Polybenzyl ether dendrimers for the complexation of [60]fullerenes

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The formation of host-guest complexes between C_{60} and polybenzyl ether dendrimers with different central cores (phloroglucinol, *meso*-tetraphenylporphyrin, cyclotriveratrylene) has been investigated in organic solvents by means of ^{13}C-NMR and UV-Vis spectroscopy. The interior of the dendrimers with a phloroglucinol core provides the correctly sized space for the inclusion of [60]fullerene and ^{13}C-NMR studies suggest that the guest resides near the central core. In the dendrimers containing a *meso*-tetraphenylporphyrin (TPP) core, the absorbance of the porphyrin Soret band is substantially reduced in the presence of [60]fullerene, thus providing evidence for close vicinity of the fullerene guest to the central core. In solution, the cyclotriveratrylene (CTV) unit alone is a poor receptor for fullerene, but its functionalization with polybenzyl ether dendrons affords an internal cavity with a more appropriate shape and dimension, thus allowing complexation. Indeed, the K_a values (order of magnitude 10^1–10^2 L mol^{-1}) increase significantly with the generation number of the surrounding dendritic substituents.

In light of their multifunctionality and specific shape, dendrimers have been regarded as attractive candidates for applications in host-guest chemistry. Several approaches are possible when using such architectures for the complexation of guest molecules.[1–3] Effectively, all three topologically distinct regions (core, branching shell, and surface) of dendrimers can be used for association with suitable substrates.[2,3] Newkome *et al.*, as well as others, have previously demonstrated that water-soluble hydrophobic dendrimers are able to act analogously to micelles and encapsulate hydrophobic guest molecules within their internal cavities.[4] It has also been shown that the reverse strategy is possible, where in this case a hydrophilic dendritic core with a fluorinated surface was used to extract hydrophilic molecules from water into supercritical CO_2 by encapsulation.[5] Meijer *et al.* demonstrated the "dendritic box" function with a fifth generation poly(propyleneimine)-type dendrimer,[6] which is capable of retaining substrates trapped during the synthesis with diffusion out of the box being prevented since the dendrimer is closely packed with the branches spreading from a small initiator core. In all of the systems mentioned above, no clearly defined binding units have been incorporated into the dendritic structure and the dendrimer acts as an "unimolecular micelle" capable of "dissolving" small guest molecules. Where dendrimers with defined recognition sites are concerned, one possible approach is to functionalise either the dendritic surface or the branches with multiple recognition sites.[3] In such cases, an enhanced efficiency through simultaneous association with several substrates has been observed.[7] Research by the groups of Shinkai[8] and Astruc[9] has also shown increased sensory responses to guest binding on a dendritic surface. Alternatively, the central core of the dendrimer can be a cyclophane with well defined complexation ability.[3] Diederich *et al.* recently described examples of such dendritic host molecules, which they call dendrophanes.[10] The dendritic core is, at least to some extent, shielded from its medium,[11] implying a typical microenvironment inside the dendrimer and such structures can serve as models for globular proteins.[3,10,12]

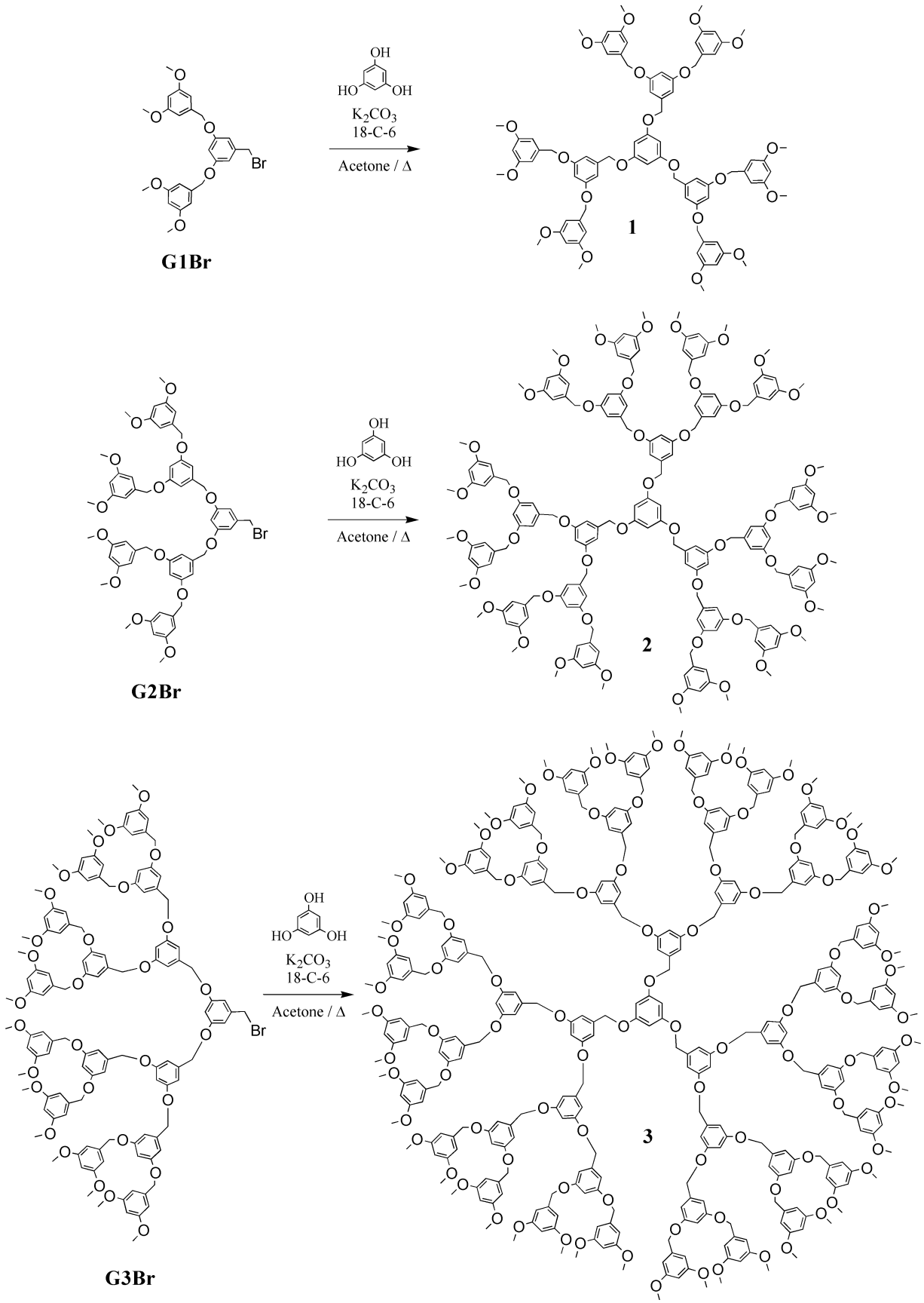
Within the framework of this research line, we now report on the complexation of fullerenes[13] with Fréchet-type dendrimers.[14] In fact, judging from the CPK (Corey–Pauling–Koltun) molecular models such dendrimers can provide a cavity size compatible with [60]fullerene and also a number of electron-rich resorcinyl ether groups capable of giving rise to π-π interactions with the electron-deficient fullerene sphere. Effectively, we found that the interior cavity of our dendrimers is able to bind [60]fullerene in toluene solvent. We also show that this fullerene-dendrimer interaction can be useful for modulating the binding properties of a dendrophane with a fullerene macrocyclic receptor as the central core.

Results and discussion

Dendrimers with a phloroglucinol core

The benzyl ether dendrimers with a phloroglucinol core (**1**–**3**) were synthesised as shown in Scheme 1. The dendrons **G1**–**3Br** were prepared by a convergent approach[15] as previously described by Jin and Aida.[16] Treatment of phloroglucinol with **G1**–**3Br** in refluxing acetone in the presence of K_2CO_3 and 18-crown-6 afforded compounds **1**–**3** in 60–70% yields. Dendrimers **1**–**3** were identified by ^{1}H-NMR and mass spectral evidence† and elemental analyses.

† TOF-MS (dithranol, $NaClO_4$): **1**, *m/z* 1450 $[M + Na]^+$; **2**, *m/z* 3053 $[M + Na]^+$; **3**, *m/z* 6354 $[M + Na]^+$.



Scheme 1

The formation of complexes between [60]fullerene and **1**–**3** in toluene solution was followed by the continuous changes observed in the UV/Vis spectra upon successive additions of dendrimers to solutions of fullerene (Fig. 1).

Each new addition of **1**, **2** or **3** to the [60]fullerene solution led to an increase in absorption, the most pronounced effect being observed at *ca.* 440 nm. These spectral changes are not attributable to the added dendrimer, which does not absorb in this spectral region. Indeed, they are an indication of fullerene complexation, as previously reported in the literature for supramolecular adducts containing [60]fullerene.[17–20] It is noteworthy that these changes in absorption were more and

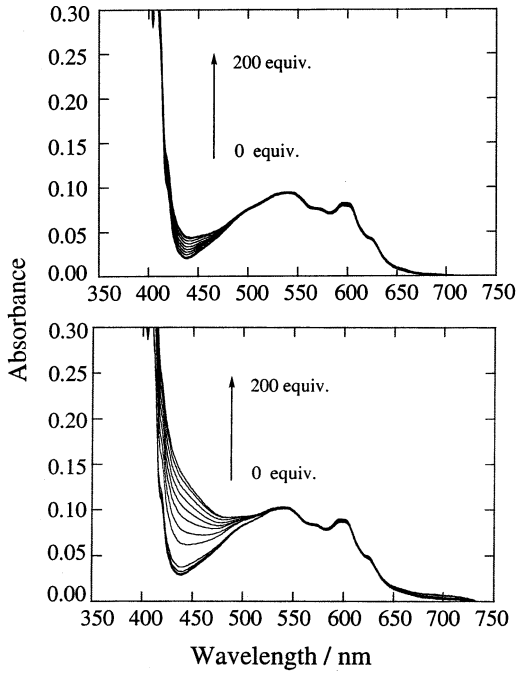


Fig. 1 Changes in the absorption spectra of a [60]fullerene toluene solution containing increasing amount of **1** (top) and **3** (bottom) at 298 K.

more pronounced upon increasing the generation number of the dendrimer. Furthermore, in the case of the highest generation dendrimer **3**, a plot of A_{440} *vs.* [**3**] showed a clear saturation dependence (Fig. 2). Assuming a 1 : 1 stoichiometry, the association constants (K_a) for the binding of [60]fullerene to **1**–**3** were determined by standard UV/Vis titrations in toluene at 298 K. The K_a values for **1**, **2** and **3** were estimated to be 5 ± 2, 12 ± 1 and 68 ± 4 L mol^{-1}, respectively.

The increase of the K_a values in parallel with the generation number of the dendrimers could be attributed to the increasing number of aromatic units, thus allowing a higher number of π-π interactions with the fullerene sphere. However, we also believe that along the series the interior space of the dendrimers tends to approach the appropriate size for the inclusion of [60]fullerene. Therefore, we assume that the internal cavity within the dendrimers becomes more suitably defined as the dendrimer becomes larger. In order to gain further insight, it was decided to follow the changes in the absorption spectra of [60]fullerene upon successive addition of tri-*O*-methylphloroglucinol, which was used as the central core for dendrimers **1**–**3**. As shown in Fig. 3, spectral changes were barely observed. These findings indicate that very weak interactions (if any) occur between tri-*O*-methylphloroglucinol and [60]fullerene. The clear difference in behaviour between tri-*O*-

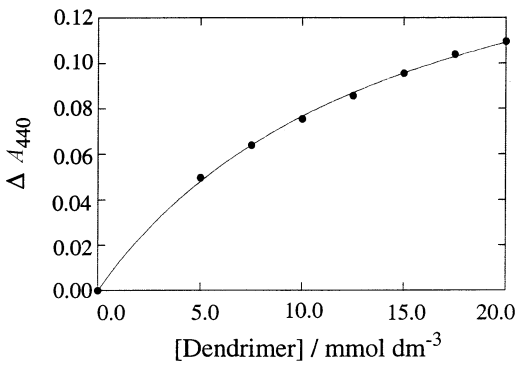


Fig. 2 Plot of the absorption changes at 440 nm observed upon successive addition of **3** to a [60]fullerene toluene solution at 298 K *vs.* the concentration of **3**.

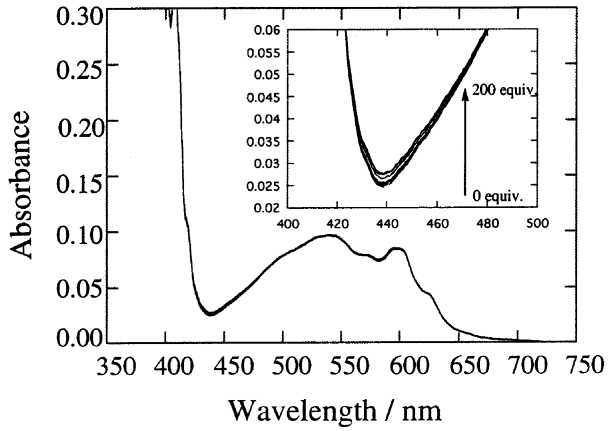


Fig. 3 Changes in the absorption spectra of a [60]fullerene toluene solution containing increasing amounts of tri-*O*-methylphloroglucinol at 298 K.

methylphloroglucinol and **1**–**3** obviously implies that the observed spectral changes could not be simply rationalised by the formation of π-π interactions between [60]fullerene and the phloroglucinol core. In other words, the dendritic structure appears to be indispensable for the formation of a complex with [60]fullerene.

In order to provide more definitive evidence, ^{13}C-NMR studies have also been carried out. The results are summarised in Fig. 4 and Table 1. In toluene-d_8 at 25 °C, the ^{13}C-enriched (10–15%) [60]fullerene peak appeared at 143.200 ppm, which shifted to 143.197 ppm in the presence of an equimolar amount of **3** (2.0 mmol dm^{-3}). Whereas the change in chemical shift was not very informative at 25 °C, it became significant at −60 °C when the exchange became slower (from 143.232 to 142.942 ppm in the presence of **3**). A similar chemical shift change was also observed for **1** and **2**: at −60 °C: 142.958 ppm in the presence of **1** and 142.946 ppm in the presence of **2** (Table 1). As shown in Fig. 4, the peaks in **3** were also shifted in the presence of C_{60} but the largest shift was observed for the phloroglucinol carbons. These results suggest that the [60]fullerene guest mainly resides in the space around the phloroglucinol moiety. A similar trend in the chemical shift change was also observed for the complexation with **1** and **2** (Fig. 4), but the magnitude was smaller than that observed for **3**. These important observations are in full agreement with our hypothesis that the interior region of the branching shell located close to the central core of the polyaryl ether dendrimers, is capable of providing the cavity size necessary for the inclusion of [60]fullerene.

Dendrimers with a *meso*-tetraphenylporphyrin (TPP) core

To obtain further evidence for the binding of [60]fullerene into the branching shell close to the central core, investigations were also carried out with dendrimers **4**–**6** containing a TPP core. It has been effectively shown that the interaction of [60]fullerene with porphyrins substantially reduces the

Table 1 Chemical shift changes of [60]fullerene in the presence of dendrimers **1**–**3** at 25 and −60 °C (150 MHz, toluene-d_8), [**1**–**3**] = [C_{60}] = 2.0 mmol dm^{-3}

	1	**2**	**3**
$T = 25$ °C			
δ_{free}	143.200	143.200	143.200
$\delta_{complex}$	143.200	143.200	143.197
$\Delta\delta$ ($=\delta_{complex} - \delta_{free}$)	0.000	0.000	−0.003
$T = -60$ °C			
δ_{free}	143.232	143.232	143.232
$\delta_{complex}$	142.958	142.946	142.942
$\Delta\delta$ ($=\delta_{complex} - \delta_{free}$)	−0.274	−0.286	−0.290

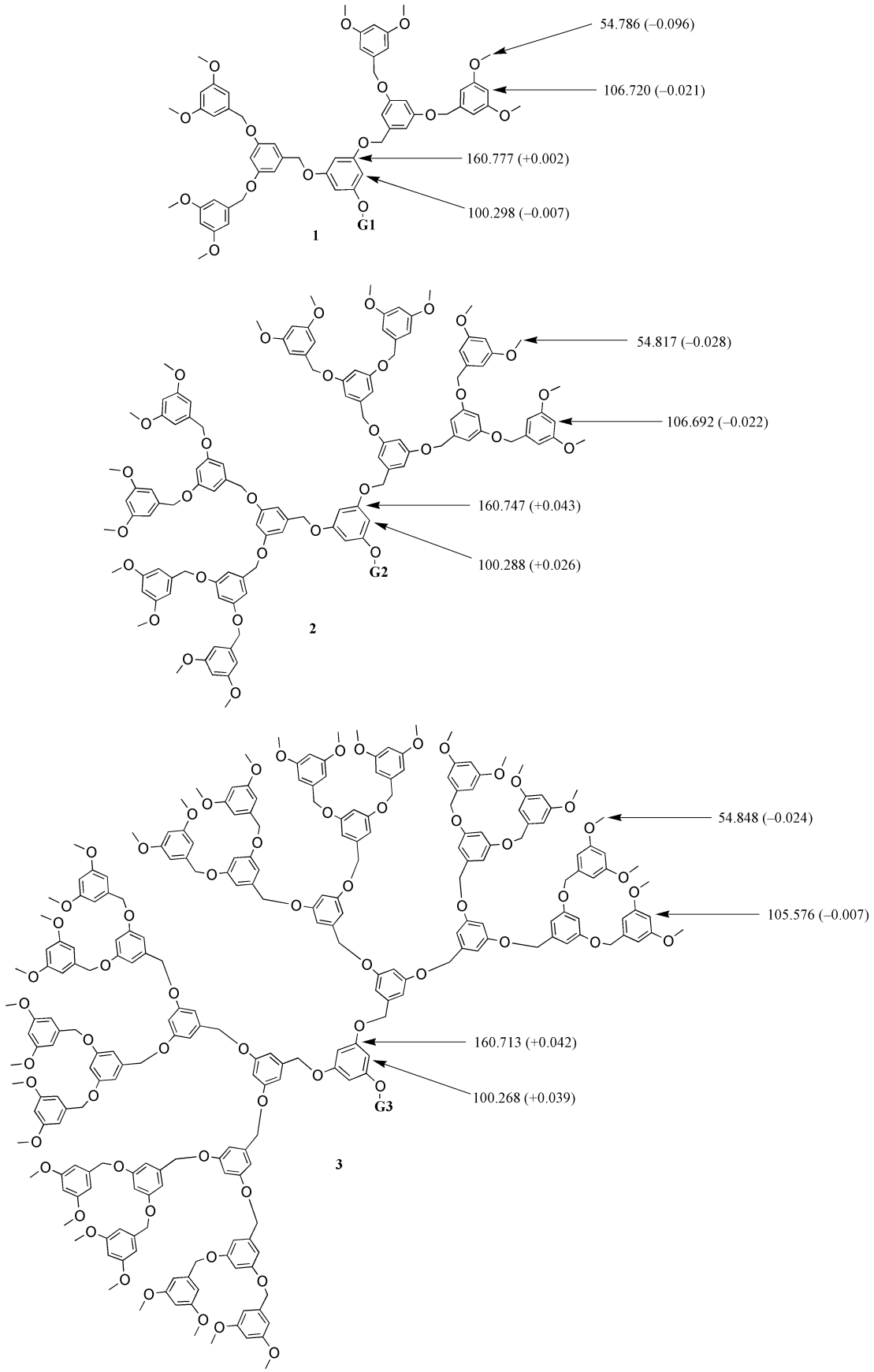
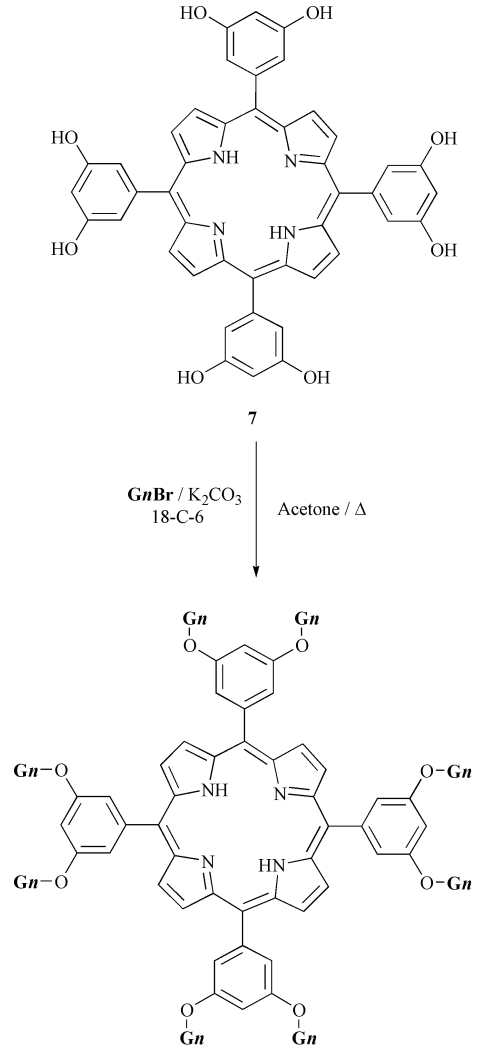


Fig. 4 Chemical shifts (ppm) of carbon peaks in dendrimers **1**–**3** in the presence of [60]fullerene (150 MHz, toluene-d_8, 25 °C, [**1**–**3**] = [C_{60}] = 2.0 mmol dm^{-3}); the numbers in parentheses denote the shift from uncomplexed dendrimer (+ to lower magnetic field, − to higher magnetic field).

absorbance of the Soret band.[21] Compounds **4**–**6** were prepared from **G1**–**3Br** and porphyrin **7** according to the procedure described by Jin and Aida (Scheme 2).[16] The UV/Vis spectra of **4**, **5** and **6** were recorded in toluene solution in the presence and absence of [60]fullerene. Interestingly, the absorbance of the Soret band (λ_{max} 424.0 nm in toluene at 25 °C) in **4**, **5** and **6** was significantly decreased in the presence of [60]fullerene as shown in Fig. 5 for dendrimer **6**. In the



Scheme 2

presence of [60]fullerene (10 equiv.), the absorbance at 424 nm was 90% relative to a solution of pure **6**. Under the same conditions, the absorbance of the Soret band in **4** and **5** was decreased to 94% and 89%, respectively. The interaction between **7** and [60]fullerene could not be estimated in toluene because of the poor solubility of **7**. Judging from the preceding examples, however, the "intermolecular" interaction should be negligible or very weak (if any). One may thus consider that the affinity observed for **5** and **6** originates from the dendritic branches. The larger affinity of **5** and **6** compared to juvenile **4** also supports this view. All these findings suggest that (*i*) the dendritic branches are necessary to give complexation and (*ii*) the [60]fullerene is in close vicinity to the TPP moiety.

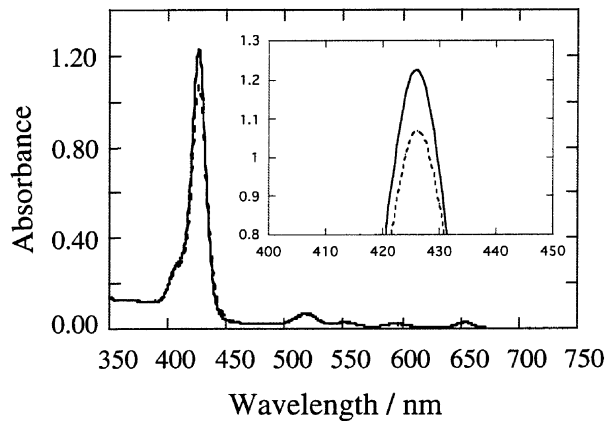


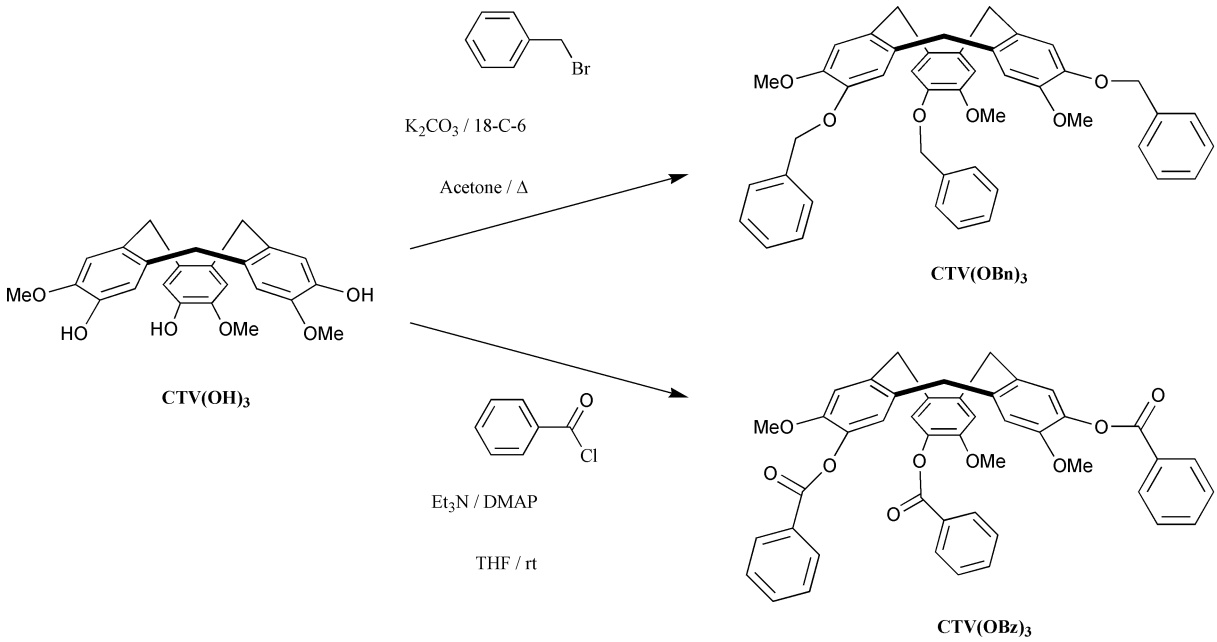
Fig. 5 Absorption spectra of dendrimer **6** ([**6**] = 0.025 mmol dm^{-3}) in the absence (full line) and in the presence of [60]fullerene (10 equiv., dotted line) in toluene at 298 K.

Dendrimers with a cyclotriveratrylene (CTV) core

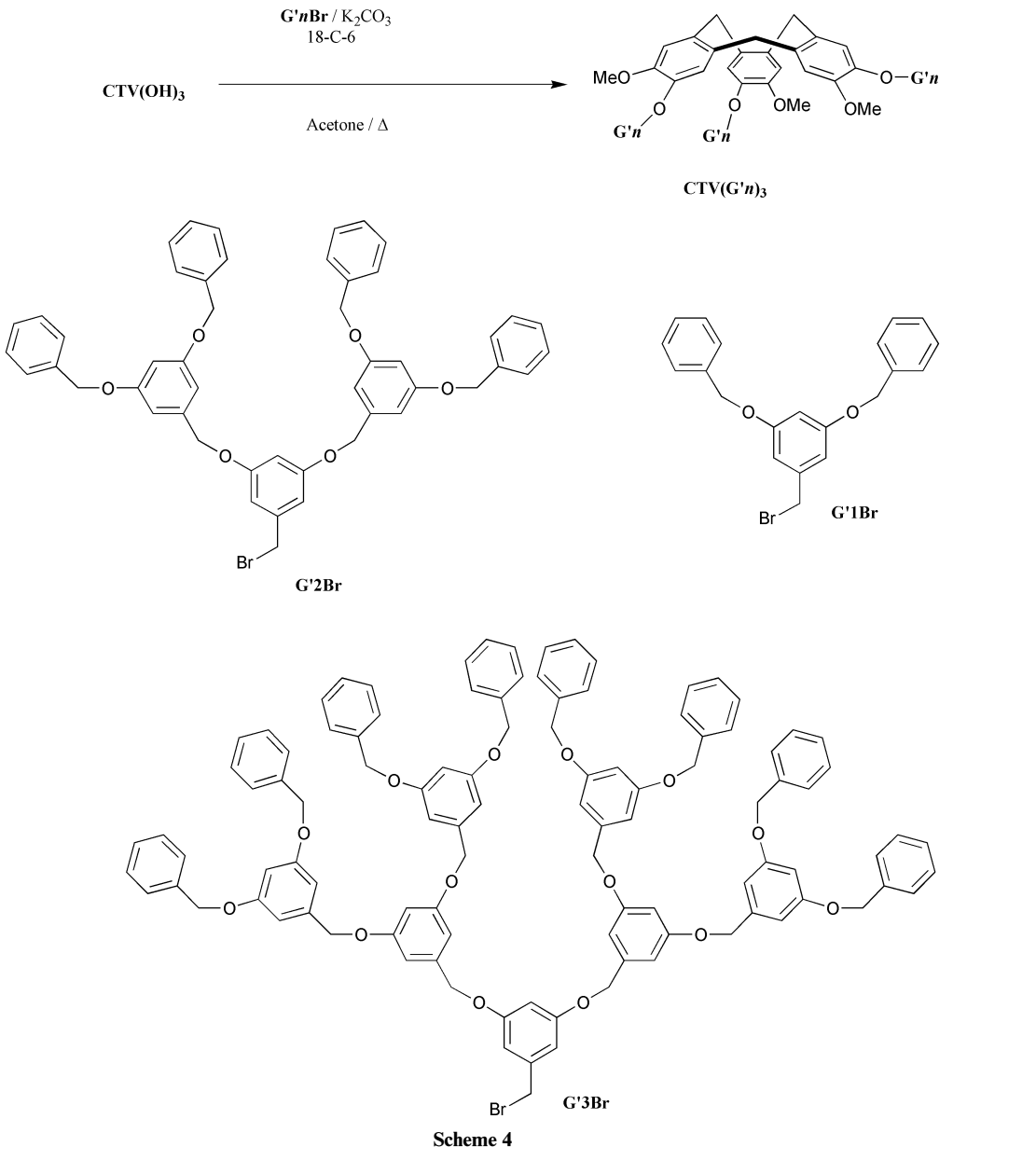
Growing attention is currently being devoted to the study of supramolecular complexes of fullerenes with a variety of macrocyclic host systems[13] including calixarenes,[17] cyclotriveratrylene (CTV)[18,19] and γ-cyclodextrin.[20] As a part of this research, we became interested in the utilisation of derivatives **CTV(OBn)$_3$** and **CTV(OBz)$_3$** for the inclusion of C_{60} in organic solvents. The preparation of the CTV derivatives is depicted in Scheme 3. Precursor **CTV(OH)$_3$** was obtained in three steps from commercially available vanillyl alcohol according to the procedure reported by Collet and co-workers.[22] Treatment of **CTV(OH)$_3$** with benzyl bromide in the presence of K_2CO_3 and 18-crown-6 in refluxing acetone afforded **CTV(OBn)$_3$** in 77% yield. The CTV derivative bearing the three benzoyl groups **CTV(OBz)$_3$** was obtained from **CTV(OH)$_3$** and benzoyl chloride according to the procedure described by Matsubara and co-workers.[19]

The formation of host-guest complexes in C_6H_6 solutions between [60]fullerene and **CTV(OBz)$_3$** was evidenced by the continuous changes of the UV/Vis spectra upon successive additions of the host to the fullerene solutions. As previously shown by Matsubara and co-workers,[19] a Job's plot[23] provided evidence for 1 : 1 complex formation in benzene solution. However, the association constant for the binding of [60]fullerene to **CTV(OBz)$_3$** in C_6H_6 at 298 K, determined with the Benesi–Hildebrand equation,[24,25] was found to be much lower (90 ± 15 dm^3 mol^{-1}) than that reported[19] by Matsubara and co-workers (9000 ± 130 dm^3 mol^{-1}). The result obtained *via* the Benesi–Hildebrand treatment was confirmed using non-linear regression analysis curve-fitting software developed in the laboratory of Diederich.[26] Furthermore, the colour change from violet to light yellow, described by Matsubara and co-workers[19] upon the addition of **CTV(OBz)$_3$** to C_{60} solutions, was never observed. When a large excess of this CTV derivative was added, we obtained precipitation of a brown solid. We believe that the following two points should be highlighted: (*i*) Matsubara and co-workers used the Benesi–Hildebrand equation although the condition [guest] ≫ [host] was not maintained and (*ii*) under their conditions, the solution became partly turbid, which eventually increased the absorbance and apparently resulted in a too large K_a value. The K_a value for the binding of [60]fullerene to **CTV(OBn)$_3$** could not be determined in C_6H_6 due to the poor solubility of the host in benzene, but was determined in CH_2Cl_2 and found to be 85 ± 15 dm^3 mol^{-1}.

Even if the shape and the dimension of the CTV macrocycle appears well predetermined for the complexation of the [60]fullerene sphere, the binding constants found in organic solvents for [60]fullerene with both **CTV(OBn)$_3$** and **CTV(OBz)$_3$** are very low. This could be due to the fact that only a small part of the [60]fullerene surface is actually in contact with the cavity of the macrocyclic CTV receptor. Based on the results obtained with dendrimers **1**–**6**, CTV derivatives bearing polybenzyl ether dendrons should provide an internal cavity capable of interacting with the main part of the fullerene's surface. Therefore, one can expect that the surrounding dendritic branches will be able to increase the inclusion abilities of the CTV central core for fullerenes. The preparation of the dendritic CTV derivatives is shown in Scheme 4. The dendrons **G′1**–**3Br** were prepared as previously described by Hawker and Fréchet.[15] Treatment of **CTV(OH)$_3$** with **G′1**–**3Br** in the presence of K_2CO_3 and 18-crown-6 in refluxing acetone afforded **CTV(G′1–3)$_3$** in 68 to 75% yield.



Scheme 3



Scheme 4

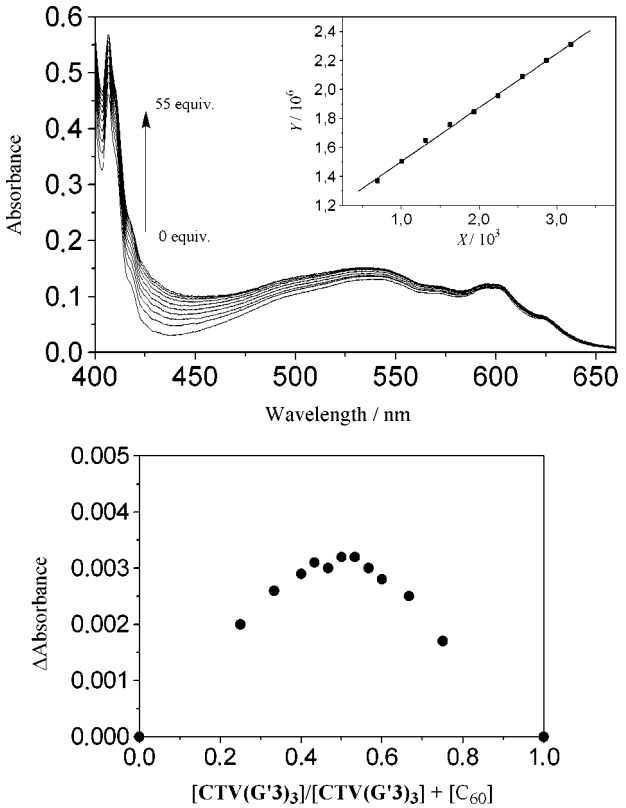


Fig. 6 Top: changes in the absorption spectra of a [60]fullerene benzene solution containing increasing amounts of **CTV(G′3)$_3$** at 298 K; the inset shows the Benesi–Hildebrand plot for determining the association constant between **CTV(G′3)$_3$** and C_{60} *via* UV/Vis titration $\{X = [\mathbf{CTV(G'_3)_3}] + [C_{60}]$; $Y = ([\mathbf{CTV(G'_3)_3}] \cdot [C_{60}])/\Delta A_{430}\}$. Bottom: continuous variation plot obtained with **CTV(G′3)$_3$** in C_6H_6.

Table 2 Association constants (dm^3 mol^{-1}) from UV/Vis binding titrations for 1 : 1 complexes of [60]fullerene with **CTV(G′1–3)$_3$** in CH_2Cl_2 and C_6H_6 at 298 K[a]

	CH_2Cl_2	C_6H_6
CTV(G′1)$_3$	120 ± 20	115 ± 15
CTV(G′2)$_3$	200 ± 10	190 ± 20
CTV(G′3)$_3$	340 ± 20	345 ± 20

[a] The association constants have been determined by monitoring the variations in absorbance at different wavelengths in the 430–440 nm region where the strongest spectral changes are observed. Identical results within the error range in triplicate runs were obtained, and average values are reported.

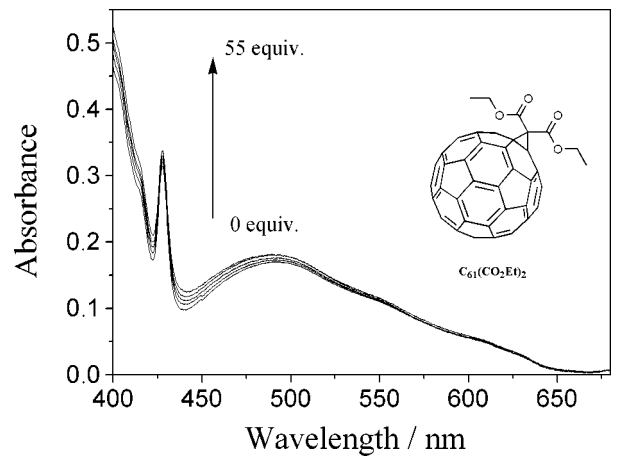


Fig. 7 Changes in the absorption spectra of a $C_{61}(CO_2Et)_2$ benzene solution containing increasing amount of **CTV(G′3)$_3$** at 298 K.

Table 3 Association constants (dm^3 mol^{-1}) from UV/Vis binding titrations for 1 : 1 complexes of $C_{61}(CO_2Et)_2$ to **CTV(OBn)$_3$** and **CTV(G′1–3)$_3$** in CH_2Cl_2 and C_6H_6 at 298 K[a]

	CH_2Cl_2	C_6H_6
CTV(OBn)$_3$	90 ± 30	N.D.[b]
CTV(G′1)$_3$	130 ± 20	110 ± 30
CTV(G′2)$_3$	190 ± 20	180 ± 20
CTV(G′3)$_3$	300 ± 30	290 ± 30

[a] The association constants have been determined by monitoring the variations in absorbance at different wavelengths in the 430–440 nm region where the strongest spectral changes are observed. Identical results within the error range in triplicate runs were obtained, and average values are reported. [b] Not determined due to the poor solubility of **CTV(OBn)$_3$** in C_6H_6.

All of the ^{1}H- and ^{13}C-NMR data were consistent with the proposed molecular structures and elemental analysis also gave satisfactory results.

As already described for dendrimers **1**–**3**, the formation of host-guest complexes between [60]fullerene and **CTV(G′1–3)$_3$** was shown by the continuous changes observed in the UV/Vis spectra upon successive additions of the host to [60]fullerene solutions. This is illustrated in Fig. 6 for **CTV(G′3)$_3$**. The association constants for the binding of [60]fullerene to **CTV(G′1–3)$_3$** were determined by standard UV/Vis titrations in C_6H_6 and CH_2Cl_2 at 298 K (Fig. 6). Treatment of the titration data with the Benesi–Hildebrand equation[24,25] gave the association constants values reported in Table 2. The results obtained through the Benesi–Hildebrand equation were all confirmed by the use of non-linear regression analysis curve-fitting software[26] with the binding isotherms also providing a good fit for a 1 : 1 stoichiometry. For all the dendritic CTV derivatives, Job's plots[23] provided good evidence for 1 : 1 complex formation in solution. The continuous variation plot obtained with **CTV(G′3)$_3$** in C_6H_6 at 298 K (where $[\mathbf{CTV(G'3)_3}] + [C_{60}] = 0.10$ mmol dm^{-3}) is shown in Fig. 6; the maximum at 0.5 indicates 1 : 1 complex formation at these low concentration levels.

The formation of host-guest complexes in CH_2Cl_2 or C_6H_6 solutions between methanofullerene $C_{61}(CO_2Et)_2$ and the dendritic CTV derivatives was also investigated. An example of the continuous changes observed in the UV/Vis spectra by successive additions of a CTV dendrimer is shown in Fig. 7. The association constant values, determined by standard UV/Vis titrations, are summarised in Table 3.

Interestingly, in both solvents (CH_2Cl_2 and C_6H_6) and for both substrates (C_{60} and $C_{61}(CO_2Et)_2$), the K_a values significantly increase as the generation number of the dendritic substituents of the CTV core increases. Therefore, the surrounding dendritic branches appear to be able to increase the inclusion ability of the CTV central core for fullerenes. This effect could be attributed to additional electronic donor-acceptor π-π interactions between the polyaryl ether dendrons and the fullerene guest. However, we also believe that the additional phenyl subunits are not the sole explanation for the observed effect; the dendritic structure itself must play an important role for the binding of [60]fullerene as shown with **1**–**6**. The CTV core itself is a poor receptor for the complexation of fullerenes in solution and its functionalisation with polybenzyl ether dendrons is able to generate an internal cavity with more appropriate shape and dimensions for interactions with the fullerene guest. This effect is more pronounced as the size of the dendritic substituents is increased. As a result, the K_a values increase when the surrounding dendrons become larger.

Conclusion

In this study, we have shown that the branching shell of polybenzyl ether dendrimers provides the correctly sized site for

the inclusion of [60]fullerene in dendrimers containing phloroglucinol, *meso*-tetraphenylporphyrin (TPP), and cyclotriveratrylene (CTV) as central cores. ^{13}C-NMR (for phloroglucinol) and UV/Vis (for TPP) studies suggest that the [60]fullerene guest mainly resides in the space region around the central core. Dendrophanes with a CTV core have been investigated and, although CTV alone is a poor receptor for the complexation of fullerenes in solution, its functionalisation with polybenzyl ether dendrons is capable of generating an internal cavity with more appropriate shape and dimensions for interactions with the carbon sphere. In fact, the K_a values increased significantly as the generation number of the surrounding dendritic substituents increased. Therefore, we have shown that the functionalisation of a macrocyclic receptor with dendritic branches is not only able to isolate a central functional core, thus mimicking natural globular proteins, but can also modulate the binding properties of the core by means of the size and the nature of the surrounding dendrons.

The host-guest association constants that we found (10^1–10^2 L mol^{-1}) are still rather low, in line with other recent reports.[17–19] Indeed, further research efforts aimed at the preparation of more efficient and water-soluble hosts for [60]fullerene can be expected shortly, owing to the interesting perspectives for practical applications, especially in the field of medicinal chemistry.[27]

Experimental

General methods

Reagents and solvents were purchased as reagent grade and used without further purification. Acetone was dried with anhydrous sodium sulfate. Toluene and benzene were refluxed over sodium under N_2 and distilled just before use. CH_2Cl_2 was distilled over CaH_2. Compounds **G*n*Br**,[16] **G′*n*Br**,[15] **4**–**7**,[16] **CTV(OH)$_3$**,[22] and **CTV(OBz)$_3$**[19] were prepared according to literature procedures. All reactions were performed in standard glassware under an inert Ar or N_2 atmosphere. Evaporation and concentration were done at water aspirator pressure and drying *in vacuo* at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. Thin layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualisation by UV light. Melting points were measured on an Electrothermal Digital Melting Point apparatus and are uncorrected. UV/Vis spectra were measured on a Hitachi U-3000 spectrophotometer or on a Shimadzu UV-2500PC using a quartz cell of 1 cm or 0.1 cm path length. IR spectra were recorded on a Shimadzu FT-IR-8700. NMR spectra were recorded on a Bruker AC 200 (200 MHz) or on a Bruker DRX-600 (600 MHz) with solvent peaks as internal reference, chemical shifts were referenced to tetramethylsilane (0.00 ppm).

General procedure for the synthesis of dendritic deivatives 1–3

A mixture of the appropriate dendritic benzyl bromide (3 equiv.), phloroglucinol (1 equiv.), potassium carbonate (30 equiv.) and *cis*-dicyclohexano-18-crown-6 (0.6 equiv.) in dry acetone was heated at reflux and stirred vigorously under nitrogen for 24 to 72 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and $CHCl_3$ and the aqueous layer extracted with $CHCl_3$ (3 ×). The combined organic layers were then dried (Na_2SO_4) and evaporated to dryness. The crude product was purified as outlined in the following text.

1. This was prepared from **G1Br** and purified by column chromatography (SiO_2, $CHCl_3$) to give **1** as a colourless glassy product: yield 60%; FT-IR (KBr, cm^{-1}): 2934, 1597, 1202, 1155; ^{1}H-NMR ($CDCl_3$, 250 MHz): δ 3.77 (s, 36H), 4.92 (s, 6H), 4.95 (s, 12H), 6.23 (s, 3H), 6.40 (br, 6H), 6.56 (br, 15H), 6.66 (br, 6H); MALDI-TOF-MS: 1418 $[M + Na]^+$; Anal. calcd. for $C_{81}H_{84}O_{21}$: C, 69.81, H 6.08, O 24.11; found: C 69.65, H 6.24, O 24.11.

2. It was prepared from **G2Br** and purified by column chromatography (SiO_2, $CHCl_3$) to give **2** as a colourless glassy product: yield 60%; FT-IR (KBr, cm^{-1}): 2934, 1595, 1205, 1152; ^{1}H-NMR ($CDCl_3$, 600 MHz) δ 3.74 (s, 72H), 4.93 (s, 42H), 6.23 (s, 3H), 6.38 (br, 12H), 6.54 (br, 33H), 6.65 (br, 18H); MALDI-TOF-MS: 3053 $[M + Na]^+$; Anal. calcd. for $C_{177}H_{180}O_{45} \cdot 0.5\ CHCl_3$: C 69.06, H 5.89, O 23.32; found: C 69.44, H 6.01, O 24.55.

3. It was prepared from **G3Br** and purified by column chromatography (SiO_2, $CHCl_3$) to give **3** as a colourless glassy product: yield 70%; FT-IR (KBr, cm^{-1}) 2934, 1597, 1205, 1151; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 3.71 (s, 144H), 4.88 (br, 90H), 6.21 (s, 3H), 6.35 (br, 24H), 6.51 (br, 81H), 6.62 (br, 18H); MALDI-TOF-MS: 6325 $[M + Na]^+$; Anal. calcd. for $C_{369}H_{378}O_{93} \cdot 0.5\ CHCl_3$: C 69.83, H 6.09, O 24.08. found: C 69.77, H 6.00, O 23.39.

General procedure for the synthesis of the CTV derivatives

A mixture of the appropriate dendritic benzyl bromide (3 equiv.), **CTV(OH)$_3$** (1 equiv.), potassium carbonate (4 equiv.) and 18-crown-6 (0.3 equiv.) in dry acetone was heated at reflux and stirred vigorously under Ar for 48 h. The mixture was allowed to cool and evaporated to dryness under reduced pressure. The residue was partitioned between water and CH_2Cl_2 and the aqueous layer extracted with CH_2Cl_2 (2 ×). The combined organic layers were then dried ($MgSO_4$) and evaporated to dryness. The crude product was purified as outlined in the following text.

CTV(OBn)$_3$. It was prepared from benzyl bromide and purified by column chromatography (SiO_2, CH_2Cl_2) to give **CTV(OBn)$_3$** as a white crystalline solid: yield 77%; mp 149 °C; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.45 (d, *J* 14, 3H), 3.71 (s, 9H), 4.70 (d, *J* 14, 3H), 5.13 (AB, *J* 13.5, 6H), 6.67 (s, 3H), 6.84 (s, 3H), 7.28–7.44 (m, 15H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 36.49, 56.23, 71.51, 113.67, 115.91, 126.95, 127.82, 128.61, 131.67, 132.52, 137.57, 147.12, 148.37; Anal. calcd. for $C_{45}H_{42}O_6$: C 79.62, H 6.24; found: C 79.60, H 6.27.

CTV(G′1)$_3$. It was prepared from **G′1Br** and purified by column chromatography (SiO_2, CH_2Cl_2–hexane 9 : 1) to give **CTV(G′1)$_3$** as a colourless glassy product: yield 72%; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.45 (d, $J = 14$, 3H), 3.67 (s, 9H), 4.69 (d, $J = 14$, 3H), 4.99 (s, 12H), 5.05 (AB, $J = 13$, 6H), 6.54 (t, $J = 2$, 3H), 6.63 (s, 3H), 6.67 (d, $J = 2$, 6H), 6.81 (s, 3H), 7.24–7.40 (m, 30H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 36.41, 56.01, 69.98, 71.45, 101.29, 105.47, 113.39, 115.81, 127.49, 127.94, 128.49, 131.51, 132.49, 136.62, 140.17, 146.94, 148.23, 160.11; Anal. calcd. for $C_{87}H_{78}O_{12}$: C 79.43, H 5.98; found: C 79.33, H 6.04.

CTV(G′2)$_3$. It was prepared from **G′2Br** and purified by column chromatography (SiO_2, CH_2Cl_2–hexane 9 : 1) to give **CTV(G′2)$_3$** as a colourless glassy product: yield 68%; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.41 (d, $J = 14$, 3H), 3.70 (s, 9H), 4.61 (d, $J = 14$, 3H), 4.92 (s, 12H), 4.98 (s, 30H), 6.50 (t, $J = 2$, 3H), 6.55 (t, $J = 2$, 6H), 6.65 (m, 21H), 6.82 (s, 3H), 7.28–7.40 (m, 60H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 36.38, 56.06, 69.86, 69.97, 71.65, 101.28, 101.45, 105.74, 106.30, 113.54, 118.16, 127.49, 127.91, 128.49, 131.59, 132.60, 136.66, 139.08, 140.17, 146.99, 148.33, 160.00, 160.04; Anal. calcd. for $C_{171}H_{150}O_{24}$: C 79.33, H 5.84; found: C 79.17, H 5.80.

CTV(G′3)$_3$. It was prepared from **G′3Br** and purified by column chromatography (SiO_2, CH_2Cl_2–hexane 9 : 1) to give **CTV(G′3)$_3$** as a colourless glassy product: yield 75%; ^{1}H-NMR ($CDCl_3$, 200 MHz) δ 3.36 (d, $J = 14$, 3H), 3.66 (s, 9H), 4.55 (d, $J = 14$, 3H), 4.87 (s, 36H), 4.95 (s, 54H), 6.50 (m, 9H), 6.54 (t, $J = 2$, 12H), 6.63 (m, 45H), 6.78 (s, 3H), 7.25–7.40 (m, 120H); ^{13}C-NMR ($CDCl_3$, 50 MHz) δ 36.33, 56.03, 69.82, 69.92, 71.61, 101.43, 105.69, 106.26, 113.54, 116.20, 127.46, 127.88, 128.45, 131.57, 132.60, 136.65, 139.08, 140.19, 146.93, 148.30, 159.92, 160.00; Anal. calcd. for $C_{339}H_{294}O_{48}$: C 79.28, H 5.77; found: C 79.04, H 5.99.

Determination of the association constants

Binding studies were performed in toluene, benzene, or dichloromethane solution at 298 ± 1 K. In a typical experiment, a 1 ml volume of a [60]fullerene solution (typical concentration: 0.1 to 0.2 mM) was placed in the sample cell. An aliquot of a stock solution of the host compound (typical concentration: 10 to 20 mM) was added to the sample cell and, after homogenisation, the absorption spectrum was recorded. Additional aliquots of the host compound were added to the sample cell, and the spectrum was recorded after each addition. The association constants were calculated from the absorption intensity changes observed at 430 or 440 nm, compared to pure C_{60} using the Benesi–Hildebrand equation.[24,25] All experiments were performed in at least triplicate runs.

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