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Synthesis and incorporation in Langmuir films of oligophenylenevinylene dendrimers bearing a polar head group and different dendritic poly(benzyl ether) branches

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ABSTRACT

Oligophenylenevinylene (OPV) units containing a hydroxyl polar head group and different dendritic poly(benzyl ether) branches bearing aliphatic chains (*n*-propyl and *n*-dodecyl) have been synthesized. The obtained dendrimers were characterized by ^{1}H and ^{13}C NMR, FTIR and absorption spectroscopies. Optical properties of the dendrimers have been studied in toluene and dichloromethane solutions. Changes in the maximum absorption wavelength were observed for the dendrimers OPV core. Increasing the dendron branches generation gave rise to a hypsochromic shift of the maximum absorption band of the OPV core. The ability of all dendrimers to form Langmuir films at the air–water interface was also investigated; the obtained films were characterized by surface pressure versus molecular area isotherms, and by compression–expansion cycles (hysteresis curves). All dendrimers were able to form stable Langmuir monolayers in the air–water interface, and exhibited a good reversible behavior upon successive compression/expansion cycles. The terminal alkyl chains length of the dendritic branches has a remarkable influence on the packing of highest generation dendrimers in the monolayers. These dendrimers can be promising prospects for the preparation of Langmuir–Blodgett films, in view of optical and electronic potential applications.

1. Introduction

Dendrimers are hyperbranched molecules with a well-defined three-dimensional molecular structure, which can be easily prepared by two synthetic routes: divergent [1] and convergent [2] methods. Over the past decade, a wide variety of dendrimers bearing different functional groups in their structure, have been synthesized and characterized [3]. Nowadays, the research in the design and synthesis of new-dendritic structures increased considerably because of the interesting structural characteristics of these molecules (highly branched, globular architecture, three-dimensional structure, etc.) as well as their interesting properties, which differ from those of analogous linear polymers [4]. That is why these molecules attracted the attention of several chemists working on interdisciplinary fields of research, with technical applications in material science: catalysis [5], biotechnology [6], medicine [7] and nanotechnology [8].

Recently, there has been a considerable interest in the incorporation of π-conjugated systems in dendritic architectures due to its outstanding electronic, conducting and electroluminescent properties [9]. Dendritic structures containing π-conjugated systems as core [10], peripheral subunits [11] or at each branch [12] have been prepared. Oligophenylenevinylene systems are of particular interest since their totally conjugated structure facilitates the electron mobility; therefore, such systems are good candidates for electronic and optoelectronic applications. However, the efficiency of many electronic devices based on π-conjugated systems depends in a big measure on the quality, homogeneity and morphology of the thin films. The preparation and study of thin films based on organic materials are of great interest in many science and technology fields. For example, the formation and transfer of well-ordered functional molecules from thin films to solid surfaces, find use in several nanotechnology applications such as molecular sensors, [13] electronic and optoelectronic devices [14], nonlinear optical properties [15], conducting and semiconductor organic materials [16]. Thin films of flat substrates based on organic materials can be prepared by the spin-coating technique; nevertheless, the homogeneity and morphology of such films are usually of

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very-low quality. One possible approach towards the preparation of thin films with controlled structure and morphology is the Langmuir–Blodgett technique, which allows us to prepare thin films in the air–water interface [17,18]. To form a monolayer, the molecules of interest are dissolved in a volatile organic solvent unable to react with or to dissolve into the water surface. A small amount of this solution is poured on the interface air–water. After the solvent evaporates, the molecules are deposited on the water surface, with the amphiphilic part touching the water-phase and the hydrophobic groups are oriented towards the air-phase. Then, the available surface area of the molecules in the Langmuir trough is reduced by a barrier system, forcing the molecules to comply. The formation of monolayers is characterized by their surface pressure versus molecular area isotherms.

In this paper, we report the synthesis and characterization of two novel series of dendrimers with an oligophenylenevinylene (OPV) core containing a polar head group, end-capped with alkyl chains of different lengths, as well as their incorporation in Langmuir films. Optical properties of these compounds have been studied by absorption spectroscopy in solution. As the generation of hyper-branches increases, these dendrimers exhibit a blue shift in the maximum absorption band of the OPV unit. Surprisingly, a hypsochromic shift in absorption band of OPV unit is also observed with increasing aliphatic chains' length. Langmuir films of all dendrimers have been prepared on the air–water interface, and they were characterized by surface pressure versus molecular area (Π/A) isotherms and hysteresis curves.

2. Experimental part

2.1. Materials and equipments

Solvents and compounds reagent grade used in the synthesis were purchased from Aldrich and used without further purification. Acetone was distilled over calcium chloride; tetrahydrofuran was distilled over sodium and benzophenone. Column chromatography was performed on Merck silica gel 60 Å (70–230 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz instrument, using tetramethylsilane (TMS) as an internal reference. Infrared (FTIR) spectra of the dendrons in film were recorded on a Perkin–Elmer Paragon 500 spectrophotometer. Absorption spectra were carried out in a UV–vis Varian Cary 100 Fast Scan spectrophotometer, in toluene and dichloromethane at room temperature. Langmuir film data were collected with a KSV 5000 system 3, using a Teflon trough and symmetrical hydrophilic barriers. The trough was set in a Plexiglas enclosure in order to protect it from drafts and dust, and the temperature variation was limited to $\pm$0.1 °C. All isotherms were recorded at 20 °C. Ultra-pure water used for the Langmuir trough was obtained from a Milli-DI/Milli-Q 185 Simplicity ultra purification system from Millipore. Surface pressure was measured by the means of a platinum Wilhelmy plate. Solutions at $\sim$1 mg/mL concentration were prepared using chloroform (HPLC grade from Aldrich). Films were left to equilibrate for 20 min prior to start measurement. The monolayers were compressed, using a barrier speed of 4 mm/min. Typical uncertainties on the collapse pressure and final molecular area data are $\pm$1.0 and $\pm$2.5%, respectively.

2.2. Synthesis

2.2.1. General procedure for dendrons' synthesis

Dendrons have been obtained via a convergent synthesis, using a modified Fréchet type methodology based upon the alkylation of 3,5-dihydroxybenzyl alcohol with different alkyl bromides, followed by bromination of the hydroxyl group with carbon tetrabromide and triphenylphosphine [19].

A mixture of 3,5-dihydroxybenzyl alcohol **1** (5 g, 35.678 mmol), 1-bromopropane (2.4 equiv) (or 1-bromododecane), a catalytic amount of 18-crown-6 and K_2CO_3 (4 equiv) in acetone (150 mL) was heated at reflux for 48 h. After cooling, the mixture was filtered on Celite and evaporated to dryness. The brown residue was extracted with CH_2Cl_2; then the organic layer was washed with a saturated NaCl aqueous solution, dried with Na_2SO_4, filtered, and concentrated at reduced pressure. The resulting product was purified by column chromatography to yield **2(s or m)**. The intermediate **2(s or m)** was treated with carbon tetrabromide (1.3 equiv) and triphenylphosphine (1.3 equiv) in dry THF (100 mL) at 0 °C. The resulting solution was stirred for 6 h, and THF was evaporated. The obtained product was extracted with CH_2Cl_2; the organic layer was dried with Na_2SO_4, filtered and concentrated at reduced pressure. The crude product was purified by column chromatography yielding the first generation dendron **3(s or m)**. Subsequently, 3,5-dihydroxybenzyl alcohol was reacted with 2.3 equiv of first generation dendron **3(s or m)**, 4 equiv of K_2CO_3 and a catalytic amount of 18-crown-6 in dry acetone (100 mL); the reaction mixture was heated to reflux for 48 h. After cooling, the mixture was filtered on Celite and evaporated to dryness. The resulting product was purified by column chromatography to give **4(s or m)**. Compound **4(s or m)** was reacted in the presence of carbon tetrabromide (1.3 equiv) and triphenylphosphine (1.3 equiv) in dry THF (100 mL) at 0 °C for 6 h. THF was evaporated and the product was extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4, filtered and concentrated at reduced pressure. Purification by column chromatography of the resulting product gave **5(s or m)**. Furthermore **5(s or m)** (2.3 equiv) was reacted in the presence of 3,5-dihydroxybenzyl alcohol (1 equiv), K_2CO_3 (4 equiv) and a catalytic amount of 18-crown-6 in dry acetone (100 mL) for 48 h. After cooling, the reaction mixture was filtered on Celite and evaporated to dryness. The resulting product was purified by column chromatography to give dendron **6(s or m)**. Finally, dendron **6(s or m)** was treated in the presence of carbon tetrabromide (1.3 equiv) and triphenylphosphine (1.3 equiv) in dry THF (100 mL) at 0 °C for 6 h; then THF was evaporated to dryness and the resulting product was extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4, filtered and concentrated at reduced pressure. Purification by column chromatography of the crude product gave bromide-dendron **7(s or m)**.

2.2.1.1. Dendrons with propenyloxy chains

*2.2.1.1.1. Compound **2s**, (3,5-dipropoxy-phenyl)-methanol.* Column chromatography (SiO_2, CH_2Cl_2/hexane 3:2) gave **2s** (6.48 g, 28.89 mmol). Yield: 81% (colorless oil). IR (CH_2Cl_2): 3607 (O–H) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.02 (t, J = 7.4 Hz, 6H), 1.80 (m, 4H), 3.90 (t, J = 6.6 Hz, 4H), 4.61 (d, J = 0.4 Hz, 2H), 6.38 (t, J = 2.3 Hz, 1H), 6.5 (d, J = 2.3 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.49, 22.53, 65.39, 69.52, 100.49, 105.01, 143.17, 160.46. Elemental analysis: calcd for $C_{13}H_{20}O_3$: C, 69.61%; H, 8.99%. Found: C, 69.58%; H, 8.97%.

*2.2.1.1.2. Compound **3s**, 1-bromomethyl-3,5-dipropoxy-benzene.* Column chromatography (SiO_2, CH_2Cl_2/hexane 1:9) gave **3s** (2.90 g, 10.09 mmol). Yield: 87% (colorless oil). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.02 (t, J = 7.3 Hz, 6H), 1.79 (m, 4H), 3.89 (t, J = 6.4 Hz, 4H), 4.4 (s, 2H), 6.38 (t, J = 2.4 Hz, 1H), 6.51 (d, J = 2.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.49, 22.53, 33.76, 69.60, 101.44, 107.40, 139.52, 160.40. Elemental analysis: calcd for $C_{13}H_{19}BrO_2$: C, 54.37%; H, 6.67%. Found: C, 54.34%; H, 6.63%.

*2.2.1.1.3. Compound **4s**, [3,5-bis-(3,5-dipropoxy-benzyloxy)-phenyl]-methanol.* Column chromatography (SiO_2, CH_2Cl_2/hexane 3:2) gave **4s** (2.93 g, 2.93 mmol). Yield: 80% (colorless viscous oil). IR ($CHCl_3$): 3421 (O–H) cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.02 (t, J = 7.4 Hz, 12H), 1.78 (m, 8H), 3.90 (t, J = 6.6 Hz, 8H), 4.61 (s, 4H), 4.95 (s, 2H), 6.38 (t, J = 2.3 Hz, 2H), 6.40 (t,

$J = 2.3$ Hz, 1H), 6.5 (d, $J = 2.3$ Hz, 4H), 6.65 (d, $J = 2.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.51, 22.54, 65.31, 69.54, 70.06, 100.77, 101.30, 105.68, 138.98, 143.34, 160.11, 160.47. Elemental analysis: calcd for $C_{33}H_{44}O_7$: C, 71.71%; H, 8.02%. Found: C, 71.69%; H, 7.98%.

*2.2.1.1.4. Compound **5s**, [3,5-bis-(3,5-dipropoxy-benzyloxy)-phenyl]-1-bromomethyl.* Column chromatography (SiO_2, CH_2Cl_2/hexane 1:9) gave **5s** (2.45 g, 3.98 mmol). Yield: 75% (colorless viscous oil). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.02 (t, $J = 7.5$ Hz, 12H), 1.79 (m, 8H), 3.90 (t, $J = 6.4$ Hz, 8H), 4.41 (s, 2H), 4.94 (s, 4H), 6.41 (t, $J = 2.4$ Hz, 2H), 6.53 (t, $J = 2.5$ Hz, 1H), 6.54 (d, $J = 2.1$ Hz, 4H), 6.62 (d, $J = 2.1$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.51, 22.56, 33.60, 69.57, 70.18, 100.90, 102.23, 105.74, 108.14, 138.76, 139.70, 160.02, 160.50. Elemental analysis: calcd for $C_{33}H_{43}BrO_6$: C, 64.39%; H, 7.04%. Found: C, 64.37%; H, 7.01%.

*2.2.1.1.5. Compound **6s**, (3,5-bis-[3,5-bis-(3,5-dipropoxy-benzyloxy)-benzyloxy]-phenyl)-methanol.* Column chromatography (SiO_2, CH_2Cl_2/hexane 9:1) gave **6s** (1.80 g, 1.49 mmol). Yield: 65% (colorless viscous oil). IR ($CHCl_3$): 3436 (O–H) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.02 (t, $J = 7.3$ Hz, 24H), 1.78 (m, 16H), 3.89 (t, $J = 6.6$ Hz, 16H), 4.95 (s, 8H), 4.96 (s, 4H), 6.40 (t, $J = 2.4$ Hz, 4H), 6.52 (t, $J = 2.4$ Hz, 2H), 6.55 (d, $J = 2.1$ Hz, 8H), 6.56 (s, 1H), 6.59 (d, $J = 2.1$ Hz, 2H), 6.65 (d, $J = 2.1$ Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.49, 22.55, 29.26, 31.69, 53.82, 65.28, 69.59, 69.99, 70.16, 100.91, 101.31, 101.64, 105.75, 106.35, 138.98, 139.24, 160.15, 160.51. Elemental analysis: calcd for $C_{73}H_{92}O_{15}$: C, 72.49%; H, 7.67%. Found: C, 72.45%; H, 7.62%.

*2.2.1.1.6. Compound **7s**, (3,5-bis-[3,5-bis-(3,5-dipropoxy-phenoxy)-benzyloxy]-phenyl)-1-bromomethyl.* Column chromatography (SiO_2, CH_2Cl_2/hexane 1:9) yielded **7** (1.67 g, 1.31 mmol). Yield: 80% (colorless viscous oil). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 1.02 (t, $J = 7.4$ Hz, 24H), 1.78 (m, 16H), 3.89 (t, $J = 6.6$ Hz, 16H), 4.41 (s, 2H), 4.95 (s, 12H), 6.40 (t, $J = 2.2$ Hz, 4H), 6.53 (s, 2H), 6.55 (d, $J = 2.2$ Hz, 8H), 6.57 (s, 1H), 6.62 (d, $J = 2.2$ Hz, 2H), 6.66 (d, $J = 2.2$ Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.51, 22.53, 33.58, 69.62, 70.03, 70.12, 100.80, 101.61, 102.13, 105.69, 106.36, 108.12, 138.89, 139.74, 159.94, 160.11, 160.46. Elemental analysis: calcd for $C_{73}H_{91}BrO_{14}$: C, 68.91%; H, 7.21%. Found: C, 68.88%; H, 7.17%.

2.2.1.2. Dendrons with dodecyloxy chains

*2.2.1.2.1. Compound **2m**, (3,5-bis-dodecyloxy-phenyl)-methanol.* Column chromatography (SiO_2, CH_2Cl_2/hexane 3:2) gave **2m** (28.90 g, 6.06 mmol). Yield: 85% (white solid). IR (film): 3608 (O–H) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.88 (t, $J = 6.6$ Hz, 6H), 1.26 (s, 36H), 1.76 (m, 4H), 3.93 (t, $J = 6.6$ Hz, 4H), 4.61 (s, 2H), 6.37 (t, $J = 2.2$ Hz, 1H), 6.49 (d, $J = 1.2$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.09, 22.87, 25.7, 26.02, 29.25, 29.36, 29.58, 31.90, 32.79, 63.08, 65.44, 68.03, 100.52, 105.02, 143.16, 160.52. Elemental analysis: calcd for $C_{31}H_{56}O_3$: C, 78.09%; H, 11.84%. Found: C, 78.01%; H, 11.82%.

*2.2.1.2.2. Compound **3m**, 1-bromomethyl-3,5-bis-dodecyloxy-benzene.* Column chromatography (SiO_2, CH_2Cl_2/hexane 1:4) gave **3m** (3.34 g, 6.19 mmol). Yield: 78% (white solid). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.88 (t, $J = 6.7$ Hz, 6H), 1.26 (s, 36H), 1.71–1.80 (m, 4H), 3.92 (t, $J = 6.6$ Hz, 4H), 4.4 (s, 2H), 6.37 (t, $J = 2.2$ Hz, 1H), 6.51 (d, $J = 2.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.10, 22.68, 26.02, 29.20, 29.33, 29.37, 29.56, 29.58, 29.62, 29.65, 31.91, 68.1, 101.42, 107.38, 139.50, 160.41. Elemental analysis: calcd for $C_{31}H_{55}BrO_2$: C, 68.99%; H, 10.27%. Found: C, 68.94%; H, 10.23%.

*2.2.1.2.3. Compound **4m**, [3,5-bis-(3,5-bis-dodecyloxy-benzyloxy)-phenyl]-methanol.* Column chromatography (SiO_2, CH_2Cl_2/hexane 3:2) gave **4m** (5.20 g, 4.91 mmol). Yield: 75% (colorless oil). IR ($CHCl_3$): 3419 (O–H) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.87 (t, $J = 6.7$ Hz, 12H), 1.26 (s, 72H), 1.76 (m, 8H), 3.93 (t, $J = 6.6$ Hz, 8H), 4.62 (s, 2H), 4.94 (s, 4H), 6.39 (t, $J = 2.2$ Hz, 2H), 6.53 (t, $J = 2.2$ Hz, 1H), 6.54 (d, $J = 2.1$ Hz, 4H), 6.6 (d, $J = 2.1$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.09, 22.67, 26.05, 29.26, 29.33, 29.40, 29.61, 31.91, 65.34, 68.08, 70.12, 100.8, 101.34, 105.7, 138.97, 143.34, 160.16, 160.51. Elemental analysis: calcd for $C_{69}H_{116}O_7$: C, 78.36%; H, 11.05%. Found: C, 78.32%; H, 11.01%.

*2.2.1.2.4. Compound **5m**, [3,5-bis-(3,5-bis-dodecyloxy-benzyloxy)-phenyl]-1-bromometyl.* Column chromatography (SiO_2, CH_2Cl_2/hexane 1:4) gave **5m** (5.17 g, 4.61 mmol). Yield: 84% (white solid). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.88 (t, $J = 6.7$ Hz, 12H), 1.26 (s, 72), 1.74 (m, 8H), 3.93 (t, $J = 6.4$ Hz, 8H), 4.62 (s, 2H), 4.95 (s, 4H), 6.4 (t, $J = 2.2$ Hz, 2H), 6.53 (t, $J = 2$ Hz, 1H), 6.55 (d, $J = 2.1$ Hz, 4H), 6.61 (d, $J = 2.4$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.11, 22.67, 26.06, 29.26, 29.35, 29.41, 29.6, 29.63, 29.66, 31.91, 65.34, 68.08, 70.11, 100.8, 101.32, 105.71, 138.97, 143.35, 160.16, 160.51. Elemental analysis: calcd for $C_{69}H_{115}BrO_6$: C, 73.96%; H, 10.34%. Found: C, 73.94%; H, 10.30%.

*2.2.1.2.5. Compound **6m**, (3,5-bis-[3,5-bis-(3,5-didodecyloxy-benzyloxy)-benzyloxy]-phenyl)-methanol.* Column chromatography (SiO_2, CH_2Cl_2/hexane 3:2) gave **6m** (4.10 g, 1.85 mmol). Yield: 75% (colorless viscous oil). IR ($CHCl_3$): 3422 (O–H) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.87 (t, $J = 6.6$ Hz, 24H), 1.26 (s, 144), 1.76 (m, 16H), 3.93 (t, $J = 6.6$ Hz, 16H), 4.62 (s, 4H), 4.95 (s, 8H), 6.39 (t, $J = 2.2$ Hz, 4H), 6.52 (t, $J = 2.4$ Hz, 2H), 6.54 (d, $J = 2$ Hz, 8H), 6.57 (d, $J = 2$ Hz, 2H), 6.6 (d, $J = 2.3$ Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.10, 22.68, 26.05, 29.26, 29.41, 29.58, 29.63, 29.66, 31.91, 65.36, 68.07, 70.13, 100.8, 101.33, 105.7, 138.97, 143.35, 160.18, 160.51. Elemental analysis: calcd for $C_{146}H_{238}O_{15}$: C, 78.51%; H, 10.74%. Found: C, 78.48%; H, 10.70%.

*2.2.1.2.6. Compound **7m**, (3,5-bis-[3,5-bis-(3,5-didodecyloxy-benzyloxy)-benzyloxy]-phenyl)-1-bromomethyl.* Column chromatography (SiO_2, CH_2Cl_2/hexane 1:9) gave **7m** (1.67 g, 0. 731 mmol). Yield: 88% (colorless viscous oil). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.88 (t, $J = 6.7$ Hz, 24H), 1.29 (s, 144H), 1.75 (m, 16H), 3.96 (t, $J = 6.4$ Hz, 16H), 4.56 (s, 2H), 5.0 (s, 12H), 6.41 (t, $J = 2.2$ Hz, 4H), 6.52 (t, $J = 2.2$ Hz, 2H), 5.54 (s, 1H), 6.58 (d, $J = 2.4$ Hz, 2H), 6.6 (d, $J = 2.4$ Hz, 8H), 6.63 (d, $J = 2.4$ Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.1, 22.68, 26.05, 29.26, 29.35, 29.41, 29.6, 29.63, 29.66, 31.92, 65.34, 68.08, 70.12, 100.8, 101.32, 105.7, 138.97, 143.35, 160.16, 160.51. Elemental analysis: calcd for $C_{146}H_{237}BrO_{14}$: C, 76.36%; H, 10.40%. Found: C, 76.32%; H, 10.38%.

2.2.2. Synthesis of the π-conjugated OPV core

*2.2.2.1. Compound **9**, 4-(5,5-dimethyl-1,3-dioxan-2-yl)-benzaldehyde.* A solution of terephthaldehyde (10 g, 74.55 mmol), 2,2-dimethylpropane-1,3-diol (7.76 g, 74.55 mmol), and a catalytic amount of *p*-toluenesulfonic acid (100 mg) in benzene (300 mL) was refluxed for 24 h using a Dean–Stark trap. After cooling, the solution was evaporated to dryness and the resulting product was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) to yield **9** (9.86 g, 4.47 mmol). Yield: 60% (white crystalline solid). ^1H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.82 (s, 3H), 1.292 (s, 3H), 3.63 (AB, $J = 10.5$ Hz, 2H) 3.76 (AB, $J = 10$ Hz, 2H), 5.45 (s, 1H), 7.68 (A_2B_2, $J = 8.4$ Hz, 2H), 7.89 (A_2B_2, $J = 8.4$ Hz, 2H), 10.02 (s, 1H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 21.81, 22.97, 30.23, 77.67, 100.71, 126.02, 126.89, 136.62, 144.56, 192.03. Elemental analysis: calcd for $C_{13}H_{16}O_3$: C, 70.89%; H, 7.32%. Found: C, 70.85%; H, 7.29%.

*2.2.2.2. Compound **10**, 5,5-dimethyl-2-(4-vinyl-phenyl)-1,3-dioxane.* *t*-BuOK (4.32 g, 38.52 mmol) was added to a solution of **9** (7.71 g, 35.02 mmol) and methyltriphenylphosphonium bromide (13.76 mg, 38.52 mmol) in dry THF (100 mL) at 0 °C. The solution was stirred for 4 h; then a few drops of water were added and the resulting mixture was concentrated. The aqueous layer was extracted with CH_2Cl_2. The organic layer was dried with Na_2SO_4, and evaporated at reduced pressure. Column chromatography

(SiO_2, CH_2Cl_2/hexane 3:7) gave **10** (3.66 g, 16.76 mmol). Yield: 48%. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.79 (s, 3H), 1.29 (s, 3H), 3.63 (d, J = 10.8 Hz, 2H), 3.76 (d, J = 9.99 Hz, 2H), 5.24 (dd, J = 10.83 Hz, 1H), 5.74 (dd, J = 17.6 Hz, 1H), 6.71 (dd, J = 17.58 Hz, 1H), 7.43 (A_2B_2, J = 17.73 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 21.86, 23.02, 77.64, 101.50, 114.16, 126.12, 126.32, 136.55, 137.99, 138.10. Elemental analysis: calcd for $C_{14}H_{18}O_2$: C, 77.03%; H, 8.31%. Found: C, 76.99%; H, 8.28%.

*2.2.2.3. Compound **12**, 2-(4-{(*E*)-2-[2,5-bis-dodecyloxy-4-((*E*)-5,-5-dimethyl-2-phenyl-[1,3]dioxane)-phenyl]-vinyl}-phenyl)-5,5-dimethyl-[1,3]dioxane.* A mixture of **10** (2.63 g, 12.04 mmol), **11** (3.03 g, 5.01 mmol), $Pd(OAc)_2$ (112 mg, 0.50 mmol), and tri-*o*-tolylphosphine POT (763 mg, 2.51 mmol) in Et_3N/DMF 1:1 (30 mL) was stirred under N_2 at 120 °C for 48 h. After cooling, the resulting mixture was filtered and evaporated. Purification by column chromatography (SiO_2, CH_2Cl_2/hexane 2:3) gave **12** (3.75 g, 4.26 mmol). Yield: 85% (yellow solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.80 (s, 3H), 0.88 (t, J = 6.75 Hz, 6H), 1.26 (s, 36H), 1.31 (s, 3H), 1.86 (m, 4H), 3.65 (d, J = 10.8 Hz, 2H), 3.78 (d, J = 11.1 Hz, 2H), 4.04 (t, J = 6.45 Hz, 4H), 7.11 (s, 2H), 7.12 (d, J = 16.5 Hz, 2H), 7.47 (d, J = 17.1 Hz, 2H), 7.5 (A_2B_2, J = 13.8 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.09, 21.88, 22.67, 23.04, 26.26, 29.34, 29.45, 29.63, 30.22, 69.57, 77.65, 101.60, 110.67, 123.84, 126.40, 126.84, 128.45, 137.51, 138.54, 151.11. Elemental analysis: calcd for $C_{58}H_{86}O_6$: C, 79.22%; H, 9.86%. Found: C, 79.19%; H, 9.82%.

*2.2.2.4. Compound **13**, 4,4′-(1*E*,1′E)-2,2′-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)dibenzaldehyde.* CF_3COOH (15 mL) was added to a solution of **12** (2.64 g, 3 mmol) in CH_2Cl_2/H_2O (50 mL/2 mL). The solution was stirred at room temperature for 2 h. The organic layer was then washed with water (2 × 100 mL), dried with Na_2SO_4, filtered, and evaporated to dryness. Purification by column chromatography (SiO_2, CH_2Cl_2/hexane 3:2) gave **13** (1.26 g, 1.79 mmol). Yield: 85% (orange solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.87 (t, J = 6.6 Hz, 6H), 1.25 (s, 36H), 1.89 (m, 4H), 4.08 (t, J = 6.45 Hz, 4H), 7.13 (s, 2H), 7.20 (d, J = 16.5 Hz, 2H), 7.63 (d, J = 16.5 Hz, 2H), 7.66 (A_2B_2, J = 8.1 Hz, 4H), 7.87 (A_2B_2, J = 8.4 Hz, 4H), 9.99 (s, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.10, 22.67, 26.27, 29.33, 29.42, 29.64, 31.89, 69.51, 110.81, 126.89, 127.89, 130.22, 135.21, 143.99, 151.40, 191.51. Elemental analysis: calcd for $C_{48}H_{66}O_4$: C, 81.54%; H, 9.41%. Found: C, 81.50%; H, 9.38%.

*2.2.2.5. Compound **14**, (4,4′-(1*E*,1′E)-2,2′-(2,5-bis(dodecyloxy)-1,4-phenylene)bis(ethene-2,1-diyl)bis(4,1-phenylene))dimethanol.* A 1 M solution of $LiAlH_4$ in THF (3.94 mL, 3.94 mmol) was slowly added to a solution of **13** (1.26 g, 1.79 mmol) in dry THF (100 mL) at 0 °C under N_2 atmosphere. The resulting mixture was stirred for 7 h; then a few drops of MeOH and 5 mL of water were carefully added. The resulting mixture was filtered on Celite and evaporated. Purification by column chromatography (SiO_2, MeOH/CH_2Cl_2 1/99) gave **14** (1.05 g, 1.47 mmol). Yield: 82% (yellow solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.87 (t, J = 6.7 Hz, 6H), 1.26 (s, 36H), 1.68 (t, J = 8.8 Hz, 2H), 4.05 (t, J = 6.4 Hz, 4H), 4.69 (s, 4H), 7.12 (s, 2H), 7.13 (d, J = 16.5 Hz, 2H), 7.35 (A_2B_2, J = 8.1 Hz, 4H), 7.47 (d, J = 16.5 Hz, 2H), 7.52 (A_2B_2, J = 8.1 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.13, 22.7, 26.29, 29.37, 29.47, 29.66, 31.93, 65.21, 69.6, 110.67, 123.58, 126.66, 126.84, 127.34, 128.34, 137.46, 139.95, 151.08. Elemental analysis: calcd for $C_{48}H_{70}O_4$: C, 81.08%; H, 9.92%. Found: C, 81.07%; H, 9.89%.

2.2.3. General procedure for dendrimers synthesis

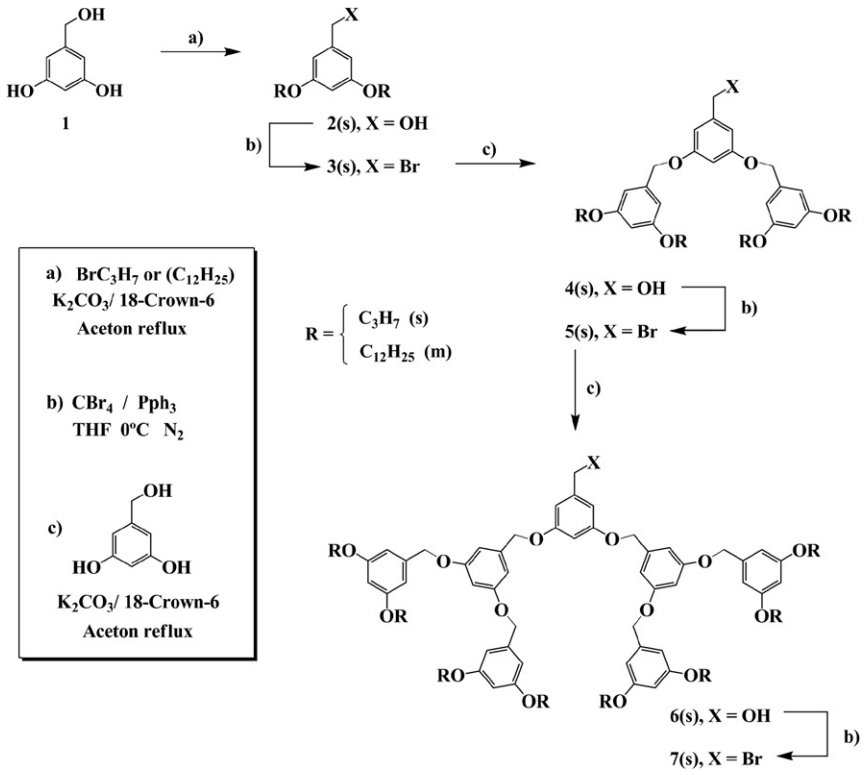
t-BuOK (0.5 equiv) was added to a solution of the OPV unit **16** (100 mg) in dry DMF (50 mL); the solution was heated at 120 °C and stirred under N_2 atmosphere for 30 min. Then, a solution of 0.5 equiv of dendron **3(s or m)**, or **5(s or m)**, or **7(s or m)** in dry DMF (10 mL) was added dropwise and the resulting solution was stirred and heated for 48 h. After cooling, DMF was removed at reduced pressure and the resulting product was purified by column chromatography (SiO_2) to give dendrimers **15** or **16**, **17** or **18**, **19** or **20**, respectively.

2.2.3.1. Dendrimers with propenyloxy chains

*2.2.3.1.1. Dendrimer **15** (4-(4-(4-((3,5-dipropoxy-benzyloxy)-methyl)styryl)-2,5-bis(dodecyloxy)styryl)phenyl) methanol.* Purification by column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) gave **15** (63 mg, 6.867×10^{-5} mmol). Yield: 40% (yellow solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.88 (t, J = 6.7 Hz, 6H), 1.05 (t, J = 7.5 Hz, 12H), 1.26 (s, 36H), 1.51–1.6 (m, 4H), 1.70–1.91 (m, 8H), 3.90 (t, J = 6.5 Hz, 8H), 4.07 (q, J = 12.6, Hz, 4H), 4.43 (s, 4H), 4.46 (s, 4H), 6.38 (t, J = 2.3 Hz, 2H), 6.5 (d, J = 2.3 Hz, 4H), 7.12 (s, 1H), 7.13 (s, 1H), 7.15 (d, J = 17.5 Hz, 1H), 7.18 (d, J = 16.4 Hz, 1H), 7.36 (A_2B_2, J = 8.2 Hz, 2H), 7.48 (d, J = 16.4 Hz, 1H), 7.52 (A_2B_2, J = 8.1 Hz, 2H), 7.63 (d, J = 16.4 Hz, 1H), 7.66 (A_2B_2, J = 8.2 Hz, 2H), 7.86 (A_2B_2, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.51, 14.11, 22.67, 26.05, 26.29, 29.33, 29.44, 29.64, 31.90, 65.20, 65.48, 68.08, 69.60, 100.58, 105.06, 110.57, 110.95, 123.44, 126.75, 126.82, 127.13, 127.38, 128.95, 130.22, 132.26, 135.08, 137.33, 140.17, 143.16, 144.20, 151.05, 151.49, 160.54. Elemental analysis: calcd for $C_{61}H_{88}O_6$: C, 79.87%; H, 9.67%. Found: C, 79.85%; H, 9.63%.

*2.2.3.1.2. Dendrimer **16**, (4-(4-(4-((3,5-bis(3,5-dipropoxy-benzyloxy)benzyloxy)methyl)styryl)-2,5-bis(dodecyloxy)styryl)phenyl)methanol.* Purification by column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) gave **16** (88 mg, 7.064×10^{-5} mmol). Yield: 35% (yellow solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.87 (t, J = 6.7 Hz, 6H), 1.05 (t, J = 6.5 Hz, 24H), 1.25 (s, 36H), 1.49–1.61 (m, 4H), 1.70–1.91 (m, 16H), 3.91 (t, J = 6.5 Hz, 16H), 4.06 (q, J = 12.6, Hz, 4H), 4.62 (s, 4H), 4.71 (s, 8H), 4.94 (s, 4H), 6.40 (t, J = 2.3 Hz, 4H), 4.53 (s, 2H), 6.55 (d, J = 2.2 Hz, 8H), 6.61 (d, J = 2.2 Hz, 4H), 7.13 (s, 1H), 7.14 (s, 1H), 7.15 (d, J = 16.5 Hz, 1H), 7.18 (d, J = 16.4 Hz, 1H), 7.37 (A_2B_2, J = 8.1 Hz, 2H), 7.48 (d, J = 17 Hz, 1H), 7.53 (A_2B_2, J = 7.8 Hz, 2H), 7.63 (d, J = 16.5 Hz, 1H), 7.66 (A_2B_2, J = 8.2 Hz, 2H), 7.87 (A_2B_2, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.49, 14.09, 22.67, 26.04, 26.27, 29.25, 29.32, 29.39, 29.57, 29.6, 29.69, 65.15, 68.08, 69.57, 70.23, 100.84, 105.82, 108.94, 110.67, 123.56, 126.67, 126.85, 127.35, 128.36, 137.44, 138.73, 140.05, 151.1, 160.15, 160.48. Elemental analysis: calcd for $C_{81}H_{112}O_{10}$: C, 78.09%; H, 9.06%. Found: C, 78.06%; H, 9.02%.

*2.2.3.1.3. Dendrimer **17**, (4-(4-(4-((3,5-bis(3,5-bis(3,5-dipropoxy-benzyloxy)benzyloxy)benzyloxy)methyl)styryl)-2,5-bis(dodecyloxy)-styryl)phenyl)methanol.* Purification by column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) gave **17** (50 mg, 2.628×10^{-5} mmol). Yield: 15% (yellow solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.88 (t, J = 6.6 Hz, 6H), 1.01 (t, J = 7.3 Hz, 48H), 1.25 (s, 36H), 1.71–1.81 (m, 32H), 1.84–1.91 (m, 4H), 3.89 (t, J = 6.6 Hz, 32H), 3.96 (t, J = 6.4 Hz, 4H), 4.61 (s, 4H), 4.70 (s, 4H), 4.94 (s, 16H), 4.96 (s, 8H), 6.4 (t, J = 2.2 Hz, 8H), 6.53 (t, J = 2.1 Hz, 4H), 6.55 (d, J = 3 Hz, 16H), 6.56 (s, 2H), 6.59 (d, J = 2.1 Hz, 4H), 6.65 (d, J = 2.1 Hz, 8H), 7.12 (s, 1H), 7.13 (s, 1H), 7.15 (d, J = 17.7 Hz, 1H), 7.18 (d, J = 16.5 Hz, 1H), 7.36 (A_2B_2, J = 8.4 Hz, 2H), 7.47 (d, J = 16.8 Hz, 1H), 7.53 (A_2B_2, J = 8.1 Hz, 2H), 7.63 (d, J = 16.5 Hz, 1H), 7.65 (A_2B_2, J = 8.1 Hz, 2H), 7.86 (A_2B_2, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 10.51, 14.10, 22.55, 22.68, 26.28, 29.34, 29.45, 29.62, 29.65, 29.70, 31.91, 65.19, 65.58, 70.15, 100.88, 105.74, 106.34, 110.56, 110.94, 123.44, 125.93, 126.75, 126.82, 127.14, 127.36, 127.90, 128.96, 130.23, 135.1, 137.32, 138.96, 139.2, 140.19, 144.18, 151.06, 151.50, 160.14, 160.49. Elemental analysis: calcd for $C_{121}H_{160}O_{18}$: C, 76.39%; H, 8.48%. Found: C, 76.33%; H, 8.45%.



Scheme 1. Preparation of the *n*-alkyl (*n*-propyl and *n*-dodecyl) end-capped dendrons. Reagents and conditions: (a) 1-bromopropane (or 1-bromododecane), K_2CO_3, 18-Crown-6 (cat.), acetone (reflux), 72 h; (b) CBr_4/PPh_3, THF, 0 °C, 6 h; (c) 3,5-dihydroxybenzyl alcohol, K_2CO_3, 18-Crown-6 (cat.), acetone (reflux), 72 h.

2.2.3.2. Dendrimers with dodecyloxy chains

2.2.3.2.1. Dendrimer ***18****, (4-(4-(4-((3,5-bis(dodecyloxy)benzyloxy)-methyl)styryl)-2,5-bis(dodecyloxy)styryl)phenyl)methanol.* Purification by column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) gave **18** (63 mg, 5.385×10^{-5} mmol). Yield: 63% (yellow solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.88 (t, J = 6.6 Hz, 18H), 1.25 (s, 108H), 1.68–1.81 (m, 4H), 1.83–1.91 (m, 8H), 3.93 (t, J = 6.4 Hz, 8H), 4.06 (q, J = 12.5, Hz, 4H), 4.61 (s, 4H), 4.71 (s, 4H), 7.12 (s, 1H), 7.13 (s, 1H), 7.15 (d, J = 17 Hz, 1H), 7.18 (d, J = 16.5 Hz, 1H), 7.37 (A_2B_2, J = 8.4 Hz, 2H), 7.48 (d, J = 16.5 Hz, 1H), 7.53 (A_2B_2, J = 8.1 Hz, 2H), 7.63 (d, J = 16.5 Hz, 1H), 7.66 (A_2B_2, J = 8.1 Hz, 2H), 7.87 (A_2B_2, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.1, 22.67, 26.04, 26.29, 29.34, 29.44, 29.64, 65.18, 65.48, 68.08, 69.6, 100.58, 105.06, 110.57, 110.95, 123.44, 125.93, 126.75, 126.82, 127.13, 127.38, 128.95, 130.22, 132.26, 135.09, 137.33, 138.59, 140.17, 143.16, 144.2, 148.96, 151.05, 151.49, 160.54. Elemental analysis: calcd for $C_{79}H_{124}O_6$: C, 81.11%; H, 10.68%. Found: C, 81.09%; H, 10.64%.

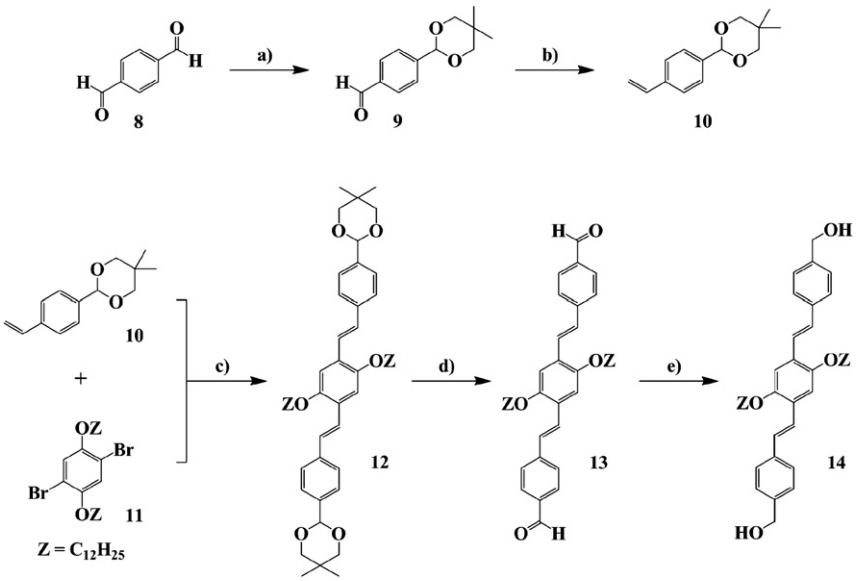
2.2.3.2.2. Dendrimer ***19****, (4-(4-(4-((3,5-bis(3,5-bis(dodecyloxy)-benzyloxy)benzyloxy)methyl)styryl)-2,5-bis(dodecyloxy)styryl)phenyl)-methanol.* Purification by column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) gave **19** (70 mg, 3.998×10^{-5} mmol). Yield: 51% (yellow solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.87 (t, J = 6 Hz, 18H), 1.25 (s, 180H), 1.67–1.80 (m, 16H), 1.83–1.91 (m, 4H), 3.92 (t, J = 6.4 Hz, 16H), 4.06 (q, J = 12.6, Hz, 4H), 4.63 (s, 4H), 4.70 (s, 12H), 6.37 (t, J = 2.1 Hz, 4H), 6.48 (s, 2H), 6.49 (d, J = 2.1 Hz, 8H), 6.75 (d, J = 2.1 Hz, 4H), 7.12 (s, 1H), 7.13 (s, 1H), 7.15 (d, J = 17 Hz, 1H), 7.17 (d, J = 16.5 Hz, 1H), 7.36 (A_2B_2, J = 8.1 Hz, 2H), 7.47 (d, J = 16.5 Hz, 1H), 7.53 (A_2B_2, J = 8.1 Hz, 2H), 7.62 (d, J = 16.5 Hz, 1H), 7.65 (A_2B_2, J = 8.4 Hz, 2H), 7.86 (A_2B_2, J = 8.1 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.10, 22.68, 26.05, 26.28, 29.26, 29.34, 29.45, 29.65, 29.70, 65.19, 65.48, 68.07, 68.47, 69.51, 69.61, 100.57, 105.06, 109.29, 110.56, 110.96, 123.44, 125.93, 126.76, 126.82, 127.14, 127.38, 127.91, 128.96, 130.23, 135.1, 137.34, 140.16, 144.19, 151.06, 151.05, 160.55, 160.90. Elemental analysis: calcd for $C_{117}H_{184}O_{10}$: C, 80.27%; H, 10.59%. Found: C, 80.25%; H, 10.54%.

2.2.3.2.3. Dendrimer ***20****, (4-(4-(4-((3,5-bis(3,5-bis(3,5-bis-(dodecyloxy)benzyloxy)benzyloxy)benzyloxy)methyl)styryl)-2,5-bis-(dodecyloxy)styryl)phenyl)methanol.* Purification by column chromatography (SiO_2, CH_2Cl_2/hexane 7:3) gave **20** (100 mg, 3.433×10^{-5} mmol). Yield: 17% (yellow solid). ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) = 0.87 (t, J = 6.4 Hz, 54H), 1.25 (s, 324H), 1.72–1.82 (m, 32H), 1.84–1.91 (m, 4H), 3.89 (t, J = 6.4 Hz, 32H), 4.06 (q, J = 12.6 Hz, 4H), 4.71 (s, 8H), 4.95 (s, 16H), 5.01 (s, 8H), 6.38 (t, J = 2.6 Hz, 2H), 6.40 (t, J = 2.2 Hz, 8H), 6.5 (d, J = 2.3 Hz, 4H), 6.55 (d, J = 2 Hz, 16H), 6.57 (d, J = 2.2 Hz, 4H), 6.66 (d, J = 2 Hz), 7.12 (s, 1H), 7.13 (s, 1H), 7.15 (d, J = 17 Hz, 1H), 7.18 (d, J = 16.4 Hz, 1H), 7.36 (A_2B_2, J = 8.2 Hz, 2H), 7.48 (d, J = 17 Hz, 1H), 7.53 (A_2B_2, J = 7.9 Hz, 2H), 7.63 (d, J = 16.4 Hz, 1H), 7.66 (A_2B_2, J = 8.2 Hz, 2H), 7.86 (A_2B_2, J = 8.2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75.4 MHz): δ (ppm) = 14.10, 22.55, 22.68, 26.28, 29.34, 29.45, 29.62, 29.65, 29.70, 31.91, 65.19, 65.58, 70.15, 100.88, 105.74, 106.34, 110.56, 110.94, 123.44, 125.93, 126.75, 126.82, 127.14, 127.36, 127.90, 128.96, 130.23, 135.1, 137.32, 138.96, 139.2, 140.19, 144.18, 151.06, 151.50, 160.14, 160.49. Elemental analysis: calcd for $C_{193}H_{304}O_{18}$: C, 79.59%; H, 10.52%. Found: C, 79.54%; H, 10.48%.

3. Results and discussion

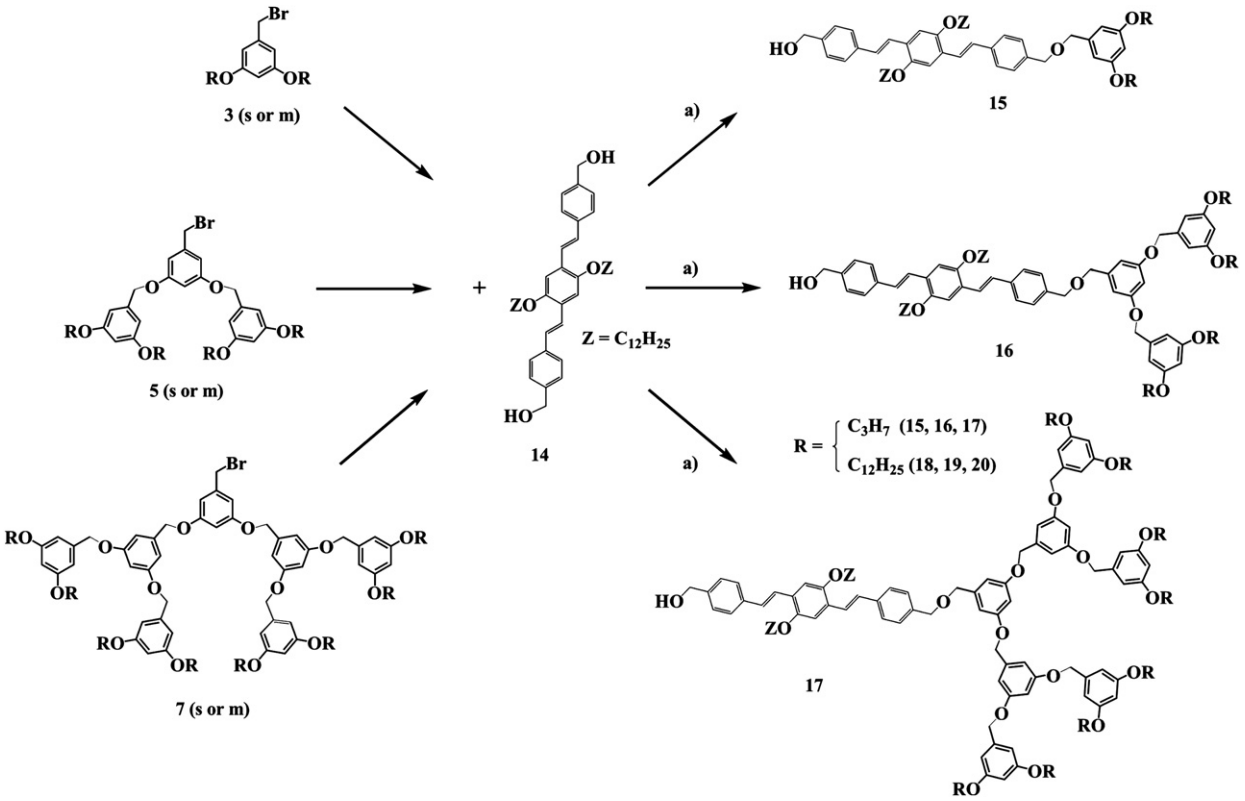
3.1. Synthesis of the dendritic branches

The preparation of the end-capped alkylated (*n*-propyl and *n*-dodecyl) dendritic branches is illustrated in Scheme 1. Such dendritic branches have been prepared, using a typical convergent method [19]. Particularly, dendritic branches with *n*-dodecyl chains were prepared according to the procedure previously reported in the literature [20].



Scheme 2. Preparation of the π-conjugated system OPV. Reagents and conditions: (a) 2,2-dimethyl-1,3-propanediol, PTSA (cat.), benzene, Δ, 12 h, (60%); (b) $CH_3P(Ph)_3Br$, *t*-BuOK, THF, 0 °C, 3 h (48%); (c) tri-*o*-tolylphosphine, $Pd(AcO)_2$ (cat.), Et_3N/DMF, 80 °C, 16 h (85%); (d) CF_3COOH/H_2O, CH_2Cl_2, r.t, 30 min, (85%); (e) $LiAlH_4$, THF, 0 °C, 4 h (82%).

The alkylated dendritic branches synthesis started with the alkylation of 3,5-dihydroxybenzyl alcohol **1** in the presence of 1-bromopropane (or 1-bromododecane) and K_2CO_3, which were heated to reflux in acetone with a catalytic amount of 18-crown-6. Further reaction of the resulting 3,5-dipropyloxybenzyl alcohol **2(s)** with carbon tetrabromide (CBr_4) and triphenylphosphine (PPh_3) in dry THF at 0 °C, leaded to the formation of the corresponding bromide of generation zero **3(s)**. Later bromide **3(s)** was reacted with 3,5-dihydroxybenzyl alcohol, in the presence of K_2CO_3 and a catalytic amount of 18-crown-6 in refluxing acetone, to give the first dendron generation with a terminal hydroxyl group **4(s)**. Subsequent treatment of **4(s)** with CBr_4 and PPh_3 in dry THF at 0 °C, yielded the dendron-bromide of first generation **5(s)**. Further reaction of **5(s)** with 3,5-dihydroxybenzyl alcohol in the presence of K_2CO_3 in refluxing acetone with catalytic amount of 18-crown-6, gave a dendron-alcohol **6(s)**. Finally, the higher generation dendron-bromide **7(s)** was obtained by bromination of **6(s)** in the presence of CBr_4 and PPh_3 in dry THF at 0 °C.



Scheme 3. Synthesis of dendrimers with an OPV core and peripheral alkyl chains. Reagents and conditions: (a) *t*-BuOK (1 equiv), DMF, 80 °C, N_2, 48 h.

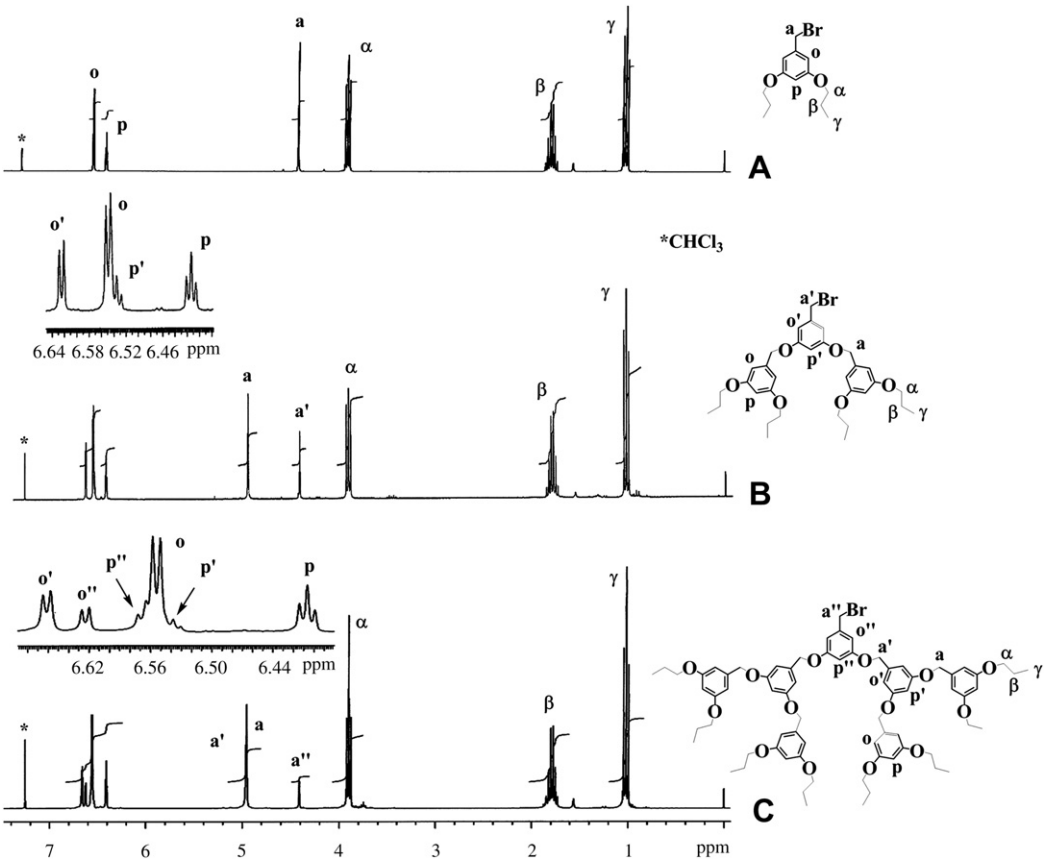


Fig. 1. ^{1}H NMR ($CDCl_3$, 300 MHz, $CDCl_3$) spectra of dendrons: **3s** (A), **5s** (B) and **7s** (C).

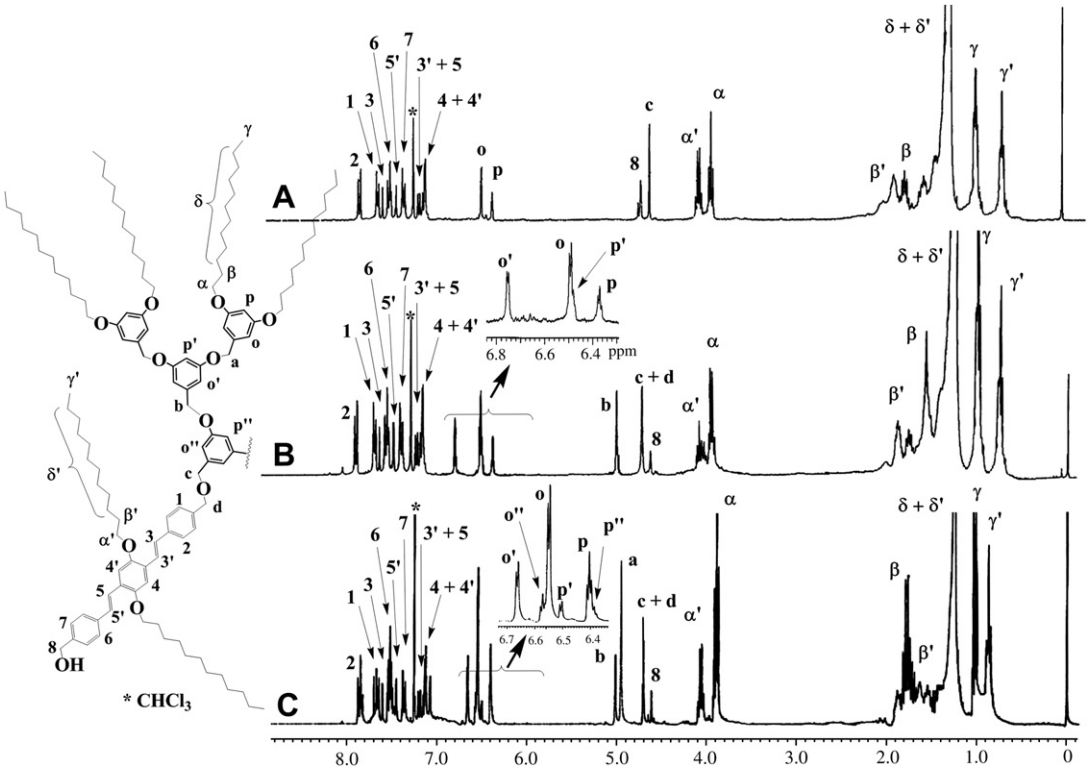


Fig. 2. ^{1}H NMR ($CDCl_3$, 300 MHz, $CDCl_3$) spectra of dendrimers: **18** (A), **19** (B) and **20** (C).

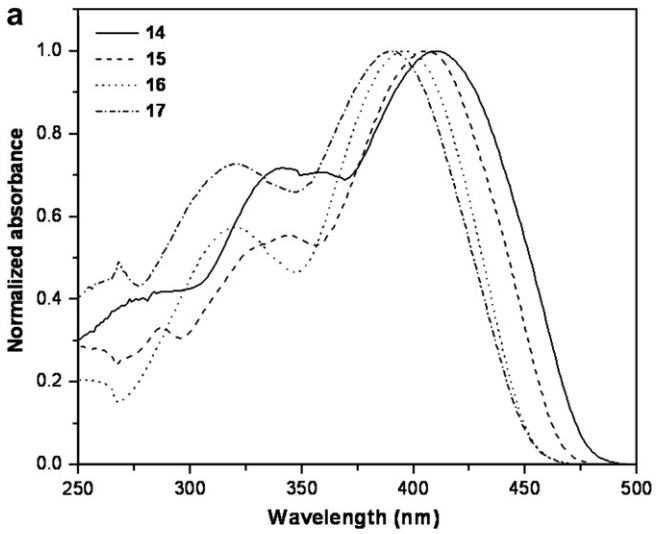


Fig. 3. Normalized absorption spectra of the dendrimers **15**–**17**: in toluene (a) and dichloromethane (b) at room temperature.

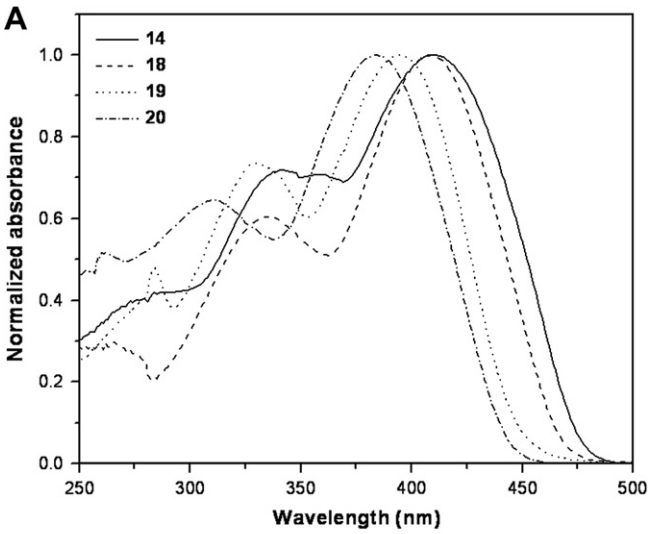


Fig. 4. Normalized absorption spectra of the dendrimers **18**–**20**: in toluene (A) and dichloromethane (B) at room temperature.

3.2. Synthesis of the π-conjugated system

The synthesis of the oligophenylenevinylene (OPV) unit was achieved in five steps, according to the synthetic sequence illustrated in Scheme 2.

The synthesis of the OPV moiety started with the reaction of terephthaldehyde (**8**) with 2,2-dimethyl-1,3-propanediol in refluxing benzene, in the presence of a catalytic amount of *p*-toluenesulfonic acid (PTSA), to give the mono-protected aldehyde **9** with 60% yield. Subsequent treatment of **9** with methyl triphenylphosphine bromide in dry THF in the presence of *t*-BuOK, under Wittig reaction conditions, afforded the corresponding stilbene **10**. Di-bromide **11** was synthesized according to the procedure reported in the literature [21]. Furthermore, **10** was reacted with **11** via a Heck reaction [22] using $Pd(OAc)_2$ as catalyst and DMF–Et_3N as solvent, in the presence of tri-*o*-tolylphosphine (POT) at 80 °C to give the di-ketal **12**. Subsequent cleavage of **12** in the presence of CF_3COOH in CH_2Cl_2/H_2O [23] leaded to the formation of the di-aldehyde **13**. Further treatment of **13** with $LiAlH_4$ in dry THF gave **14** in a 75% overall yield. Thanks to the presence of two dodecyloxy substituents, compound **14** is highly soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, toluene and THF, that is why the complete spectroscopic characterization of dendrimers and dendrons was easily achieved. ^1H NMR spectrum of **14** in $CDCl_3$ solution shows all the expected signals. Coupling constants of ca. 17 Hz for the two AB signals, corresponding to the two sets of vinylic protons, confirmed the *E* stereochemistry of both C=C double bonds of the OPV moiety.

3.3. Synthesis of the dendrimers

The strategy used for the synthesis of the dendrimers is described in Scheme 3. The incorporation of 1 equiv of dendron branches **3(s or m)**, **5(s or m)** and **7(s or m)** to the OPV moiety was achieved in one step by the reaction of the OPV moiety **14** with each one of the dendron arms.

Table 1
Optical properties of OPV unit **14** and dendrimers **15**–**20**, in toluene and dichloromethane at room temperature

Solvent	OPV unit	Dendrimers					
	14	**15**	**16**	**17**	**18**	**19**	**20**
λ_{max} toluene (nm)	410	406	396	390	409	395	384
λ_{max} CH_2Cl_2 (nm)	420	417	412	406	409	390	381

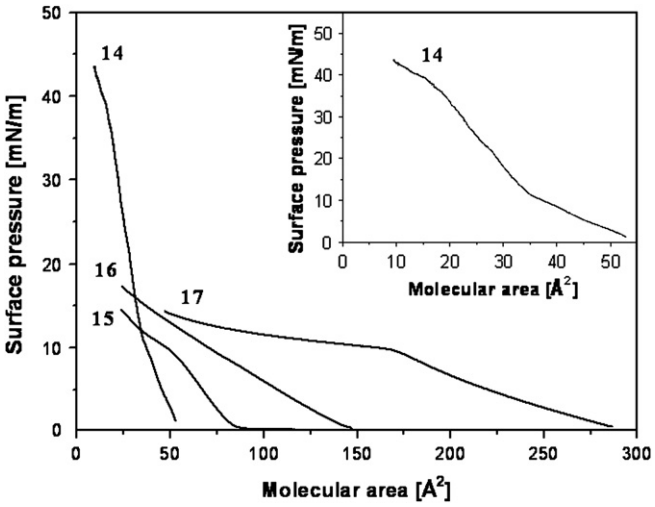


Fig. 5. Surface pressure–molecular area (Π/A) isotherms recorded at 20 °C, for Langmuir monolayers from dendrimers **15**–**17** with short alkyl chains (C_3H_7), and reference compound **14** lacking alkyl chains.

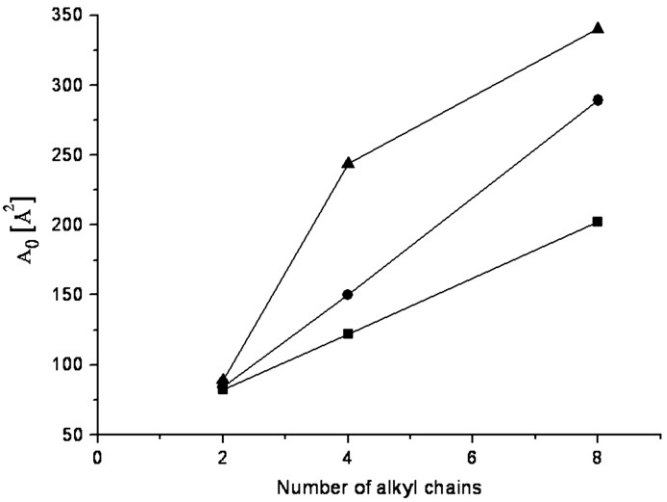


Fig. 7. Variation of cross-sectional area per molecule of the monolayers as a function of the number of alkyl chains in the dendrimers: (■) calculated for a given number of alkyl chains in vertical orientation, (●) experimentally measured for dendrimers with short alkyl chains (C_3H_7), and (▲) experimentally measured for dendrimers with long alkyl chains ($C_{12}H_{25}$).

3.4. Characterization of the obtained dendritic branches and dendrimers

Dendritic branches **3(s or m)**, **5(s or m)** and **7(s or m)** as well as the OPV unit **14** and dendrimers **15**–**20** showed to be highly soluble in common organic solvents (dichloromethane, chloroform, hexane, etc.). All compounds were fully characterized by FTIR, UV–vis, ^{1}H and ^{13}C NMR spectroscopies.

Fig. 1 shows the ^{1}H NMR spectra of dendrons **3(s)**, **5(s)** and **7(s)** with short alkyl chains (C_3H_7) in $CDCl_3$ solution. In the range between $\delta = 0.9$–4 ppm, we can observe the signals corresponding to the aliphatic protons H_α (O–CH_2–), H_β (O–CH_2–) and H_γ (O–CH_3) of the propenyloxy chains. Additional signals due to methylene protons H_a (ArO–CH_2–Ar), $H_{a'}$ (ArO–CH_2–Ar) and $H_{a''}$ ($ArCH_2$–Br) neighbor to the aromatic rings for each dendron generation appear at $\delta = 3.8$–5 ppm. The signals which appear at $\delta = 6.2$–6.8 ppm are assigned to the aromatic protons (Ar–H): H_o, H_p, $H_{o'}$, $H_{p'}$, $H_{o''}$ and $H_{p''}$, in each dendron generation. As expected, the ^{1}H NMR spectrum of dendron **7** clearly shows the signals corresponding to three [3,5-(benzyloxy)phenyl] subunits in a 4:2:1 ratio, which is in full agreement with the proposed dendritic structure. Finally, the ^{1}H NMR spectra of dendrons **3(m)**, **5(m)** and **7(m)** containing long alkyl chains ($C_{12}H_{25}$) are very similar to those of dendrons bearing short alkyl chains.

Dendrimers **15**–**20** were also characterized by ^{1}H and ^{13}C NMR. Fig. 2 shows the ^{1}H NMR spectra of dendrimers **18**–**20** in $CDCl_3$ solution. In the range between $\delta = 0.8$–4.2 ppm, we can observe a series of signals corresponding to all aliphatic protons H_α, $H_{\alpha'}$ (O–CH_2–), H_β, $H_{\beta'}$ (O–CH_2–) and H_γ, $H_{\gamma'}$ (O–CH_3) present in the dodecylyloxy chains. Besides, the signals corresponding to methylene protons H_a (ArO–CH_2–Ar), H_b (ArO–CH_2–Ar), H_c ($ArCH_2$–O), neighbor to the aromatic rings for each dendron generation and methylene protons H_d (O–CH_2–Ar) and H_8 (Ar–CH_2–OH) of OPV unit appear in the $\delta = 4.5$–5.2 ppm region. On the other hand, the signals which appear at $\delta = 6$–7 ppm are assigned to the aromatic protons (Ar–H): H_o, H_p, $H_{o'}$, $H_{p'}$, $H_{o''}$ and $H_{p''}$ in dendritic branches. Finally, the signals present in the region $\delta = 7$–8 ppm are due to the aromatic protons (Ar–H): H_1, H_2, H_4, $H_{4'}$, H_6, H_7 and vinyl protons (–CH=CH–): H_3, $H_{3'}$, H_5 and $H_{5'}$ of the OPV moiety.

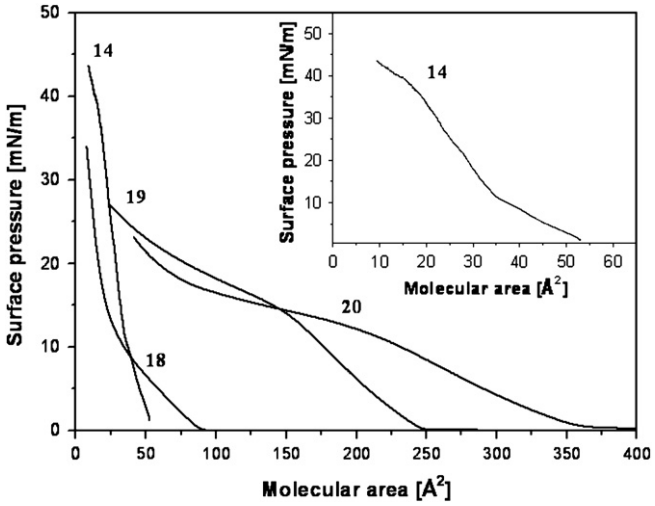


Fig. 6. Surface pressure–molecular area (Π/A) isotherms recorded at 20 °C, for Langmuir monolayers from dendrimers **18**–**20** with short alkyl chains ($C_{12}H_{25}$), and reference compound **14** lacking alkyl chains.

3.5. Optical properties of the dendrimers

The absorption spectra of the OPV unit **14** and dendrimers **15**–**20** were recorded in toluene and dichloromethane at room temperature. The UV–vis spectra are shown in Figs. 3 and 4; the most important features of the optical properties of these compounds are summarized in Table 1.

The absorption spectrum of OPV unit **14** exhibited a characteristic absorption band due to the characteristic π–π^* transition at $\lambda = 410$ nm in toluene, which appears at $\lambda = 420$ nm in dichloromethane. It is interesting to note that dendrimers bearing propyloxy chains (**15**–**17**) showed a blue shift of the absorption band of OPV core. This hypsochromic shift is more significant as the size or generation of dendritic arms increases. On the other hand, for dendrimers containing dodecyloxy chains **18**–**20**, this shift is still higher. This effect reveals that there is a significant influence of the size of dendritic branches and the OPV core unit, which increases the charge transfer character of the molecule, thereby making it more sensitive to the polarity of the solvent. Consequently, there are solvatation of the alkyl chains, and strong intramolecular interactions between the OPV core unit and the dendritic branches. These observed spectral changes are in agreement with those previously described for other dendrimers containing π-conjugated systems [10b,11,24].

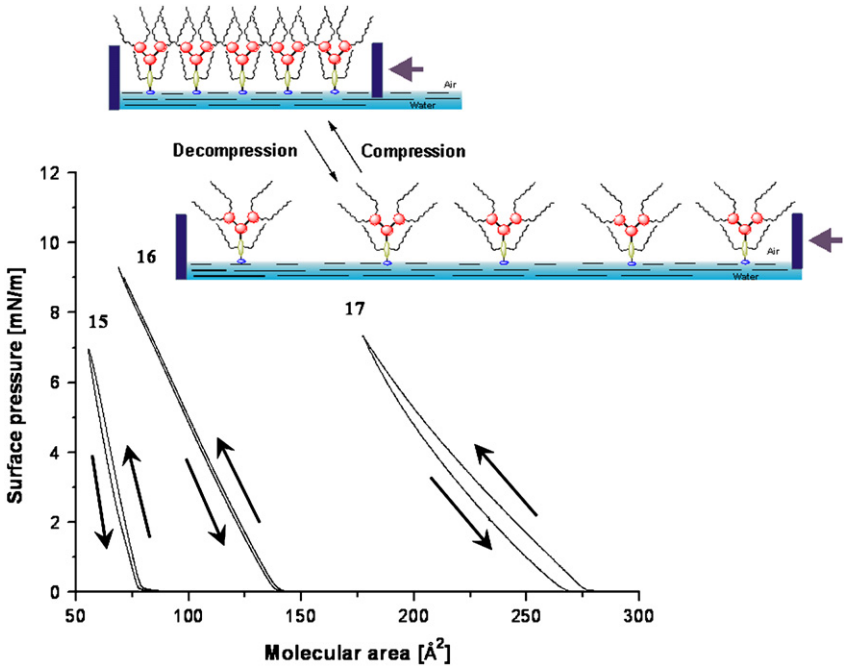


Fig. 8. Hysteresis curves show monolayer reversibility upon successive "compression/decompression" cycles for dendrimers **15**–**17**. Arrows pointing upward indicate compression, and those pointing downward indicate decompression. The barrie speed for the "compression/decompression" cycles was of 4 mm/min. Inset: An idealized representation showing a monolayer "compression/decompression" cycle for a dendrimer.

3.6. Preparation of Langmuir monolayers

Langmuir monolayers of all dendrimers (**15**–**20**) were prepared and characterized by plotting their surface pressure versus molecular area isotherms (Π/A), and hysteresis curves. The isotherms recorded at 20 °C for all dendrimers are shown in Figs. 5 and 6. All dendrimers are able to form stable Langmuir monolayers at the air–water interface. It is worth to point out that the surface pressure increases as the surface area of the molecules is reduced by compression of the barriers, thereby showing a classic amphiphilic behavior. This is more evident if we compare the data obtained for dendrimers with those of reference compound **14**. Such behavior is in good agreement with that previously reported for other analogous dendritic structures containing terminal alkyl chains [25].

As expected, an increase in the size of dendritic branches causes a shift in the Π/A isotherm to higher cross-sectional area per molecule, A_0. These values of molecular areas extrapolated at zero surface pressure A_0 are 84, 150 and 289 Å^2/molecule for dendrimers **15**–**17**, respectively; and 89, 244 and 340 Å^2/molecule for **18**–**20**, respectively.

The cross-sectional area (A_0) for molecules with one alkyl chain such as stearic acid is well known, approximately 20 Å^2, this value considers that alkyl chains are in a straight position [26]. The reference compound **14** containing two alkyl chains, displays a cross-sectional area per molecule of 41 Å^2. Simple area values' comparison shows that the cross-sectional area for **14** can be estimated by multiplying A_0 of a single alkyl chain by the number of alkyl chains in **14**, which suggests a suitable dense packing. Therefore, the expected cross-sectional area for each dendrimer can be estimated assuming a dense surface packing and straight orientation of alkyl chains within monolayer, by multiplying the A_0 of a single alkyl chain by the number of chains in a dendrimer molecule, and adding this value to A_0 of the reference compound **14** (41 Å^2), which contains two alkyl chains.

Indeed, the experimental cross-sectional areas obtained for dendrimers with two alkyl chains (**15** and **18**) are close to the calculated values. This is an indication that a dense packing of vertical oriented chains in monolayers of these dendrimers predominates. However, for dendrimers with four and eight short alkyl chains (**16** and **17**), the A_0 values are 23 and 43% higher than the calculated theoretical values, respectively. Besides, for dendrimers with four and eight long alkyl chains **19** and **20**, A_0 values are 100 and 68% higher than their estimated theoretical values, respectively (Fig. 7). These deviations suggest that steric limitations, which avoid a suitable dense packing of higher generation dendrimers, cause the alkyl chains adopt a favored orientation along the radial direction of the focal point, thereby occupying a larger area than vertically aligned chains.

It is also interesting to notice that the isotherms of all dendrimers display different phases at the air–water interface, within increasing of the size of the dendritic arms. These phase features are similar to those found in other similar dendrimers bearing alkyl chains [25a,c–e].

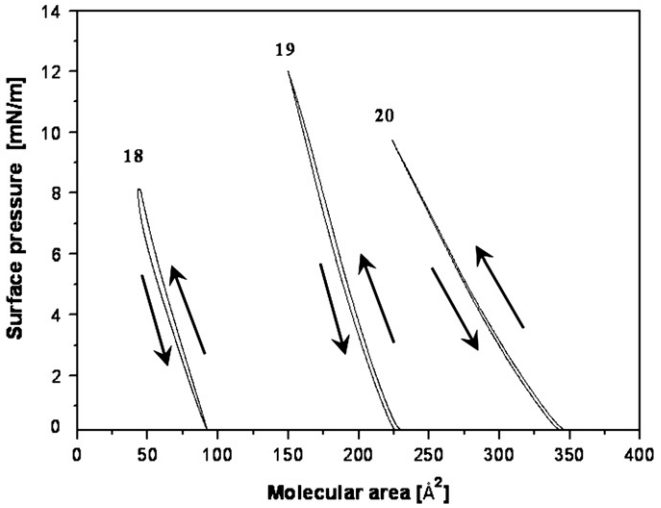


Fig. 9. Hysteresis curves show monolayer reversibility upon successive "compression/decompression" cycles for dendrimers **18**–**20**. Arrows pointing upward indicate compression, and those pointing downward indicate decompression. The barrie speed for the "compression/decompression" cycles was of 4 mm/min.

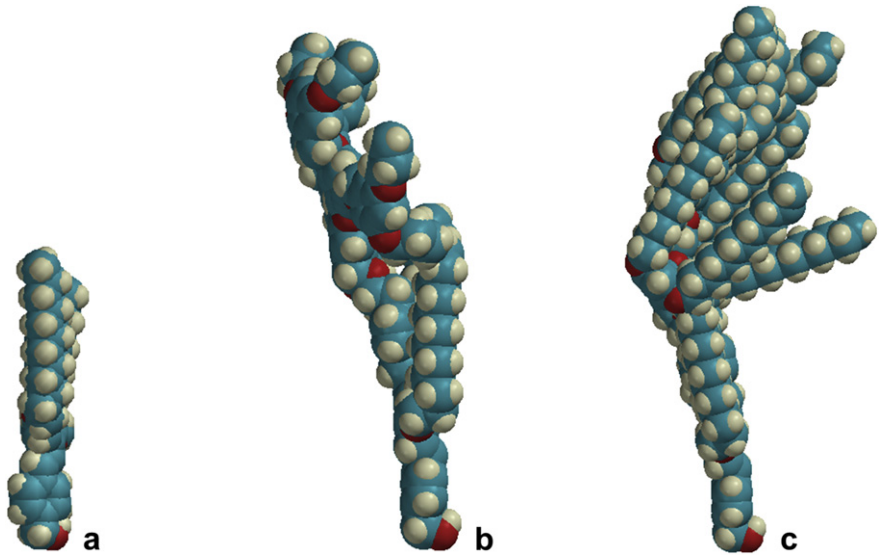


Fig. 10. Optimized geometries obtained with Spartan 04 molecular modeling software in order to estimate the molecular areas: (a) **14**, (b) **17** and (c) **20**.

The reference compound **14** shows a two-dimensional gas state at a molecular area > 53 Å^2; when the pressure is increased to 52 Å^2/molecule, so that the isotherm showed a gas state to liquid-expanded (LE) phase transition. An additional transition appears at a surface pressure of $\Pi = 11$ mN/m, which may be attributed to the existence of two phases in equilibrium liquid-expanded phase and liquid-condensed (LC) phase [27]. The isotherm of dendrimer **15** shows also a transition to LE phase in a pressure range of 0.38–10 mN/m, whereas the isotherm of dendrimer **17** shows a plateau, due to the coexistence of LE and LC phases in the range of $9.7 < \Pi < 14$ mN/m. Besides, the isotherm of dendrimer **16** does not show any structural transition, which reveals the coexistence of several phases in equilibrium [28].

On the other hand, an increase of the alkyl chains' length of the dendritic arms stabilizes the transition from a non-ordered LE phase to an ordered LC phase. The isotherms of dendrimers **19** and **20** show this transition phase in the range between $68 < \Pi < 140$ mN/m for **19**, and $86 < \Pi < 193$ mN/m for **20**. Besides for the dendrimer **18**, its isotherm shows the presence of two phases in equilibrium (LE–LC) [28].

Except for dendrimer **17**, hysteresis studies showed that the Langmuir monolayers of all dendrimers exhibit an excellent reversibility upon successive compression/decompression cycles, as long as the collapsed pressure π_c is not exceeded (hysteresis curves, Figs. 8 and 9); thus these films showed to be highly stable. The monolayer of dendrimer **17** showed a very limited reversibility, which can be due to the formation of aggregates because of strong intermolecular interactions between neighbor dendrimer molecules [29].

Optimized geometries were estimated for compound **14** and all dendrimers (**15**–**20**) by molecular modeling, using the semi-empirical method AM1, integrated in Spartan 04 molecular modeling software. Predicted geometries calculated for compound **14** and dendrimers **17** and **20** are shown in Fig. 10. We used these molecular models in order to estimate the molecular areas of all dendrimers. The experimental molecular areas extrapolated at zero surface pressure A_0 match well with the values obtained by molecular modeling. Theoretical and experimental molecular areas of all compounds are summarized in Table 2.

Table 2
Theoretical and experimental molecular areas of OPV unit **14** and dendrimers **15**–**20**

	Compound						
	14	**15**	**16**	**17**	**18**	**19**	**20**
Theoretical molecular areas (Å^2)	40	85	147	290	90	242	238
Experimental molecular areas (Å^2)	41	84	150	289	89	244	340

4. Conclusion

We described the synthesis and characterization of different generation dendrimers, containing an oligophenylenevinylene (OPV) core unit with a polar head group and terminal alkyl chains with different lengths. All dendrons were characterized by ^{1}H and ^{13}C NMR, FTIR and absorption spectroscopies. UV–vis spectra of all dendrimers in toluene and dichloromethane showed changes in the absorption spectrum of OPV core. The blue shift of the maximum absorption band of the OPV core increases as a function of the dendron generation number.

We demonstrated that all dendrimers are able to form stable Langmuir monolayers in the air–water interface and exhibit a good reversible behavior upon successive compression/expansion cycles. We also observed that the surrounding alkyl chains' length of the dendritic branches has a remarkable influence on the isotherm phases as well as on the appropriate packing of highest generation dendrimers in the monolayers.

We are currently working on the transference of the Langmuir monolayers onto solid substrates, using the Langmuir–Blodgett technique in order to study of optical and electronic properties of resulting films, in view of optical and electronic potential applications.

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