Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Synthesis of OligoPhenyleneVinylene Dendrimers with Resorcinarene Core and their Supramolecular Complexes with Fullerene C_{60}

I. V. Lijanova[a]; T. K. Berestneva[b]; M. M. García[a]
[a] Instituto de Química, Universidad Nacional Autónoma de México, México D.F., Mexico [b] Facultad de Química, Universidad Nacional Autónoma de México, México D.F., México

To cite this Article Lijanova, I. V. , Berestneva, T. K. and García, M. M.(2007) 'Synthesis of OligoPhenyleneVinylene Dendrimers with Resorcinarene Core and their Supramolecular Complexes with Fullerene C_{60}', Supramolecular Chemistry, 19: 8, 655 — 662
To link to this Article: DOI: 10.1080/10610270701402919
URL: http://dx.doi.org/10.1080/10610270701402919

Supramolecular Chemistry, December 2007 Vol. 19 (8), pp. 655–662

Taylor & Francis
Taylor & Francis Group

Synthesis of OligoPhenyleneVinylene Dendrimers with Resorcinarene Core and their Supramolecular Complexes with Fullerene C_{60}

I. V. LIJANOVA[a], T. K. BERESTNEVA[b] and M. M. GARCÍA[a,*]

[a]*Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, Circuito Exterior, Coyoacán, C.P., 04510 México D.F., Mexico;*
[b]*Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria. Circuito Interior, Coyoacán C.P, 04510 México D.F., México*

(Received 7 February 2007; Accepted 16 April 2007)

Dendritic branches of Oligophenylvinylene chains have been attached to a resorcinarene core. The supramolecular complexes with fullerene C_{60} were studied with two dendrimers of first and second generation. All the compounds were characterized by ^{1}H, ^{13}C NMR, FTIR, UV–vis spectroscopy, MALDI-TOF, FAB + mass spectra and elemental analysis.

Keywords: OPV; π-Conjugated system; Resorcinarene; Dendrimers; Supramolecular complexes; Fullerene C_{60}

INTRODUCTION

Since the advent of dendrimers, a great variety of these well-defined structures have been synthesized [1] and now they represent the center of an important interdisciplinary field of research with possible technical applications in material science, catalysis, biotechnology, and medicine [2–4]. In recent years, there has been a considerable interest in incorporating π-conjugated systems into dendrimers aimed at an access to electroluminescent compounds [5,6]. Dendrimers with π-conjugated systems representing cores [7,8] or peripheral subunits [9] and included into each branching unit [10] have been documented. The core in the dendritic structures offers a unique opportunity to vary the physical and electronic properties independently, and the high molecular weight dendrimers possess a regulated nanospace. These well defined nanospaces can provide cavities for inclusion of big molecules. We are interested in resorcinarenes because of their ease of synthesis and the possibility to be obtained only in their *rccc* conformation, making them less affected by steric constraints [11]. In this paper we report the synthesis of dendrimers with π-conjugated systems oligophenylenevinylene (OPV) using resorcinarenes with an *rccc* conformation as core molecules and their supramolecular complexes with fullerene C_{60}.

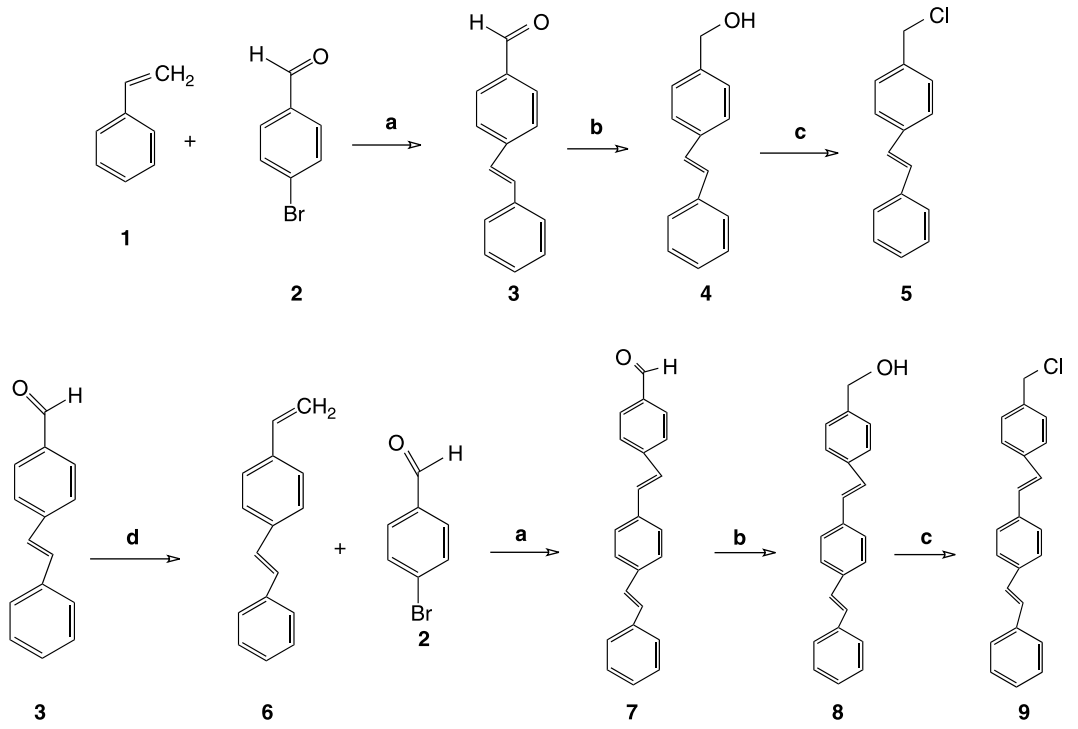
RESULTS AND DISCUSSION

Dendrons containing phenyl vinyl groups were prepared according to the convergent Fréchet approach [12]. Styrene was obtained from Aldrich reagents and used in the Heck reaction coupling of the 4-bromo-benzaldehyde **2** in dimethyl formamide and triethylamine using palladium acetate as catalyst to afford **3**. The aldehyde **3** was reduced with $LiAlH_4$ in THF at 0°C to give alcohol **4**, which was converted into the chloride **5** upon treatment with thionyl chloride and pyridine in dichloromethane at 0°C. This chloride was used as the reagent for the synthesis of the first generation of stilbene containing dendrimers (Scheme 1).

After synthesizing the first generation, the higher generation can be formed by applying the same set of reactions; Wittig of **3** to obtain the (E)-1-styryl-4-vinylbenzene **6**, which reacted by Heck reaction with 4-bromo-benzaldehyde under the same conditions to afford aldehyde **7**, followed by the reduction of the aldehyde group to benzylic alcohol **8** and chlorination of the benzylic alcohol to obtain the dendron **9**. Dendrons **5** and **9** were characterized by ^{1}H— and ^{13}C-NMR, IR, FAB + mass spectrometry. The ^{1}H

*Corresponding author. E-mail: margar@servidor.unam.mx

ISSN 1061-0278 print/ISSN 1029-0478 online © 2007 Taylor & Francis
DOI: 10.1080/10610270701402919



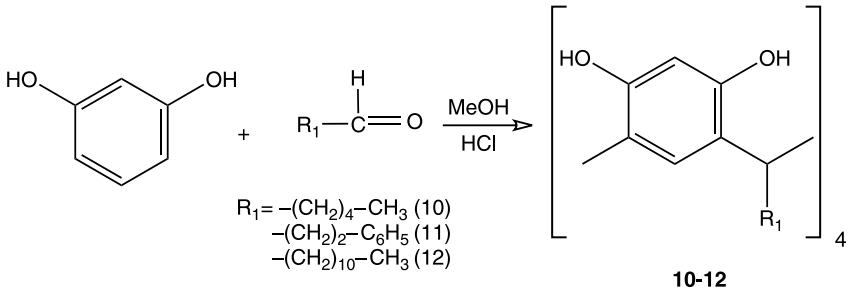
SCHEME 1 Synthesis of lineal dendrons of first and second generation; a) $Pd(OAc)_2$/ TOP, DMF/ET_3N, 120°C b) THF, $LiAlH_4$, 0°C c) Py, CH_2Cl_2, $SOCl_2$, 0°C d) $CH_3(Ph)_3PBr$, n-BuLi, THF, 10°C.

NMR spectra of the dendrons **5**, **9** contain signals at δ_H 4.60 for the methylene protons Ar—CH_2—Cl, for the vinylic protons were observed a singlet at δ_H 7.10. In agreement with the ^{1}H NMR data all the π-conjugated systems showed *trans*-configuration and the coupling constant was $J = 16.8$ Hz.

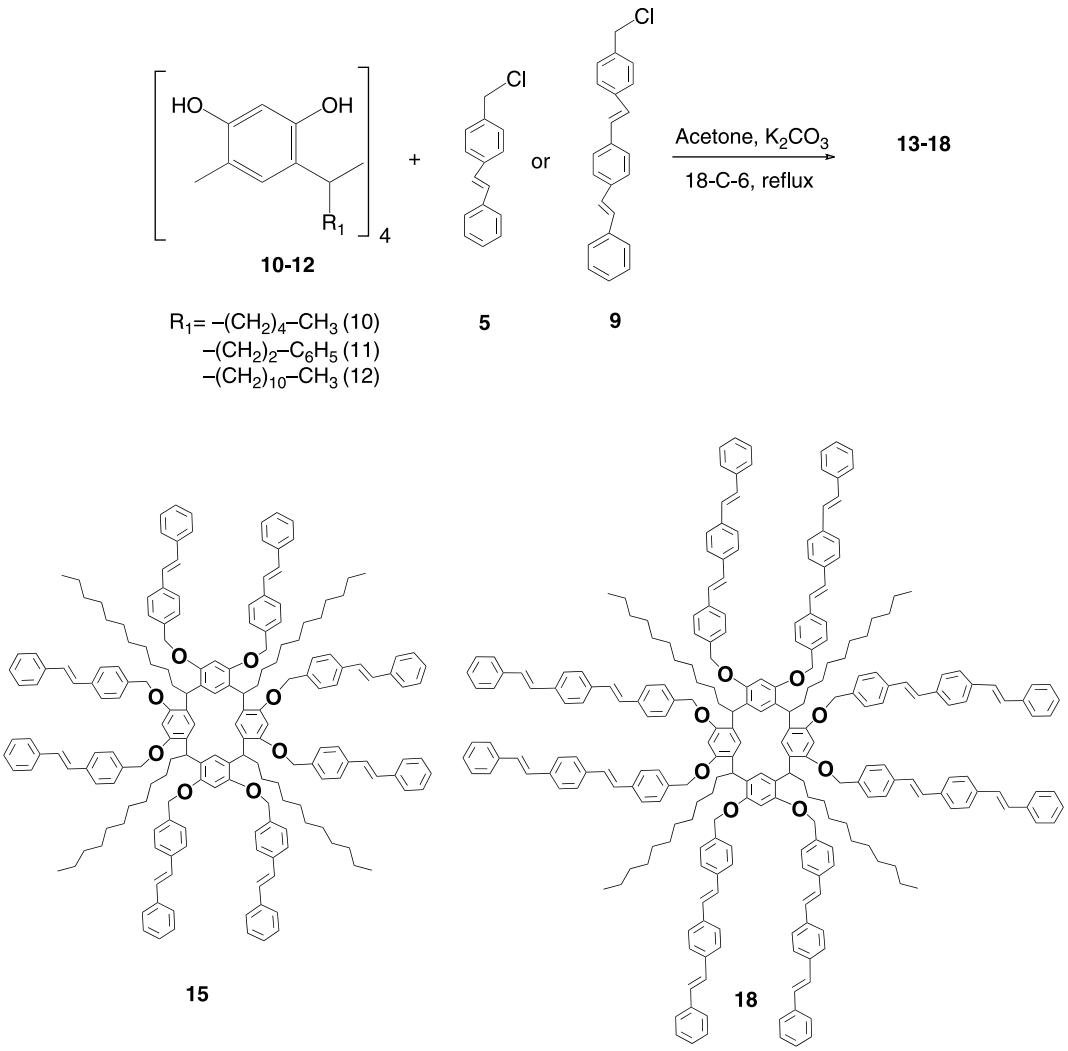
Resorcinarenes were obtained from resorcinol and three different aldehydes, hydrocinnamaldehyde, hexanal and dodecanal (Scheme 2). The structure of these resorcinarenes was confirmed by NMR and FAB + mass spectrometry. Cyclic tetramers gave a well resolved triplet at δ_H 4.36, which is attributed to methine protons with an *rccc* conformation [11].

The iterative convergent strategy used for the styrene-focused dendrimers synthesis is shown in Scheme 3. As illustrated, the one step for dendrimer **13**–**18** formation involves a simple Williamson reaction between the dendrons **5** and **9** and resorcinarenes **10**–**12** in acetone and K_2CO_3 at reflux for 3 days. The structures of **13**–**18** dendrimers were confirmed by ^{1}H— and ^{13}C-NMR, IR, and for the dendrimers **13**, **14** and **15** by MALDI-TOF mass spectrometry with all of the dendrimers having a molecular ion at the expected mass (Fig. 1). The molecular masses of the second generation dendrimers **16**, **17** and **18** could not be determined by MALDI-TOF mass spectrometry due to their poor volatility properties. However, gel-permeation chromatography (gpc) against polystyrene standards showed that all the dendrimers were monodisperse as would be expected from their well ordered construction.

The obtained **13**–**18** dendrimers are readily soluble in common organic solvents. The ^{1}H NMR spectrum of the dendrimer **15** showed one broad signal at δ_H 0.85 due to the CH_3 groups, two broad signals at δ_H 1.22 and 1.60 assigned to the CH_2 groups for the aliphatic chain, one singlet at δ_H 3.66



SCHEME 2 Synthesis of resorcinarenes.



SCHEME 3 Synthesis of dendrimers of first and second generation.

due to the methine protons at the resorcinarene ring, one broad signal at δ_H 5.13 for the —CH_2—O protons, one multiplet at δ_H 7.01–7.15 due to the vinylic protons, and finally one broad signal at δ_H 7.26–7.48 for the aromatic protons was observed. The presence of one singlet at δ_H 3.66 confirmed the *rccc* conformation of the resorcinarene-dendrimers [11].

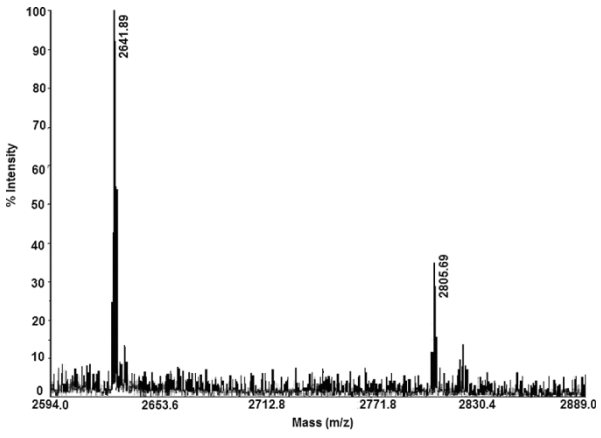
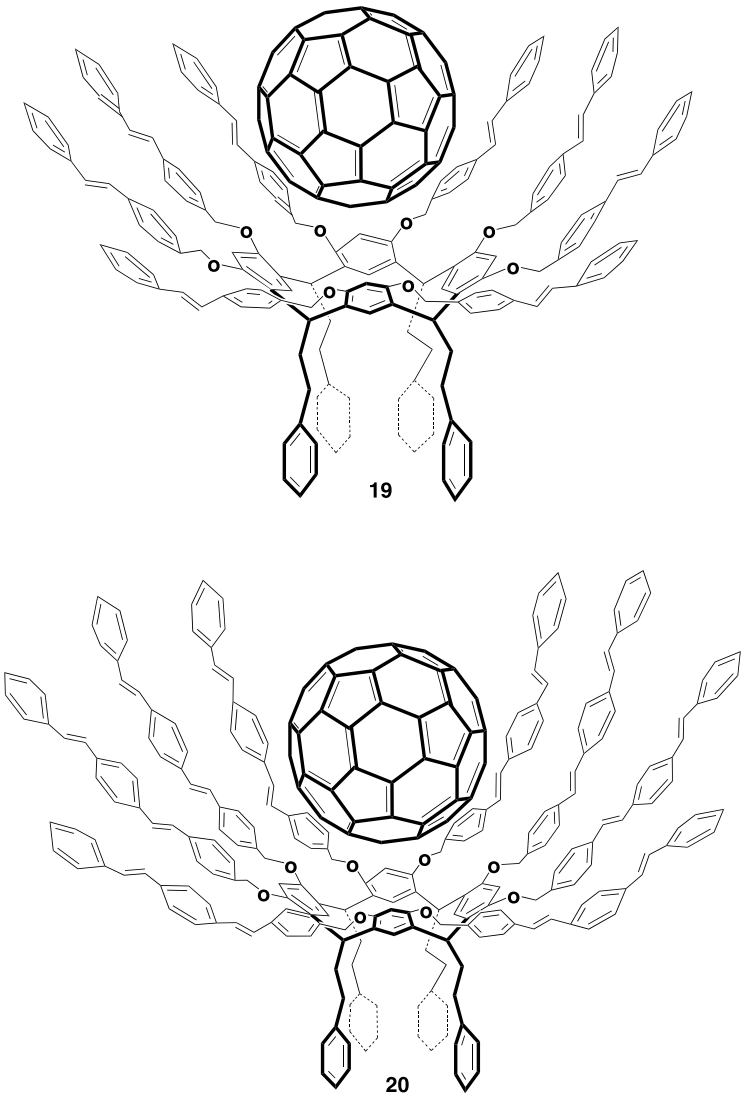


FIGURE 1 MALDI-TOF mass spectrum of **15** first generation dendrimer.

The supramolecular complexes were obtained from the resorcinarene-dendrimers **14** and **17** with fullerene C_{60} (Scheme 4). To a toluene solution of equimolar amounts of the fullerene, the dendrimer **14** or **17** was added. The reaction was stirred at reflux for 7 days. The solvent was evaporated in vacuum and the solid was carefully washed with small quantities of toluene to remove the traces of free fullerene and dendrimer, affording complexes **19** and **20** in 40 and 45% yields, respectively. Elemental analysis of the residual solid was consistent with the 1:1 stoichiometry.

The comparison of the solid-state ^{13}C CP-MAS NMR spectrum of **14** with that of the **14**:C_{60} 1:1complex **19** shows some conformational changes in **14** (Fig. 2). The signal at δ_c 35.62 for the ethylene and methine groups was shifted upfield to δ_c 35.34. No changes for Ar—CH_2—O groups were observed. The signal assigned for the carbons at the resorcinarene ring at δ_c 102.50 in the complex was diminished.



SCHEME 4 Supramolecular complexes **19** and **20**.

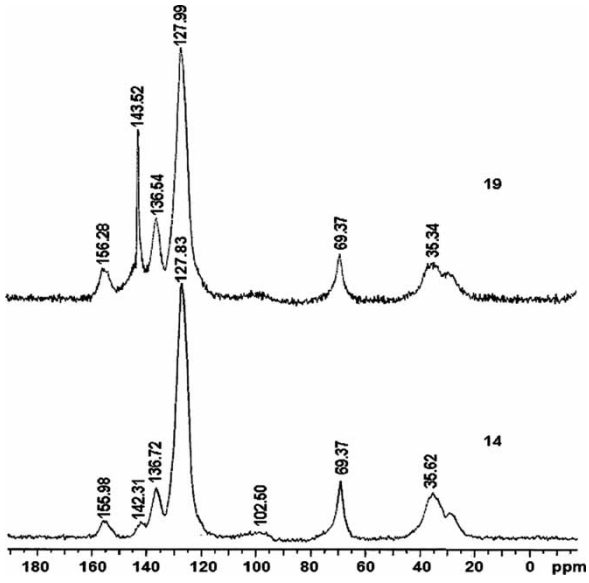


FIGURE 2 ^{13}C CP-MAS NMR spectra of the resorcinarene-dendrimer **14** and of the supramolecular complex **19**.

For the aromatic and vinylic carbons, the strong broad signal at δ_c 127.83 in the resorcinarene-dendrimer was shifted in the complex at δ_c 127.99. The signal observed at 136.72 in the compound **14** is shifted to upfield together with the fullerene signal at δ_c 136.54 in the complex **19**, but the other signal at δ_c 142.31 for **14** is shifthed downfield at δ_c 143.52 in **19**. One additional signal for the $C_{Ar}O$ groups at δ_c 155.98 in the resorcinarene-dendrimer free was shifted at δ_c 156.28.

The solid state ^{13}C CP-MAS NMR spectrum of the **17**:C_{60} 1:1 complex **20** shows some conformational changes for **17** (Fig. 3). For the ethylene and methine carbons the signal at δ_c 35.58 was shifted upfield at δ_c 33.64. The signal assigned to the Ar—CH_2—O groups δ_c 69.61 was shifted 0.15 ppm. The signal assigned for the carbons at resorcinarene ring at δ_c 104.36 in the complex was diminished. For the aromatic carbons, two signals, one broad strong signal at δ_c 128.62 and one small signal at δ_c 135.55 due to the carbons C_{ipso} were observed. The signal assigned to the fullerene

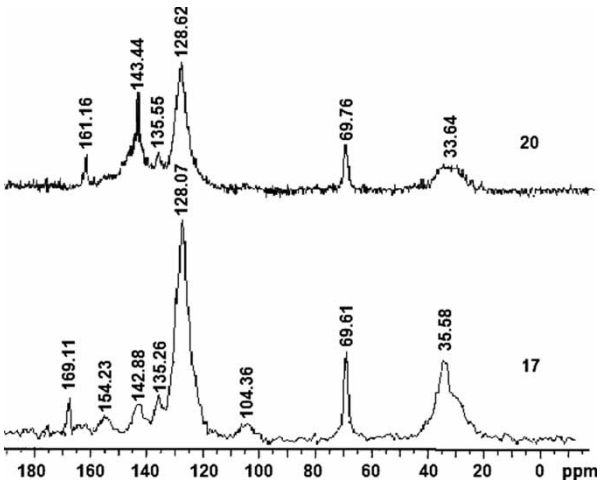


FIGURE 3 ^{13}C CP-MAS NMR spectra of the resorcinarene-dendrimer **17** and of the supramolecular complex **20**.

was observed at δ_c 143.44, and finally the two signals for the C_{Ar}—O groups at δ_c 154.23 and 169.11 observed in the resorcinarene-dendrimer free, in the complex appear together at δ_c 161.16.

CONCLUSIONS

Two generations of resorcinarene-dendrimers were synthesized by convergent building method obtaining relative good yields with preservation of the resorcinarene *rccc* conformation. The fixed nanospace constructed from the OPV system of 16 and 24 benzene rings around the resorcinarene core give the multipoint interaction to host the fullerene C_{60}. Two new supramolecular complexes between resorcinarene-dendrimers and fullerene C_{60} were also obtained, and π−π n-π interactions were observed in the complexes.

EXPERIMENTAL SECTION

Solvents and reagents were purchased as reagent grade and used without further purification. Acetone was distilled over calcium chloride. Tetrahydrofuran was distilled from sodium and benzophenone. Column chromatography was performed on Merck silica gel 60 Å (70–230 mesh). ^1H and ^{13}C NMR were recorded on a Varian-Unity-300 MHz with tetramethylsilane (TMS) as an internal reference. Infrared (IR) spectra were measured on a spectrophotometer Nicolet FT-SSX. Elemental analysis was determined by Galbraith Laboratories, INC Knoxville. FAB + mass spectra were taken on a JEOL JMS AX505 HA instrument. Matrix-assisted laser desorption/ionization were taken with a TofSpec spectrometer.

(E)-4-Styrylbenzaldehyde 3

A mixture of **1** 2.8 g (27.02 mmol), **2** 5 g (27.02 mmol), $Pd(OAc)_2$ 3 mg (1.3 mmol), and tri-o-tolylphosphine POT 1 g (3.28 mmol) in Et_3N/DMF 1:5 (120 mL) was stirred under N_2 at 120°C for 24 h. After cooling, the resulting mixture was filtered and the solvents evaporated. The crude product was purified by column chromatography (SiO_2, hexane) to yield 5.4 g, (70%) as a yellow-pale powder, UV CH_2Cl_2 (nm): 231, 328. IR (KBr, cm^{-1}): 3431, 3024, 1624, 1445, 1119, 966, 828, 691. ^1H-NMR ($CDCl_3$), δ (ppm): 7.11 (d, 1H, CH═, $J = 16.2$ Hz), 7.25 (d, 1H, CH═, $J = 16.4$ Hz), 7.31–7.56 (m, 5H, Ar), 7.83 (d, 2H, Ar, $J = 1.8$ Hz), 7.87 (d, 2H, Ar, $J = 2.0$ Hz), 9.97 (s, 1H, —HC═O). ^{13}C NMR ($CDCl_3$), δ (ppm): 126.8 (Ar), 127.2 (CH═), 128.4 (CH═), 128.7 (Ar), 130.1 (Ar), 132.1 (Ar), 135.2 (Ar), 136.4 (Ar), 143.3 (Ar_{ipso}), 191.5 (C═O). Ms (m/z): 208. Anal. Calcd. for $C_{15}H_{12}O$: C 86.51, H 5.81%. Found: C 86.50, H 5.81%.

(E)-(4-Styrylphenyl)methanol 4

0.56 g (15.0 mmol) of 97% lithium aluminum hydride were dissolved in 50 mL of dry THF. To this emulsion, 2.1 g (10.0 mmol) of (E)-4-styrylbenzaldehyde **3** dissolved in 15 mL of dry THF were added drop wise using an addition funnel. The reaction was carried in acetone-ice bath for 4 h. After this time, 10 mL of water were added and the reaction mixture was filtered in Celite®. The solvent was evaporated and the residue was dissolved in dichloromethane. The resulting solution was dried with sodium sulfate, filtered and the product was vacuum dried to yield 1.5 g (70%) as a yellow powder, UV CH_2Cl_2 (nm): 232, 300, 313. IR (KBr, cm^{-1}): 3331, 3023, 2866, 1446, 1073, 997, 967, 780, 749, 690, 525. ^1H-NMR ($CDCl_3$), δ (ppm): 1.76 (s, 1H, —OH), 4.69 (s, 2H, CH_2), 7.10 (s, 2H, CH═), 7.25–7.40 (m, 5H, Ar), 7.49 (s, 2H, Ar), 7.53 (t, 2H, Ar, $J = 1.0$ Hz). ^{13}C NMR ($CDCl_3$), δ (ppm): 65.1 (CH_2), 126.5, 126.6, 127.3 (Ar), 127.6 (CH═), 128.2 (CH═), 128.6, 128.7 (Ar), 136.8, 137.2 (Ar), 140.2 (Ar_{ipso}). Ms (m/z): 210. Anal. Calcd. for $C_{15}H_{14}O$: C 85.68, H 6.71%. Found: C 85.67, H 6.70%.

(E)-1-(Chloromethyl)-4-styrylbenzene 5

3 g (14.0 mmol) of (E)-(4-styrylphenyl) methanol **4**, 1 mL (14.0 mmol) of pyridine and 1.45 ml (14.0 mmol) of $SOCl_2$ were dissolved in 100 mL of dry CH_2Cl_2, and this mixture was cooled to 10°C. The reaction was carried out under nitrogen in ice bath for 7 h. After this period, the solvent was evaporated and the resulting oil was dry supported and purified in a silica gel (60–240 pore size) column using a mixture of hexane-CH_2Cl_2 2:1 as eluent to yield 2.9 g (95%) as a yellow–brown powder, UV $CHCl_3$ (nm): 241, 304, 315. IR (KBr, cm^{-1}): 3025, 2958, 1489, 1446, 1264, 967, 821, 755, 691, 667, 539. ^1H-NMR ($CDCl_3$), δ (ppm):

4.60 (s, 2H, CH_2), 7.10 (s, 2H, CH═), 7.26–7.39 (m, 5H, Ar), 7.45–7.54 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$), δ (ppm): 46.0 (CH_2), 126.5, 126.8 (Ar), 127.8 (CH═), 128.0 (Ar), 128.7 (Ar), 129.5 (Ar), 130.1 (Ar_{ipso}). Ms (m/z): 228 m/z. Anal. Calcd. for $C_{15}H_{13}O$: C 78.77, H 5.73%. Found: C 78.76, H 5.71%.

(E)-1-Styryl-4-vinylbenzene 6

n-BuLi 1.6 g (25.0 mmol) was added to a solution of **3** 5.2 g (25.00 mmol) and methyltriphenylphosphonium bromide 8.94 g (25.00 mmol) in dry THF (100 mL) at −10°C. The solution was stirred for 12 h, then a few drops of water were added and the resulting mixture was concentrated. The organic layer was extracted with CH_2Cl_2 and dried with Na_2SO_4, evaporated and purified by column chromatography (SiO_2, CH_2Cl_2/hexane 2:8) to give the (E)-1-styryl-4-vinylbenzene **6**, in 95% (5.0 g) yield as a yellow powder, UV $CHCl_3$ (nm): 242, 328. IR (KBr, cm^{-1}): 3080, 3023, 2924, 1914, 1815, 1624, 1448, 1405, 1073, 993, 965, 904, 521. ^1H-NMR ($CDCl_3$), δ (ppm): 5.25 (d, 1H, CH_2═, $J = 11.0$ Hz), 5.80 (d, 1H, CH_2═, $J = 17.6$ Hz), 6.71 (q, 1H, CH═), 7.10 (s, 2H, CH═), 7.26–7.42 (m, 5H, Ar), 7.46–7.54 (m, 4H, Ar). ^{13}C NMR ($CDCl_3$), δ (ppm): 113.7 (CH_2═), 126.4, 126.5, 126.6, 127.6 (Ar), 128.2 (CH═), 128.6 (Ar), 136.4 (Ar), 136.8 (Ar), 137.3 (Ar_{ipso}). Ms (m/z): 206 m/z. Anal. Calcd. for $C_{16}H_{14}$: C 93.16, H 6.84%. Found: C 93.14, H 6.84%.

4-((E)-4-(E)-Styrylstyryl)benzaldehyde 7

A mixture of **6** 2 g (9.7 mmol), **2** 1.8 g (9.7 mmol), $Pd(OAc)_2$ 3 mg (1.3 mmol), and tri-o-tolylphosphine POT 0.9 g (2.6 mmol) in Et_3N/DMF 1:5 (60 mL) was stirred under N_2 at 120°C for 24 h. After cooling, the resulting mixture was filtered and the solvents evaporated. The crude product was purified by column chromatography (SiO_2, hexane) to yield 2.3 g (60%) of 4-((E)-4-(E)-styrylstyryl)benzaldehyde **7** as a yellow powder, UV $CHCl_3$ (nm): 245, 376. IR (KBr, cm^{-1}): 3023, 2825, 1698, 1595, 1166, 967, 826, 545. ^1H NMR ($CDCl_3$), δ (ppm): 7.16 (d, 2H, CH═, $J = 14.7$ Hz), 7.18 (d, 2H, CH═, $J = 16.5$ Hz), 7.24–7.27 (m, 2H, Ar), 7.30 (t, 1H, Ar, $J = 1.0$ Hz,), 7.35–7.40 (m, 2H, Ar), 7.52–7.57 (m, 4H, Ar), 7.66 (d, 2H, Ar, $J = 6$ Hz), 7.87 (d, 2H, Ar, $J = 9$ Hz), 10.00 (s, 1H, C═O). ^{13}C NMR ($CDCl_3$), δ (ppm): 126.5, 126.8, 126.9, 127.1 (Ar), 127.2 (CH═), 127.8 (CH═), 128.7, 129.2, 130.2, 131.7, 135.3, 135.8, 137.2, 137.6, 143.4 (Ar). Ms (m/z): 310 m/z. Anal. Calcd. for $C_{23}H_{18}O$: C 89.00, H 5.85%. Found: C 89.01, H 5.85%.

(4-((E)-4-(E)-Styrylstyryl)phenyl)methanol 8

0.56 g (15.0 mmol) of 97% lithium aluminum hydride were dissolved in 50 mL of dry THF. To this emulsion, 3 g (10.0 mmol) of 4-((E)-4-(E)-styrylstyryl)-benzaldehyde **7** dissolved in 15 mL of dry THF were added drop wise using an addition funnel. The reaction was carried out in acetone-ice bath for 4 h. After this time, 10 mL of water were added and the reaction mixture was filtered in Celite®. The solvent was evaporated and the residue was dissolved in dichloromethane. The resulting solution was dried with sodium sulfate, filtered and the product was vacuum dried to yield 3.6 g (70%) as a yellow powder, UV $CHCl_3$ (nm): 242, 358. IR (KBr, cm^{-1}): 3326, 2959, 2872, 1728, 1285, 1073, 966, 748, 548. ^1H NMR ($CDCl_3$), δ (ppm): 4.69 (s, 2H, CH_2), 4.74 (s, 1H, —OH), 7.12 (s, 1H, Ar), 7.29 (br, 4H, CH═), 7.33 (br, 2H, Ar), 7.36 (br, 2H, Ar), 7.39 (br, 2H, Ar), 7.51 (br, 4H, Ar), 7.54 (br, 2H, Ar). ^{13}C NMR ($CDCl_3$, DMSO-D_6), δ (ppm): 64.7 (CH_2—OH), 109.2 (Ar), 126.5, 126.7, 128.1, 128.6 (Ar). Ms (m/z): 312 m/z. Anal. Calcd. for $C_{23}H_{20}O$: C 88.43, H 6.45%. Found: C 88.43, H 6.44%.

1-(Chloromethyl)-4-((E)-4-(E)-styrylstyryl)benzene 9

4.3 g (14.0 mmol) of (4-((E)-4-(E)-styrylstyryl)phenyl)methanol **8**, 1.12 ml (14.0 mmol) of pyridine and 1 mL (14.0 mmol) of $SOCl_2$ were dissolved in 100 mL of dry CH_2Cl_2, this mixture was cooled to 10°C. The reaction was carried out under nitrogen in ice bath for 7 h. After this period, the solvent was evaporated and the resulting oil was dry supported and purified in a silica gel (60–240 pore size) column using a mixture of hexane–dichloromethane 2:1 as eluent to yield 4.1 g (95%) as a yellow powder, UV $CHCl_3$ (nm): 243, 358. IR (KBr, cm^{-1}): 3361, 3023, 2945, 1635, 1513, 1420, 1087, 966, 825. ^1H NMR (DMSO-d_6), δ (ppm): 4.49 (s, 2H, CH_2), 7.26 (br, 1H, Ar), 7.30 (d, 2H, CH═, $J = 16.8$ Hz), 7.35 (d, 2H, CH═, $J = 16.8$ Hz), 7.41 (br, 2H, Ar), 7.54 (br, 4H, Ar), 7.58–7.62 (br, 6H, Ar). ^{13}C NMR (DMSO-d_6), δ (ppm): 46.0 (CH_2), 126.4 (CH═), 126.6 (Ar), 127.7 (Ar), 128.6 (Ar), 128.9 (Ar), 129.2 (Ar), 136.8 (Ar), 137.0 (Ar). Ms (m/z): 330 m/z. Anal. Calcd. for $C_{23}H_{19}Cl$: C 83.50, H 5.79%. Found: C 83.52, H 5.79%.

The resorcinarenes were obtained in agreement with reference [11].

General Procedure for Dendrimers

A mixture of 1 mmol of the respective monochloride generation of dendron **5** or **9**, potassium carbonate (21.2 mmol) and 18-crown-6 0.56 g (2.12 mmol) in dry acetone (80 ml) was heated to reflux and stirred vigorously under nitrogen after 20 min. The compounds **10**–**12** (0.0125 mmol) dissolved in dry acetone (40 ml) were added dropwise and the reaction was continued for 7 days. The mixture was allowed to cool and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. The residue dissolved in diethyl ether was washed with an aqueous solution of 5% Na_2CO_3 (3 times). The organic layer was dried

and evaporated to dryness and reprecipitated with dichloromethane–methanol.

Dendrimer **G1 13**. Resorcinarene **10**; **5**; brown powder 0.29 g (90%), UV $CHCl_3$ (nm): 242, 302, 315. IR (KBr, cm^{-1}): 3416, 3054, 2926, 2858, 1606, 1494, 1290, 1117, 962. ^1H NMR ($CDCl_3$), δ (ppm): 0.83 (br, 12H, CH_3), 1.27 (br, 24H, CH_2), 2.17 (br, 8H, CH_2), 3.60 (br, 4H, CH), 4.82 (br, 16H, CH_2—O), 6.42 (br, 4H, Ar), 7.12 (br, 16H, CH═), 7.25 (br, 76H, Ar). ^{13}C NMR ($CDCl_3$), δ (ppm): 14.1 (CH_3), 22.7 (CH_2), 27.7 (CH_2), 32.2 (CH), 70.0 (CH_2—O), 101.0 (Ar), 126.4 (Ar), 127.5 (CH═), 128.6 (Ar), 131.0 (Ar ipso), 134.0 (Ar_{ipso}), 136.4 (Ar), 137.2 (Ar), 139.3 (Ar_{ipso}), 154.3 (Ar—O). MALDI TOF: 2305 m/z. Anal. Calcd. for $C_{168}H_{160}O_8$: C 87.46, H 6.99%. Found: C 87.45, H 6.98%.

Dendrimer **G1 14**. Resorcinarene **11**; **5**; brown–red powder 0.21 g (91%), UV $CHCl_3$ (nm): 242, 301, 315. IR (KBr, cm^{-1}): 3427, 3025, 2918, 1607, 1495, 1291, 1107. ^1H RMN ($CDCl_3$), δ (ppm): 2.31 (br, 8H, CH_2), 2.78 (br. 8H, CH_2) 3.62 (s, 16H, CH_2—O), 4.82–4.91 (t, 4H, CH, $J = 1.5$ Hz), 6.45 (s, 4H, Ar), 7.01 (br, 16H, CH═), 7.06–7.43 (m, 96H, Ar). ^{13}C NMR ($CDCl_3$), δ (ppm): 34.6 (CH_2), 34.9 (CH), 70.0 (CH_2—O), 126.5 (CH═), 127.5 (Ar), 128.3 (Ar), 128.6 (Ar), 136.5 (Ar), 137.1 (Ar). ^{13}C CP-MAS NMR δ (ppm): 35.62 (CH), 69.37 (CH_2—O), 102.50 (Ar), 127.83 (CH═, Ar), 136.72 (Ar), 142.31 (Ar), 155.98 (Ar—O). MALDI TOF: 2441 m/z. Anal. Calcd. for $C_{180}H_{152}O_8$: C 88.49, H 6.27%. Found: C 88.50, H 6.27%.

Dendrimer **G1 15**. Resorcinarene **12**; **5** brown powder 0.20 g (85%), UV $CHCl_3$ (nm): 242, 301, 315. IR (KBr, cm^{-1}): 3419, 2924, 2852, 1497, 1108, 961. ^1H NMR ($CDCl_3$), δ (ppm): 0.85 (br, 12H, CH_3), 1.22 (br, 72H, CH_2), 1.60 (br, 8H, CH_2), 3.66 (s, 4H, CH), 5.13 (br, 16H, CH_2—O), 7.01–7.15 (m, 16H, CH═), 7.26–7.48 (br, 80H, Ar). ^{13}C NMR ($CDCl_3$), δ (ppm): 14.1 (CH_3), 22.6 (CH_2), 29.4 (CH_2), 29.7 (CH_2), 31.9 (CH), 70.2 (CH_2—O), 126.4 (CH═), 127.5 (Ar), 128.6 (Ar), 137.1 (Ar). MALDI TOF: 2641 m/z. Anal. Calcd. for $C_{192}H_{208}O_8$: C 87.23, H 7.93%. Found: C 88.25, H 7.92%.

Dendrimer **G2 16**. Resorcinarene **10**; **9** brown powder 0.38 g (90%), UV $CHCl_3$ (nm): 243, 296, 359. IR (KBr, cm^{-1}): 3422, 2925, 1613, 1461, 1107, 962. ^1H NMR ($CDCl_3$), δ (ppm): 0.89 (br, 12H, CH_3), 1.25 (br, 24H, CH_2), 2.19 (br, 8H, CH_2), 3.59 (br, 16H, CH_2—O), 4.33 (t, 4H, CH, $J = 1.5$ Hz), 6.13 (br, 4H, Ar), 7.12 (br, 32H, CH═), 7.26–7.38 (m, 76H, Ar), 7.52 (br, 32H, Ar). ^{13}C NMR ($CDCl_3$), δ (ppm): 13.5 (CH_3), 22.2 (CH_2), 27.6 (CH_2), 28.7 (CH_2), 31.6 (CH), 69.4 (CH_2—O), 125.9 (CH═), 126.3 (Ar), 126.7 (Ar), 127.1 (Ar), 127.6 (Ar), 128.2 (Ar), 136.0 (Ar). Anal. Calcd. for $C_{232}H_{208}O_8$: C 89.19, H 6.71%. Found: C 89.19, H 6.72%.

Dendrimer **G2 17**. Resorcinarene **11**; **9** brown–red powder 0.31 g (92%), UV $CHCl_3$ (nm): 243, 297, 359. IR (KBr, cm^{-1}): 3386, 2923, 1654, 1400, 1106, 961. ^1H NMR ($CDCl_3$), δ (ppm): 2.63 (br, 16H, CH_2), 3.51 (br, 16H, CH_2—O), 4.56 (br, 4H, CH), 6.32 (br, 4H, Ar), 6.92 (br, 32H, CH═), 7.12–7.54 (m, 128H, Ar). ^{13}C NMR ($CDCl_3$), δ (ppm): 13.5 (CH_3), 22.2 (CH_2), 31.2 (CH_2), 31.6 (CH), 69.9 (CH_2—O), 122.0 (Ar), 125.6 (Ar), 126.5 (Ar), 126.8 (Ar), 128.3 (CH═), 130.8 (Ar), 136.6 (Ar), 137.3 (Ar), 142.9 (Ar), 152.6 (Ar). ^{13}C CP-MAS NMR δ (ppm): 35.58 (CH), 69.61 (CH_2—O), 104.36 (Ar), 128.07 (CH═, Ar), 135.26 (Ar), 142.88 (Ar), 154.23 (Ar—O), 169.11(Ar—O). Anal. Calcd. for $C_{244}H_{200}O_8$: C 89.89, H 6.18%. Found: C 89.89, H 6.16%.

Dendrimer **G2 18**. Resorcinarene **12**; **9** brown powder 0.30 g (90%), UV $CHCl_3$ (nm): 243, 359. IR (KBr, cm^{-1}): 3396, 2924, 2853, 1623, 1458, 1253, 1108, 963. ^1H NMR ($CDCl_3$), δ (ppm): 0.85 (br, 12H, CH_3), 1.25 (br, 72H, CH_2), 2.11 (br, 8H, CH_2), 3.60 (br, 16H, CH_2—O), 4.33 (m, 4H, CH), 6.13 (br, 4H, Ar), 7.12 (br, 32H, CH═), 7.26–7.52 (m, 108H, Ar). ^{13}C NMR ($CDCl_3$), δ (ppm): 13.5 (CH_3), 22.1 (CH_2), 29.5 (CH_2), 69.4 (CH_2—O), 125.9 (Ar), 126.3 (Ar), 128.2 (Ar), 135.6 (Ar), 136.8 (Ar). Anal. Calcd. for $C_{256}H_{256}O_8$: C 88.85, H 7.46%. Found: C 89.87, H 7.46%.

Complexes 19 and 20

A solution of **14** or **17** (0.138 mmol) in toluene (50 ml) was added to a toluene solution (100 ml) of C_{60} (0.138 mmol), and the mixture was stirred vigorously at 80°C for 7 days. After this period, the solvent was evaporated to dryness and the solid obtained was carefully washed with small quantities of toluene.

Supramolecular complex 19

Brown powder 80 mg (40% yield). UV–Vis (solid state) nm: 249, 365. IR (cm^{-1}), 3430, 2927, 3055, 3024, 2916, 2862, 1602, 1494, 1426, 1288, 1178, 1104, 1014, 959, 807, 747, 694, 574,524. ^{13}C CP-MAS NMR δ_c (ppm): 35.34 (CH, CH_2), 69.37 (CH_2—O), 102.50 (Ar), 127.99 (CH═, Ar), 136.54 (Ar), 143.52 (Ar, C_{60}), 156.28 (Ar—O). Anal. Calcd. for $C_{240}H_{152}NaO_8$: C 90.45, H 4.81%; found C 90.47, H 4.81%.

Supramolecular complex 20

Brown powder 90 mg (45% yield). UV–Vis (solid state) nm: 249, 365. IR (cm^{-1}), 3406, 3026, 2919, 2620, 1628, 1403, 1373, 1104, 1005, 967, 831, 749, 701, 573, 524; ^{13}C CP-MAS NMR δ_c (ppm): 33.64 (CH, CH_2), 69.76 (CH_2—O), 128.62 (CH═, Ar), 135.55 (Ar), 143.44 (Ar, C_{60}), 161.16 (Ar—O). Anal. Calcd. for $C_{304}H_{200}NaO_8$: C 91.72, H 5.06%; found C 91.70, H 5.08%.

Acknowledgements

This work was supported by the DGAPA (IN209106). We would also like to thank Nieves, Z. S. M.; Rios, O. H.; Velasco, L., Pérez P. J.; Patiño, M. M. R. and Cedillo, V. G. for technical assistance.

References

[1] Vögtle, F.; Gestermann, S.; Hesse, R.; Schwierz, H.; Windisch, B. *Prog. Polym. Sci.* **2000**, *25*, 987.
[2] Tully, D. C.; Fréchet, J. M. J. *Chem. Commun.* **2001**, 1229.
[3] Inoue, K. *Prog. Polym. Sci.* **2000**, *25*, 453.
[4] Bosman, A. W.; Janssen, H. M.; Meijer, E. W. *Chem. Rev.* **1999**, *99*, 1665.
[5] Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201.
[6] McQuade, D. T.; Pullen, A. E.; Swager, T.M. *Chem. Rev.* **2000**, *100*, 2537.
[7] Sato, T.; Jiang, D.-L.; Aida, T. J. *Am. Chem. Soc.* **1999**, *121*, 10658.
[8] Balogh, L.; de Leuze-Jallouli, A.; Dvornic, P.; Kunugi, Y.; Blumstein, A.; Tomalia, D. A. *Macromolecules* **1999**, *32*, 1036.
[9] Schenning, A. P. H. J.; Peeters, E.; Mijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489.
[10] Swallena, S. F.; Kopelmana, R.; Mooreb, J. S.; Devadossb, C. *J. Mol. Struct.* **1999**, *485*, 585.
[11] García, M. A.; Klimova, E.; Klimova, T.; Flores, P. B.; Romero, A. M.; Hernandez, O. S.; Martínez, G. M. *Fullerenes Nanot. Carbon Nanostruct.* **2005**, *13*, 171.
[12] Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.