First hyperpolarizabilities of hexa(ethynyl)benzene derivatives: effect of conjugation length

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A variety of dipolar and octupolar molecules containing C≡C bonds as the conjugation bridge have been synthesized and the linear and nonlinear optical properties (β) were studied. The $\beta(0)$ value of the dipole increases with conjugation length, whereas that of the octupole decreases from **2a** to **2b** with concomitant decrease in λ_{max}. A further increase in the conjugation length to **3a–c** increased $\beta(0)$ because of the larger oscillator strength. Moreover, **3a** with the most distorted structure shows the largest $\beta(0)$, probably because of the dipolar contribution. On the other hand, β_{yyy}/β_{zzz} ratios are smaller than unity, probably because β_{zzz} is overestimated by the errors involved in the resonance correction.

1. Introduction

Much effort is being focused to develop octupolar nonlinear optical (NLO) materials for possible applications in electro-optic devices.[1–5] The advantages of octupoles in comparison to the more conventional dipolar molecules include easier noncentrosymmetric arrangements and the polarization-independent second harmonic response.[1d,4] Also, there is a design strategy for the synthesis of octupoles with large first hyperpolarizabilities.[5] According to the VB-3CT model, the β value of two-dimensional octupoles should increase with the extent of charge transfer. Hence, the β values of such molecules can be enhanced by simultaneously increasing the donor–acceptor strength, conjugation length, and by using a more efficient conjugation bridge.

Earlier, we reported that 1,3,5-trinitro-2,4,6-tris(stryryl)benzene derivatives show significant first hyperpolarizabilities that increased with the conjugation length.[3a] However, the β values were not much larger than the corresponding dipoles because of the distorted structures that hampered the intramolecular charge transfer (ICT). When sterically less hindered acceptor groups were employed, the structure became more planar and the β of the octupole showed significant enhancement in comparison to the dipole, *i.e.* β_{yyy} of 1,3,5-tricyano-2,4,6-tris(*p*-diethylaminostyryl)benzene was larger by a factor of 3.5 than β_{zzz} of 4-cyano-4′-diethylaminostilbene.[3a,f] The large enhancement has been attributed to the effect of the sharing of the central phenyl group by the three dipolar units that induced efficient delocalization of the molecular orbital and enhanced ICT. Furthermore, this compound produced noncentrosymmetric crystals that showed one of the largest second harmonic generations (SHGs) known in the literature.[4b] Very recently, we reported that 1,3,5-tricyano-2,4,6-tris(*p*-diethylaminophenylethynyl)benzene, which is the triple bond analogue of 1,3,5-tricyano-2,4,6-tris(*p*-diethylaminostyryl)benzene, shows a similar first hyperpolarizability to that of the latter. Also, 1,3,5-tris(*p*-diethylaminophenylethynyl)-2,4,6-tris(*p*-nitrophenylethynyl)benzene has been shown to exhibit a large first hyperpolarizability.[2g] These results seem to indicate that the poor conjugation ability of the C≡C bond is largely compensated by the more planar structure. However, there is no report on the β of the octupoles with a more extended conjugation length.

Here, we have studied a series of dipolar and octupolar molecules containing donor–acceptor groups and triple bonds as the conjugation bridge. We were interested in learning the effects of extending the conjugation length from **2a** to **2b**, to **3a–c** (Scheme 1). Compounds **1a** and **1b** are dipolar references to the octupolar analogues **2a** and **2b**. Compounds **3b** and **3c** are essentially the same except for the *para* substituent in the peripheral phenyl groups, whereas **3a** may be distorted due to the steric hindrance. Hence, the effects of planarity on the octupoles could be assessed by comparing **3a** with **3b,c**. The first hyperpolarizabilities were measured by the frequency-resolved hyper-Rayleigh scattering (HRS) experiments.[6] By this method, the β values of **1–3** can be measured accurately without the possibility of overestimation due to multi-photon fluorescence (MPF).[3j]The results of these studies are now reported.

2. Experimental

Synthesis

Synthesis of **1a**, **1b**, **2b**, and **3a–c** is described below. Except for **3b** and **3c**, whose solubility was too low to obtain ^{13}C NMR spectra, all new compounds were thoroughly characterized by IR, ^{1}H and ^{13}C NMR, and elemental analysis.

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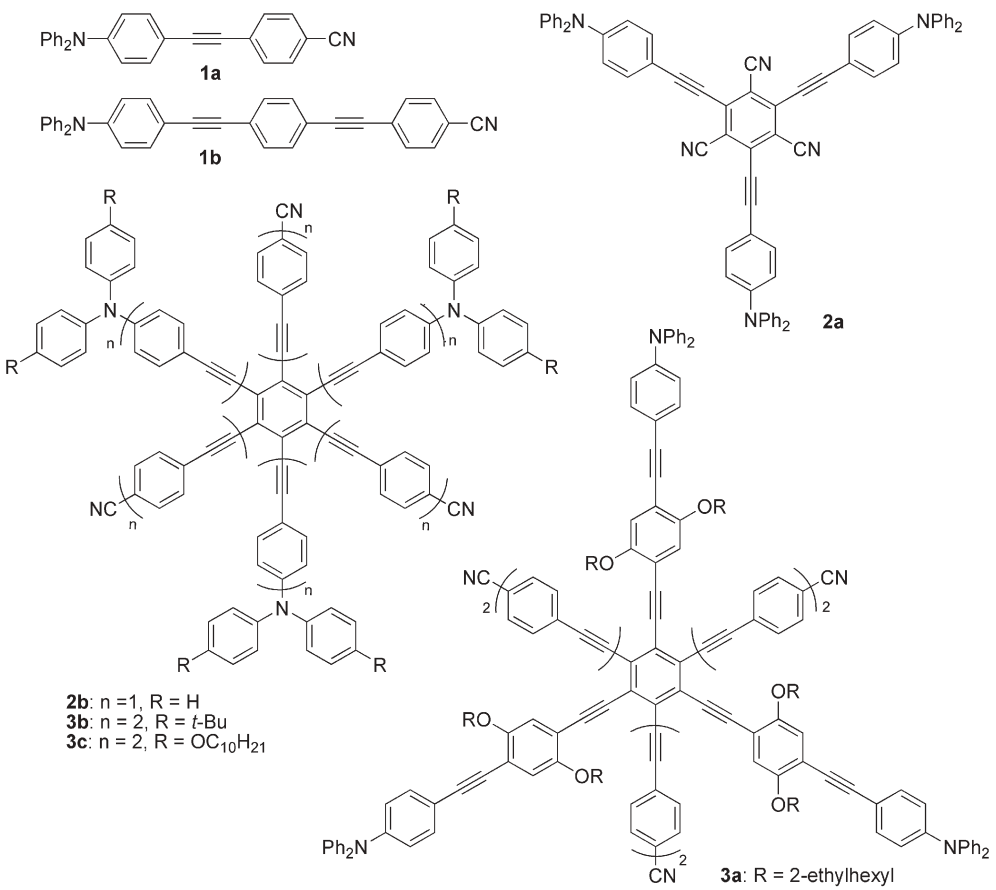


Scheme 1 Structures of **1–3**.

4-[4-(Diphenylamino)phenylethynyl]iodobenzene (A1). Et_3N (10 mL) was added to a stirred solution of $Pd_2Cl_2(PPh_3)_2$ (0.065 g, 0.093 mmol), CuI (0.020 g, 0.11 mmol), 4-(diphenylamino)phenylacetylene[7] (1.0 g, 3.7 mmol), and 1,4-diiodobenzene (2.5 g, 7.6 mmol) in anhydrous THF (20 mL) at RT under nitrogen. The mixture was stirred for 12 h. After evaporating off the THF and a standard work-up procedure, the crude product was purified on a silica gel column using CH_2Cl_2–hexane (1 : 17) as eluent. Yield: 1.1 g (63%); mp 166 °C; IR (KBr, cm^{-1}): 2204; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.3 Hz, 2H), 7.35 (d, J = 8.7 Hz, 2H), 7.27 (dd, J = 7.8, 7.2 Hz, 4H), 7.21 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 7.8 Hz, 4H), 7.06 (t, J = 7.2 Hz, 2H), 6.99 ppm (d, J = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.37, 147.33, 137.68, 133.18, 132.76, 129.65, 125.29, 123.87, 123.40, 122.36, 115.77, 93.83, 91.41, 97.93 ppm; Elemental analysis: calcd (%) for $C_{26}H_{18}IN$: C 66.25, H 3.85, N 2.97; found: C 66.30, H 3.64, N 2.90.

4-(4-Cyanophenylethynyl)iodobenzene (A2). Synthesized from 4-ethynylbenzonitrile[8] by the same procedure as described for **A1**. Yield: 50%; mp 182 °C; IR (KBr, cm^{-1}): 2224, 2214; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 8.4 Hz, 2H), 7.26 ppm (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 137.95, 133.40, 132.32, 132.29, 128.07, 121.92, 118.67, 111.98, 95.54, 92.97, 89.24 ppm; Elemental analysis: calcd (%) for $C_{15}H_8IN$: C 54.74, H 2.45, N 4.26; found: C 54.76, H 2.81, N 4.12.

1,4-Bis(2-ethylhexyloxy)benzene (B1). Synthesized from *p*-hydroquinone and 2-ethylhexyl bromide by a known method.[9] Yield: 74%; ^1H NMR (300 MHz, $CDCl_3$): δ = 6.82 (s, 4H), 3.78 (d, J = 5.7 Hz, 4H), 1.69 (m, 2H), 1.42 (m, 8H), 1.33 (m, 8H), 0.92 (t, J = 7.5 Hz, 6H), 0.90 ppm (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.63, 115.56, 71.40, 39.67, 30.74, 29.31, 24.06, 23.30, 14.34, 11.34 ppm; Elemental analysis: calcd (%) for $C_{22}H_{38}O_2$: C 78.99, H 11.45; found: C 78.94, H 11.48.

1,4-Bis(2-ethylhexyloxy)-2,5-diiodobenzene (B2). Synthesized from **B1** by a known method.[9] Yield: 67%; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.16 (s, 2H), 3.82 (d, J = 5.4 Hz, 4H), 1.73 (m, 2H), 1.49 (m, 8H), 1.33 (m, 8H), 0.94 (t, J = 7.5 Hz, 6H), 0.91 ppm (t, J = 6.6 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 153.04, 122.52, 86.25, 72.51, 39.66, 30.73, 29.28, 24.16, 23.29, 14.38, 11.46 ppm; Elemental analysis: calcd (%) for $C_{22}H_{36}I_2O_2$: C 45.07, H 6.19; found: C 45.12, H 6.19.

2,5-Bis(2-ethylhexyloxy)-1-iodo-4-[(*p*-diphenylamino)phenylethynyl]benzene (B3). Synthesized from 4-(diphenylamino)phenylacetylene[7] and 2 equiv. of **B2** by the same procedure as described for **A1**. Yield: 51%; IR (KBr, cm^{-1}): 2206; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.4 Hz, 2H), 7.28 (dd, J = 7.8, 7.5 Hz, 4H), 7.25 (s, 1H), 7.11 (d, J = 7.8 Hz, 4H), 7.06 (t, J = 7.5 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.88 (s, 1H), 3.87 (d, J = 5.1 Hz, 2H), 3.85 (d, J = 5.1 Hz, 2H), 1.75 (m, 2H), 1.53

(m, 8H), 1.35 (m, 8H), 0.92 (t, J = 7.5 Hz, 6H), 0.87 ppm (t, J = 6.9 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.62, 152.10, 148.09, 147.43, 132.66, 129.62, 125.22, 123.76, 123.74, 122.48, 116.57, 115.62, 114.18, 94.74, 86.91, 85.14, 72.39, 72.35, 39.85, 39.71, 30.87, 30.79, 29.40, 29.32, 24.21, 23.31, 14.39, 14.35, 11.52, 11.48 ppm; Elemental analysis: calcd (%) for $C_{42}H_{50}INO_2$: C 69.32, H 6.92, N 1.92; found: C 69.39, H 7.00, N 1.83.

***N,N*-Bis(4-*tert*-butylphenyl)-4-(triisopropylsilylethynyl)aniline (C1).** Sodium *tert*-butoxide (1.8 g, 19 mmol) and 4-(triisopropylsilylethynyl)aniline[10] (1.0 g, 3.7 mmol) were added to a stirred solution of $Pd_2(dba)_3$ (0.13 g, 0.14 mmol), DPPF (0.12 g, 0.22 mmol) and 4-*tert*-butylbromobenzene (2.0 g, 9.4 mmol) in dry toluene (80 mL) under nitrogen. The mixture was stirred at RT for 30 min and then heated at 90 °C for 24 h. The cooled mixture was filtered and the solvent was evaporated. The crude product was taken up in CH_2Cl_2 (50 mL) and the organic layer was washed several times with water. The solvent was evaporated, and the product was purified on a silica gel column chromatography using CH_2Cl_2–hexane (1 : 20) as the eluent. Yield: 1.4 g (71%); mp 133 °C; IR (KBr, cm^{-1}): 2149; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, J = 8.9 Hz, 2H), 7.26 (d, J = 8.6 Hz, 4H), 7.00 (d, J = 8.6 Hz, 4H), 6.94 (d, J = 8.9 Hz, 2H), 1.31 (s, 18H), 1.11 ppm (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.46, 146.49, 144.70, 133.09, 126.36, 124.63, 121.83, 115.90, 107.83, 89.13, 34.57, 31.66, 18.95, 11.61 ppm; Elemental analysis: calcd (%) for $C_{37}H_{51}NSi$: C 82.62, H 9.56, N 2.60; found: C 82.49, H 9.86, N 2.73.

***N,N*-Bis(4-decyloxyphenyl)-4-(triisopropylsilylethynyl)aniline (C2).** Synthesized by the same procedure described for **C1** using 4-(decyloxy)bromobenzene[11] in place of 4-*tert*-butylbromobenzene. Yield: 82%; IR (KBr, cm^{-1}): 2149; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 9.0 Hz, 4H), 6.80 (d, J = 9.0 Hz, 4H), 6.79 (d, J = 8.9 Hz, 2H), 3.91 (t, J = 6.5 Hz, 4H), 1.77 (m, 4H), 1.30 (m, 28H), 1.11 (m, 21H), 0.88 ppm (t, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.04, 149.08, 140.34, 133.08, 127.12, 119.54, 115.53, 114.61, 108.10, 88.60, 68.45, 32.20, 29.90, 29.87, 29.72, 29.65, 29.64, 26.38, 22.99, 18.99, 14.42, 11.67 ppm; Elemental analysis: calcd (%) for $C_{49}H_{75}NO_2Si$: C 79.72, H 10.24, N 1.90; found: C 79.85, H 10.45, N 1.79.

***N,N*-Bis(4-*tert*-butylphenyl)-4-ethynylaniline (D1).** $Bu_4N^+F^-$ in THF (3.7 mL, 3.7 mmol) was added into the solution of **C1** (1.0 g, 1.9 mmol) in THF dropwise. The mixture was stirred at RT for 30 min. Solvent was evaporated and the mixture was dissolved in CH_2Cl_2. After usual work-up, the product was purified on a silica gel column chromatography using CH_2Cl_2–hexane (1 : 5) as the eluent. Yield: 0.59 g (83%); mp 157 °C; IR (KBr, cm^{-1}): 2104; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, J = 8.7 Hz, 2H), 7.34 (d, J = 8.8 Hz, 4H), 7.10 (d, J = 8.8 Hz, 4H), 7.00 (d, J = 8.7 Hz, 2H), 3.03 (s, 1H), 1.40 ppm (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.89, 146.77, 144.52, 133.13, 126.42, 124.94, 121.22, 113.86, 84.43, 76.04, 34.59, 31.65 ppm; Elemental analysis: calcd (%) for $C_{28}H_{31}N$: C 88.14, H 8.19, N 3.67; found: C 88.45, H 8.37, N 3.53.

***N,N*-Bis(4-decyloxyphenyl)-4-ethynylaniline (D2).** Synthesized from **C2** by the same procedure described for **D1**. Yield: 65% (brown oil); IR (KBr, cm^{-1}): 2104; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, J = 8.8 Hz, 2H), 7.04 (d, J = 8.7 Hz, 4H), 6.82 (d, J = 8.7 Hz, 4H), 6.80 (d, J = 8.8 Hz, 2H), 3.92 (t, J = 6.6 Hz, 4H), 2.98 (s, 1H), 1.77 (m, 4H), 1.30 (m, 28H), 0.88 ppm (t, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.20, 149.48, 140.11, 133.13, 127.38, 119.02, 115.58, 112.65, 84.58, 75.77, 68.46, 32.17, 29.87, 29.84, 29.68, 29.61, 29.60, 26.35, 22.96, 14.40 ppm; Elemental analysis: calcd (%) for $C_{40}H_{55}NO_2$: C 82.57, H 9.53, N 2.41; found: C 82.37, H 9.72, N 2.52.

***N,N*-Bis(4-*tert*-butylphenyl)-4-(*p*-iodophenylethynyl)aniline (E1).** Synthesized from **D1** by the same procedure as described for **A1**. Yield: 63%; mp 204 °C; IR (KBr, cm^{-1}): 2214; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.7 Hz, 2H), 7.32 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.8 Hz, 4H), 7.22 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 8.8 Hz, 4H), 6.96 (d, J = 8.7 Hz, 2H), 1.32 ppm (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.70, 146.79, 144.53, 137.65, 133.16, 132.63, 126.44, 124.96, 123.54, 121.34, 114.70, 93.67, 91.72, 87.63, 34.60, 31.67 ppm; Elemental analysis: calcd (%) for $C_{34}H_{34}IN$: C 69.98, H 5.87, N 2.40; found: C 69.92, H 5.88, N 2.38.

***N,N*-Bis(4-decyloxyphenyl)-4-(*p*-iodophenylethynyl)aniline (E2).** Synthesized from **D2** by the same procedure as described for **A1**. Yield: 61%; IR (KBr, cm^{-1}): 2210; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.9 Hz, 2H), 7.20 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.8 Hz, 4H), 6.83 (d, J = 8.8 Hz, 4H), 6.82 (d, J = 8.9 Hz, 2H), 3.93 (t, J = 6.6 Hz, 4H), 1.77 (m, 4H), 1.30 (m, 28H), 0.88 ppm (t, J = 6.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.20, 149.30, 140.07, 137.62, 133.10, 132.60, 127.38, 123.65, 119.13, 115.56, 113.40, 93.49, 91.88, 87.35, 68.48, 32.13, 29.82, 29.80, 29.64, 29.57, 29.56, 26.31, 22.92, 14.36 ppm; Elemental analysis: calcd (%) for $C_{46}H_{58}INO_2$: C 70.48, H 7.46, N 1.79; found: C 70.48, H 7.53, N 1.80.

4-(4-Diphenylaminophenylethynyl)benzonitrile (1a). Synthesized from 4-ethynylbenzonitrile[7] and 4-(diphenylamino)iodobenzene[12] by the same procedure as described for **A1**. Yield: 59%; mp 159 °C; IR (KBr, cm^{-1}): 2226, 2214; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.8 Hz, 2H), 7.56 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 9.0 Hz, 2H), 7.30 (dd, J = 8.8, 7.2 Hz, 4H), 7.12 (d, J = 8.8 Hz, 4H), 7.09 (t, J = 7.2 Hz, 2H), 7.00 ppm (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.93, 147.15, 133.00, 132.23, 132.04, 129.71, 128.91, 125.51, 124.15, 121.93, 118.91, 114.69, 111.13, 94.74, 87.39 ppm; Elemental analysis: calcd (%) for $C_{27}H_{18}N_2$: C 87.54, H 4.90, N 7.56; found: C 87.56, H 5.07, N 7.51.

4-{4-[4-(*N,N*-Diphenylamino)phenylethynyl]phenylethynyl} benzonitrile (1b). Synthesized from 4-ethynylbenzonitrile[8] and **A1** by the same procedure as described for **A1**. Yield: 49%; mp 202 °C; IR (KBr, cm^{-1}): 2228, 2206; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.50 (s, 4H), 7.38 (d, J = 8.5 Hz, 2H), 7.29 (dd, J = 7.8, 7.2 Hz, 4H), 7.12 (d, J = 7.8 Hz, 4H), 7.08 (t, J = 7.2 Hz, 2H), 7.01 ppm

(d, J = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.47, 147.30, 132.82, 132.31, 132.28, 131.92, 131.68 129.66, 128.28, 125.34, 124.74, 123.94, 122.26, 121.67, 118.73, 115.63, 111.81, 93.80, 92.56, 89.52, 88.41 ppm; Elemental analysis: calcd (%) for $C_{35}H_{22}N_2$: C 89.33, H 4.71, N 5.95; found: C 89.30, H 4.60, N 5.91.

1,3,5-Trichloro-2,4,6-tris-[4-(diphenylamino)phenylethynyl] benzene (I). Diisopropylamine (1.3 mL) was added to a stirred solution of $Pd_2Cl_2(PPh_3)_2$ (0.088 g, 0.13 mmol), CuI (0.024 g, 0.13 mmol), 1,3,5-trichloro-2,4,6-triiodobenzene[13] (1.4 g, 2.5 mmol) and *N,N*-diphenyl-4-ethynylaniline[14] (3.0 g, 11 mmol) in anhydrous THF (20 mL) under nitrogen. The mixture was heated at 90 °C for 24 h. After cooling, the solvent was evaporated and the mixture was purified on a silica gel column using CH_2Cl_2–hexane (1 : 5) as eluent. Yield: 0.84 g (34%); mp 230 °C; IR (KBr, cm^{-1}): 2208; ^{1}H NMR (300 Hz, $CDCl_3$): δ = 7.45 (d, J = 8.7 Hz, 6H), 7.29 (dd, J = 7.8, 7.2 Hz, 12H), 7.13 (d, J = 7.8 Hz, 12H), 7.08 (t, J = 7.2 Hz, 6H), 7.02 ppm (d, J = 8.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 148.81, 146.95, 136.89, 132.93, 129.45, 125.19, 123.83, 123.11, 121.84, 114.70, 101.32, 82.78 ppm; Elemental analysis: calcd (%) for $C_{66}H_{42}Cl_3N_3$: C 80.61, H 4.30, N 4.27; found: C 80.58, H 4.43, N 4.36.

1,3,5-Tris[4-(diphenylamino)phenylethynyl]-2,4,6-tris(4-cyanophenylethynyl)benzene (2b). A mixture of **I** (0.10 g, 0.10 mmol), 4-ethynylbenzonitrile[8] (64.0 mg, 0.50 mmol), $PdCl_2(PPh_3)_2$ (1.0 mg, 0.001 mmol), CuI (2.0 mg, 0.010 mmol), PPh_3 (8.0 mg, 0.31 mmol) and Et_3N–DMF(1 : 3) (10 mL) in a pressure tube was heated in a microwave oven for 10 s and cooled to RT to avoid overheating. This procedure was repeated 10 times. The mixture was poured into water and extracted with CH_2Cl_2. The product was purified on a silica gel column using CH_2Cl_2 as eluent. Yield: 0.030 g (24%); mp > 280 °C; IR (KBr, cm^{-1}): 2228, 2198; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.1 Hz, 6H), 7.55 (d, J = 8.1 Hz, 6H), 7.35 (d, J = 8.4 Hz, 6H), 7.32 (dd, J = 7.8, 7.2 Hz, 12H), 7.13 (t, J = 7.2 Hz, 6H), 7.12 (d, J = 7.8 Hz, 12H), 6.96 ppm (d, J = 8.4 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 149.09, 146.71, 132.69, 132.15, 132.07, 129.60, 129.25, 127.90, 125.50, 125.46, 124.32, 121.28, 118.31, 114.46, 111.98, 101.59, 96.81, 91.48, 86.42 ppm; Elemental analysis: calcd (%) for $C_{93}H_{54}N_6$: C 88.97, H 4.34, N 6.69; found: C 88.96, H 4.12, N 6.56.

1,3,5-Triethynyl-2,4,6-tris{2,5-bis(2-ethylhexyloxy)-4-[4-(diphenylamino)phenyl-ethynyl]phenylethynyl}benzene (II). Synthesized from 1,3,5-triethynyl-2,4,6-tris[(trimethylsilyl) ethynyl]benzene[15] and 4 equiv. of **B3** by the same procedure as described for **A1**, followed by the deprotection of TMS with $Bu_4N^+F^-$ (TBAF) in THF. Yield: 31;. mp 69 °C; IR (KBr, cm^{-1}): 2195; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.7 Hz, 6H), 7.28 (t, J = 7.8 Hz, 12H), 7.12 (d, J = 7.8 Hz, 12H), 7.09 (s, 3H), 7.06 (t, J = 7.8 Hz, 6H), 7.01 (d, J = 8.7 Hz, 6H), 7.00 (s, 3H), 3.94 (d, J = 6.0 Hz, 6H), 3.91 (d, J = 6.0 Hz, 6H), 3.65 (s, 3H), 1.79 (m, 6H), 1.53 (m, 24H), 1.32 (m, 24H), 0.96 (t, J = 7.8 Hz, 9H), 0.93 (t, J = 7.8 Hz, 9H), 0.90 (t, J = 6.6 Hz, 9H), 0.87 ppm (t, J = 6.6 Hz, 9H); ^{13}C (75 MHz, $CDCl_3$): δ = 154.26, 153.74, 148.17, 147.40, 132.74, 130.15, 129.63, 125.98, 125.26, 123.80, 122.41, 118.03, 116.71, 116.46, 115.83, 112.92, 97.05, 95.94, 91.49, 87.09, 85.60, 80.81, 72.25, 72.09, 39.83, 39.60, 30.88, 30.54, 29.94, 29.40, 29.27, 24.21, 23.95, 23.32, 23.31, 14.35, 11.52, 11.25; Elemental analysis: calcd (%) for $C_{144}H_{153}N_3O_6$: C 85.55, H 7.63, N 2.08; found: C 85.62, H 7.83, N 2.06.

1,3,5-Tris-{2,5-bis-(ethylhexyloxy)-4-[4-(diphenylamino)phenylethynyl]phenylethynyl}-2,4,6-tris-[4-(4-cyanophenylethynyl) phenylethynyl]benzene (3a). Synthesized from **II** and 6 equiv. of **A2** by the same procedure as described for **2b**. Yield: 41%; mp 96 °C; IR (KBr, cm^{-1}): 2226, 2195; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, J = 8.4 Hz, 6H), 7.62 (d, J = 8.1 Hz, 6H), 7.59 (d, J = 8.4 Hz, 6H), 7.46 (d, J = 8.1 Hz, 6H), 7.39 (d, J = 8.7, 6H), 7.30 (t, J = 7.8 Hz, 12H), 7.13 (d, J = 7.8 Hz, 12H), 7.09 (s, 3H), 7.08 (s, 3H), 7.07 (t, J = 7.8 Hz, 6H), 7.02 (d, J = 8.7 Hz, 6H), 3.86 (d, J = 5.7 Hz, 6H), 3.75 (d, J = 5.7 Hz, 6H), 1.75 (m, 6H), 1.52 (m, 24H), 1.26 (m, 24H), 0.92, (t, J = 7.2 Hz, 9H), 0.83 (t, J = 6.6 Hz, 9H), 0.78 (t, J = 6.6 Hz, 9H), 0.74 ppm (t, J = 7.2 Hz, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 154.20, 153.77, 148.05, 147.13, 132.49, 132.25, 132.09, 132.04, 131.60, 129.42, 128.08, 127.93, 126.99, 125.08, 124.00, 123.66, 122.46, 122.09, 118.45, 117.39, 116.65, 116.08, 115.39, 113.25, 111.70, 98.91, 96.93, 95.90, 93.36, 91.86, 89.88, 89.76, 85.22, 73.00, 71.78, 39.59, 39.14, 30.64, 30.38, 29.69, 29.15, 29.06, 23.96, 23.69, 23.06, 23.02, 14.06, 11.27, 10.86 ppm; Elemental analysis: calcd (%) for $C_{189}H_{174}N_6O_6$: C 86.46, H 6.68, N 3.20; found: C 86.42, H 6.65, N 3.02.

1,3,5-Triethynyl-2,4,6-tris(4-{4-[*N,N*-bis(4-*tert*-butylphenyl) amino]phenylethynyl}phenylethynyl)benzene (III). Synthesized from 1,3,5-triethynyl-2,4,6-tris[(trimethylsilyl)ethynyl]benzene[15] and 4 equiv. of **E1** by the same procedure as described for **II**, followed by the deprotection of TMS with $Bu_4N^+F^-$ (TBAF) in THF. Yield: 23%; mp > 280 °C; IR (KBr, cm^{-1}): 2204; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.5 Hz, 6H), 7.50 (d, J = 8.5 Hz, 6H), 7.36 (d, J = 8.8 Hz, 6H), 7.28 (d, J = 8.7 Hz, 12H), 7.04 (d, J = 8.7 Hz, 12H), 6.98 (d, J = 8.8 Hz, 6H), 3.78 (s, 3H), 1.32 ppm (s, 54H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.76, 146.82, 144.53, 132.72, 132.19, 131.57, 129.73, 126.45, 126.28, 125.00, 124.89, 122.05, 121.31, 114.70, 99.89, 92.90, 88.41, 88.18, 80.49, 77.46, 34.61, 31.67; Elemental analysis: calcd (%) for $C_{120}H_{105}N_3$: C 90.70, H 6.66, N 2.64; found: C 90.62, H 6.46, N 2.68.

1,3,5-Triethynyl-2,4,6-tris(4-{4-[*N,N*-bis(4-decyloxyphenyl) amino]phenylethynyl}phenylethynyl)benzene (IV). Synthesized from 1,3,5-triethynyl-2,4,6-tris[(trimethylsilyl)ethynyl]benzene[15] and **E2** by the same procedure as described for **II**. Yield: 27%; mp 54 °C; IR (KBr, cm^{-1}): 2203; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.0 Hz, 6H), 7.48 (d, J = 8.0 Hz, 6H), 7.30 (d, J = 8.3 Hz, 6H), 7.06 (d, J = 8.3 Hz, 12H), 6.84 (d, J = 8.3 Hz, 12H), 6.83 (d, J = 8.3 Hz, 6H), 3.93 (t, J = 6.5 Hz, 12H), 3.77 (s, 3H), 1.77 (m, 12H), 1.28 (m, 84H), 0.89 ppm (t, J = 6.8 Hz, 18H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.23, 149.36, 140.07, 132.72, 132.17, 131.51, 129.75, 127.42, 126.25, 125.02, 121.94, 119.11, 115.59, 113.42, 99.93, 93.11, 88.17, 87.46, 80.51, 77.46, 68.48, 32.15, 29.84, 29.82, 29.67, 29.59, 29.58, 26.34, 22.94, 14.38; Elemental analysis: calcd (%)

for $C_{156}H_{177}N_3O_6$: C 85.55, H 8.15, N 1.92; found: C 85.38, H 8.35, N 1.82.

1,3,5-Tris-(4-{4-[*N*,*N*-bis(4-*tert*-butylphenyl)amino]phenylethynyl}phenylethynyl)-2,4,6-tris-[4-(4-cyanophenylethynyl)phenylethynyl]benzene (3b). Synthesized from **III** and 6 equiv. of **A2** by the same procedure as described for **2b**. Yield: 33%; mp > 280 °C; IR (KBr, cm^{-1}): 2228, 2212; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54 (d, J = 8.7 Hz, 6H), 7.48 (d, J = 8.7 Hz, 6H), 7.43 (d, J = 8.4 Hz, 6H), 7.38 (s, 12H), 7.36 (d, J = 8.7, 6H), 7.31 (d, J = 8.8 Hz, 6H), 7.30 (d, J = 8.8 Hz, 12H), 7.04 (d, J = 8.8 Hz, 12H), 6.92 (d, J = 8.8 Hz, 6H), 1.33 ppm (s, 54H); Elemental analysis: calcd (%) for $C_{165}H_{126}N_6$: C 90.38, H 5.79, N 3.83; found: C 90.39, H 5.71, N 3.83.

1,3,5-Tris-(4-{4-[*N*,*N*-bis(4-decyloxyphenyl)amino]phenylethynyl}phenylethynyl)-2,4,6-tris-[4-(4-cyanophenylethynyl)phenylethynyl]benzene (3c). Synthesized from **IV** and 6 equiv. of **A2** by the same procedure as described for **2b**. Yield: 47%; mp 170 °C; IR (KBr, cm^{-1}): 2226, 2204; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.4 Hz, 6H), 7.44 (d, J = 8.4 Hz, 6H), 7.38 (d, J = 8.5 Hz, 6H), 7.35 (s, 12H), 7.30 (d, J = 8.5, 6H), 7.26 (d, J = 8.7 Hz, 6H), 7.08 (d, J = 9.0 Hz, 12H), 6.86 (d, J = 9.0 Hz, 12H), 6.80 (d, J = 8.7 Hz, 6H), 3.95 (t, J = 6.5 Hz, 12H), 1.79 (m, 12H), 1.29 (m, 84H), 0.89 ppm (t, J = 6.8 Hz, 18H); Elemental analysis: calcd (%) for $C_{201}H_{198}N_6O_6$: C 86.41, H 7.14, N 3.01; found: C 86.41, H 7.35, N 3.02.

Spectroscopic measurements

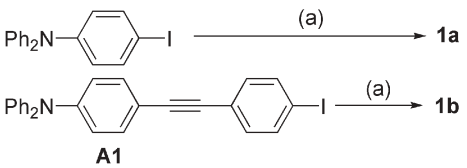
All spectroscopic measurements were performed on THF solutions. Absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer, and the fluorescence spectra were obtained with a Amico Bowman series 2 luminescence spectrometer. The first hyperpolarizabilities of **1–3** were measured in THF by the frequency-resolved HRS experiments following a previously described protocol.[6,7]

3. Results and discussion

Synthesis

Compound **2a** was available from a previous study.[3j] Compounds **1a** and **1b** were synthesized by the Sonogashira coupling of *p*-diphenylaminoiodobenzene and 4-[4-(diphenylamino)phenylethynyl]iodobenzene (**A1**) with *p*-cyanophenylacetylene, respectively (Scheme 2).

Synthesis of the other compounds is summarized in Scheme 3. Compound **2b** was synthesized by the Sonogashira coupling of 1,3,5-trichloro-2,4,6-triiodobenzene with *p*-diphenylaminophenylacetylene to obtain the intermediate **I**, followed by the coupling of **I** with *p*-cyanophenylacetylene under microwave conditions. To synthesize **3a**, 1,3,5-tri(ethynyl)-2,4,6-tris(trimethylsilylethynyl)benzene was reacted with 4-[(*p*-diphenylaminophenyl)ethynyl]-2,5-bis(2-ethylhexyloxy)iodobenzene and the trimethylsilyl groups were removed by treatment with TBAF. The intermediate **II** was then reacted with *p*-[(*p*-cyanophenyl)ethynyl]iodobenzene to obtain the desired product. Compounds **3b** and **3c** were synthesized by the same procedure as described for **3a**, except that *p*-[di(arylaminophenyl)ethynyl]iodobenzene was used in place of 4-[(*p*-diphenylaminophenyl)ethynyl]-2,5-bis(2-ethylhexyloxy)iodobenzene. Except for **3b** and **3c**, whose solubility was too low to obtain the ^{13}C NMR spectra, the structures of the new compounds were unambiguously confirmed by ^1H and ^{13}C NMR, IR, and elemental analysis.

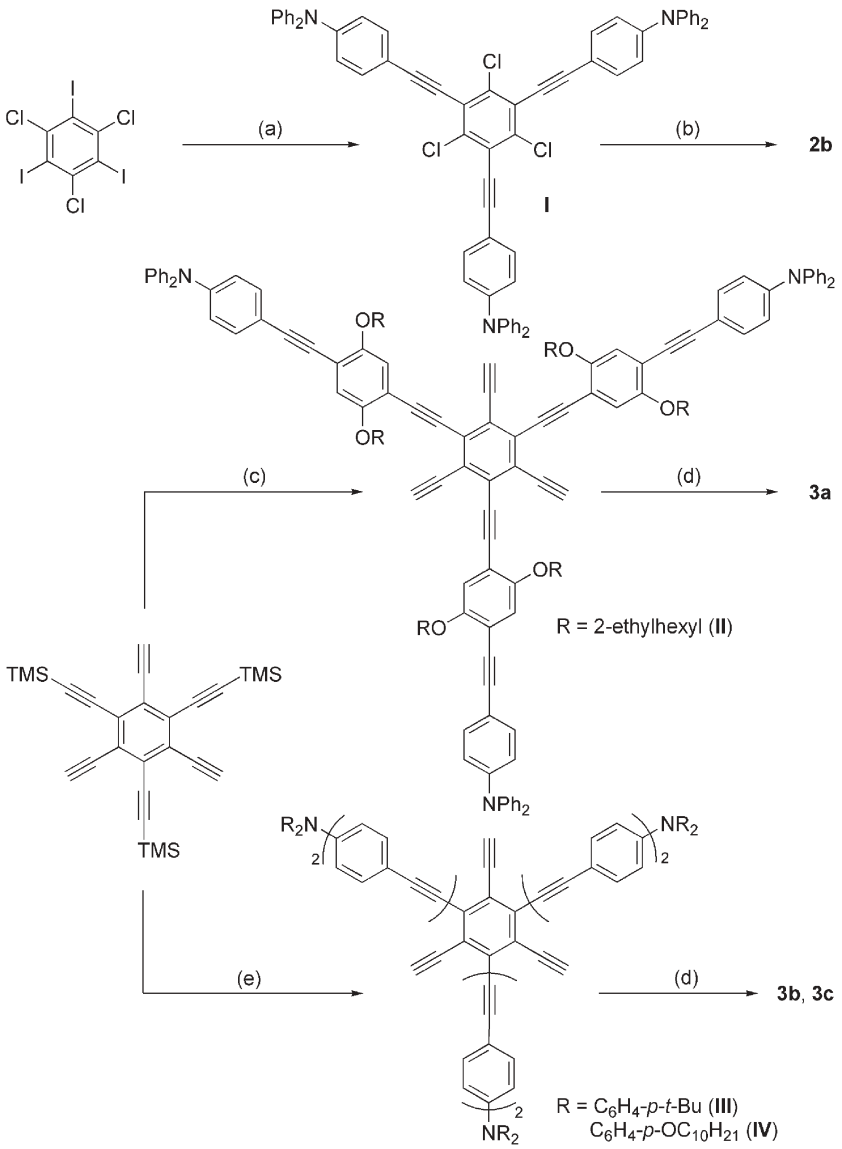


Scheme 2 *Reagents and conditions*: (a) *p*-$CNC_6H_4C{\equiv}CH$/$Pd(PPh_3)_2Cl_2$/CuI/Et_3N/THF.

Linear optical properties

Fig. 1 shows that the λ_{max} values of **1a** and **1b** are nearly the same. This indicates the poor conjugation ability of the C≡C bond for the intramolecular charge transfer (ICT). However, the oscillator strength (f), which is proportional to the square of the transition moment (μ_{10}), increases with the conjugation length. When the molecular structure is changed from **1a** to **2a**, λ_{max} is red-shifted by more than 100 nm, indicating that ICT increases significantly as the three dipolar units share the central phenyl group as the conjugation path. Also, the oscillator strength increases by 3-fold from **1a** to **2a** (Table 1). Hence, **2a** is almost the same as three molecules of **1a** in terms of transition dipole moment. On the other hand, **2b** shows a smaller red-shift (60 nm) and a modest increase in the oscillator strength (2 fold) in comparison to **1b**, indicating that the effect of sharing the central phenyl group becomes less important as the conjugation length increases. The net result of these effects is the decrease in λ_{max} from **2a** to **2b** without changing the oscillator strength (Table 1). When the conjugation length is further increased to **3a–c**, the λ_{max} decreases with concomitant increase in the localized bands (Fig. 1). The poorly conjugating C≡C bonds seem to have attenuated the ICT to distort the structures and break the symmetry of the molecules. Consistently, **3a** with bulky substituents exhibits more distinct localized bands (Fig. 1).

The fluorescence spectra of **1–3** are displayed in Fig. 2. Compared with the absorption spectra, λ_{max}^{fl} of **1b** shows a greater bathochromic shift and hence a larger Stokes shift in comparison to **1a**, indicating that the ICT is more efficient in the excited than in the ground state (Table 1). Interestingly, the Stokes shifts of **1a**, **2a**, and **2b** are nearly the same, that is, the energy gap between the ground and the Franck–Condon states is more or less the same. However, a further increase in the conjugation length to **3a–c** results in a large increase in the Stokes shift, probably because the excited state is more planar than the ground state. Also, λ_{max}^{fl} of **3a** is shorter than **3b** and **3c**, indicating that the former is more distorted in the excited state. Except for **3c**, which emits little fluorescence, all compounds emitted strong fluorescence with the fluorescence lifetime ranging from 3 to 6 ns. The much weaker fluorescence of **3c** can be attributed to the long chain alkoxy group, which may facilitate the nonradiative pathways.

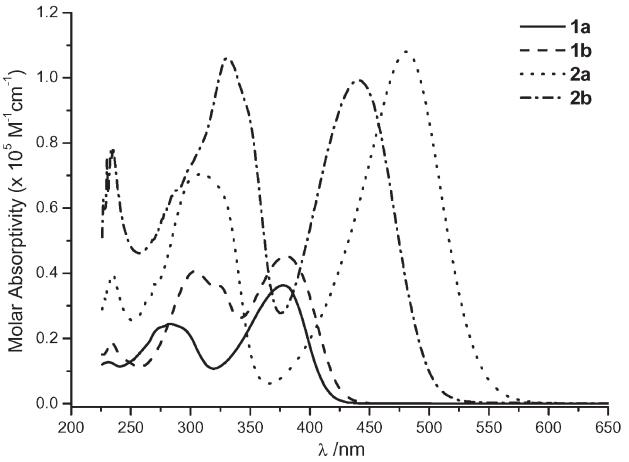


Scheme 3 *Reagents and conditions*: (a) *p*-$Ph_2NC_6H_4C{\equiv}CH$/Cat(I)/THF, 90 °C; (b) *p*-$CNC_6H_4C{\equiv}CH$/Cat(II)/PPh_3/DMF, microwave; (c) i) *p*-$Ph_2NC_6H_4C{\equiv}CC_6H_2$-2,5-$(Oeh)_2$-4-I/Cat(II)/THF/RT, ii) TBAF/THF; (d) *p*-$CNC_6H_4C{\equiv}CC_6H_4$-*p*-I/Cat(II)/PPh_3/DMF, microwave; (e) i) *p*-$R_2NC_6H_4C{\equiv}CC_6H_4$-*p*-I [R = C_6H_4-*p*-*tert*-Bu (**III**), C_6H_4-*p*-$OC_{10}H_{21}$ (**IV**)]/Cat(II)/THF, RT, ii) TBAF/THF. Oeh: 2-ethylhexyloxy; Cat(I): $Pd_2Cl_2(PPh_3)_2$/CuI/$(i\text{-}Pr)_2NH$; Cat(II): $Pd_2Cl_2(PPh_3)_2$/CuI/Et_3N.

Nonlinear optical properties

Since octupolar molecules do not possess a dipole moment, hyper-Rayleigh scattering (HRS) is the only measurement technique that is capable of determining the molecular second-order nonlinear polarizability (or first hyperpolarizability). HRS is the second-order analogue of the linear Rayleigh scattering process.[16] In HRS, the signal is comprised of incoherently scattered photons at the second-harmonic wavelength. Multi-photon fluorescence (MPF) can also result in such photons at exactly the same wavelength. Different techniques have been proposed to discriminate between HRS and MPF. In the spectral domain, the narrow HRS peak can be isolated from the broad MPF band by background subtraction. In the time domain, a narrow and early temporal gate around the infrared laser pulse can largely suppress the long-lived and time-delayed MPF. We have implemented a frequency-domain technique that relies on the demodulation (decrease in amplitude) and phase delay between HRS and MPF. By measuring the amplitude and phase as a function of amplitude modulation frequency, it is possible to extract an accurate value for the hyperpolarizability that is not over-estimated due to MPF. By simultaneously analyzing the frequency-dependent demodulation and phase data towards the hyperpolarizability value, the fluorescence contribution and the fluorescence lifetime, a relatively precise value can also be obtained.

We have performed frequency-resolved HRS experiments in THF at two different near-infrared wavelengths. At 800 nm, the reference is the octupolar β_{yyy} of crystal violet in methanol, 340×10^{-30} esu.[6a] At 1300 nm, we used the dipolar β_{zzz} of Disperse Red 1 of 54×10^{-30} esu in chloroform as the



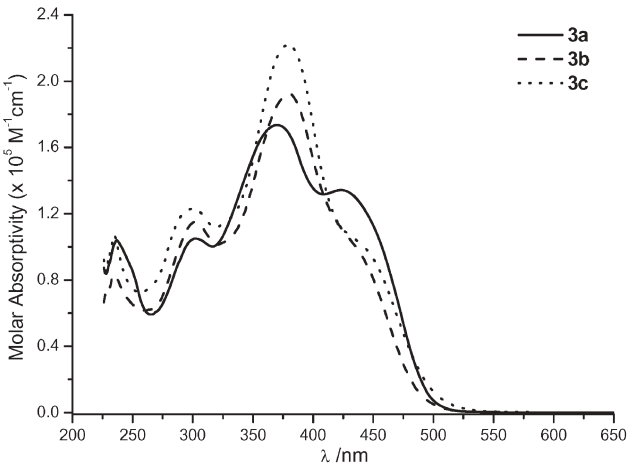
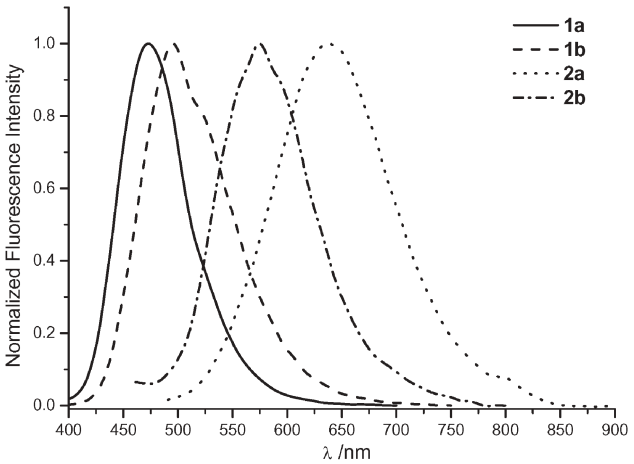


Fig. 1 Molar absorptivity spectra for **1–3**.



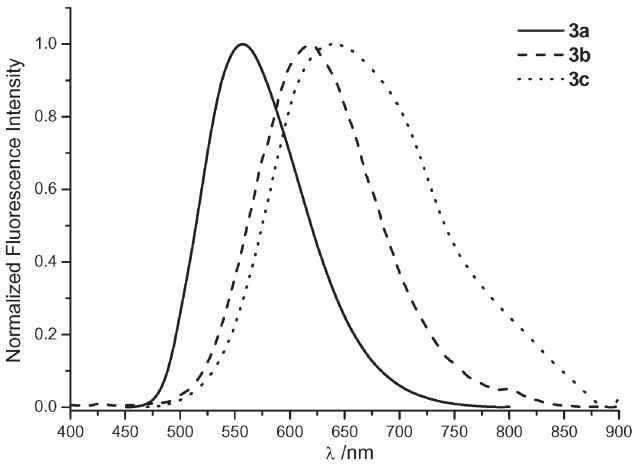


Fig. 2 Fluorescence spectra for **1–3**.

reference.[6b] At this wavelength, the difference in symmetry between the reference and the octupolar compounds as well as the local field corrections factors from the difference in refractive index between THF and methanol or chloroform were taken into account. The femtosecond pulses at 1300 nm are derived from a femtosecond optical parametric oscillator (Spectra-Physics, model OPAL), pumped by an 800 nm femtosecond laser (Spectra-Physics, model Tsunami). Hence, the pulses at 1300 nm have lower peak power. Also, the resonance enhancement factors for the first hyperpolarizability values at 800 nm are larger than at 1300 nm. Therefore, the HRS measurements at 1300 nm are more difficult and result in a less precise result. However, they do confirm the results obtained at 800 nm. The results for the linear and nonlinear optical properties are given in Table 1.

For the dipolar model compound **1a**, we did observe significant MPF at 400 nm. This is clearly seen from Fig. 3, which shows the demodulation (decrease in amplitude for higher frequencies) and the phase shift between the MPF and HRS signals. At 480 MHz, the MPF contribution is

Table 1 Linear and nonlinear optical properties of dipolar and octupolar molecules (**1–3**)

	λ_{max}[a]/nm	λ_{max}^{fl}[a]/nm	$\Delta\nu_{ST}$[b]	f[c]	β_{800}[d]	$\beta_{0,800}$[d,e]	τ/ns[f]	β_{1300}[d]	$\beta_{0,1300}$[d,e]	τ/ns[f]
1a	378	473	5313	0.46	1340 ± 70	111 ± 6[g]	2.7 ± 0.4	nm[h]	nm[h]	nm[h]
1b	380	495	6114	0.73	2260 ± 100	170 ± 7[g]	3.0 ± 3.5	nm[h]	nm[h]	nm[h]
2a	481	637	5135	1.4	450 ± 45	128 ± 13[i]	nf[j]	125 ± 90	50 ± 36	3 ± 3
2b	441	575	5284	1.5	500 ± 50	76 ± 8[i]	nf[j]	55 ± 70	27 ± 35	6 ± 4
3a	371	557	9001	3.7	1750 ± 175	192 ± 19	nf[j]	170 ± 70	106 ± 40	5 ± 2
3b	382	619	10 023	4.1	1760 ± 175	120 ± 12	nf[j]	90 ± 70	60 ± 40	5 ± 3
3c	379	640	10 760	4.0	1125 ± 110	90 ± 10	nf[j]	nm[h]	nm[h]	nm[h]

[a] λ_{max} of the one-photon absorption and emission spectra in nm. [b] Stokes shift in cm^{-1} $(1/\lambda_{max} - 1/\lambda_{max}^{fl})$. [c] Oscillator strength estimated by the relationship: $f = 4.319 \times 10^{-9} \cdot \varepsilon \cdot \nu_{1/2}$, where $\nu_{1/2}$ is the band width at half-height in THF. [d] 10^{-30} esu. [e] Static hyperpolarizability corrected by using two- and three-level models for the dipolar and octupolar molecules, respectively.[1a,18] [f] Fluorescence lifetime. [g] β_{zzz} values calculated from the relationships, $<\beta^2> = (6/35)\beta_{zzz}^2$ are 268 $\times$ 10^{-30} and 411 $\times$ 10^{-30} esu for **1a** and **1b**, respectively. [h] Not measurable. [i] β_{yyy} values calculated from the relationships, $<\beta^2> = (8/21)\beta_{yyy}^2$ are 207 $\times$ 10^{-30} and 123 $\times$ 10^{-30} esu for **2a** and **2b**, respectively. [j] No fluorescence contribution to the HRS observed.

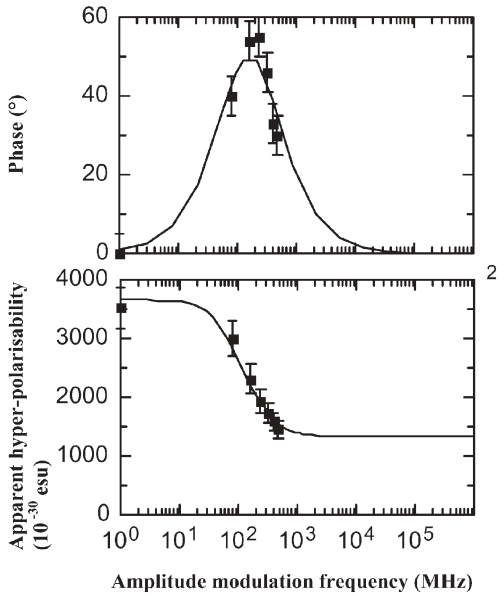


Fig. 3 Demodulation (bottom) and phase (top) for the femtosecond HRS measurement at 800 nm for compound **1a** as a function of amplitude modulation frequency.

completely demodulated and the fluorescence-free dynamic hyperpolarizability value [(1340 ± 70) × 10^{-30} esu] is obtained. Therefore, a precise value for the fluorescence lifetime [(2.7 ± 0.4) ns] could be determined. From the much smaller MPF contribution at 400 nm for **2a**, it was not possible to do so, but the resulting value for the dynamic hyperpolarizability [(450 ± 100) × 10^{-30} esu] is more precise. Because of the absence of MPF and the small resonance enhancement at 1300 nm, no values could be obtained at this longer fundamental wavelength. For comparison, $\beta(0)$ values of **1b** and **2a** measured by the nanosecond pulses are 95 × 10^{-30} and 273 × 10^{-30} esu, respectively. The larger value of 170 × 10^{-30} esu for **1b** measured by the femtosecond pulses may be because of the shorter wavelength of the fundamemtal wave,[17] or imperfect resonance correction (*vide infra*). On the other hand, the larger value of **2a** measured with nanosecond pulses may be due to the MPF contribution (*vide infra*).

The first hyperpolarizability of a D_3 symmetric molecule can be expressed by the three-level model [eqn. (1)], where μ_{10} is the transition moment between the ground and degenerate first excited CT state, μ_{21} is the transition moment connecting the degenerate excited states, ω_{10} is the CT energy and ω is the energy of the incident laser light.[1a] The equation is identical to that of the two-level model of molecular nonlinearity for the dipoles if μ_{21} 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.[18]

$$\beta_{yyy} = \frac{1}{\hbar^2} \times \frac{\mu_{10}^2 \mu_{21}}{\omega_{10}^2} \times \frac{\omega_{10}^4}{(\omega_{10}^2 - 4\omega^2)(\omega_{10}^2 - \omega^2)} \quad (1)$$

Table 1 shows that there is a sizeable enhancement of the first hyperpolarizability with the extension of the conjugation length from **2a** to **3a**. Owing to the similarity in wavelength of maximal absorption, the static hyperpolarizability values (without resonance enhancement) show the same trend. Since the resonance energy is not shifting significantly, this enhancement cannot be attributed to a more efficient conjugation but to the large increase in oscillator strength (Table 1).

For the octupolar compounds **2a** and **2b**, no MPF was observed at 400 nm. A constant hyperpolarizability value was observed for increasing modulation frequencies. For these compounds, we could perform additional HRS experiments at 1300 nm, but at two modulation frequencies only. Because of the small hyperpolarizability values and the large MPF contributions with nanosecond lifetime, the signal is already demodulated at the second modulation frequency (80 MHz). From the resulting very limited number of data, the precision in hyperpolarizability and lifetime value is very low, but these data confirm the results based on the much better data at 800 nm. While the dynamic hyperpolarizability values for **2a** and **2b** at 800 nm are similar, the static values, after correction for the resonance enhancement, show the opposite trend when compared to **1a** and **1b**. The octupolar version **2b** of the dipolar model compound **1b** has a smaller hyperpolarizability value than **2a**. This corresponds well with the smaller wavelength of maximal absorption, pointing towards less efficient conjugation for the molecularly more elaborated octupole **2b** [eqn. (1)]. For comparison, β_{zzz} of 1,3,5-tris(*p*-diethylaminophenylethynyl)-2,4,6-tris(*p*-nitrophenylethynyl)benzene measured by the nanosecond pulses is 1670 × 10^{-50} Cm^3 V^{-2}.[2g] After conversion from SI to esu unit and considering the difference in the β values of the reference,[2e,2g,19] the $\beta(0)_{zzz}$ value becomes 228 × 10^{-50} esu, which is approximately 2-fold larger than $\beta(0)_{zzz}$ = 123 × 10^{-50} esu measured for **2b** in this work (*vide infra*). The larger value of $\beta(0)_{zzz}$ for the former is consistent with the larger λ_{max} (453 nm *vs.* 441 nm), but not with the smaller ε (10 100 vs. 99 300). To make a direct comparison, a further study is needed to measure the first hyperpolarizability by the femtosecond pulses.

For the most elaborated octupolar series **3a**, **3b** and **3c**, no MPF was observed at 400 nm, while for **3a** and **3b**, as shown for **2a** and **2b**, low-precision data at 1300 nm confirm the trend. For **3c** at 1300 nm, no signal could be obtained because the MPF was very weak. It is observed from linear (one-photon) fluorescence experiments that **3c** has a very weak emission. Very large dynamic hyperpolarizabilities are observed at 800 nm, largely due to the strong resonance enhancement. The enhancement factors are very similar, as a consequence of the similar wavelength of maximal absorption for **3a**, **3b** and **3c**. In terms of linear optical properties, these three molecules behave very similarly, with the exception of the quenching of the fluorescence in **3c**. However, in terms of second-order nonlinear optical properties, we observe a significant improvement for **3a**. Because this compound is more distorted than others, the symmetry may be broken to induce dipolar contribution and increase the first hyperpolarizability.

The β_{zzz} values of **1a** and **1b**, calculated from the relationship $<\beta^2>$ = (6/35)β_{zzz}^2, are 268 × 10^{-30} and 411 × 10^{-30} esu, respectively.[20] Similarly, β_{yyy} values calculated from $<\beta^2>$ = (8/21)β_{yyy}^2 are 207 × 10^{-30} and 123 × 10^{-30} esu for **2a** and **2b**, respectively (Table 1).[20] Hence, β_{yyy}(**2a**)/β_{zzz}(**1a**) = 0.77 and β_{yyy}(**2b**)/β_{zzz}(**1b**) = 0.30. The smaller ratio in the latter is apparently due to the large decrease in β from **2a** to **2b**

(*vide supra*). However, it is not readily apparent why both values are smaller than the reported value of β_{yyy}(**2a**)/β_{zzz}(**1a**) = 3.9 based on the nanosecond experiment.[3j] Furthermore, this ratio is consistent with the large bathochromic shift and 3-fold increase in the oscillator strength from **1a** to **2a** (Table 1). The dichotomy could be explained if β_{zzz}(**1a**) and β_{zzz}(**1b**) measured by the femtosecond pulses are overestimated. As can be seen in Table 1, $\beta_{0,1300}$ of **2a** and **2b** are 50×10^{-30} and 27×10^{-30} esu, respectively, whereas those of **1a** and **1b** are not measurable. This implies that the former may be a more efficient NLO-phore than the latter. In sharp contrast, $\beta_{0,800}$ values of **1a** and **1b** are either comparable to or much larger than those of **2a** and **2b**. This raises a strong possibility that the $\beta_{0,800}$ values of **1a** and **1b** may be overestimated by resonance enhancement, that is, the resonance correction based on the three-level model may not be perfect. Note that the resonance enhancement factor of **1a** and **1b** are 12 and 13, respectively. Alternatively, it may also be possible that β_{yyy}(**2a**) determined by the nanosecond experiment may be overestimated by MPF, despite the base line correction,[12] to give rise to a large β_{yyy}(**2a**)/β_{zzz}(**1a**) value (*vide supra*).

4. Conclusions

We have studied linear and nonlinear optical properties of a variety of newly synthesized dipolar and octupolar molecules containing C≡C bonds as the conjugation bridge. The $\beta(0)$ value of dipole increased with conjugation length, whereas that of the octupole decreased from **2a** to **2b** with concomitant decrease in λ_{max}. The λ_{max} further decreased by the increase in the conjugation length from **2b** to **3a–c**, but $\beta(0)$ increased because of the larger oscillator strength. Moreover, **3a**, with the most distorted structure, shows the largest $\beta(0)$, probably because of the dipolar contribution. Among the octupoles studied in this work, $\beta(0)$/MW is optimized in **2a**. Owing to the similarity in structure to 1,3,5-tricyano-2,4,6-tris(*p*-diethylaminostyryl)benzene, **2a** may produce noncentrosymmetric crystals. Therefore, a further study is needed to develop octupolar materials with large SHG based on this molecule. Furthermore, the smaller β_{yyy}/β_{zzz} ratio than the reported values indicate that the resonance correction based on the three-level model in the femtosecond measurement and the base line correction in the nanosecond measurement may not be perfect.

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