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Propeller-Shaped Octupolar Molecules Derived from Triphenylbenzene for Nonlinear Optics: Synthesis and Optical Studies

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Nanoscale propeller-shaped conjugated molecules based on a central triphenylbenzene core bearing three oligomeric phenylene−vinylene branches having either electron-donating *or* electron-withdrawing peripheral groups have been synthesized. These octupolar derivatives show definite solvatochromic behavior (in absorption and even more in emission), which reveals a multidimensional intramolecular charge transfer (MDICT) taking place between the center and the periphery of the molecules. Correlations between the solvatochromism magnitude and the nonlinear responses (first-order hyperpolarizabilities β) of such derivatives have been established. Accordingly, boosting of the MDICT phenomenon (by means of elongation of the branches and benefit from appropriate peripheral groups) allowed achievement of very high hyperpolarizabilities while maintaining wide transparency in the visible region (up to $||\beta|| = 810 \times 10^{-30}$ esu for $\lambda_{\max} = 377$ nm).

Introduction

The field of molecular nonlinear optics (NLO) has attracted increasing attention over the past 20 years,[1−3] owing to its connection with fundamental issues such as charge transfer and higher order polarizabilities or conjugation, as well as to numerous applications in various fields such as telecommunications,[4] optical data storage and information processing,[5] microfabrication,[6−8] biological sensors, and so forth.[9,10] Second-order NLO effects such as second-harmonic generation (SHG) or electro-optic modulation require the design of chromophores that exhibit enhanced quadratic responses. Molecular engineering of one-dimensional (1-D) chromophores has been particularly active, leading to push−pull derivatives displaying giant off-resonance first-order (β)[11,12] hyperpolarizabilities. Such chromophores however display an intense absorption band in the visible region due to a strong intramolecular charge transfer (ICT) transition. Novel strategies were thus needed for optimizing the efficiency-transparency trade-off, especially in the context of the search for effective materials for SHG in the visible. In this perspective, the octupolar route pioneered by Lehn, Zyss, and coworkers[13,14] offers a wide range of possibilities toward enhanced NLO responses.

There has been in recent years a growing number of studies devoted to novel multidimensional and multipolar structures taking advantage of the tensorial nature of hyperpolarizabilities.[3,15,16] With 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) as the prototypical structure,[13,17−19] a variety of octupolar molecules with a two-dimensional (2D) character and a 3-fold rotational

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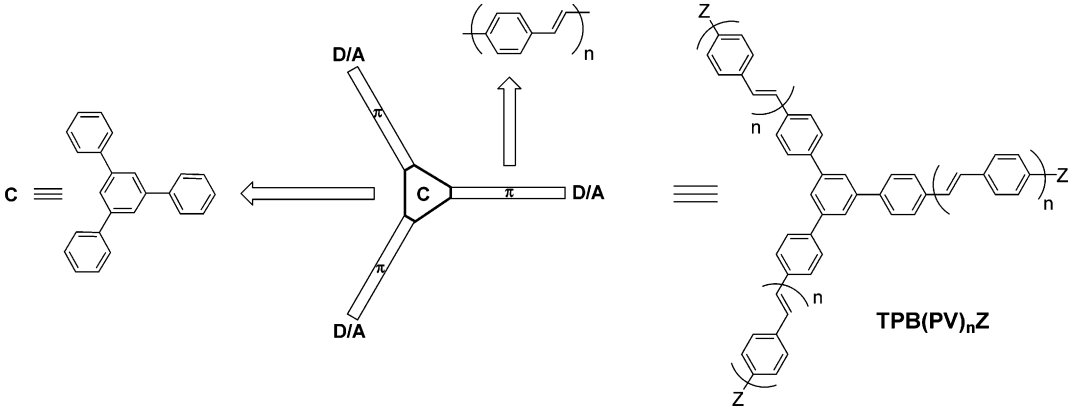

Figure 1. Molecular design of propeller-shaped octupolar molecules **TPB(PV)$_n$Z** derived from a triphenylbenzene core (**TPB**) functionalized with three phenylene–vinylene oligomers **(PV)$_n$** conjugated arms (n = 1, 2), bearing either electron-releasing or electron-withdrawing end groups (**Z** = **D** or **A**).

symmetry axis have been investigated, such as those derived from trisubstituted[20,21] and hexasubstituted[19,22–27] benzenes, 1,3,5-triazine,[20,22,23,28–31] triarylamines,[32–35] hexaazatriphenylene,[36] calixarenes,[37] tricyanomethanide anion,[38] crystal violet[19,21,39,40] and other triarylmethyl cations,[31,41] cyclopropenylium,[19] and cyanines.[22,42] 3D octupolar molecules of approximated tetrahedral symmetry have also been designed,[35,43–48] as well as subphthalocyanines,[49,50] 2D and 3D organometallic complexes,[36,51–56] and molecularly bridged nanoparticle arrays.[57]

To achieve improved nonlinearity-transparency tradeoff while taking benefit from the multidimensional tensorial nature of the β tensor, we have prepared and investigated nanoscale propeller-shaped molecules that combine wide transparency in the visible region and enhanced first-order hyperpolarizabilities in connection with a 2-D intramolecular charge transfer taking place between the center and the periphery of the molecules.[58,59] In this paper we describe in detail their design, synthesis, and optical properties (absorption,

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fluorescence, quadratic optical nonlinearities), in relation to the transparency-nonlinearity tradeoff issue. Their molecular design is based on the grafting of three conjugated branches bearing either an electron-withdrawing or an electron-releasing tip on an ambivalent conjugated core that can act either as a (weak) donor or acceptor center depending on the nature of its counterpart peripheral substituents (Figure 1). By using tris-donor or tris-acceptor substituted molecules derived from a 1,3,5-triphenylbenzene core, we aimed at achieving improved transparency as compared to tris-donor/tris-acceptor compounds such as molecules derived from 1,3,5-triamino-2,4,6-trinitrobenzene (TATB)[19,22−27] or 1,3,5-triazine.[22,23,31] Phenylene−vinylene oligomers were selected as conjugated rods to ensure effective electronic conjugation between the core and the periphery of the molecules while preserving suitable transparency. The triphenylbenzene core maintains large distance between the conjugated branches, thus preventing strong through-space electronic interactions between arms as well as sterical hindrances which could hamper intramolecular charge redistribution.

We hereafter present the detailed synthesis and experimental studies of the linear and nonlinear optical properties of a series of octupolar derivatives bearing different terminal groups and of various sizes (with diameter varying from 2.5 to 3.5 nm).

Experimental Section

General. Melting points were determined with a Büchi 510 capillary apparatus or a Electrothermal IA9300 digital melting point instrument. ^{1}H and ^{13}C NMR spectra were recorded at room temperature on AM 200, AM 250, AV 300, or AM 400 Bruker spectrometers; ^{1}H chemical shifts (δ) are reported in ppm relative to the protonated solvent peaks (^{1}H, $CHCl_3$ in $CDCl_3$ 7.26 ppm, CHD_2SOCD_3 in CD_3SOCD_3 2.49 ppm); ^{13}C chemical shifts are reported relative to the deuterated solvent peaks ($^{13}CDCl_3$ in $CDCl_3$ 77.0 ppm, $^{13}CD_3SOCD_3$ in CD_3SOCD_3 39.6 ppm); coupling constants (J) are given in Hz. Mass spectra (chemical ionization with NH_3 or CH_4 and positive FAB) were performed by the Service de Spectrométrie de Masse de l'Ecole Normale Supérieure (Paris) or at the Centre Régional de Mesures Physiques de l'Ouest (Rennes). Microanalyses were performed by the Service de Microanalyses de l'Université Pierre et Marie Curie (Paris) or at I.C.S.N.−C.N.R.S. (Gif-sur-Yvette). All air- or water-sensitive reactions were carried out under nitrogen. Solvents were generally dried and distilled prior to use. Column chromatography was performed on silica gel 60 (0.040−0.063 mm) Merck. Phosphonium salt **6a** was synthesized from *N*,*N*-dihexylbenzenamine, analogously to the literature procedures.[60] Phosphonium salt **6b**,[61] as well as phosphonates **7a**,[62] **7b**,[63] and **7c**,[64] were synthesized according to the respective literature procedures. Diethyl(4-nitrobenzyl)-phosphonate (**7d**) was purchased from Acros.

1,3,5-Tris(4-bromophenyl)benzene (1). 4-Bromoacetophenone (10.0 g, 50.2 mmol) and trifluoromethanesulfonic acid (90 μL, 1.00 mmol) were stirred at 140 °C without any solvent, until total conversion (3 h). The crude solid was washed with EtOH and Et_2O and then recrystallized from AcOH to afford **1** (8.09 g, 89%) as white needles: mp 261−262 °C (lit.[65] mp 262 °C, lit.[66] mp 259−262 °C). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.69 (s, 3H), 7.61 (d, J = 8.5 Hz, 6H), 7.53 (d, J = 8.5 Hz, 6H). ^{13}C NMR ($CDCl_3$, 50.32 MHz): δ 137.2, 135.6, 132.3, 129.6, 125.3, 122.0.

1,3,5-Tris(4-formylphenyl)benzene (2). To a stirred solution of **1** (5.0 g, 9.2 mmol) in anhydrous benzene (150 mL) under an atmosphere of nitrogen was slowly added *n*-BuLi (1.6 M in hexanes, 50 mL, 80 mmol) and the mixture turned violet. Then, the solution was warmed at 60 °C for 4 h. After cooling at 0 °C, the mixture was cannulated into another flask containing *N*-formylpiperidine (15 mL, 130 mmol). After being stirred for 4 h at room temperature, the yellow solution was hydrolyzed with aqueous HCl (3 N, 100 mL) and the organic layer was separated and evaporated. CH_2Cl_2 (50 mL) was added to the resulting orange oil, and this solution was washed twice with 30-mL portions of water. The organic layer was dried ($MgSO_4$) and the solvent was removed. Addition of Et_2O (50 mL) and filtration afforded **2** (2.70 g, 75%), as a white crystalline product which can be recrystallized from AcOH: mp 230−231 °C (lit[66] mp 231−232 °C). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 10.11 (s, 3H), 8.03 (d, J = 8.3 Hz, 6H), 7.91 (s, 3H), 7.88 (d, J = 8.3 Hz, 6H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 191.8, 146.3, 141.6, 135.7, 130.4, 128.0, 126.5. IR (KBr): ν 1693 cm^{-1}.

1,3,5-Tris[4-(hydroxymethyl)phenyl]benzene (3). To a solution of **2** (500 mg, 1.28 mmol) in 300 mL of CH_2Cl_2/EtOH (5/1) was added KBH_4 (105 mg, 1.94 mmol). After the solution was stirred for 4 h at room temperature, water (10 mL) was added and the mixture was concentrated to remove CH_2Cl_2 and a part of EtOH. A gummy white solid precipitated, which was redissolved in CH_2Cl_2 (50 mL). The organic layer was washed with water (2 × 20 mL) and dried ($MgSO_4$), and the solvents were removed under reduced pressure, to afford **3** in a quantitative yield. ^{1}H NMR (DMSO, 200.13 MHz): δ 7.85 (s, 3H), 7.83 (d, J = 7.9 Hz, 6H), 7.45 (d, J = 7.9 Hz, 6H), 5.26 (t, J = 5.6 Hz, 3H), 4.57 (d, J = 5.6 Hz, 6H).^{13}C NMR (DMSO, 50.32 MHz): δ 142.3, 141.7, 138.7, 127.2, 127.0, 124.1, 62.8. MS (CI, NH_3): m/z (%) 414 ([M + NH_4^+], 100), 397 ([M + H^+], 33), 379 ([M + H^+ − H_2O], 37).

1,3,5-Tris[(4-bromomethyl)phenyl]benzene (4). A solution of **3** (1.26 g, 3.2 mmol) in concentrated HBr (400 mL) was refluxed for 5 h. After the solution was cooled to room temperature, CH_2Cl_2 (100 mL) was added and the organic layer was separated, washed with 0.1 N NaOH (2 × 20 mL), and dried ($MgSO_4$). The solvent was removed to yield 1.68 g of **4** (90%). ^{1}H NMR ($CDCl_3$, 250.13 MHz): δ 7.75 (s, 3H), 7.66 (d, J = 8.1 Hz, 6H), 7.51 (d, J = 8.1 Hz, 6H), 4.58 (s, 6H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 141.8, 141.0, 137.3, 129.6, 127.7, 125.3, 33.2. MS (CI, NH_3): m/z 600 [$C_{27}H_{21}{}^{79}Br_3 + NH_4^+$], 583 [$C_{27}H_{21}{}^{79}Br_3 + H^+$], 521 [$C_{27}H_{21}{}^{79}Br_2 + NH_4^+$], 504 [$C_{27}H_{21}{}^{79}Br_2 + H^+$].

1,3,5-Tris[4-[(diethoxyphosphinyl)methyl]phenyl]-benzene (5). A solution of **4** (500 mg, 0.85 mmol) in triethyl phosphite (40 mL, 340 mmol) was stirred at 80 °C for 16 h under nitrogen. The excess triethyl phosphite was then distilled under reduced pressure. Water (25 mL) and CH_2Cl_2 (25 mL) were added. The organic layer was separated and dried ($MgSO_4$). The solvent was evaporated to yield 556 mg of **5** (86%). ^{1}H NMR ($CDCl_3$, 200.13 MHz): δ 7.76 (s, 3H), 7.65 (d, J = 8.1 Hz, 6H), 7.42 (dd, J = 8.1, 2.4 Hz, 6H), 4.10 (quint, J = 7.1 Hz, 12H), 3.22 (d, J = 21.7 Hz, 6H), 1.28 (t, J = 7.1 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75.48 MHz): δ 141.6, 139.3, 130.7 (d, J = 8.8 Hz), 130.0 (d, J = 6.6 Hz), 127.1, 124.5, 61.9 (d, J = 6.6 Hz), 33.1 (d, J = 138.4 Hz), 16.1 (d, J = 6.6 Hz). ^{31}P NMR ($CDCl_3$, 121.49 MHz): δ 26.4. HRMS (CI, CH_4): calcd for $C_{39}H_{52}O_9P_3$ ([M + H]$^+$) m/z 757.2824, found 757.2820.

4-[(1*E*)-2-[4-(Dihexylamino)phenyl]ethenyl]benzaldehyde (9a). To a solution of **6a** (1.045 g, 1.57 mmol) and

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8 (0.329 g, 1.58 mmol) in anhydrous CH_2Cl_2 (15 mL) were added *t*-BuOK (0.185 g, 1.65 mmol) and a catalytic amount of 18-crown-6 (1.2 mg). The mixture was stirred at room temperature for 24 h. The reaction mixture was filtered through a short pad of silica gel. Evaporation of the solvents afforded the crude acetal, which was hydrolyzed at room temperature for 1 h, using 10% HCl (25 mL) in THF (50 mL). Thereafter, THF was evaporated and CH_2Cl_2 was added. The two layers were separated and the organic layer was washed with aqueous $NaHCO_3$, dried (Na_2SO_4), and evaporated. The residue was dissolved in CH_2Cl_2, a catalytic amount of I_2 (1.2 mg) was added, and the solution was stirred at room temperature for 3 h under light exposure (75 W lamp). The organic layer was washed with aqueous $Na_2S_2O_3$ and dried (Na_2SO_4). After evaporation of the solvent, the crude product was purified by column chromatography (cyclohexane/CH_2Cl_2 20:80) to yield 0.517 g (84%) of **9a**. ^1H NMR ($CDCl_3$, 250.13 MHz): δ 9.96 (s, 1H), 7.83 (d, $J = 8.2$ Hz, 2H), 7.59 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 16.2$ Hz, 1H), 6.90 (d, $J = 16.2$ Hz, 1H), 6.63 (d, $J = 8.8$ Hz, 2H), 3.29 (t, $J = 7.7$ Hz, 4H), 1.60 (m, 4H), 1.32 (m, 12H), 0.91 (t, $J = 6.5$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 191.6, 148.5, 144.8, 134.4, 132.7, 130.3, 128.4, 126.1, 123.6, 121.9, 111.6, 51.1, 31.7, 27.3, 26.8, 22.7, 14.1. HRMS (CI, CH_4): calcd for $C_{27}H_{38}NO$ ($[M + H]^+$) *m/z* 392.2953, found 392.2951.

4-[(1*E*)-2-[4-(Methylsulfonyl)phenyl]ethenyl]benzaldehyde (9b). To a solution of **7c**[64] (1.00 g, 3.3 mmol) and **8** (0.748 g, 3.6 mmol) in anhydrous THF (25 mL) was added NaH (0.160 g, 60% dispersion in mineral oil). The mixture was stirred at room temperature for 24 h. Water (25 mL) was added and THF was evaporated. Extraction with CH_2Cl_2, drying ($MgSO_4$), and removal of the solvent afforded the crude acetal, which was hydrolyzed at room temperature for 2 h, using 2 M HCl (25 mL) in THF (50 mL). Thereafter, THF was evaporated and CH_2Cl_2 was added. The two layers were separated and the organic layer was washed with water, dried ($MgSO_4$), and evaporated. Digestion of the residue with Et_2O/pentane afforded 814 mg (87%) of **9b** as a white powder: mp 166−168 °C. ^1H NMR ($CDCl_3$, 200.13 MHz): δ 10.03 (s, 1H), 7.96 (d, $J = 8.4$ Hz, 2H), 7.92 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.70 (d, $J = 8.3$ Hz, 2H), 7.29 (s, 2H), 3.09 (s, 3H). HRMS (CI, CH_4): calcd for $C_{16}H_{15}O_3S$ ($[M + H]^+$) *m/z* 287.0742, found 287.0741.

General Procedure A: Synthesis of Octupolar Molecules by Wittig Reaction. To a solution of **2** (200 mg, 0.51 mmol) and the appropriate phosphonium salt (1.69 mmol) in anhydrous CH_2Cl_2 (100 mL) were added *t*-BuOK (0.287 g, 2.56 mmol) and a catalytic amount of 18-crown-6 (1.2 mg). The originally yellow mixture turned red in a few minutes, and the stirring was continued at room temperature for 4 h. Then the mixture was filtered through Celite, and a catalytic amount of I_2 (1.2 mg) was added. The solution was stirred at room temperature for 24 h under light exposure. The organic layer was washed with aqueous $Na_2S_2O_3$ and dried ($MgSO_4$). After evaporation of the solvent, the crude product was purified by column chromatography (cyclohexane/CH_2Cl_2).

1,3,5-Tris[4-[(1E)-2-[4-(dihexylamino)phenyl]ethenyl]phenyl]benzene ***(TPB(PV)₁NHex₂).*** **TPB(PV)₁NHex₂** was prepared following the general procedure A, from **2** and **6a** in 82% yield. ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.79 (s, 3H), 7.68 (d, $J = 8.5$ Hz, 6H), 7.58 (d, $J = 8.5$ Hz, 6H), 7.41 (d, $J = 8.8$ Hz, 6H), 7.11 (d, $J = 16.2$ Hz, 3H), 6.93 (d, $J = 16.2$ Hz, 3H), 6.63 (d, $J = 8.8$ Hz, 6H), 3.29 (t, $J = 7.5$ Hz, 12H), 1.60 (m, 12H), 1.32 (m, 36H), 0.91 (t, $J = 6.0$ Hz, 18H). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 147.8, 141.9, 139.1, 137.9, 129.8, 129.1, 127.8, 127.4, 126.3, 124.4, 123.0, 111.6, 51.0, 31.9, 27.2, 26.8, 22.8, 14.0. HRMS (FAB$^+$): calcd for $C_{84}H_{111}N_3$ ($M^{+\cdot}$) *m/z* 1161.8778, found 1161.8778. Anal. Calcd for $C_{84}H_{111}N_3$ (1162.83): C, 86.76; H, 9.62; N, 3.61. Found: C, 86.51; H, 9.83; N, 3.54.

1,3,5-Tris[4-[(1E)-2-[4-(octyloxy)phenyl]ethenyl]phenyl]benzene ***(TPB(PV)₁OOct).*** **TPB(PV)₁OOct** was prepared following the general procedure A, from **2** and **6b**[61] in 63% yield: mp 161 °C. ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.81 (s, 3H), 7.70 (d, $J = 8.1$ Hz, 6H), 7.60 (d, $J = 8.1$ Hz, 6H), 7.48 (d, $J = 8.6$ Hz, 6H), 7.15 (d, $J = 16.4$ Hz, 3H), 7.02 (d, $J = 16.4$ Hz, 3H), 6.91 (d, $J = 8.6$ Hz, 6H), 3.98 (t, $J = 6.5$ Hz, 6H), 1.79 (m, 6H), 1.33 (m, 30H), 0.91 (t, $J = 6.9$ Hz, 9H). MS (FAB$^+$): *m/z* 996.8 [$M^{+\cdot}$].

General Procedure B: Synthesis of First-Generation Octupolar Molecules by Horner-Wadsworth-Emmons Reaction. To a solution of **2** (200 mg, 0.51 mmol) and the appropriate phosphonate (1.69 mmol) in anhydrous THF (100 mL) were added NaH (102 mg, 60% dispersion in mineral oil) and a catalytic amount of 18-crown-6 (1.2 mg). The originally yellow mixture turned red or purple in a few minutes, and the stirring was continued at room temperature for 4 h. Water (50 mL) was then added, and a precipitate separated, which was collected by filtration and washed with water, cold EtOH, and Et_2O, successively.

1,3,5-Tris[4-[(1E)-2-[4-(trifluoromethyl)phenyl]ethenyl]phenyl]benzene ***(TPB(PV)₁CF₃).*** **TPB(PV)₁CF₃** was prepared following the general procedure B, from **2** and **7a**[62] in 52% yield: mp > 300 °C. ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.85 (s, 3H), 7.76 (d, $J = 8.4$ Hz, 6H), 7.66 (d, $J = 8.4$ Hz, 6H), 7.64 (s, 12H), 7.30 (d, $J = 16.0$ Hz, 3H), 7.18 (d, $J = 16.0$ Hz, 3H). MS (FAB$^+$): *m/z* 817.5 [$M + H^+$].

1,3,5-Tris[4-[(1E)-2-(4-cyanophenyl)ethenyl]phenyl]benzene ***(TPB(PV)₁CN).*** **TPB(PV)₁CN** was prepared following the general procedure B, from **2** and **7b**[63] in 53% yield: mp > 300 °C. ^1H NMR ($CDCl_3$, 250.13 MHz): δ 7.84 (s, 3H), 7.75 (d, $J = 8.4$ Hz, 6H), 7.67 (d, $J = 8.2$ Hz, 6H), 7.66 (d, $J = 8.2$ Hz, 6H), 7.62 (d, $J = 8.2$ Hz, 6H), 7.29 (d, $J = 16.3$ Hz, 3H), 7.17 (d, $J = 16.3$ Hz, 3H). MS (FAB$^+$): *m/z* 688.4 [$M + H^+$].

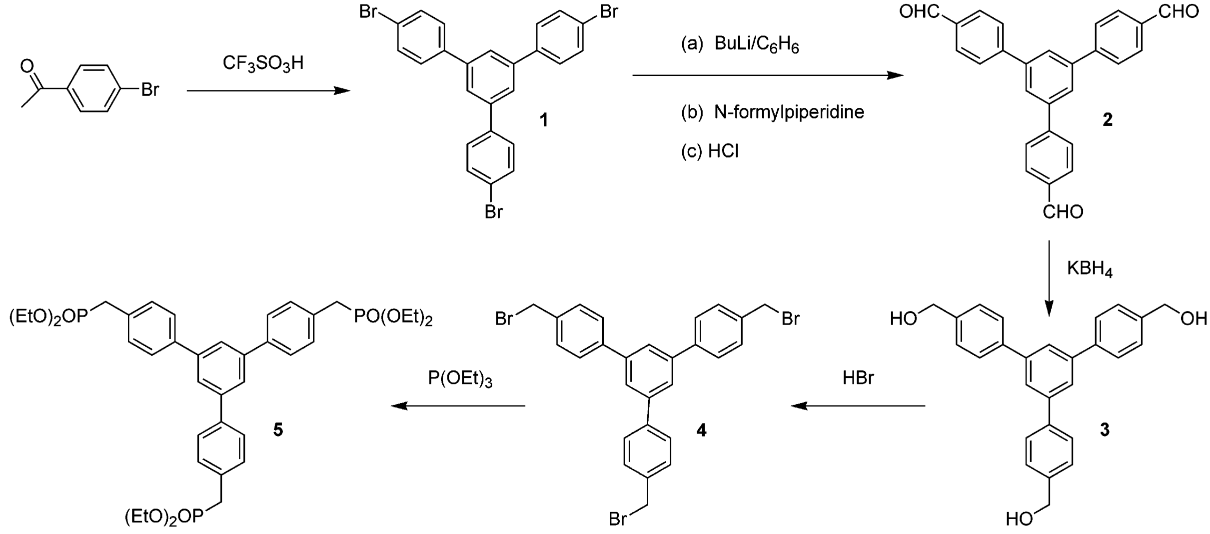
1,3,5-Tris[4-[(1E)-2-[4-(methylsulfonyl)phenyl]ethenyl]phenyl]benzene ***(TPB(PV)₁SO₂Me).*** **TPB(PV)₁SO₂Me** was prepared following the general procedure B, from **2** and **7c**[64] in 65% yield: mp > 300 °C. ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.95 (d, $J = 8.4$ Hz, 6H), 7.85 (s, 3H), 7.76 (d, $J = 8.3$ Hz, 6H), 7.72 (d, $J = 8.4$ Hz, 6H), 7.68 (d, $J = 8.3$ Hz, 6H), 7.34 (d, $J = 16.3$ Hz, 3H), 7.21 (d, $J = 16.3$ Hz, 3H), 3.09 (s, 9H). MS (FAB$^+$): *m/z* 847.3 [$M + H^+$]. Anal. Calcd for $C_{51}H_{42}O_6S_3$ (847.09): C, 72.31; H, 5.00; S, 11.36. Found: C, 72.45; H, 4.91; S, 11.55.

1,3,5-Tris[4-[(1E)-2-(4-nitrophenyl)ethenyl]phenyl]benzene ***(TPB(PV)₁NO₂).*** **TPB(PV)₁NO₂** was prepared following the general procedure B, from **2** and **7d** in 74% yield: mp > 300 °C. ^1H NMR (DMSO, 400.13 MHz): δ 8.49 (d, $J = 8.9$ Hz, 6H), 8.26 (s, 3H), 8.23 (d, $J = 8.3$ Hz, 6H), 8.15 (d, $J = 8.9$ Hz, 6H), 8.07 (d, $J = 8.3$ Hz, 6H), 7.87 (d, $J = 16.4$ Hz, 3H), 7.77 (d, $J = 16.4$ Hz, 3H). MS (CI, NH_3): *m/z* 765 [$M + NH_4^+$], 748 [$M + H^+$]. Anal. Calcd for $C_{48}H_{33}N_3O_6$ (747.81): C, 77.10; H, 4.45; N, 5.62. Found: C, 77.12; H, 4.51; N, 5.55.

General Procedure C: Synthesis of Second-Generation Octupolar Molecules by Horner-Wadsworth-Emmons Reaction. To a solution of **5** (250 mg, 0.33 mmol) and the appropriate extended aldehyde (1.09 mmol) in anhydrous CH_2Cl_2 (100 mL) were added *t*-BuOK (0.185 g, 1.65 mmol) and a catalytic amount of 18-crown-6 (0.8 mg). The mixture turned red in a few minutes, and the stirring was continued at room temperature for 24 h. Water was then added, the two layers were separated, and the organic layer was washed with water, dried (Na_2SO_4), and evaporated. Digestion of the residue with Et_2O/pentane afforded a precipitate, which was collected by filtration and washed with water, cold EtOH, and Et_2O, successively.

1,3,5-Tris[4-[(1E)-2-[4-[(1E)-2-[4-(dihexylamino)phenyl]ethenyl]phenyl]ethenyl]phenyl]benzene ***(TPB(PV)₂NHex₂).*** **TPB(PV)₂NHex₂** was prepared following the general procedure C, from **5** and **9a** in 65% yield: mp 95−96 °C. ^1H NMR ($CDCl_3$, 200.13 MHz): δ 7.84 (s, 3H), 7.73 (d, 6H, $J = 8.2$ Hz), 7.64 (d, 6H, $J = 8.2$ Hz), 7.50 (s, 12H), 7.39 (d, 6H, $J = 8.2$ Hz), 7.18 (s, 6H), 7.08 (d, 3H, $J = 16.2$ Hz), 6.88 (d, 3H, $J = 16.2$ Hz), 6.62 (d, 6H, $J = 8.2$ Hz), 3.29 (t, 12H, $J = 7.0$ Hz), 1.56 (m, 12H), 1.32 (m, 36H), 0.88 (t, 18H, $J = 6.7$ Hz). ^{13}C NMR ($CDCl_3$, 62.90 MHz): δ 148.0, 142.0, 140.1, 138.0, 137.0, 129.8, 129.1, 128.8, 127.9, 127.6, 127.0, 126.9, 126.3, 124.6, 124.3, 124.2, 122.8, 111.7, 51.1, 31.8, 27.3, 27.1, 22.7, 14.1. HRMS (CI, CH_4): calcd for $C_{108}H_{130}N_3$ ($[M + H]^+$): *m/z* 1469.0265, found 1469.0271. Anal. Calcd for $C_{108}H_{129}N_3$ (1469.24): C, 88.29; H, 8.85; N, 2.86. Found: C, 88.58; H, 8.91; N, 2.71.

Scheme 1. Synthesis of Core Reagents Derived from 1,3,5-Triphenylbenzene



*1,3,5-Tris[4-[(1E)-2-[4-[(1E)-2-[4-(methylsulfonyl)phenyl]ethenyl]phenyl]ethenyl]phenyl]benzene (**TPB(PV)$_2$SO$_2$Me**).* **TPB(PV)$_2$SO$_2$Me** was prepared following the general procedure C, from **5** and **9b** in 78% yield: mp 190 °C. ^{1}H NMR (CDCl$_3$, 200.13 MHz): δ 7.93 (d, $J = 8.4$ Hz, 6H), 7.81 (s, 3H), 7.74 (d, $J = 8.2$ Hz, 6H), 7.68 (d, $J = 8.4$ Hz, 6H), 7.65 (d, $J = 8.2$ Hz, 6H), 7.58 (s, 12H), 7.29 (d, $J = 15.9$ Hz, 3H), 7.21 (s, 6H), 7.16 (d, $J = 15.9$ Hz, 3H), 3.09 (s, 9H). MS (CI, NH$_3$): *m*/*z* 1170.4 [M + NH$_4^+$]. Anal. Calcd for $C_{75}H_{60}O_6S_3$ (1153.48): C, 78.09; H, 5.24. Found: C, 77.59; H, 5.37.

Photophysical Measurements. All experiments were performed at 25 °C. The solvents were of spectroscopic grade. The UV/Vis absorption spectra were recorded on a Kontron Uvikon 930 spectrophotometer and the corrected fluorescence spectra were obtained with a PTI spectrometer (LPS-220B) in photon-counting mode. Fluorescence quantum yields were measured on degassed samples; fluorescein in 0.1 N NaOH was used as a standard ($\phi = 0.90$ at $\lambda_{ex} = 470$ nm).

NLO Measurements. The first hyperpolarizabilities β were determined by performing harmonic light scattering (HLS) experiments in solution. This technique, initially introduced by Terhune and Maker,[67] is based on the analysis of the incoherent scattered second-harmonic signal from an isotropic medium. As resulting from an incoherent process, the scattered nonlinear intensity $I^{2\omega}$ can be expressed as $I^{2\omega} = G(N_1\langle\beta_1^2\rangle + N\langle\beta^2\rangle)(I^{\omega})^2$ for a solution with N (respectively N_1) chromophores (respectively solvent) per milliliter of solution, where the G coefficient embodies geometrical factors and experimental correction terms and the brackets refer to statistical isotropic orientational averaging. G evaluation proceeds from the calibration of the experiment, by means of a reference CCl$_4$ solution with $\sqrt{\langle\beta_1^2\rangle} = 0.26 \times 10^{-30}$ esu.[66] The $\sqrt{\langle\beta^2\rangle}$ value of the solute molecules can be inferred from the determination of the linear dependence of the harmonic intensity as a function of the square of the I^{ω} fundamental intensity for different molecular concentrations. Measurements were carried out in chloroform with pure solvent (leading to $\sqrt{\langle\beta_1^2\rangle} = (0.19 \pm 0.03) \times 10^{-30}$ esu) and various concentrations of the solute chromophores. HLS experiments were performed either at 1.064 or 1.340 μm, to locate the second-harmonic signal in the transparency region of the chromophores and avoid contamination by two-photon fluorescence. More precisely, we were cautious about performing the HRS measurement at *experimental wavelengths not allowing two-photon-excitation*, that is, at much longer wavelengths than twice the one-photon absorption wavelength (see Table 3). In those experimental conditions, the emissive excited state could thus not be reached via two-photon absorption.[68]

HLS measurements were conducted with a transverse and longitudinal single-mode Nd^{3+}:YAG laser emitting pulses of 10-MW peak power and 10-ns duration at 10-Hz repetition rate. The incident intensity I^{ω} is monitored by a half-wave plate and a Glan polarizer. A fraction of the incident beam is removed by a glass plate at a low reflection angle and sent onto a reference NPP frequency doubling calibrated powder. The fundamental beam is focused in a cell which contains the adequately filtered solutions. The scattered harmonic signal is then collected at a right angle on a second photomultiplier after spectral selection through an interferential filter with 3-nm spectral resolution. These experiments were performed using, for each molecule, solutions of increasing concentration in chloroform or in a few cases DMSO. The experimental accuracy is estimated to be ±10%.

Results and Discussion

Synthesis Methodology. The synthesis of octupolar molecules **TPB(PV)$_n$Z** derived from triphenylbenzene is based on the symmetrical triple functionalization of core reagents derived from 1,3,5-triphenylbenzene via Wittig or Horner-Wadsworth-Emmons reactions. According to this methodology, we synthesized two key core reagents with 3-fold rotational symmetry: trisaldehyde **2** and tris-phosphonate **5** (Scheme 1). The core reagent **2** was prepared in a three-step procedure based on cyclotrimerization of 4-bromoacetophenone, followed by lithiation and formylation (Scheme 1). 1,3,5-Tris(4-bromophenyl)benzene (**1**) was synthesized by condensation of three molecules of 4-bromoacetophenone with 89% yield in the presence of catalytic trifluoromethanesulfonic acid,[69] using a more efficient and convenient procedure than the previously reported ones.[65,70,71] The conversion of **1** into **2** was achieved with 75% yield by modifying and improving the previously reported pro-

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[68] To confirm the validity of this methodology on one example, we have measured the two-photon absorption spectrum of molecule **TPB(PV)$_1$NHex$_2$**—which shows the highest fluorescence quantum yield of the series (Table 2)—and checked that the TPA cross section vanishes totally at wavelengths longer than 940 nm.

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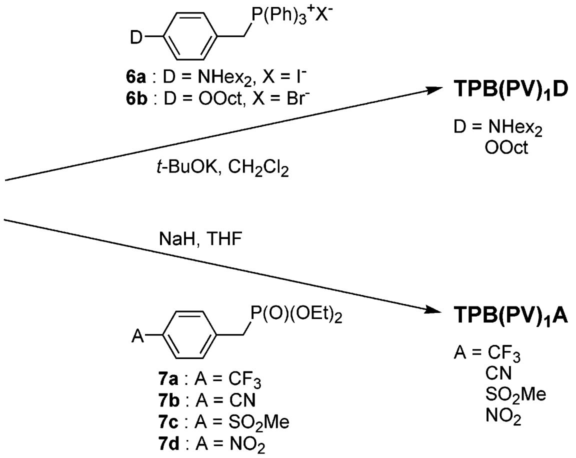
[71] Plater, M. J.; McKay, M.; Jackson, T. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2695–2701.

Scheme 2. Synthesis of First-Generation Octupolar Molecules ($n = 1$)



tocol.[66] The key reagent **5** was synthesized from **2** with 76% overall yield in a three-step sequence based on a reduction followed by a bromination and a Michaelis-Arbuzov reaction.

The first-generation molecules ($n = 1$) were prepared from core reagent **2** and phosphoniums salts **6a**,**b** or phosphonates **7a**−**d**, via a triple Wittig or Horner-Wadsworth-Emmons reaction using solid−liquid-phase transfer conditions (Scheme 2).

On the other hand, the second-generation molecules ($n = 2$) were obtained from core reagent **5** via a triple Horner-Wadsworth-Emmons condensation with extended aldehydes **9a**,**b** in solid−liquid-phase transfer conditions (Scheme 3). The extended aldehydes **9a**,**b** were prepared by reacting terephthalaldehyde mono-(diethylacetal) (**8**) with 1 equiv of phosphonium salt **6a** or of phosphonate reagent **7c**, respectively, followed by acid-catalyzed hydrolysis (Scheme 3).

Photostability. Photochemical stability of all octupolar molecules was tested by exposing (i) ca. 10^{-6} M solutions of them in toluene, $CHCl_3$, and DMSO to 100-W lamp irradiation for 100 h, (ii) ca. 10^{-6} M solutions in $CHCl_3$ to daylight for 1 year, and (iii) various concentrations solutions in $CHCl_3$ or DMSO to pulsed laser irradiation (nanosecond pulses for 1 h). In any of those conditions, no noticeable photodegradation was observed. This provides evidence that such molecules are relevant candidates toward further orientation of NLO guest−host systems via optical poling.[72−74]

Linear Optical Properties. *Absorption.* All molecules show good transparency in a wide range of the visible region and intense absorption in the near UV-blue visible range (Table 1). The absorption maxima depend both on the nature of the peripheral substituents and on the length of the conjugated arms. As expected, a red shift of the absorption band is observed with increasing the electron-withdrawing or electron-releasing strength of the end groups (Figure 2). Interestingly, the octupolar derivatives bearing electron-withdrawing end groups show improved transparency as compared to those bearing electron-releasing end groups, indicative of a higher energy cost associated with multidimensional intramolecular charge transfer from the triphenylbenzene core toward accepting end groups (i.e., center to periphery) than the reverse intramolecular charge transfer from donating end groups toward the triphenylcore (i.e., periphery to center). A bathochromic shift is observed with increasing the length of the conjugated arms (Table 1). However, we note that this transparency reduction is less pronounced for the octupolar derivatives bearing electron-releasing end groups: the absorption of **TPB(PV)$_2$NHex$_2$** exhibits a bathochromic shift of 1270 cm^{-1} as compared to that of **TPB(PV)$_1$NHex$_2$**, whereas a more than twice higher shift (2710 cm^{-1}) is observed for the absorption of **TPB(PV)$_2$SO$_2$Me** as compared to that of **TPB(PV)$_1$SO$_2$Me.**

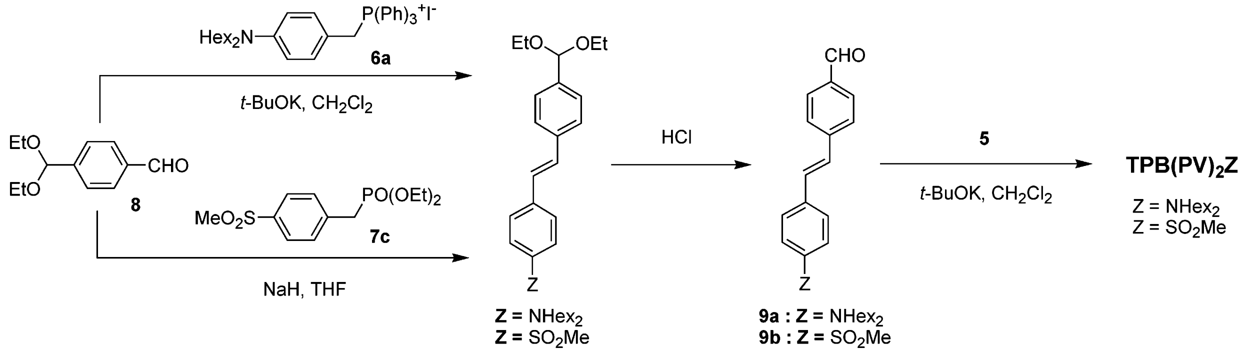
Table 1. Absorption Properties of Octupolar Molecules Derived from Triphenylbenzene

compound	λ_{max}[a] (nm)	$\lambda_{cut-off}$[b] (nm)	log ϵ	$\Delta\tilde{\nu}_{abs}$[c] (cm^{-1})
TPB(PV)$_1$NHex$_2$	387	437	4.85	730
TPB(PV)$_1$OOct	344	383	4.96	170
TPB(PV)$_1$CF$_3$	334	376	5.11	*d*
TPB(PV)$_1$CN	345	390	5.04	*d*
TPB(PV)$_1$SO$_2$Me	342	384	5.11	510
TPB(PV)$_1$NO$_2$	372	460	4.73	1060
TPB(PV)$_2$NHex$_2$	407	468	4.91	1195
TPB(PV)$_2$SO$_2$Me	377	431	5.11	1830

[a] Absorption maximum in $CHCl_3$. [b] Wavelength at which the transmittance is 95%, in $CHCl_3$. [c] Absorption solvatochromic shift $= 1/\lambda_{max}(\text{toluene}) - 1/\lambda_{max}(\text{DMSO})$. [d] Undetermined due to solubility restrictions.

All octupolar derivatives show definite solvatochromic behavior:[75] a bathochromic shift of the absorption band is observed with increasing solvent polarity (Figure 3). This positive solvatochromism is indicative of a larger stabilization of the excited state as compared to the ground state by a polar solvent. This suggests that a significant charge redistribution takes place upon excitation, consistent with a multidimensional intramolecular charge transfer (MDICT) occurring between

Scheme 3. Synthesis of Second-Generation Octupolar Molecules ($n = 2$)



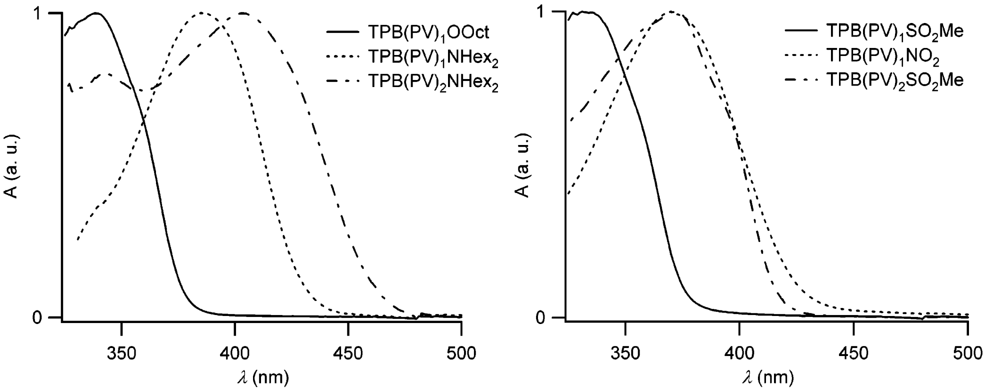


Figure 2. Normalized absorption spectra of octupoles bearing either electron-donating end groups (left)—**TPB(PV)$_1$OOct**, **TPB(PV)$_1$NHex$_2$**, and **TPB(PV)$_2$NHex$_2$**—or electron-withdrawing end groups (right)—**TPB(PV)$_1$SO$_2$Me**, **TPB(PV)$_1$NO$_2$**, and **TPB(PV)$_2$SO$_2$Me**—in CHCl$_3$.

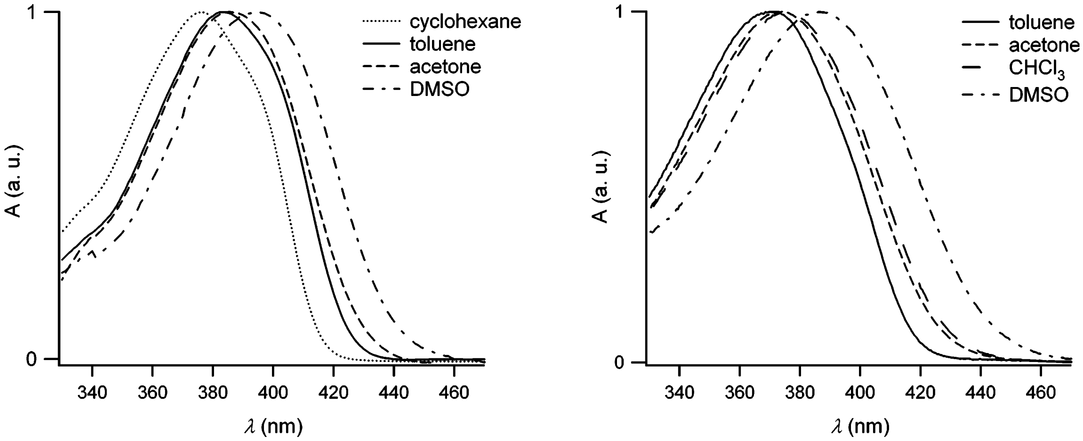


Figure 3. Solvatochromic absorption behavior of molecule **TPB(PV)$_1$NHex$_2$** (left) and **TPB(PV)$_1$NO$_2$** (right).

the core and the peripheral groups. We note that increasing the strength of the peripheral substituents (either electron-donating or electron-accepting) or the length of the conjugated arms leads to a marked increase of the solvatochromic shift (Table 1), indicative of an enlargement of the extent of the MDICT phenomenon. In addition, we observe that tris-acceptor derivatives show definitely larger solvatochromic shift than tris-donor molecules, suggesting that the MDICT could be facilitated in tris-acceptor as compared to tris-donor molecules. This is coherent with the resonance-donating character of the phenyl ring.[76]

Emission. An even more pronounced positive solvatochromism is observed in emission (Figure 4). Such characteristic behavior, as well as the large Stokes shift values (Table 2) which reveals that a significant degree of nuclear reorganization is taking place after excitation as a result of a significant electronic redistribution occurring upon excitation, provide evidence of the MDICT phenomenon. We note that stronger peripheral accepting end groups and increasing arm length lead to an increase of both Stokes shifts and fluorescence solvatochromic shifts, in agreement with a more pronounced MDICT. This interpretation is confirmed by calculations, conducted using the Gaussian 98 package[77] with the B3LYP[78] density functional and the 6-31G* basis set, that show that a periphery to center (for prototypical **TPB(PV)$_1$NMe$_2$** molecule) or center to periphery (for prototypical **TPB(PV)$_1$NO$_2$** molecule) intramolecular charge transfer actually occurs upon excitation (Figure 5). Interestingly, the MDICT phenomenon is more pronounced for the tris-acceptor molecule than for the tris-donor molecule, and this is consistent with the experimental observation that octupole **TPB(PV)$_1$NO$_2$** shows a Stokes shift value 2 times larger than octupole **TPB(PV)$_1$NHex$_2$** (Table 2).

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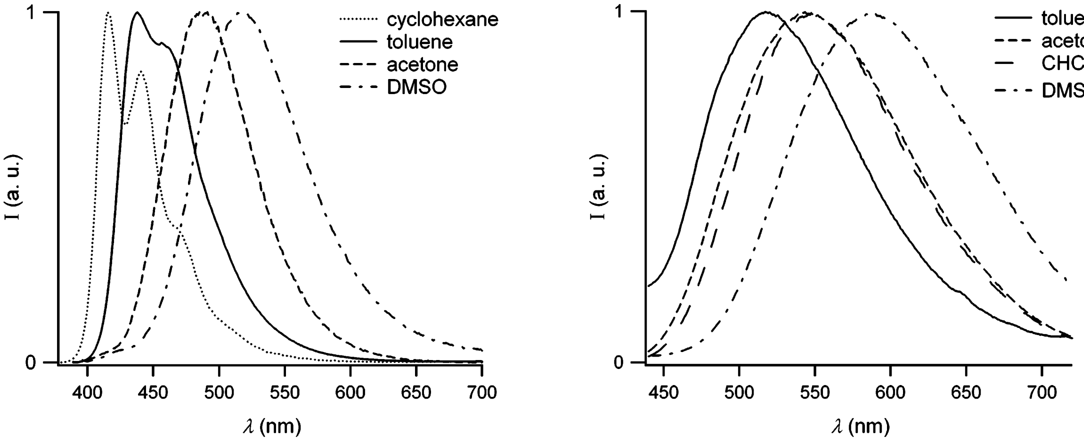

Figure 4. Solvatochromic emission behavior of molecule **TPB(PV)$_1$NHex$_2$** (left) and **TPB(PV)$_1$NO$_2$** (right).

Table 2. Emission Properties of Octupolar Molecules Derived from Triphenylbenzene

compound	λ_{em}[a] (nm)	Φ[b]	Stokes shift[c] (cm^{-1})
TPB(PV)$_1$NHex$_2$	459	0.29	4050
TPB(PV)$_1$OOct	410	0.17	4680
TPB(PV)$_1$CF$_3$	370, 389	0.22	2910
TPB(PV)$_1$CN	394, 409	0.23	3600
TPB(PV)$_1$SO$_2$Me	407	0.11	4670
TPB(PV)$_1$NO$_2$	535	0.09	8190
TPB(PV)$_2$NHex$_2$	520	0.20	5340
TPB(PV)$_2$SO$_2$Me	458	0.05	4690

[a] In CHCl$_3$. [b] Fluorescence quantum yield in CHCl$_3$. [c] Stokes shift = $(1/\lambda_{abs} - 1/\lambda_{em})$.

Molecular Nonlinearities. The β^X convention was used throughout the paper.[79] The nonlinear $\sqrt{\langle\beta^2\rangle} = \beta_{HLS}$ coefficients obtained for octupolar tristilbenylbenzenes are collected in Table 3. The modulus $||\beta|| = \sqrt{\sum_{ijk}\beta_{ijk}^2}$ values, which are commonly used to compare β values of molecules with different symmetries, are also included. For molecules with C_{3h} symmetry, $||\beta||$ is evaluated from the HLS molecular averaged hyperpolarizability according to $||\beta|| = \sqrt{21/2}\beta_{HLS}$. For 1D dipolar chromophores with only one longitudinal component β_{zzz}, $||\beta||$ is derived from β_{HLS} according to $||\beta|| = \beta_{zzz} = \sqrt{35/6}\beta_{HLS}$. The corresponding static values $\beta_{HLS}(0)$ and $||\beta_{(0)}||$ are calculated using a degenerated three-level dispersion factor.[2] The molecular figure of merit $||\beta_0||$/MW values are also included. These data allow for comparison of molecules of different symmetries and sizes via normalization by the molecular weight MW.[23] Such a figure of merit can be helpful when material applications are considered.

Effect of End Groups: Hammett Correlation. Comparison of octupoles bearing acceptor peripheral groups clearly indicates that increasing the accepting strength of the three terminal substituents results in a significant enhancement of β. **TPB(PV)$_1$NO$_2$** shows a molecular optical nonlinearity about 20 times larger than molecule **TPB(PV)$_1$CF$_3$**, providing evidence that MDICT between the core and the periphery of the molecule controls the nonlinear responses. We note that this MDICT phenomenon actually results in an improved efficiency-transparency tradeoff: **TPB(PV)$_1$NO$_2$** displays a $||\beta_0||$ value about 2 times larger than the benchmark 1-D push–pull chromophore DR1 while remaining blue-shifted by 100 nm. Similarly, comparison of molecules bearing electron-releasing end groups shows that increasing the electron-donating strength actually leads to a marked increase of β: **TPB(PV)$_1$NHex$_2$** shows a molecular nonlinearity about 6 times larger than molecule **TPB(PV)$_1$OOct** which have weaker donating peripheral substituents. This confirms that MDICT either from the periphery to the core of the propeller-shaped octupolar molecules or vice versa plays a definite role in governing the nonlinear responses and that the triphenylbenzene core actually acts as either a donor or an acceptor core moiety depending on its counterparts.

Interestingly, we observe that—for a series of octupolar derivatives of similar size and bearing either donating or accepting end groups—the values of the hyperpolarizability correlate with the Hammett σ_p constants of the peripheral groups (Figure 6). The $\beta-\sigma$ correlation for octupolar molecules has been theoretically predicted by Cho and colleagues,[80] and to the best of our knowledge, this is the first experimental corroboration. Furthermore, we note that the $\beta-\sigma$ dependence is much steeper for the series of tris-acceptor molecules than for the series of tris-donor molecules, demonstrating that MDICT from the core to the periphery is favored. This is consistent with the larger Stokes shift values and solvatochromic shifts observed for the tris-acceptor series as compared to those for the tris-donor series, in relation to a more pronounced MDICT.

Correlation between First Hyperpolarizability and Solvatochromism. Interestingly, examination of the series of tris-acceptor molecules (and of the tris-donor) molecules reveals a correlation between the $||\beta_0||$ values and the solvatochromic shift values for molecules of similar type either tris-acceptor or tris-donor) as shown in Figure 7. Whereas the connection between solvatochromism and hyperpolarizabilities of dipolar compounds has been recognized before, this is the first time to our knowledge that such correlation is underlined for octupolar systems. This behavior confirms the correla-

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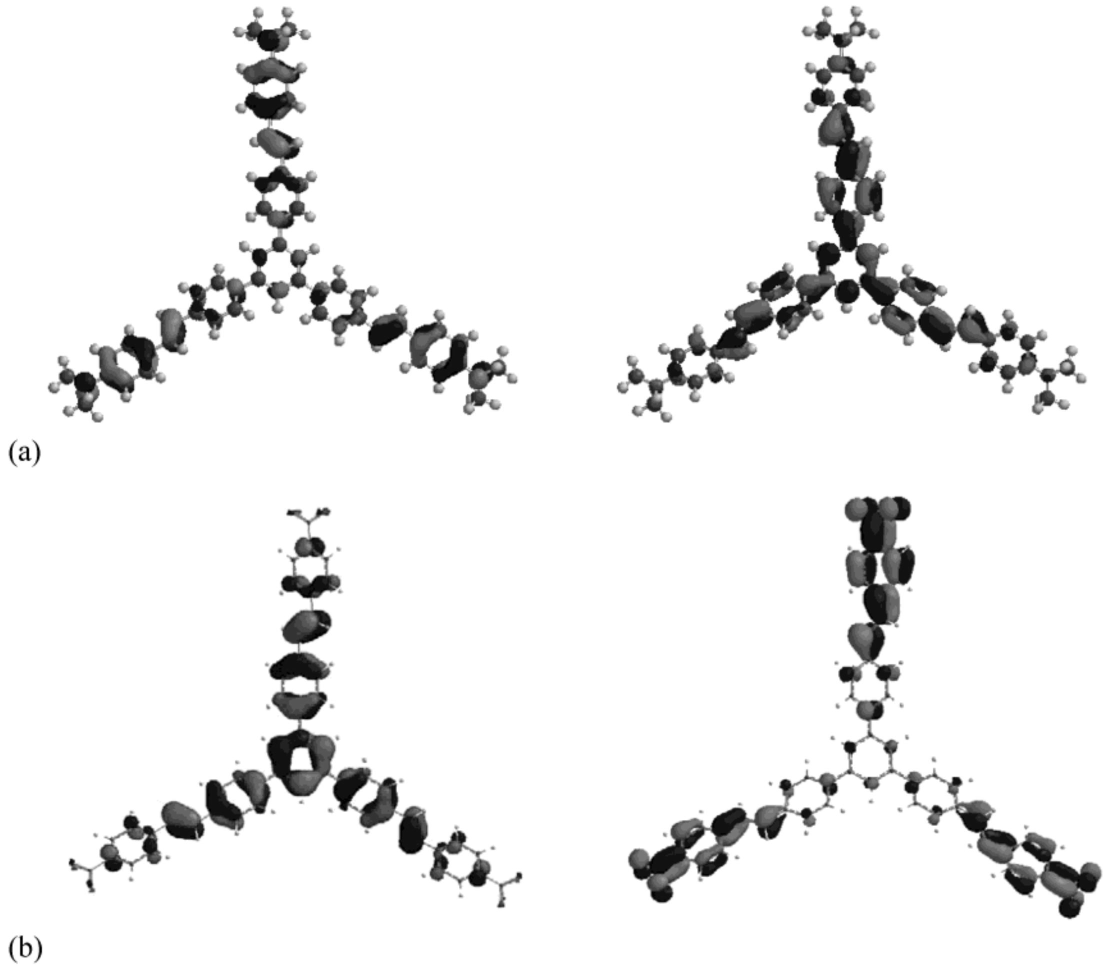

Figure 5. Contour surfaces of HOMO, HOMO − 1 (left) and LUMO, LUMO + 1 (right) of **TPB(PV)$_1$NMe$_2$** (a) and **TPB(PV)$_1$NO$_2$** (b) obtained from B3LYP/6-31G* calculations.

Table 3. Molecular Nonlinearities (β) of Octupolar Molecules Derived from Triphenylbenzene Determined from HLS Experiments in CHCl$_3$ Solution[a]

compound	λ_{max} (nm)	λ_{HLS} (nm)	β_{HLS} (10^{-30} esu)	$\|\|\beta\|\|$ (10^{-30} esu)	$\|\|\beta_0\|\|$ (10^{-30} esu)	$\|\|\beta_0\|\|$/MW (10^{-32} esu·g^{-1}·mol)
TPB(PV)$_1$NHex$_2$	387	1064	36	117	48	4.1
TPB(PV)$_1$OOct	344	1064	5	16	8	0.8
TPB(PV)$_1$CF$_3$	334	1064	4	13	7	0.9
TPB(PV)$_1$CN	345	1064	6	19	10	1.5
TPB(PV)$_1$SO$_2$Me	342	1064	30	97	51	6.0
TPB(PV)$_1$NO$_2$[b]	387	1340	70	227	139	19
TPB(PV)$_2$NHex$_2$	407	1340	150	486	278	19
TPB(PV)$_2$SO$_2$Me	377	1340	250	810	510	44
*p*NA	348	1064	10	32	12	8.7

[a] Data for prototypical 1-D dipolar molecules *p*NA are also included for comparison. [b] In DMSO.

tion between the MDICT phenomenon and the nonlinear responses. Following this observation, increasing the distance between the core and the periphery appeared as a rational approach to increase the nonlinear responses.[81]

Size Effect. Increasing the distance between the core and the periphery of the molecules results in a dramatic increase of the linear responses, in agreement with an increase of the magnitude of MDICT. **TPB(PV)$_2$NHex$_2$** exhibits a $||\beta_0||$ value about 6 times larger than molecule **TPB(PV)$_1$NHex$_2$** at the expense of an increase in molecular weight of only 26% and of a red shift of no more than 20 nm. The length effect is even more pronounced for octupolar derivatives having accepting end groups: **TPB(PV)$_2$SO$_2$Me** displays a first-order hyperpolarizability *1 order of magnitude larger* than its shorter analogue, while increasing by no more than 36% in weight and maintaining suitable transparency in the visible region. This leads to a superior efficiency-transparency tradeoff: **TPB(PV)$_2$SO$_2$Me** exhibits a $||\beta_0||$ value more than 40 times larger than the prototypical push−pull compound *p*-nitroaniline (*p*NA), with a molecular weight about 8 times larger.[82] As illustrated in Figure 8, we observe that nanoscale elongated octupolar derivatives having strong accepting peripheral groups actually lead to *superior transparency-efficiency tradeoff* with a molecular figure of

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(81) We note that this strategy has proven to be successful in other types of octupolar molecules.[25]

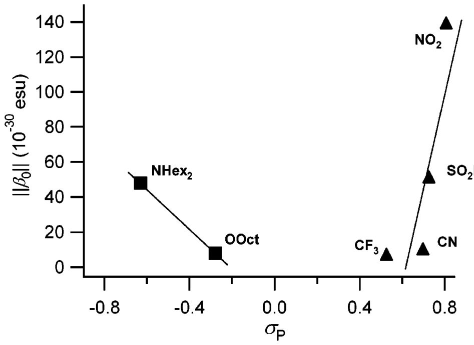

Figure 6. Hammett correlation of the first hyperpolarizability of the first generation of triphenylbenzene-derived octupolar molecules **TPB(PV)$_1$Z**, bearing donor (■) or acceptor (▲) peripheral groups.

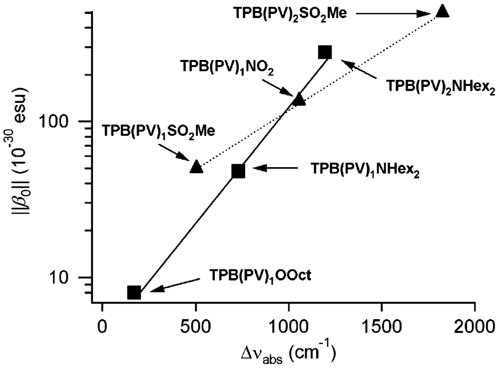

Figure 7. MDICT-nonlinearity correlation between the absorption solvatochromic shift ($\Delta\tilde{\nu}_{abs} = 1/\lambda_{max}$(toluene) − $1/\lambda_{max}$(DMSO)) and the nonlinear response ($||\beta_0||$) of triphenylbenzene-derived octupolar molecules bearing donor (■) or acceptor (▲) peripheral groups.

merit comparable to the best octupolar molecules reported up to now.[23,25]

Conclusion

By grafting of either electron-releasing or electron-withdrawing groups on the ends of conjugated blades branched on a triphenylbenzene core, three-branched propeller-shaped molecules exhibiting high NLO properties and wide transparency in the visible range have been designed. The pronounced solvatochromic behavior points to a mutidimensional intramolecular charge-transfer phenomenon occurring between the center and the periphery upon excitation. Correlation between the solvatochromism magnitude and the optical nonlinearities have been established, providing evidence that the MDICT phenomenon controls the nonlinear responses of these derivatives.[83] Consequently, boosting the MDICT by using strong acceptor end groups and increasing the distance between the core and the periphery leads to molecules presenting superior transparency-nonlinearity tradeoff ($||\beta|| = 810 \times 10^{-30}$ esu, $\lambda_{max} = 377$ nm). The nanoscale derivatives are thus attractive candidates for the elaboration of SHG active material. As far as the subsequent octupolar material formation step is concerned, the challenge of achieving non-centrosymmetric octupolar organization at the macroscopic level could possibly be addressed by an “all-optical” poling configuration. Coherent multiphoton interactions between laser beams in octupolar guest−host solid solutions at room temperature could allow for the imprint of the tensorial symmetry of the write beams polarization states into a thin film or a waveguide structure and provide challenging material engineering possibilities which are out of reach for the traditional electric field poling technique.[72−74] The molecules possess the desired photochemical stability required for such methodology.

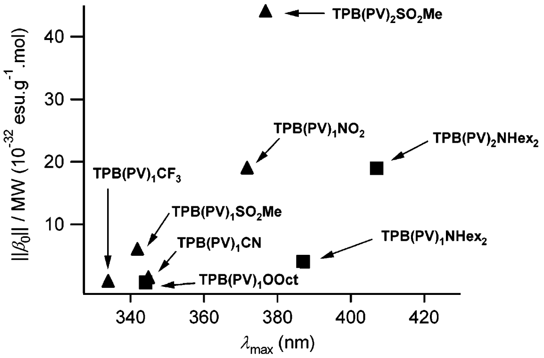

Figure 8. Nonlinearity-transparency tradeoff of triphenylbenzene-derived octupolar molecules bearing donor (■) or acceptor (▲) peripheral groups.

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(82) On the basis of the experimental evidence, we expect the **TPB(PV)$_2$NO$_2$** molecule to be even more effective. Unfortunately, this derivative, which could be prepared via a methodology analogous to that described in Scheme 3, is highly insoluble, and thus not interesting for potential developments, neither allowing a reliable determination of its hyperpolarizability. A decrease of solubility was also observed in the derivatives bearing SO$_2$Me acceptor end groups, but molecule **TPB(PV)$_2$SO$_2$Me** remains soluble enough to allow NMR characterization and HRS experiments in solution.

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