.2, 110.9, 106.7, 105.9, 44.8, 44.6, 12.8, 12.6. Anal. Calcd for $C_{51}H_{52}N_8$: C, 78.83; H, 6.75; N, 14.42. Found: C, 78.95; H, 6.82; N, 14.23%.

*1,3,5-Tricyano-2-(diethylaminostyryl)-4,6-bis[4-(*p*-diethylaminophenylazo)styryl]benzene (**2c**).* Yield 82%; mp >300 °C; IR (KBr, cm^{-1}) 2219 (CN); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H, J = 8.7 Hz), 7.82 (d, 1H, J = 16.2 Hz), 7.77 (d, 2H, J = 16.2 Hz), 7.72 (d, 4H, J = 8.7 Hz), 7.54 (d, 2H, J = 9.0 Hz), 7.43 (d, 2H, J = 16.2 Hz), 7.22 (d, 1H, J = 16.2 Hz), 6.72 (d, 4H, J = 9.0 Hz), 6.69 (d, 4H, J = 9.0 Hz), 6.68 (d, 4H, J = 9.0 Hz), 3.47 (q, 4H, J = 7.2 Hz), 3.45 (q, 8H, J = 7.2 Hz), 1.23 (t, 6H, J = 7.2 Hz), 1.21 (t, 12H, J = 7.2 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.5, 154.2, 150.4, 149.6, 149.2, 148.7, 143.3, 143.0, 141.3, 135.7, 130.2, 129.4, 128.6, 125.7, 122.8, 121.4, 116.1, 114.9, 111.4, 111.0, 107.7, 106.8, 44.7, 44.6, 12.7, 12.6. Anal. Calcd for $C_{57}H_{56}N_{10}$: C, 77.70; H, 6.41; N, 15.90. Found: C, 77.64; H, 6.87; N, 15.49%.

Synthesis of oligomer P1

1,3,5-Tricyano-2-{*p*-[*N*-(2-*tert*-butyldimethylsilanyloxyethyl)-*N*-methylamino]styryl}-4,6-bis(diethoxyphosphorylmethyl)benzene (B′). Synthesized by the same procedure as described for **2d** except that **A** (3.6 g, 5.9 mmol), LDA (1.5 M in THF, 10 mL, 16 mmol), and 4-[*N*-(2-*tert*-butyldimethylsilanyloxyethyl)-*N*-methylamino]benzaldehyde (1.4 g, 4.7 mmol) in THF (90 mL) were used. The product was purified by column chromatography using hexane–ethyl acetate = 1 : 3 as the eluent. Yield 68%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 1H, J = 16.2 Hz), 7.52 (d, 2H, J = 8.7 Hz), 7.20 (d, 1H, J = 16.2 Hz), 6.71 (d, 2H, J = 8.7 Hz), 4.26 (q, 8H, J = 6.9 Hz), 3.78 (t, 2H, J = 5.7 Hz), 3.74 (d, 4H, J = 23.1 Hz), 3.57 (t, 2H, J = 5.7 Hz), 3.07 (s, 3H), 1.36 (t, 12H, J = 6.9 Hz), 0.88 (s, 9H), 0.24 (s, 6H).

1,3,5-Tricyano-2-{*p*-[*N*-(2-*tert*-butyldimethylsilanyloxyethyl)-*N*-methylamino]styryl}-4-(*p*-dihexylaminostyryl)-6-(diethoxyphosphorylmethyl)benzene (B″). Synthesized by the same procedure as described for **2d** except that **B**′ (3.2 g, 4.3 mmol), LDA (1.5 M in THF, 6.3 mL, 9.5 mmol), and dihexylaminobenzaldehyde (0.99 g, 3.4 mmol) in THF (120 mL) were used. The product was purified by column chromatography using hexane–ethyl acetate = 1 : 1 as the eluent. Yield 92%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.84 (d, 1H, J = 16.2 Hz), 7.82 (d, 1H, J = 16.2 Hz), 7.53 (d, 2H, J = 9.0 Hz), 7.52 (d, 2H, J = 9.0 Hz), 7.22 (d, 1H, J = 16.2 Hz), 7.20 (d, 1H, J = 16.2 Hz), 6.71 (d, 2H, J = 8.7 Hz), 6.65 (d, 2H, J = 8.7 Hz), 4.26 (q, 4H, J = 6.9 Hz), 3.78 (t, 2H, J = 5.7 Hz), 3.74 (d, 2H, J = 23.1 Hz), 3.57 (t, 2H, J = 5.7 Hz), 3.37 (t, 4H, J = 7.8 Hz), 3.07 (s, 3H), 1.64 (m, 4H), 1.36 (t, 6H, J = 6.9 Hz), 1.34 (m, 12H), 0.91 (t, 6H, J = 6.4 Hz), 0.88 (s, 9H), 0.24 (s, 6H).

1,3,5-Tricyano-2-[4-(*p*-dihexylaminophenylazo)styryl]-4-{*p*-[*N*-(2-*tert*-butyldimethylsilanyloxyethyl)-*N*-methylamino]styryl}-6-(*p*-dihexylaminostyryl)benzene (D′). Synthesized by the same procedure as described for **2d** except that **B**″ (2.1 g, 2.3 mmol), LDA (1.5 M in THF, 1.9 mL, 2.8 mmol), and 4-(*p*-dihexylaminophenylazo)benzaldehyde (1.0 g, 2.6 mmol) in THF (90 mL) were used. The product was purified by column chromatography using hexane–ethyl acetate = 1 : 1 as the eluent. Yield 92%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.86 (d, 2H, J = 8.7 Hz), 7.84 (d, 2H, J = 8.7 Hz), 7.81 (d, 1H, J = 16.5 Hz), 7.78 (d, 1H, J = 16.5 Hz), 7.74 (d, 1H, J = 16.5 Hz), 7.70 (d, 2H, J = 8.7 Hz), 7.51 (d, 2H, J = 9.0 Hz), 7.50 (d, 2H, J = 8.7 Hz), 7.41 (d, 1H, J = 16.5 Hz), 7.21 (d, 1H, J = 16.2 Hz), 7.19 (d, 1H, J = 16.2 Hz), 6.74 (d, 2H, J = 9.0 Hz), 6.68 (d, 2H, J = 9.0 Hz), 6.62 (d, 2H, J = 9.0 Hz), 3.83 (t, 2H, J = 5.5 Hz), 3.55 (t, 2H, J = 5.5 Hz), 3.36 (t, 4H, J = 7.8 Hz), 3.31 (t, 4H, J = 7.8 Hz), 3.05 (s, 3H), 1.62 (m, 4H), 1.61 (m, 4H), 1.34 (m, 12H), 1.33 (m, 12H), 0.92 (t, 6H, J = 6.4 Hz), 0.91 (t, 6H, J = 6.4 Hz), 0.88 (s, 9H), 0.02 (s, 6H).

1,3,5-Tricyano-2-[4-(*p*-dihexylaminophenylazo)styryl]-4-{*p*-[*N*-(2-hydroxyethyl)-*N*-methylamino]styryl}-6-(*p*-dihexylaminostyryl)-benzene (D). A solution of **D**′ (3.5 g, 3.1 mmol) and KF (0.71 g, 12 mmol) in DMF (80 mL) was stirred for 1 h. To this solution, HBr(aq) (38%, 4.0 mL) was slowly added and stirred overnight. The solution was neutralized with NaOH(aq), filtered, washed several times with water, and dried in air. Yield 87%; mp 116 °C; IR (KBr, cm^{-1}) 3447 (OH), 2219 (CN); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.86 (d, 2H, J = 8.7 Hz), 7.84 (d, 2H, J = 8.7 Hz), 7.80 (d, 1H, J = 16.5 Hz), 7.76 (d, 1H, J = 16.5 Hz), 7.72 (d, 1H, J = 16.5 Hz), 7.70 (d, 2H, J = 8.7 Hz), 7.53 (d, 2H, J = 9.0 Hz), 7.50 (d, 2H, J = 8.7 Hz), 7.43 (d, 1H, J = 16.5 Hz), 7.20 (d, 1H, J = 16.2 Hz), 7.19 (d, 1H, J = 16.2 Hz),

6.76 (d, 2H, J = 9.0 Hz), 6.69 (d, 2H, J = 9.0 Hz), 6.63 (d, 2H, J = 9.0 Hz), 3.84 (t, 2H, J = 5.5 Hz), 3.57 (t, 2H, J = 5.5 Hz), 3.34 (t, 4H, J = 7.8 Hz), 3.30 (t, 4H, J = 7.8 Hz), 3.07 (s, 3H), 1.62 (m, 4H), 1.61 (m, 4H), 1.34 (m, 12H), 1.33 (m, 12H), 0.92 (t, 6H, J = 6.4 Hz), 0.91 (t, 6H, J = 6.4 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 154.1, 151.1, 150.8, 149.8, 149.3, 149.2, 148.8, 143.2, 142.6, 142.2, 141.0, 135.8, 129.9, 129.7, 128.5, 125.6, 123.6, 122.7, 121.7, 116.5, 116.4, 115.2, 115.1, 112.1, 111.5, 111.1, 106.9, 106.4, 106.1, 60.2, 54.6, 51.2, 51.1, 39.0, 31.6, 27.4, 27.2, 26.7, 22.6, 14.0. Anal. Calcd for $C_{66}H_{82}N_8O$: C, 79.00; H, 8.24; N, 11.17; O, 1.59. Found: C, 79.03; H, 8.41; N, 11.12; O, 1.46%.

Monomer. To a stirred solution of **D** (0.75 g, 0.75 mmol) and Et_3N (0.31 g, 2.3 mmol) in anhydrous THF (10 mL), methacryloyl chloride (0.11 g, 1.05 mmol) was added dropwise and stirring was continued for 1 hour at 0 °C under nitrogen. The solvent was evaporated and the crude product was taken up in CH_2Cl_2. The product was isolated by the usual work up procedure and purified by column chromatography with ethyl acetate–hexane = 1 : 1 as eluent. The product was a red oil. Yield 0.53 g (66%); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H, J = 8.7 Hz), 7.86 (d, 2H, J = 8.7 Hz), 7.80 (d, 1H, J = 16.5 Hz), 7.76 (d, 1H, J = 16.5 Hz), 7.72 (d, 1H, J = 16.5 Hz), 7.70 (d, 2H, J = 8.7 Hz), 7.53 (d, 2H, J = 9.0 Hz), 7.50 (d, 2H, J = 8.7 Hz), 7.43 (d, 1H, J = 16.5 Hz), 7.20 (d, 1H, J = 16.2 Hz), 7.19 (d, 1H, J = 16.2 Hz), 6.76 (d, 2H, J = 9.0 Hz), 6.69 (d, 2H, J = 9.0 Hz), 6.63 (d, 2H, J = 9.0 Hz), 6.07 (s, 1H), 5.57 (s, 1H), 4.35 (t, 2H, J = 5.5 Hz), 3.72 (t, 2H, J = 5.5 Hz), 3.36 (t, 4H, J = 7.8 Hz), 3.32 (t, 4H, J = 7.8 Hz), 3.07 (s, 3H), 1.92 (s, 3H), 1.61 (m, 4H), 1.60 (m, 4H), 1.34 (m, 12H), 1.33 (m, 12H), 0.92 (t, 6H, J = 6.4 Hz), 0.91 (t, 6H, J = 6.4 Hz); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 167.25, 154.09, 150.75, 150.44, 149.88, 149.27, 148.78, 143.16, 142.65, 142.22, 141.01, 135.86, 135.70, 129.98, 129.73, 128.90, 128.54, 126.10, 125.54, 123.53, 122.71, 122.07, 121.67, 116.42, 116.25, 115.05, 111.92, 111.42, 111.03, 106.85, 106.11, 61.67, 51.28, 51.05, 50.72, 38.82, 38.72, 31.64, 29.67, 27.29, 27.20, 26.74, 25.31, 22.64, 18.31, 18.21, 14.03.

Oligomer P1. The monomer described above (0.62 g, 0.58 mmol), AIBN (6.0 mg, 0.04 mmol), and anhydrous THF (3 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 produce that precipitated was filtered, washed with acetone–methanol = 1 : 3 as eluent, and dried under vacuum. Yield, 0.40 g (65%); M_n = 3426, PDI = 1.87; mp 150–160 °C; IR (KBr, cm^{-1}) 2216 (CN), 1726 (C=O), 1181 (C–O); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.77 (m, 9H), 7.37 (m, 5H), 7.10 (m, 2H), 6.64 (m, 6H), 4.06 (m, 2H), 3.54 (m, 2H), 3.32 (m, 8H), 2.99 (m, 3H), 1.58 (m, 8H), 1.30 (m, 26H), 0.89 (m, 15H).

Synthesis of oligomer P2

1,3,5-Tricyano-2,4-bis{*p*-[*N*-(2-*tert*-butyldimethylsilanyloxyethyl)-*N*-methylamino]styryl}-6-(diethoxyphosphorylmethyl)benzene (C′). Synthesized by the same procedure as described for **2d** except that **A** (3.4 g, 5.6 mmol), LDA (1.5 M in THF, 12 mL, 18 mmol), and 4-[*N*-(2-*tert*-butyldimethylsilanyloxyethyl)-*N*-methylamino]benzaldehyde (1.3 g, 4.5 mmol) in THF (90 mL) were used. The product was purified by column chromatography using hexane–ethyl acetate = 1 : 3 as the eluent. Yield 83%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.81 (d, 2H, J = 16.2 Hz), 7.50 (d, 4H, J = 8.7 Hz), 7.18 (d, 2H, J = 16.2 Hz), 6.70 (d. 4H, J = 8.7 Hz), 4.24 (q, 4H, J = 6.9 Hz), 3.79 (t, 4H, J = 5.7 Hz), 3.74 (d, 2H, J = 23.1 Hz), 3.55 (t, 4H, J = 5.7 Hz), 3.07 (s, 6H), 1.36 (t, 6H, J = 6.9 Hz), 0.88 (s, 18H), 0.24 (s, 12H).

1,3,5-Tricyano-2-[4-(*p*-dihexylaminophenylazo)styryl]-4,6-bis-{*p*-[*N*-(2-*tert*-butyldimethylsilanyloxyethyl)-*N*-methyl]aminostyryl}-benzene (E′). Synthesized by same procedure as described for **2d** except that **C′** (2.5 g, 2.8 mmol), LDA (1.5 M in THF, 2.2 mL, 3.4 mmol), and 4-(*p*-dihexylaminophenylazo)benzaldehyde (1.1 g, 3.1 mmol) in THF (20 mL) were used. The product was purified by column chromatography using hexane–ethyl acetate = 1 : 1 as the eluent. Yield 87%; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.89 (d, 2H, J = 16.2 Hz), 7.88 (d, 2H, J = 8.7 Hz), 7.85 (d, 2H, J = 8.7 Hz), 7.80 (d, 1H, J = 16.2 Hz), 7.72 (d, 4H, J = 8.7 Hz), 7.53 (d, 4H, J = 8.7 Hz), 7.44 (d, 2H, J = 16.2 Hz), 7.22 (d, 1H, J = 16.2 Hz), 6.70 (d, 2H, J = 9.0 Hz), 6.68 (d, 2H, J = 9.0 Hz), 3.79 (t, 4H, J = 7.8 Hz), 3.54 (t, 4H, J = 7.8 Hz), 3.37 (t, 4H, J = 7.8 Hz), 3.07 (s, 6H), 1.62 (m, 4H), 1.34 (m, 12H), 0.91 (t, 6H, J = 6.4 Hz), 0.88 (s, 18H), 0.03 (s, 12H).

1,3,5-Tricyano-2-[4-(*p*-dihexylaminophenylazo)styryl]-4,6-bis-{*p*-[*N*-(2-hydroxyethyl)-*N*-methylamino]styryl}benzene (E). Synthesized by the same procedure as described for **D**. Yield 72%; mp 158 °C; IR (KBr, cm^{-1}) 3434 (OH), 2219 (CN); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.88 (d, 2H, J = 16.2 Hz), 7.87 (d, 2H, J = 8.7 Hz), 7.85 (d, 2H, J = 8.7 Hz), 7.78 (d, 1H, J = 16.2 Hz), 7.68 (d, 4H, J = 8.7 Hz), 7.51 (d, 4H, J = 8.7 Hz), 7.38 (d, 2H, J = 16.2 Hz), 7.19 (d, 1H, J = 16.2 Hz), 6.72 (d, 2H, J = 9.0 Hz), 6.69 (d, 2H, J = 9.0 Hz), 3.84 (t, 4H, J = 7.8 Hz), 3.55 (t, 4H, J = 7.8 Hz), 3.37 (t, 4H, J = 7.8 Hz), 3.05 (s, 6H), 1.64 (m, 4H), 1.34 (m, 12H), 0.91 (t, 6H, J = 6.4 Hz). ^{13}C-NMR (75 MHz, $CDCl_3$) δ 153.7, 151.0, 150.8, 148.8, 148.6, 143.0, 142.3, 141.0, 135.7, 129.8, 128.8, 128.5, 125.6, 123.3, 122.5, 121.5, 116.3, 115.7, 112.0, 111.1, 106.6, 106.1, 60.1, 54.6, 51.2, 38.9, 31.6, 27.3, 26.7, 22.6, 14.0. Anal. Calcd for $C_{57}H_{64}N_8O_2$: C, 76.65; H, 7.22; N, 12.55; O, 3.58. Found: C, 76.65; H, 7.26; N, 12.44; O, 3.65%.

Oligomer P2. To a three-necked flask equipped with a mechanical stirrer and a condenser, **C** (0.92 g, 1.0 mmol), tolylene-2,4-diisocyanate (0.18 g, 1.0 mmol), and DMSO–methyl isobutyl ketone (3 mL, 1 : 1) were added under nitrogen. The mixture was stirred at 70 °C until all of the reactants were dissolved, and then heated for 3 h at 120 °C. To this solution was added 10 ml of DMSO, and the mixture was then cooled to room temperature and poured into a large amount of water. The precipitate was collected and dried *in vacuo*, then purified by Soxhlet extraction for 18 h using ethyl acetate as solvent. The product was dried *in vacuo*. Yield 0.6 g (55%); M_n = 10 253, PDI = 1.49; mp 178–196 °C; IR (KBr, cm^{-1}) 3427 (N–H), 2219 (CN), 1716 (C=O), 1171 (C–O); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.83 (m, 7H), 7.68 (m, 4H), 7.45 (m, 6H), 7.10 (m, 2H), 6.67 (m, 6H), 3.79 (m, 4H), 3.55 (m, 4H), 3.35 (m, 4H), 2.99 (m, 6H), 2.30 (m, 3H), 1.62 (m, 4H), 1.34 (m, 12H), 0.91 (m, 6H).

Determination of the first hyperpolarizabilties (β)

The β values were measured at 1064 nm by the hyper-Rayleigh Scattering (HRS) method using a Nd:YAG laser (Electro-Optics Inc. Continuum PII 8000, 10 Hz, 9.3 ns pulse width).[10,11] Solutions of increasing concentrations (6×10^{-6}–3×10^{-3} M) of **1**–**2**, **P1**, and **P2** in THF were cleaned to remove microscopic particles by passing them through 0.2 μm Millipore filters. The emitted photons from the sample cuvettes were collimated and focused on the monochromator by two lenses at the right angle. The HRS and two-photon fluorescence (TPF) spectrum of **2d** was obtained by averaging 200 laser pulses at each wavelength while changing the wavelength in 0.1 nm increments from 475 to 700 nm. To determine the β values, 200 laser pulses were averaged in the wavelength range of 528–535 nm. The TPF intensity was subtracted from the total signal intensity to obtain a pure

HRS signal.[11a] The HRS intensity was further corrected for self-absorption by using eqn. (2).[11b] The corrected HRS intensities were plotted against the number density (N_c) of the chromophores. The β values of the chromophores were calculated by the external reference method using *p*-nitroaniline ($\beta_{st} = 21.4 \times 10^{-30}$ esu) as the reference (eqn. (3)).[11b,c] The estimated uncertainty of this measurement is $\pm 15\%$.

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