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

Synthesis of cyclotriveratrylene dendrimers and their supramolecular complexes with fullerene C_{60}

I. V. Lijanova[a]; J. Flores Maturano[a]; J.G. Domínguez Chávez[a]; K.E. Sánchez Montes[a]; S. Hernandez Ortega[a]; T. Klimova[b]; M. Martínez-García[a]
[a] Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, México D.F., Mexico [b] Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, México D.F., Mexico

To cite this Article Lijanova, I. V. , Flores Maturano, J. , Domínguez Chávez, J.G. , Sánchez Montes, K.E. , Hernandez Ortega, S. , Klimova, T. and Martínez-García, M.(2009) 'Synthesis of cyclotriveratrylene dendrimers and their supramolecular complexes with fullerene C_{60}', Supramolecular Chemistry, 21: 1, 24 — 34
To link to this Article: DOI: 10.1080/10610270802516674
URL: http://dx.doi.org/10.1080/10610270802516674

Supramolecular Chemistry
Vol. 21, Nos. 1–2, January–March 2009, 24–34

Taylor & Francis
Taylor & Francis Group

Synthesis of cyclotriveratrylene dendrimers and their supramolecular complexes with fullerene C_{60}

I.V. Lijanova[a], J. Flores Maturano[a], J.G. Domínguez Chávez[a], K.E. Sánchez Montes[a], S. Hernandez Ortega[a], T. Klimova[b] and M. Martínez-García[a]*

[a]*Instituto de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, México D.F., Mexico*
[b]*Facultad de Química, Universidad Nacional Autónoma de México, Cd. Universitaria, México D.F., Mexico*

(*Received 19 September 2008; final version received 22 September 2008*)

Dendrimers with cyclotriveratrylene core and polybenzyl ether branches were synthetised by a convergent Fréchet approach. The cyclotriveratrylene was obtained by trimerisation of phenolic allyl ether of vanillyl alcohol and its structure was characterised by X-ray diffraction. The synthesised dendrimers of first and second generations were used to obtain the supramolecular complexes with fullerene C_{60}. The ability of the fullerene C_{60} to form supramolecular complexes with the cyclotriveratrylene dendrimers was confirmed by ^1H and ^{13}C NMR studies. The value of the association constant $K_a = 678 \pm 60\,mol^{-1}\,dm^3$ calculated on the basis of UV–vis spectroscopic measurements for the titration of the fullerene C_{60} solution in toluene with increasing amount of the cyclotriveratrylene dendrimer suggest that the fullerene resides mainly near the central core. All the compounds were characterised by ^1H, ^{13}C NMR, FTIR, UV–vis spectroscopy, MALDI-TOF, FAB + mass spectra and elemental analysis.

Keywords: cyclotriveratrylene; polybenzyl ether; dendrimers; supramolecular complex; fullerene C_{60}

Introduction

Dendrimers are highly branched polymers with well-defined structure, uniform size and molecular weight (*1*). They are composed by a multifunctional central core to which dendritic branches are connected. According to their shape, dendrimers are divided into two types (*2*). The first one has a circular or elliptic shape in which repeated units are regularly stretched from a core, whereas the second type has a conic shape with repeated units directionally stretched from a core. Since it is possible to control dendrimer's size and structure, and at the same time introduce different kinds of functional groups into their terminal groups or core, these molecules find numerous applications in different fields such as catalysis (*3*), energy or charge-transfer systems (*4*), magnetic resonance imaging contrast agents (*5*), drug delivery (*6*), sensors (*7*), charge transfer of light-emitting layer in organic light-emitting diodes (LEDs) (*8*), DNA complexation (*9*), etc. In addition to the above advantages, dendrimers manifest a highly ordered structure and give thin films with various functional groups on top surface of substrate, making possible the creation of unique materials in which surface characteristics are controlled at the molecular level. The dendrimers are also used in the supramolecular chemistry as host molecules in which guest molecules can be located in the dendritic branches or in to the core if it has a cavity. In the present work, we reported the synthesis of polybenzyl ether dendrimers with a cyclotriveratrylene core and their supramolecular comlplexes with the fullerene C_{60}.

Results and discussion

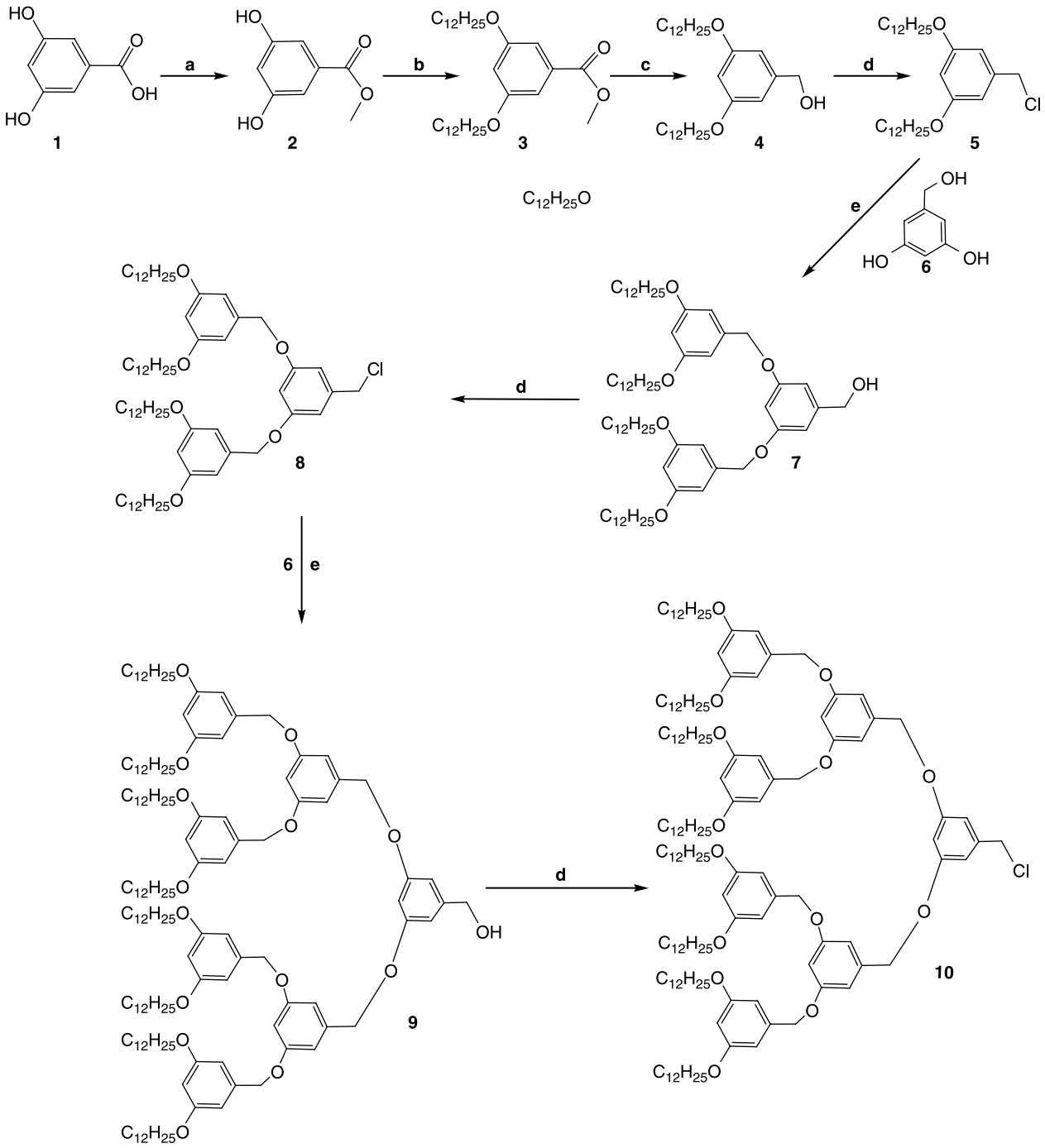
The synthesis of the three series of dendrimers with polybenzyl ethers was carried out applying the convergent Fréchet approach (*10*) that consists of three steps. The first one was the synthesis of the three dendrons, which was followed by the synthesis of the cyclotriveratrylene and finally the *O*-alkylation of the dendrons to the cyclotriveratrylene. Under this order, dendrons containing benzyloxy groups were prepared starting from the protection of the commercially available 3,5-dihidroxy-benzyl acid **1** to obtain the methyl 3,5-dihydroxybenzoate **2** in 98% yield, followed by an *O*-alkylation reaction coupling with the 1-bromododecane, to obtain the compound **3** in 87% yield. The methyl benzoate group was subjected to a reduction reaction with $LiAlH_4$ in THF at 0°C to obtain the 3,5-didodecyloxybenzyl alcohol **4** in 96% yield. Treatment of **4** with thionyl chloride in dichloromethane at 0°C yielded 85% of 1,3-didodecyloxy-5-(chloromethyl)benzene **5** that is regarded as the first generation dendron (*11*).

After being synthesised the first generation, the higher generations can be formed by applying repetitive set of reactions: alkylation with **6** and chlorination of the

*Corresponding author. Email: margar@servidor.unam.mx

ISSN 1061-0278 print/ISSN 1029-0478 online

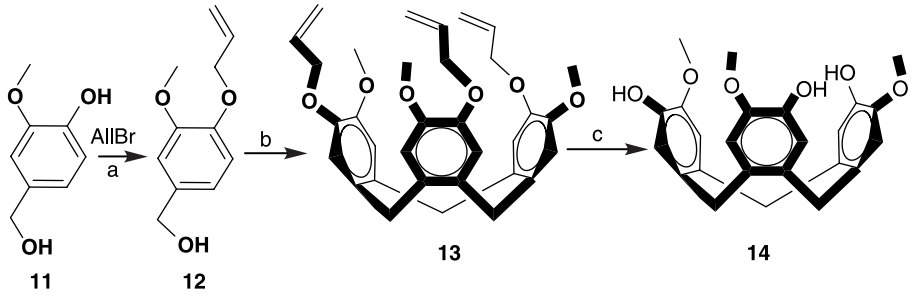
DOI: 10.1080/10610270802516674
http://www.informaworld.com



Scheme 1. Synthesis of dendrons of first, second and third generations; (a) CH_3OH, H_2SO_4, reflux, 18 h; (b) $CH_3(CH_2)_{10}CH_2Br$, K_2CO_3, KI, acetone, reflux, 24 h; (c) $LiAlH_4$, THF, 0°C to rt, 4 h; (d) Pyridine, $SOCl_2$, CH_2Cl_2, 0°C, 4 h; (e) K_2CO_3, KI, acetone, reflux.

benzylic alcohol. For instance, alkylation of two equivalents of chloride **5** with **6** in presence of K_2CO_3 and small amounts of KI in boiling acetone yielded compound **7** in 89%, which upon treatment with thionyl chloride gave the second-generation dendron **8** having the (chloromethyl)benzene group in, 77% yield. As **8** has a chloromethyl group, another cycle can be started by 3,5-dihydroxybencyl alcohol with two equivalents of **8**, to form the compound **9** which was obtained in 70% yield. Finally, after chlorination of **9**, the third generation chloride **10** was afforded in 70% yield.

Dendrons **5**, **8** and **10** were characterised by ^{1}H- and ^{13}C-NMR, FTIR and FAB + mass spectrometry. The ^{1}H NMR spectra of the dendrons of first **5**, second **8** and third



Scheme 2. Synthesis of cyclotriveratrylene; (a) K_2CO_3, acetone, reflux; (b) MeOH, F_3CCOOH, N_2; (c) Dioxane Pd/charcoal, ethanol, perchloric acid.

10 generations contain signals at δ_H 4.60 for the methylene protons Ar—CH_2—Cl, and signals for the aromatic protons (one, two and three doublets and triplets, respectively, depending on the generation).

The C_3-cyclotriguaiacylene **14** (cyclotriveratrylene) can be easily prepared in multigram quantities (*12*), according to the subsequent multistep transformations shown in Scheme 2. The (4-(allyloxy)-3-methoxyphenyl) methanol **12** undergoes smooth trimerisation in presence of trifluoracetic acid, affording the C_3-cyclotriveratrylene derivative **13** in 80% yield. The allyl ethers of **13** can then be cleaved back to the phenols under mild condition, giving **14** in *ca.* 65% (*13*).

In the ^{1}H NMR spectrum of the compound **13** were observed two doublets at δ_H 3.51 and 4.74 due to the methylene bridge groups with coupling constants $J = 13.8$ Hz, also two doublets at δ_H 5.25, 5.37 with coupling constants $J = 10.14$, 17.37 Hz, respectively, and one multiplet at δ_H 6.6 due to the vinylic protons. Finally, two singlets were observed at δ_H 6.80 and 6.85 assigned to the aromatic protons.

Crystals of 2,7,12-trihydroxy-3,8,13-trimethoxy-10,l5-dihydro-5H-tribenzo [a,d,g]cyclononene (cyclotriveratrylene) **14** suitable for X-ray crystallographic studies were obtained by crystallisation from dioxane. Figure 1 shows the crystal structure of the compound **14**.

The synthesis of dendrimers involves only one step, namely an *O*-alkylation between dendrons **5**, **8** or **10** and cyclotriveratrylene **14.** The reaction was carried out in acetone and K_2CO_3 at reflux for 7 days and the dendrimers were obtained in good yields (Scheme 3).

The dendrimers **15**, **16** and **17** are readily soluble in common organic solvents such as $CHCl_3$, CH_2Cl_2, toluene, acetonitrile. Their chemical structure was determined by ^{1}H, ^{13}C NMR and FTIR. In the ^{1}H NMR spectra, it was observed that all the dendrimers have the same resonant peaks but with different intensities. One triplet at δ 0.88 ppm was assigned to the methyl protons of the central dodecanoxy chains, signals of ethyl groups —CH_2— were centred at 1.26 ppm and the —CH_2—γ—OAr protons appeared at 1.41 ppm, while the CH_2—β—OAr and —CH_2—α—OAr signals were observed at 1.74 and 3.43 ppm, respectively. At 3.71 ppm was observed one singlet due to the methoxy group. Signals at 3.90 and 5.01 ppm were assigned to the methylene protons neighbour to the ether groups of the dendron generation —CH_2—O—Ar. The methylenic protons of the cyclotriveratrylene appeared as two doublets at 3.45 and 4.67 ppm,

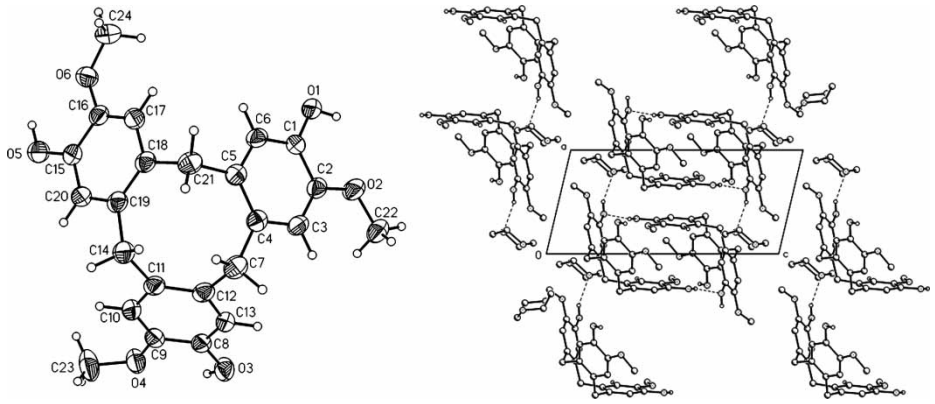
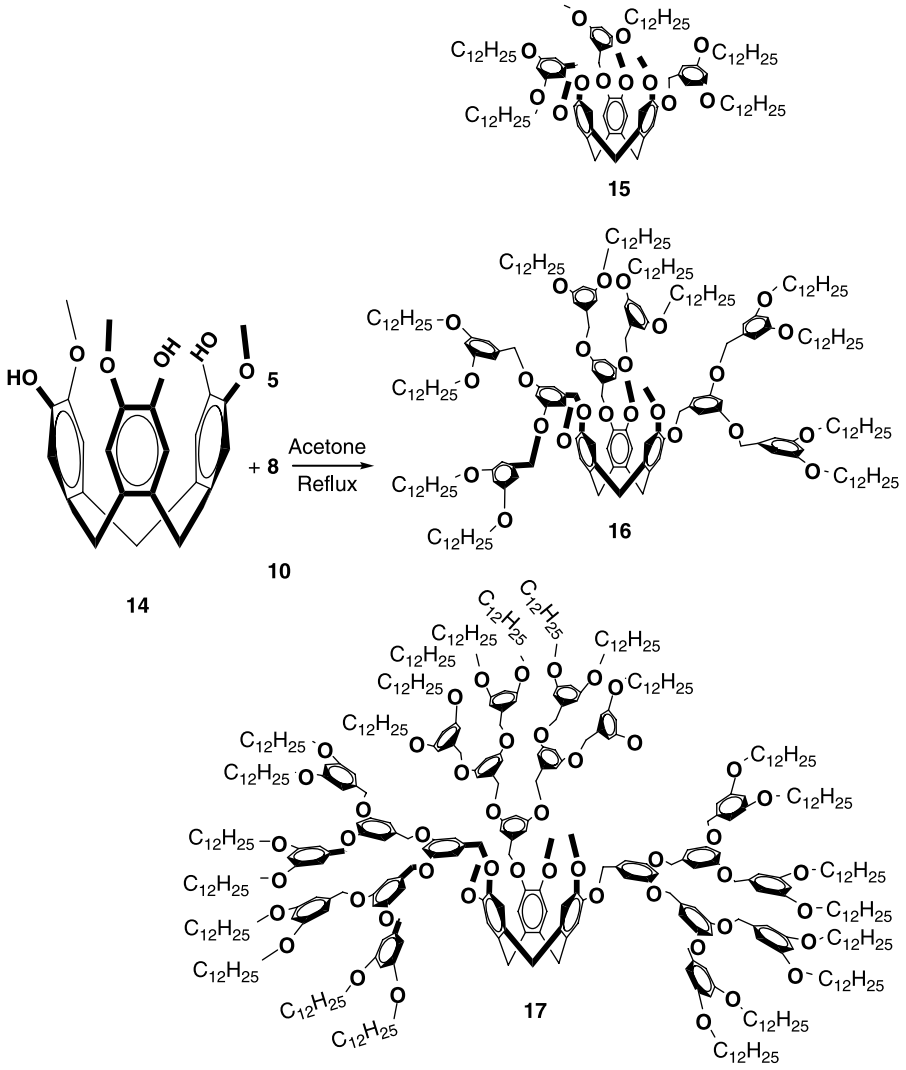


Figure 1. Crystal structure and crystal packing of compound **14**. Selected bond lengths (Å): C1—O1 = 1.369, C2—O2 = 1.365, C4—C7 = 1.514, C7—C12 = 1.524. Selected angle (°): C4—C7—C12 = 112.4.



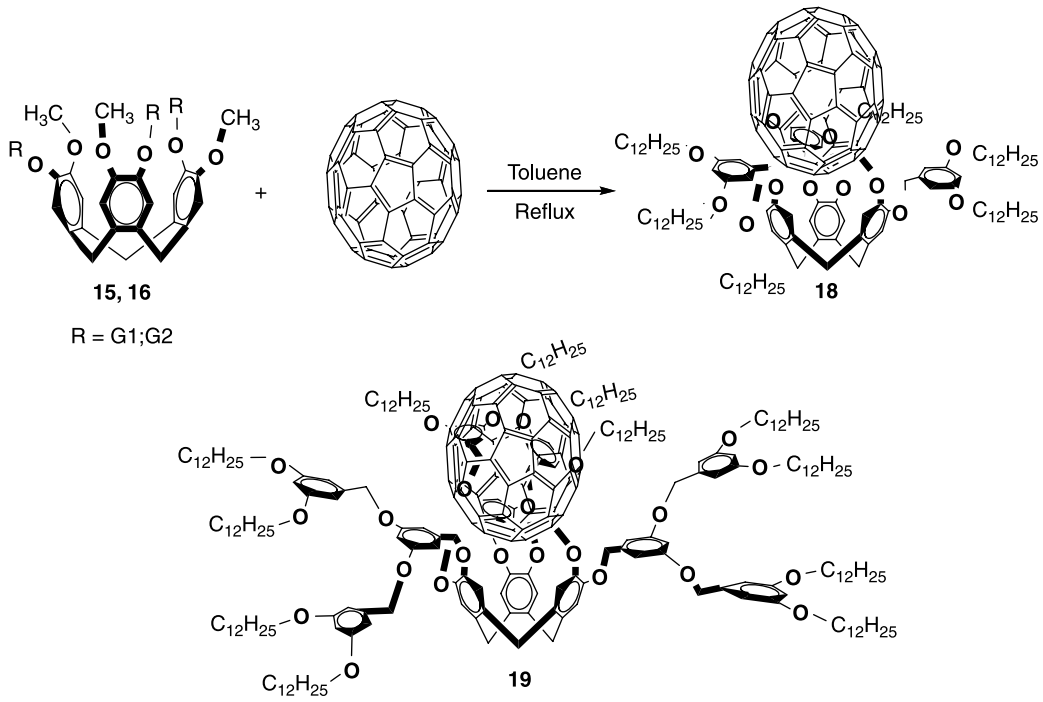
Scheme 3. Synthesis of cyclotriveratrylene dendrimers.

while those of the aromatic protons appear at δ 6.37–6.82 ppm as singlets, doublets and triplets.

The matrix-assisted laser desorption/ionisation (MALDI-TOF) or fast-atom bombardment (FAB) mass spectra confirmed the structure of the dendrimers being *m*/*z* of 1770 for **15**, *m*/*z* of 3527 for **16** and *m*/*z* of 7012 for **17**.

The cyclotriveratrylene dendrimers **15** and **16** were used for the preparation of supramolecular complexes with fullerene C_{60}. Stirring of benzene solutions with equimolar amounts of the dendrimers **15** or **16** and fullerene C_{60} for 3 days at 80°C afforded complexes **18** and **19** in 60 and 55% yields, respectively. Elemental analysis was consistent with the 1:1 stoichiometry (Scheme 4).

In order to obtain a more complete characterisation of the supramolecular complexes, ^{1}H and ^{13}C NMR studies were carried out in toluene-d_8 at 25°C. In the ^{1}H NMR spectrum of the supramolecular complex **18** were observed one triplet at δ_H 0.88 due to the CH_3 groups (Table 1), two sets of multiplets at δ_H 1.27 and 1.64 due to the CH_2 groups of the aliphatic chain, one singlet at δ_H 3.60 assigned to the CH_3—O groups and one multiplet at δ_H 4.64 ascribed to the CH_2—O groups. Two doublets appeared at δ_H 3.37 and 4.56 were assigned to the bridge —CH_2— groups. In the spectrum of free dendrimer **15**, these doublets were observed at δ_H 3.58 and 4.00. Similarly, one singlet ascribed to the CH_2—O— joined to the cyclotriveratrylene complex appeared at δ_H 4.92, whereas this signal was observed at δ_H 4.15 in the spectrum of free dendrimer **15**. The signals for the aromatic rings in the supramolecular complex **18** were observed at δ_H 6.52, 6.73, 6.81, 7.00 and 7.09. In the case of free dendrimer **15**, these signals appeared at δ_H 6.42, 6.52, 7.00 and 7.08. Similar changes were also observed in the ^{1}H NMR spectra of free **16** and in the complex **19**. Above-mentioned changes in the position of the signals



Scheme 4. Supramolecular complexes of cyclotriveratrylene dendrimers with fullerene C_{60}.

Table 1. Chemical shifts (ppm) observed in the ^{1}H NMR spectra of dendrimers **15**, **16** and supramolecular complexes **18**, **19** in toluene-d_8 at 25°C.

Group/compound	**15**	**18**	**16**	**19**
CH_3	0.88	0.87	0.88	0.93
CH_2	1.27, 1.62	1.27, 1.64	1.25–1.45, 1.75	1.29, 1.64
CH_3—O	3.61	3.60	3.74	3.59
CH_2—O	3.63, 3.73, 4.15	3.64, 4.92	3.91, 4.91, 5.02	3.73, 4.78, 4.91
CH_2	3.58, 4.00	3.37, 4.56	3.44, 4.68	3.40, 4.60
Ar—H	6.42, 6.52, 7.00, 7.08	6.52, 6.73, 6.81, 7.00, 7.09	6.39, 6.53, 6.67, 6.84	6.53, 6.65, 6.75, 6.83, 7.10

of different protons of cyclotriveratrylene unit observed upon addition of fullerene C_{60} evidence the formation of the supramolecular complex between cyclotriveratrylene **15** and fullerene C_{60}.

Further evidences of the complexation between synthesised cyclotriveratrylene dendrimers and fullerene C_{60} were obtained by ^{13}NMR spectroscopy. Thus, the comparison of the ^{13}C NMR spectrum of **16** with that of the **16**:C_{60} 1:1 complex **19** in toluene-d_8 shows some conformational changes in **16** (Figure 2). The signal at δ_C 35.73 corresponding to the O—CH_3 groups in **16** was shifted downfield to δ_C 35.93 in **19**. The signals corresponding to Ar —CH_2—O groups joined to the aliphatic chain and to the cyclotriveratrylene observed at δ_C 67.61, 69.86 and at δ_C 71.88 in the spectrum of **16** were shifted downfield to δ_C 67.99, 70.27 and to δ_C 72.06 in the spectrum of **19.** The signals assigned to aromatic carbons of the dendron arms were observed at δ_C 101.31, 107.58 and 139.40 in the case of the compound **16** and in the complex **19** were found at δ_C 101.98, 107.95, 139.40 and their intensities were diminished. The signals of the aromatic carbons of the cyclotriveratrylene (δ_C 114.36, 117.47 and 133.15) were shifted in the complex **19** to δ_C 114.56, 117.41 and 133.43. In addition, the signals for the CArO groups at δ_C 149.24, 160.37 and 160.72 ascribed to the CArO groups in free cyclotriveratrylene dendrimer **16** were shifted to δ_C 149.47, 160.76 and 161.08 in the supramolecular complex **19**.

A signal observed at δ_C 143.200 in the ^{13}C NMR spectrum of the free C_{60} also was shifted to δ_C 143.082 ppm in the supramolecular complex **18**. A similar change of chemical shift was also observed for the supramolecular complex **19** (δ_C 143.040 ppm).

The binding behaviour of fullerene C_{60} to cyclotriveratrylene **16** was also investigated by UV–vis spectroscopy and the corresponding association constant was

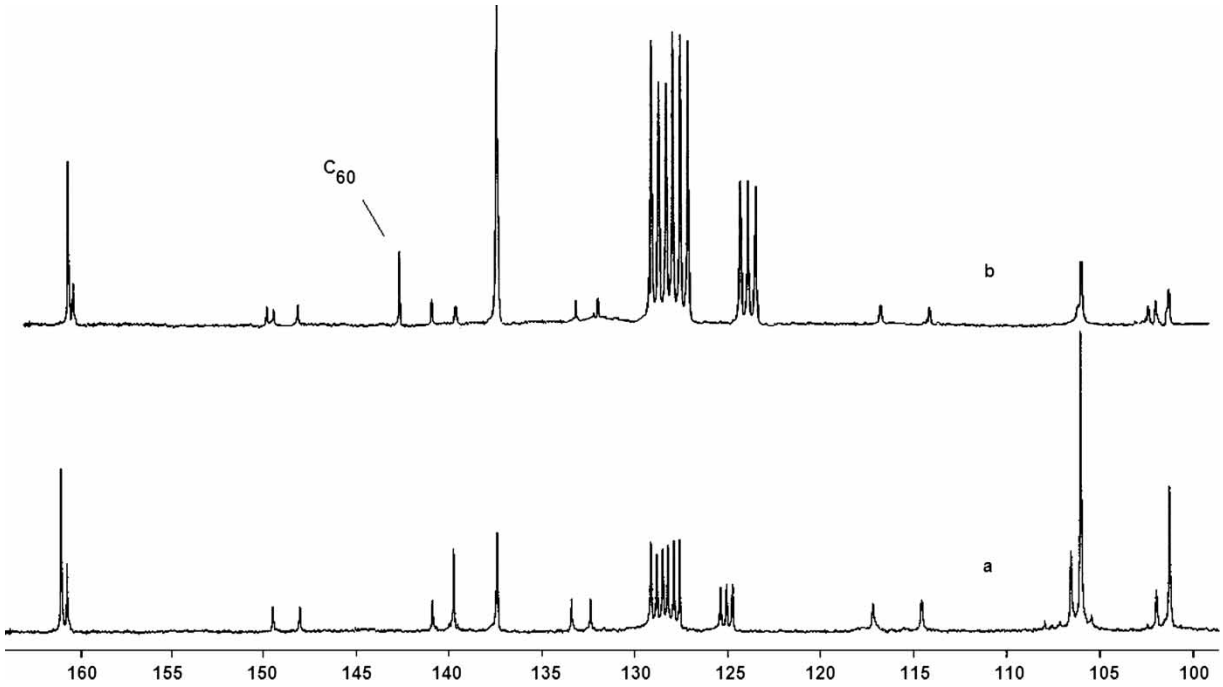


Figure 2. ^{13}C NMR spectra of the free cyclotriveratrylene dendrimer **16** (a) and of the supramolecular complex **18** (b) in toluene-d_8.

determined. For this, the titration studies of C_{60} in toluene solution with cyclotriveratrylene dendrimer **16** were conduced at 298 K (Figure 3). The spectral changes induced by the addition of different amounts of **16** to solutions of C_{60} can be clearly seen in Figure 3. The most significant changes were observed at $\lambda = 430$ nm. Specifically, addition of **16** to a toluene solution of C_{60} (1.03×10^{-4} mol dm^{-3} led to an increase in the absorption of the band at 430 nm, characteristic of complexation (Figure 3). Treatment of the titration data with the Benesi–Hildebrand equation (*14*) gave a value for the association constant $K_a = 678 \pm 60$ mol^{-1} dm^3 at 298 ± 1 K. The binding isotherm provides a good fit to 1:1 stoichiometry. This determination is in agreement with the association constants found for supramolecular complexes reported (*15*).

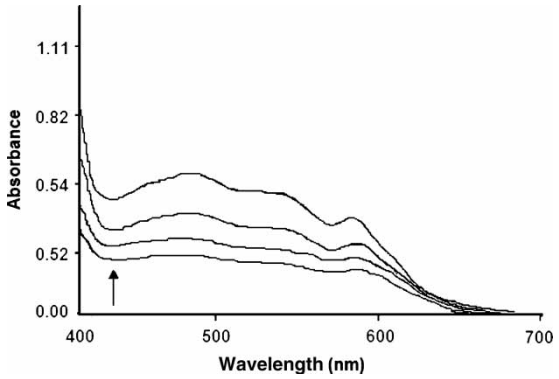


Figure 3. Absorption spectra of C_{60} (1.03×10^{-4} mol dm^{-3}) in the presence of **16** in toluene. The concentrations of **16** are: 0.0, 0.19, 0.45, 0.78 ($\times 10^{-4}$ mol dm^{-3}). Temperature: 298 K.

These results suggest that the fullerene C_{60} guest mainly resides in the space near the cyclotriveratrylene moiety. These chemical shifts are in full agreement with our hypothesis that the interior region of the branching shell located close to the central core of the polybenzyl ether dendrimers is capable of providing the cavity size necessary for the inclusion of fullerene C_{60}.

Conclusions

The synthesis of cyclotriveratrylene dendrimers with crown-ether functionalised nanocavities was realised. The formation of host–guest complexes between C_{60} and polybenzyl ether dendrimers with cyclotriveratrylene core has been investigated by ^1H and ^{13}C-NMR and UV–vis spectroscopy in toluene-d_8 at 298 K. The chemical shifts in the ^1H and ^{13}C-NMR studies and the association constant value (678 ± 60 mol^{-1} dm^{-3}) determined by UV–vis spectroscopy suggest that the fullerene C_{60} mainly resides near the central core.

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 as an internal reference. The UV–vis absorption spectra were obtained with a Shimadzu 2401 PC spectrophotometer. 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. Electrospray mass spectra were taken on a Bruker Daltonic, Esquire 6000. MALDI-TOF mass spectra were taken on a Bruker Omni FLEX.

Synthesis of dendrons

*Methyl 3,5-dihydroxybenzoate **2***

A mixture of 10 g (64.92 mmol) of 3,5-dihydroxybenzoic acid **1** in 100 ml of methanol was added to 0.5 ml of concentrated sulphuric acid, the mixture was heated to reflux and stirred vigorously under nitrogen for 13 h. Then the mixture was allowed to cool and the solvent was evaporated. The residue was dissolved in acetone and washed with an aqueous solution of 5% Na_2CO_3. The organic layer was dried using $NaSO_4$ and evaporated to yield 10.8 g (98%) of a white powder. UV–vis (nm): 303, 249. IR (cm^{-1}): 3384, 3252, 1693, 1608, 1487, 1445, 1349, 1308, 1262, 1171, 999. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.65 (br, 2H, OH), 6.99 (d, 2H, Ar —H, $J = 1.94$ Hz), 6.58 (t, ^{1}H, Ar —H, $J = 2.3$ Hz), 3.82 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 167.23 (C═O), 159.50 (Ar —OH), 133.12 (C_{ipso}), 108.66 (Ar), 107.99 (C_{ipso}), 109.20 (Ar), 52.30 (CH_3—O), Ms (*m/z*): 168 *m/z*. Calcd. for C: 57.14, H: 4.80%. Found. C: 57.13, H: 4.81%.

*Methyl 3,5-bis(dodecyloxy)benzoate **3***

A mixture of methyl 3,5-dihydroxybenzoate **2** 14.5 g (86 mmol) and the dodecyl bromide 46 ml (189 mmol), K_2CO_3, KI, in dry acetone (150 ml) was heated to reflux and stirred under nitrogen for 24 h. The mixture was allowed to cool and the precipitated was filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in diethyl ether and washed with an aqueous solution of 5% Na_2CO_3 (two times). The product was purified (SiO_2; Hexane–ethyl acetate, 4:1) to yield 49.5 g (87%) of a white powder. UV–vis (nm): 307, 254. IR (cm^{-1}): 2921, 2852, 1724, 1604, 1471, 1443, 1391, 1324, 1240, 1164, 1122, 1054, 1003, 857, 764, 720, 636. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 6H, CH_3, $J = 6.40$ Hz); 1.26–1.44 (m, 36H, CH_2), 1.77 (q, 4H, CH_2, $J = 7.77$), 3.89 (s, 3H, CH_3—O), 3.96 (t, 4H, CH_2—O, $J = 6.50$), 6.63 (t, ^{1}H, Ar —H, $J = 2.30$ Hz), 7.21 (d, 2H, Ar —H, $J = 2.30$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.67 (CH_2), 26.0 (CH_2), 29.2—29.5 (CH_2), 52.0 (CH_3—O), 68.3 (CH_2—O), 106.7 (Ar), 107.7 (Ar), 131.9 (Ar_{ipso}), 160.2 (Ar —O), 166.9 (C═O). Ms (*m/z*): 504 *m/z*. Calcd. for C: 76.19, H: 11.18%. Found. C: 76.17, H: 11.18%.

*(3,5-bis(dodecyloxy)phenyl)methanol **4***

5 g (10 mmol) of **3** in 50 ml of THF were added to a suspension of $LiAlH_4$ 0.38 g (10 mmol) in 100 ml of THF under nitrogen. The reaction mixture was stirred for 24 h at room temperature. Water (2 ml) was added dropwise. The mixture was filtered over zeolite and the residue washed with CH_2Cl_2.The solvent was evaporated *in vacuo* and the residue was chromatographed (SiO_2; hexane; ethyl acetate 80:20) to yield 4.8 g (96%) of a white powder. UV–vis (nm): 281. IR (cm^{-1}): 3513, 3102, 2921, 2854, 1612, 1591, 1470, 1397, 1313, 1168, 1060, 1027, 981, 929, 838, 714, 678, 621, 520.^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 6H, CH_3, $J = 6.96$ Hz), 1.26–1.45 (m, 36H, CH_2), 1.75 (q, 4H, CH_2, $J = 8.01$ Hz), 1.85 (s, ^{1}H, OH), 3.92 (t, 4H, CH_2—O, $J = 6.57$ Hz), 4.59 (s, 2H, CH_2—OH), 6.36 (t, ^{1}H, Ar —H, $J = 2.28$ Hz), 6.48 (d, 2H, Ar —H, $J = 2.25$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.3–29.5 (CH_2), 31.9 (CH_2), 65.4 (CH_2—OH), 68.1 (CH_2—O), 100.7 (Ar), 105.1 (Ar), 143.2 (Ar_{ipso}), 160.6 (Ar —O). Ms (*m/z*): 476 *m/z*. Calcd. for C: 78.09, H: 11.84%. Found. C: 78.10, H: 11.82%.

A mixture of **5** or **8** (10 mmol) and the 3,5-dihydroxybencyl alcohol **6** (4.4 mmol) K_2CO_3, KI, in dry acetone (150 ml) was heated to reflux and stirred under nitrogen for 24 h. The mixture was allowed to cool and the precipitate was filtered. The filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in diethyl ether and washed with an aqueous solution of 5% Na_2CO_3 (two times). The product was purified (SiO_2; Hexane–ethyl acetate, 4:1).

*(3,5-bis(3,5-bis(dodecyloxy)benzyloxy)phenyl)methanol **7***

5 g (89%) of a white powder. UV–vis (nm): 282, 232. IR (cm^{-1}): 3369, 2925, 2854, 1599, 1461, 1379, 1345, 1324, 1295, 1165, 1057, 832, 722, 684.^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 12H, CH_3, $J = 7.20$ Hz), 1.26–1.46 (m, 72H, CH_2), 1.65 (s, ^{1}H, OH), 1.76 (q, 8H, CH_2, $J = 7.80$ Hz), 3.93 (t, 8H, CH_2—O, $J = 6.60$ Hz), 4.62 (s, 2H, CH_2—OH), 4.94 (s, 4H, $ArCH_2$—O), 6.40 (t, 2H, Ar —H, $J = 2.40$ Hz), 6.45 (t, ^{1}H, Ar —H, $J = 2.40$ Hz), 6.49 (d, 2H, Ar —H, $J = 2.1$ Hz), 6.54 (d, 4H, Ar —H, $J = 2.1$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.2–29.6 (CH_2), 31.9 (CH_2), 65.4 (CH_2—OH), 68.0 (CH_2—O), 70.1 ($ArCH_2$—O), 100.5 (Ar), 100.7 (Ar), 105.0 (Ar), 105.7 (Ar), 139.0 (Ar_{ipso}), 143.2 (Ar_{ipso}), 160.17 (Ar —O), 160.5 (Ar —O). Ms (*m/z*): 1056 *m/z*. Calcd. for C: 78.36, H: 11.05%. Found. C: 78.36, H: 11.04%.

(3,5-bis(3,5-bis(3,5-bis(dodecyloxy)benzyloxy)benzyloxy) phenyl)methanol ***9***

8 g (70%) of a white powder, UV–vis (nm): 282, 231. IR (cm^{-1}): 2925, 2854, 1599, 1461, 1375, 1344, 1325, 1296, 1166, 1056, 909, 832, 734, 683. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 24H, CH_3, $J = 6.90$ Hz), 1.26–1.46 (m, 144H, CH_2), 1.65 (s, ^{1}H, OH), 1.76 (q, 16H, CH_2, $J = 7.80$ Hz), 3.92 (t, 16H, CH_2—O, $J = 6.60$ Hz), 4.61 (s, 2H, CH_2—OH), 4.94 (s, 8H, $ArCH_2$—O), 4.97 (s, 4H, $ArCH_2$—O), 6.39 (t, 4H, Ar —H, $J = 2.10$), 6.53 (t, ^{1}H, Ar —H, $J = 2.1$ Hz), 6.54 (d, 8H, Ar —H, $J = 2.1$ Hz), 6.56 (t, 2H, Ar —H, $J = 2.40$ Hz), 6.59 (d, 2H, Ar —H, $J = 2.4$ Hz), 6.66 (d, 4H, Ar —H, $J = 2.10$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.2–29.6 (CH_2), 31.9 (CH_2), 65.2 (CH_2—OH), 68.0 (CH_2—OAr), 70.1 ($ArCH_2$—OAr), 70.1 ($ArCH_2$—OAr), 100.8 (Ar), 101.3 (Ar), 101.6 (Ar), 105.7 (Ar), 106.3 (Ar), 138.9 (Ar_{ipso}), 139.2 (Ar_{ipso}), 143.4 (Ar_{ipso}), 160.1 (Ar —O), 160.1 (Ar —O), 160.5 (Ar —O) Ms (*m/z*): 2219 *m/z*. Calcd. for C: 78.47, H: 10.72%. Found. C: 78.45, H: 10.71%.

Dendron **4**, **7** or **9** (10 mmol) was added to a mixture of pyridine (1.5 ml) and CH_2Cl_2 (150 ml) at 0°C under nitrogen and vigorously stirred for 20 min. Thionyl chloride (20.29 mmol) was added dropwise, the reaction was continued for 4 h at room temperature and the solvent was evaporated *in vacuo*. The product was washed with a mixture hexane:ethyl acetate, the solvent was evaporated to give the following.

1-(chloromethyl)-3,5-bis(dodecyloxy)benzene ***5***

4.25 g (85%) of a white powder. UV–vis (nm): 284, 210. IR (cm^{-1}): 2922, 2851, 1601, 1467, 1392, 1345, 1298, 1262, 1173, 1063, 951, 836, 714, 689, 594. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 6H, CH_3, $J = 6.93$ Hz); 1.26–1.46 (m, 36H, CH_2), 1.76 (q, 4H, CH_2, $J = 7.98$ Hz), 3.92 (t, 4H, CH_2—O, $J = 6.54$ Hz), 4.49 (s, 2H, CH_2—Cl), 6.39 (t, ^{1}H, Ar —H, $J = 2.25$ Hz), 6.50 (d, 2H, Ar —H, $J = 2.22$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.2–29.5 (CH_2), 31.9 (CH_2), 46.4 (CH_2—Cl), 68.1 (CH_2—O), 101.4 (Ar), 107.01 (Ar), 139.36 (Ar_{ipso}), 160.5 (Ar —O). Ms (*m/z*): 495 *m/z*. Calcd. for C: 75.19, H: 11.19%. Found. C: 75.21, H: 11.22%.

5,5′-(5-(chloromethyl)-1,3-phenylene)bis(oxy)bis (methylene)bis(1,3-bis(dodecyloxy) benzene) ***8***

8.1 g (77%) of a white powder. UV–vis (nm): 283, 235. IR (cm^{-1}): 2925, 2854, 1598, 1461, 1376, 1346, 1324, 1297, 1167, 1056, 833, 719, 682. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 12H, CH_3, $J = 6.13$ Hz); 1.26–1.46 (m, 72H, CH_2), 1.76 (q, 8H, CH_2, $J = 6.83$ Hz), 3.93 (t, 8H, CH_2—O, $J = 6.50$ Hz), 4.50 (s, 2H, CH_2—Cl), 4.94 (s, 4H, $ArCH_2$—O), 6.40 (t, 2H, Ar —H, $J = 2.24$ Hz), 6.54 (d, 5H, Ar —H, $J = 1.75$ Hz), 6.62 (d, 2H, Ar —H, $J = 1.85$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 13.9 (CH_3), 22.65 (CH_2), 26.1 (CH_2), 29.3–29.6 (CH_2), 31.9 (CH_2), 46.2 (CH_2—Cl), 68.3 (CH_2—OAr), 70.4 ($ArCH_2$—O), 101.3 (Ar), 102.5 (Ar), 106.0 (Ar), 107.9 (Ar), 139.0 (Ar_{ipso}), 139.6 (Ar_{ipso}), 160.3 (Ar —O), 160.76 (Ar —O). Ms (*m/z*): 1076 *m/z*. Calcd. for C: 77.01, H: 10.77%. Found. C: 77.04, H: 10.74%.

5,5′,5″,5‴-(5,5′-(5-(chloromethyl)-1,3-phenylene)-bis(oxy)bis(methylene)bis(benzene-5,3,1-triyl))tetrakis (oxy)tetrakis(methylene)tetrakis(1,3-bis(dodecyloxy) benzene) ***10***

16 g (70%) of a white powder. UV–vis (nm): 283, 232. IR (cm^{-1}): 2925, 2854, 1598, 1461, 1375, 1344, 1324, 1297, 1166, 1056, 832, 720, 682. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 24H, CH_3, $J = 6.90$ Hz); 1.26–1.45 (m, 144H, CH_2), 1.76 (q, 16H, CH_2, $J = 7.80$ Hz), 3.93 (t, 16H, CH_2—O, $J = 6.60$ Hz), 4.50 (s, 2H, CH_2—Cl), 4.94 (s, 8H, $ArCH_2$—O), 4.96 (s, 4H, $ArCH_2$—O), 6.40 (t, 4H, Ar —H, $J = 2.10$), 6.54 (d, 9H, Ar —H, $J = 2.4$ Hz), 6.56 (t, 2H, Ar —H, $J = 2.10$ Hz), 6.62 (d, 2H, Ar —H, $J = 2.4$ Hz), 6.66 (d, 4H, Ar —H, $J = 2.40$ Hz). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.2–29.6 (CH_2), 31.9 (CH_2), 46.2 (CH_2—Cl), 68.1 (CH_2—OAr), 70.1 (CH_2—OAr), 70.2 (CH_2—O), 100.9 (Ar), 101.7 (Ar), 102.0 (Ar), 105.7 (Ar), 106.4 (Ar), 107.7 (Ar), 138.9 (Ar_{ipso}), 139.0 (Ar_{ipso}), 139.5 (Ar_{ipso}), 160.0 (Ar —O), 160.2 (Ar —O), 160.5 (Ar —O). Ms (*m/z*): 2235 *m/z*. Calcd. for C: 77.82, H: 10.58%. Found. C: 77.82, H: 10.54%.

(4-(allyloxy)-3-methoxyphenyl)methanol ***12***

A mixture of vanillyl alcohol 10 g (65 mmol) **11**, allyl bromide (6.3 ml, 73 mmol) and potassium carbonate 10 g (65 mmol) in 100 ml of acetone was refluxed for 12 h with magnetic stirring. Then, after most of the solvent was stripped off, water was added and the organic material was extracted with dichloromethane. This product was recrystallised from 100 ml of diethyl ether to yield 14 g (80%) of a white powder. UV–vis (nm): 281. 234. IR (cm^{-1}): 3335, 3257, 3075, 2994, 2976, 2942, 2906, 2856, 2842, 2042, 1942, 1861, 1784, 1704, 1647, 1592, 1514, 1457, 1420, 1364, 1322, 1294, 1254, 1233, 1139, 1061, 1025, 1005, 991, 926, 853, 805, 742. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 2.08 (s, ^{1}H, OH), 3.86 (s, 3H, CH_3—O), 4.59 (m, 4H, CH_2—O—CH_2—OH), 5.28 (d, d, ^{1}H, CH_2=C, $J_{cis} = 10.50$ Hz, $J_{gem} = 1.5$ Hz), 5.40 (d, d, ^{1}H, CH_2=C, $J_{trans} = 17.40$ Hz, $J_{gem} = 1.8$ Hz), 6.07 (m, ^{1}H, —CH=C), 6.83 (s, ^{1}H, Ar —H), 6.84 (s, ^{1}H,

Ar —H), 6.91 (s, ^{1}H, Ar —H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 55.7 (CH_3—O), 65.0 (CH_2—OH), 69.8 (OCH_2), 110.7 (Ar), 113.3 (Ar), 117.86 (CH_2═), 119.1 (Ar), 133.2 (HC═), 133.9 (Ar_{ipso}), 147.3 (Ar —O), 149.4 (Ar —O). Ms (*m/z*): 194 *m/z*. Calcd. for C: 68.02, H: 7.27%. Found. C: 68.01, H: 7.24%.

2,7,12-Trimethoxy-3,8,13-tris(2-propenyloxy)-10,15-dihydro-5Htribenzo[a,d,g]cyclononene ***13***

About 20 ml of trifluoroacetic acid was added dropwise to a solution of the phenol protected vanillyl alcohol 12.5 g (26 mmol) in methanol (600 ml), cooled in an ice bath and magnetically stirred. The resulting pink solution was stayed under nitrogen at room temperature for 18 h. The reaction mixture was redissolved by addition of dichloromethane and the organic phase was thoroughly washed with water until neutral pH. The dichloromethane solution was partially dried over sodium sulphate and evaporated under vacuum, and added ether, affording a crystalline residue, which was purified by digestion in 200 ml of ether overnight and finally isolated by suction filtration, to yield 1.75 g (35%), of a white powder. UV–vis (nm): 289. 235. IR (cm^{-1}): 3075, 2906, 2844, 1647, 1604, 1510, 1458, 1437, 1401, 1336, 1276, 1193, 1165, 1101, 998, 930, 882, 851, 787, 751, 614, 569. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 3.51 (d, 3H, CH_2, $J = 13.80$ Hz), 3.84 (s, 9H, O—CH_3), 4.59 (m, 6H, O—CH_2), 4.74 (d, 3H, CH_2, $J = 13.60$ Hz), 5.25 (d, d, 3H, CH_2═C, $J_{cis} = 10.40$ Hz, $J_{gem} = 1.4$ Hz), 5.37 (d, d, 3H, CH_2═C, $J_{trans} = 17.20$ Hz, $J_{gem} = 1.4$ Hz), 6.06 (m, 3H, —CH═C), 6.80 (s, 3H, Ar —H), 6.85(s, 3H, Ar —H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 36.5 (CH_2), 56.2 (CH_3—O), 70.3 (OCH_2), 114.0 (Ar), 116.0 (Ar), 117.4 (CH_2═), 131.9 (Ar —CH_2), 132.5 (Ar —CH_2), 133.8 (HC═), 146.9 (Ar —O), 148.4 (Ar —O). Ms (*m/z*): 528 *m/z*. Calcd. for C: 74.98, H: 6.86%. Found. C: 74.96, H: 6.84%.

2,7,12-Trihydroxy-3,8,13-trimethoxy-10,l5-dihydro-5H-tribenzo[a,d,g]cyclononene (cyclotriveratrylene) ***14*** *(*13*)*

The tris(allyl ether) **13**, 2.5 g (4.8 mmol) was dissolved in 15 ml of hot dioxane, and to this solution 20 ml of ethanol, 1 g of 10% palladium on charcoal and (dropwise) 0.5 ml of 70% perchloric acid were added. This mixture was stirred under nitrogen at 55–60°C for18 h. The catalyst was filtered off and washed first with 10 ml of dioxane and then with ca. 50 ml of dichloromethane. The organic filtrate was thoroughly washed with water, dried over sodium sulphate and concentrated to ca. 5 ml. The desired triphenol, which was allowed to crystallise overnight, was finally collected by suction filtration, to yield 1.6 g (65%) of white needles. UV–vis (nm): 291, 235. IR (cm^{-1}): 3414, 3029, 2964, 2932, 2842, 1707, 1618, 1592, 1512, 1470, 1447, 1360, 1275, 1214, 1176, 1141, 1084, 1011, 933, 885, 848, 744, 648, 618, 591, 526, 495, 449. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 3.48 (d, 3H, CH_2, $J = 13.80$ Hz), 3.85 (s, 9H, O—CH_3), 4.71 (d, 3H, CH_2, $J = 13.80$ Hz), 5.38 (s, 3H, OH), 6.79 (s, 3H, Ar —H), 6.88 (s, 3H, Ar —H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 35.2 (CH_2), 55.6 (CH_3—O), 113.2 (Ar), 116.3 (Ar), 130.1 (Ar —CH_2), 132.1 (Ar —CH_2), 144.6 (Ar —O), 145.7 (Ar —O). Ms (*m/z*): 408 *m/z*. Calcd. for $C_{24}H_{24}O_6$; C 70.57, H 5.92%. Found. C: 70.56, H: 5.93%.

Synthesis of dendrimers

A mixture of 1 mmol of the respective monochloride generation of dendron **5**, **8** or **10**, potassium carbonate (21.2 mmol) and 18-crown-6 (0.56 g, 2.12 mmol) in dry acetone (80 ml) were heated to reflux and stirred vigorously under nitrogen for 20 min. The compound **14** (0.033 mmol) dissolved in dry acetone (40 ml) was added dropwise and the reaction was continued for 7 days. The mixture was filtered over celite, washed with dichloromethane and evaporated under vacuum.

Dendrimer ***15***

0.4 g (82%) of a white powder. UV–vis (nm): 285, 233. IR (cm^{-1}): 2925, 2854, 1600, 1513, 1462, 1380, 1346, 1325, 1292, 1265, 1220, 1166, 1086, 1063, 849, 834, 720, 685. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 18H, CH_3, $J = 6.90$ Hz); 1.26–1.41 (m, 108H, CH_2), 1.74 (q, 12H, CH_2, $J = 7.56$ Hz), 3.43 (d, 3H, CH_2, $J = 13.8$ Hz), 3.71 (s, 9H, CH_3—O), 3.90 (t, 12H, CH_2—O, $J = 6.48$ Hz), 4.67 (d, 3H, CH_2, $J = 13.5$ Hz), 5.01 (s, 6H, ArCH_2—OCTV), 6.36 (t, 3H, Ar —H, $J = 2.40$ Hz), 6.55 (d, 6H, Ar —H, $J = 2.4$ Hz), 6.64 (s, 3H, Ar —H), 6.82 (s, 3H, Ar —H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 26.1 (CH_2), 29.3–29.6 (CH_2), 31.9 (CH_2), 36.5 (CH_2), 56.3 (CH_3—O), 68.2 (CH_2—OAr), 72.1 (ArCH_2—O), 100.9 (Ar), 105.4 (Ar), 114.2 (Ar), 116.8 (Ar), 131.9 (Ar), 132.8 (Ar), 140.1 (Ar_{ipso}), 147.5 (Ar), 148.7 (Ar), 160.7 (Ar —O). ^{1}H NMR (300 MHz, toluene-d_8), δ_H (ppm): 0.88 (t, 18H, CH_3, $J = 7.5$ Hz), 1.27 (br, 108H, CH_2), 1.62 (br, 12H, CH_2), 3.58 (s, 3H, CH_2), 3.61 (s, 9H, CH_3—O), 3.63–3.73 (m, 12H, CH_2—O), 4.00 (s, 3H, CH_2), 4.15 (s, 6H, ArCH_2—OCTV), 6.38 (br, 3H, Ar —H), 6.42 (br, 3H, Ar —H), 6.52 (s, 3H, Ar —H), 7.00 (s, 3H, Ar —H), 7.08 (s, 3H, Ar —H). ^{13}C NMR (75 MHz, toluene-*d*), δ_C (ppm): 14.36 (CH_3), 23.17 (CH_2), 26.54 (CH_2), 28.97 (CH_2), 29.20 (CH_2), 29.32 (CH_2), 29.93 (CH_2), 30.16 (CH_2), 30.82 (CH_2), 32.42 (CH_2), 46.42 (CH_3—O), 68.00 (CH_2—OAr), 99.47 (Ar), 100.77 (Ar), 101.53 (Ar), 101.78 (Ar), 105.12 (Ar), 105.90 (Ar), 107.17 (Ar), 107.39 (Ar), 107.67 (Ar), 114.2 (Ar), 139.78 (Ar), 149.49 (Ar —O), 161.02 (Ar —O). Ms (*m/z*): 1045 *m/z*.

Calcd. for C: 78.10, H: 10.23%. Found. C: 78.07, H: 10.26%.

*Dendrimer **16***

0.83 g (77%) of a white powder. UV–vis (nm): 283, 236. IR (cm^{-1}): 2925, 2854, 1599, 1513, 1461, 1375, 1344, 1324, 1295, 1266, 1165, 1061, 832, 756, 721, 684. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.88 (t, 36H, CH_3, $J = 7.20$ Hz); 1.25–1.45 (m, 216H, CH_2), 1.75 (q, 24H, CH_2, $J = 7.80$ Hz), 3.44 (d, 3H, CH_2, $J = 13.8$ Hz), 3.74 (s, 9H, CH_3—O), 3.91 (t, 24H, CH_2—O, $J = 6.60$ Hz), 4.68 (d, 3H, CH_2, $J = 13.5$ Hz), 4.91 (s, 12H, $ArCH_2$—OAr), 5.02 (s, 6H, $ArCH_2$—O), 6.39 (t, 6H, Ar —H, $J = 2.10$ Hz), 6.53 (d, 15H, Ar —H, $J = 2.1$ Hz), 6.67 (d, 9H, Ar —H, $J = 2.4$ Hz), 6.84 (s, 3H, Ar —H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.0 (CH_3), 22.6 (CH_2), 26.0 (CH_2), 29.2–29.6 (CH_2), 31.8 (CH_2), 39.4 (CH_2), 56.1 (CH_3—O), 68.0 (CH_2—O), 70.1 ($ArCH_2$—O), 71.8 ($ArCH_2$—O), 100.7 (Ar), 101.3 (Ar), 105.7 (Ar), 113.6 (Ar), 116.3 (Ar), 131.6 (Ar), 132.6 (Ar), 138.8 (Ar_{ipso}), 140.1 (Ar_{ipso}), 147.1 (Ar), 148.4 (Ar), 160.1 (Ar), 160.4 (Ar); ^{1}H NMR (300 MHz, toluene-d_8), δ_H (ppm): 0.91 (t, 36H, CH_3, $J = 6.4$ Hz); 1.26–1.33 (m, 216H, CH_2), 1.64 (m, 24H, CH_2), 3.32 (d, 3H, CH_2, $J = 13.8$ Hz), 3.50 (s, 9H, CH_3—O), 3.70 (t, 24H, CH_2—O, $J = 6.00$ Hz), 4.52 (d, 3H, CH_2, $J = 13.6$ Hz), 4.73 (s, 12H, $ArCH_2$—OAr), 4.84 (d, 6H, $ArCH_2$—O, $J = 6.00$ Hz), 6.53 (d, 9H, Ar —H, $J = 2.1$ Hz), 6.61–6.64 (m, 9H, Ar —H), 6.77 (s, 9H, Ar —H), 6.88 (s, 3H, Ar), 7.08 (s, 3H, Ar). ^{13}C NMR (75 MHz, toluene-d_8), δ_C (ppm): 14.05 (CH_3), 22.84 (CH_2), 26.25 (CH_2), 29.5–29.8 (CH_2), 32.10 (CH_2), 36.31 (CH_2), 55.73 (CH_3—O), 67.61 (CH_2—O), 69.86 (Ar —O—CH_2), 71.88 (Ar —O—CH_2), 100.85 (Ar), 101.31 (Ar), 105.62 (Ar), 105.97 (Ar), 107.58 (Ar), 114.36 (Ar), 117.47 (Ar), 132.03 (Ar), 133.15 (Ar), 139.18 (Ar), 139.40 (Ar), 140.69 (Ar_{ipso}), 147.69 (Ar_{ipso}), 149.24 (Ar —O), 160.37 (Ar —O), 160.72 (Ar —O). Ms (*m/z*): 3527 *m/z*. Calcd. for C: 78.66, H: 10.46%. Found. C: 78.69, H: 10.42%.

*Dendrimer **17***

1.6 g (73%) of a white powder. UV–vis (nm): 283, 232. IR (cm^{-1}): 2925, 2854, 1598, 1513, 1461, 1374, 1344, 1324, 1296, 1269, 1166, 1057, 832, 720, 682. ^{1}H NMR (300 MHz, $CDCl_3$), δ_H (ppm): 0.87 (t, 72H, CH_3, $J = 6.90$ Hz); 1.25–1.45 (m, 432H, CH_2), 1.73 (q, 48H, CH_2, $J = 7.50$ Hz), 3.45 (d, 3H, CH_2, $J = 13.8$ Hz), 3.76 (s, 9H, CH_3—O), 3.89 (t, 48H, CH_2—O, $J = 6.60$ Hz), 4.65 (d, 3H, CH_2, $J = 13.6$ Hz), 4.90 (s, 24H, $ArCH_2$—O), 4.92 (s, 12H, $ArCH_2$—O), 5.02 (s, 6H, $ArCH_2$—O), 6.38 (t, 12H, Ar —H, $J = 1.80$), 6.52 (d, 24H, Ar —H, $J = 2.10$ Hz), 6.54 (t, 6H, Ar —H, $J = 2.40$ Hz), 6.65 (d, 15H, Ar —H, $J = 1.80$ Hz), 6.68 (d, 6H, Ar —H), 6.72 (s, 3H, Ar —H), 6.85 (s, 3H, Ar —H). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.1 (CH_3), 22.7 (CH_2), 26.06 (CH_2), 29.3–29.6 (CH_2), 31.9 (CH_2), 36.5 (CH_2), 56.2 (CH_3—O), 68.0 (CH_2—O), 70.1 ($ArCH_2$—O), 71.8 ($ArCH_2$—O) 100.8 (Ar), 101.6 (Ar), 105.7 (Ar), 106.40 (Ar), 113.9 (ArH), 116.5 (ArH), 131.8 (Ar), 132.7 (Ar), 138.9 (Ar_{ipso}), 139.1 (Ar_{ipso}), 147.2 (Ar), 148.6 (Ar), 160.2 (Ar —O), 160.5 (Ar —O). Ms (*m/z*): 7012 *m/z*. Calcd. for C: 78.61, H: 10.43%. Found; C: 78.67, H: 10.39%.

Complexes 18 and 19

A solution of **15** or **16** (0.138 mmol) in toluene (50 ml) was added to a toluene solution of C_{60} (0.138 mmol). The mixture was stirred vigorously at 80°C for 3 days. After this period, the solvent was evaporated to dryness and the solid obtained was carefully washed with small quantities of toluene.

*Supramolecular complex **18***

0.353 g (60%) of a brown powder, UV–vis (nm): 259, 330. IR (cm^{-1}): 2923, 2853, 1598, 1512, 1464, 1378, 1345, 1323, 1292, 1264, 1219, 1166, 1088, 1065, 849, 832, 753,722, 683. ^{1}H NMR (300 MHz, toluene-*d*), δ_H (ppm): 0.87 (t, 18H, CH_3, $J = 6.6$ Hz), 1.27 (br, 108H, CH_2), 1.64 (br, 12H, CH_2), 3.37 (d, 3H, CH_2, $J = 13.2$ Hz), 3.60 (s, 9H, CH_3—O), 3.64 (br, 12H, CH_2—O), 4.56 (d, 3H, CH_2, $J = 13.5$ Hz), 4.92 (s, 6H, $ArCH_2$—OCTV), 6.52 (s, 3H, Ar —H), 6.73 (s, 3H, Ar —H), 6.81 (s, 3H, Ar —H), 7.00 (t, 3H, Ar —H, $J = 12$ Hz), 7.09 (s, 3H, Ar —H). ^{13}C NMR (75 MHz, toluene-*d*), δ_C (ppm): 14.36 (CH_3), 23.16 (CH_2), 26.59 (CH_2), 29.83 (CH_2), 29.91 (CH_2), 29.98 (CH_2), 30.20 (CH_2), 32.42 (CH_2), 36.74 (CH_2), 55.94 (CH_3—O), 67.96 (CH_2—OAr), 71.58 (Ar —O—CH_2), 72.16 (Ar —O—CH_2), 101.16 (Ar), 101.78 (Ar), 105.72 (Ar), 107.18 (Ar), 107.58 (Ar), 107.98 (Ar), 114.61 (Ar), 116.18 (Ar), 117.33 (Ar), 132.44 (Ar), 132.62 (Ar), 133.37 (Ar), 140.40 (Ar), 140.73 (Ar_{ipso}), 143.08 (C_{60}), 147.49 (Ar_{ipso}), 147.62 (Ar_{ipso}), 148.16 (Ar_{ipso}), 149.22 (Ar_{ipso}), 149.49 (Ar_{ipso}), 161.02 (Ar —O), 161.13 (Ar —O). $C_{167}H_{167}O_{12}$; Calcd. for C: 84.77, H: 7.11%. Found; C: 84.81, H: 7.14%.

*Supramolecular complex **19***

0.201 g (55%) of a brown powder. UV–vis (nm): 259, 330,591. IR (cm^{-1}): 2925, 2854, 1600, 1513, 1460, 1376, 1343, 1324, 1294, 1266, 1166, 1060, 833, 752, 722, 683. ^{1}H NMR (300 MHz, toluene-*d*), δ_H (ppm): 0.93 (t, 36H, CH_3, $J = 6.9$ Hz); 1.29 (s, 216H, CH_2), 1.64 (m, 24H, CH_2), 3.40 (d, 3H, CH_2, $J = 13.0$ Hz), 3.59 (s, 9H, CH_3—O), 3.73 (t, 24H, CH_2—O, $J = 6.00$ Hz), 4.60 (d, 3H, CH_2, $J = 13.2$ Hz), 4.78 (s, 12H, $ArCH_2$—OAr), 4.91

(an, 6H, $ArCH_2$—O), 6.53 (an, 9H, Ar —H), 6.65 (an, 9H, Ar —H), 6.75 (an, 9H, Ar —H), 6.83 (an, 3H, Ar), 7.10 (s, 3H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$), δ_C (ppm): 14.36 (CH_3), 23.15 (CH_2), 26.59 (CH_2), 29.83–30.19 (CH_2), 32.41 (CH_2), 36.76 (CH_2), 55.93 (CH_3—O), 67.99 (CH_2—O), 70.27 (Ar —O—CH_2), 72.06 (Ar —O—CH_2), 101.26 (Ar), 101.98 (Ar), 105.44 (Ar), 106.02 (Ar), 106.54 (Ar), 107.13 (Ar), 107.95 (Ar), 114.56 (Ar), 117.41 (Ar), 132.39 (Ar), 133.43 (Ar), 139.73 (Ar), 140.89 (Ar), 143.04 (C_{60}), 148.02 (Ar_{ipso}), 149.47 (Ar —O), 160.76 (Ar —O), 161.08 (Ar —O). $C_{291}H_{366}O_{24}$; Calcd. for C: 82.28, H: 8.68%. Found; C: 82.24, H: 8.73%.

X-ray crystallography

A suitable crystal of compound **14** (obtained by crystallisation from dioxane at room temperature) was rolled in epoxy resin and mounted on a glass fibre. Bruker Apex AXS CCD area detector X-ray diffractometer was the instrument used for the determination. The data were first reduced and corrected for absorption using psi-scans, and then solved using the program SHELL-XS. All non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were refined at calculated positions with thermal parameters constrained to the carbon atom on which they were attached.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 701792 for the 2,7,12-Trihydroxy-3,8,13-trimethoxy-l0,l5-dihydro-5H-tribenzo[a,d,g]cyclononene (cyclotriveratrylene) **14**.

Acknowledgements

This work was supported by the DGAPA (IN211408). We would also like to thank Nieves, Z.S.M., Rios, O.H., Velasco, L., Huerta, S.E., Patiño, M.M.R. and Peña, Gonzalez, M.A., for technical assistance.

References

(1) (a) Newkome, G.R.; Moorefield, C.N.; Vögtle, F. *Dendritic Molecules: Concepts Synthesis, Perspectives*; VCH: Weinheim, Germany, 1996. (b) Zeng, F.; Zimmerman, S.C. *Chem. Rev.* **1997**, *97*, 1681–1712. (c) Bosman, A.W.; Janssen, H.M.; Meijer, E.W. *Chem. Rev.* **1999**, *99*, 1665–1688.

(2) Rahman, K.M.A.; Durning, C.J.; Turro, N.J.; Tomalia, D.A. *Langmuir* **2000**, *16*, 10154–10160.

(3) (a) Gossage, R.A.; Jastrzebski, J.T.B.H.; van Ameijde, J.; Mulders, S.J.E.; Brouwer, A.J.; Liskamp, R.M.J.; van Koten, G. *Tetrahedron Lett.* **1999**, *40*, 1413–1416. (b) Reetz, M.T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1526–1529.

(4) (a) Jockusch, S.; Ramirez, J.; Sanghvi, K.; Nociti, R.; Turro, N.J.; Tommalia, D.A. *Macromolecules* **1999**, *32*, 4419–4423. (b) Gilat, S.L.; Adronov, A.; Fréchet, J.M.J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1422–1427. (c) Hofkens, J.; Latterini, L.; De Belder, G.; Gensch, T.; Maus, M.; Vosch, T.; Karni, Y.; Schweitzer, G.; De Schryver, F.C.; Hermann, A.; Müllen, K. *Chem. Phys. Lett*. **1999**, *304*, 1–9.

(5) (a) Weiner, E.C.; Brechbiel, M.W.; Brothers, H.; Magin, R.L.; Gansow, O.A.; Tomalia, D.A.; Lauterbur, P.C. *Magn. Reson. Med.* **1994**, *31*, 1–8. (b) Toth, E.; Pubanz, D.; Vauthey, S.; Helm, L.; Merbach, A.E. *Chem. Eur. J*. **1996**, *2*, 1607–1615.

(6) Twyman, L.J.; Beezer, A.E.; Esfand, R.; Hardy, M.J.; Mitchell, J.C. *Tetrahedron Lett.* **1999**, *40*, 1743–1746.

(7) Albrecht, M.; Gossage, R.A.; Speck, A.L.; van Koten, G. *Chem. Commun.* **1998**, *9*, 1003–1004.

(8) (a) Halim, M.; Pillow, J.N.G.; Samuel, I.D.; Burn, P.L. *Adv. Mater.* **1999**, *11*, 371–374. (b) Strohriegl, P. *Adv. Mater.* **1996**, *8*, 507–510. (c) Wang, P.W.; Liu, Y.J.; Devadoss, C.; Bharathi, P.; Moore, J.S. *Adv. Mater.* **1996**, *8*, 237–241.

(9) Bielinska, A.U.; Kukowska Latallo, J.F.; Baker, J.R. *Biochim. Biophys. Acta-Gene Struct. Expr.* **1997**, *1353*, 180–190.

(10) Tomalia, D.A.; Fréchet, J.M.J. *Dendrimers and other Dendritic Polymers*; Wiley: New York, 2001.

(11) Flores, M.J.; Domínguez, C.J.G.; Carreón, C.; Ma, P.; Gutiérrez, N.M.; Lijanova, I.; Klimova, T.; Martínez, G.M. *Supramol. Chem.* **2007**, *19*, 485–491.

(12) (a) Atwood, J.L.; Koutsantonis, G.A.; Raston, C.L. *Nature* **1994**, *348*, 229–231. (b) Raston, C.L.; Atwood, J.L.; Nichols, P.J.; Sudria, I.B.N. *Chem. Commun.* **1996**, 2615–2651. (c) Atwood, J.L.; Barbour, L.J.; Raston, C.L.; Sudria, I.B.N. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 981–983. (d) Barbour, L.J.; Orr, G.W.; Atwood, J.L. *Chem. Commun.* **1998**, 1901–1902. (e) Nierengarten, J.F.; Oswald, L.; Eckert, J.F.; Nicoud, J.F.; Armaroli, N. *Tetrahedron Lett.* **1999**, *40*, 5681–5684. (f) Huerta, E.; Cequier, E.; de Mendoza, J. *Chem. Commun.* **2007**, 5016–5018.

(13) (a) Canceill, J.; Gabart, J.; Collet, A. *J. Chem. Soc., Chem. Commun*. **1983**, 122. (b) Canceill, J.; Collet, A.; Gottarelli, G. *J. Am. Chem. Soc.* **1984**, *106*, 5997–6003.

(14) (a) Benesi, H.A.; Hildebrand, J.H. *J. Am. Chem. Soc.* **1949**, *71*, 2703–2707. (b) Rose, N.J.; Drago, R.S. *J. Am. Chem. Soc.* **1985**, *107*, 604–613.

(15) (a) Georghiou, P.E.; Mizyed, S.; Chowdhury, S. *Tetrahedron Lett.* **1999**, *40*, 611–614. (b) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed.* **1997**, *36*, 259–260. (c) Haino, T.; Yanase, M.; Fukazawa, Y. *Angew. Chem., Int. Ed.* **1998**, *37*, 997–998. (d) Tsubaki, K.; Tanaka, K.; Kinoshita, T.; Fuji, K. *Chem. Commun.* **1998**, *37*, 895–896. (e) Ikeda, A.; Yoshimura, M.; Shinkai, S. *Tetrahedron Lett.* **1997**, *38*, 2107–2110. (f) Tucci, F.C.; Rudkevitch, D.M.; Rebek, J. *J. Org. Chem.* **1999**, *64*, 4555–4559. (g) Precup-Blaga, F.S.; Garcia-Martinez, J.C.; Schenning, A.P.H.J.; Meijer, E.W. *J. Am. Chem. Soc.* **2003**, *125*, 12953–12960. (h) Gillies, E.R.; Fréchet, J.M.J. *J. Org. Chem.* **2004**, *69*, 46–53.