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Complexation of fullerenes with dendritic cyclotriveratrylene derivatives

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Abstract

Dendritic derivatives containing a cyclotriveratrylene core for the complexation of fullerenes have been prepared. The association constants for the binding of fullerene derivatives determined by UV–vis titrations in CH_2Cl_2 and C_6H_6 are significantly increased as the generation number of the dendritic substituents is increased. © 1999 Elsevier Science Ltd. All rights reserved.

Dendrimers have attracted increasing attention in the past decade because of their unique structures and properties.[1–3] Among the development of suitable protocols to synthetise monodispersed cascade molecules, the design of functional dendrimers is emphasized today as the field expands rapidly in many different directions.[2,3] Of particular current interest is the use of such architectures for complexation with guest molecules.[3] Functionalization of the dendritic surface or branches with recognition sites appears to be a possible approach to dendrimers with defined binding properties.[4] On the other hand, the central core of the dendrimer can be a cyclophane with well defined complexation ability and its binding properties can be modulated by the size or the polarity of the surrounding dendrons.[5] Growing attention is currently devoted to the study of supramolecular complexes of fullerenes with a variety of host systems including calixarenes,[6] cyclotriveratrylene[7] (CTV) and γ-cyclodextrin.[8] In this context, we now report the preparation of new CTV derivatives substituted with Fréchet dendrons and show how the size of the surrounding dendritic branches affects the inclusion abilities of the CTV central core for fullerenes in organic solvents.

The preparation of the CTV dendrimers is depicted in Fig. 1. The dendrons G1–3Br were prepared as previously reported by Hawker and Fréchet[9] and $CTV(OH)_3$ was obtained in three steps from vanillyl alcohol according to the procedure described by Collet and coworkers.[10] Treatment of $CTV(OH)_3$ (1 equiv.) with G0–3Br (3 equiv.) in the presence of K_2CO_3 (4 equiv.) and 18-crown-6 (0.3 equiv.) in

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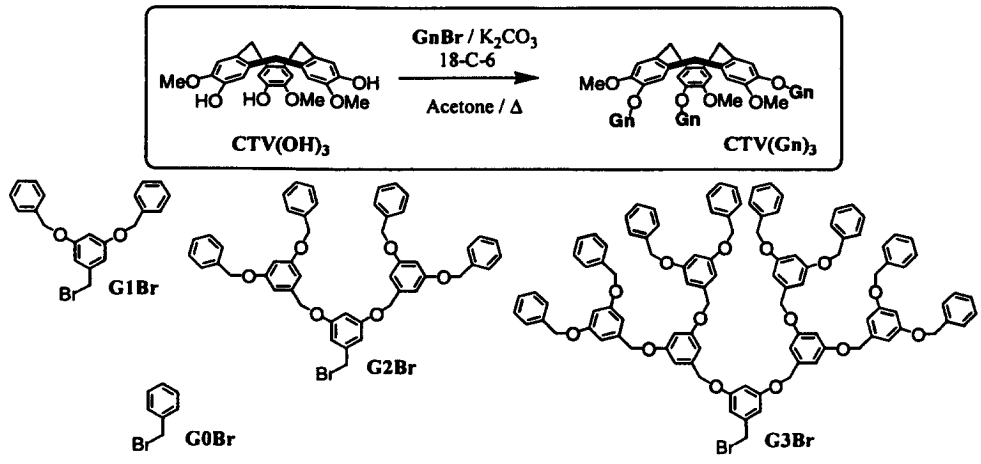

Figure 1. Preparation of the dendritic CTV derivatives

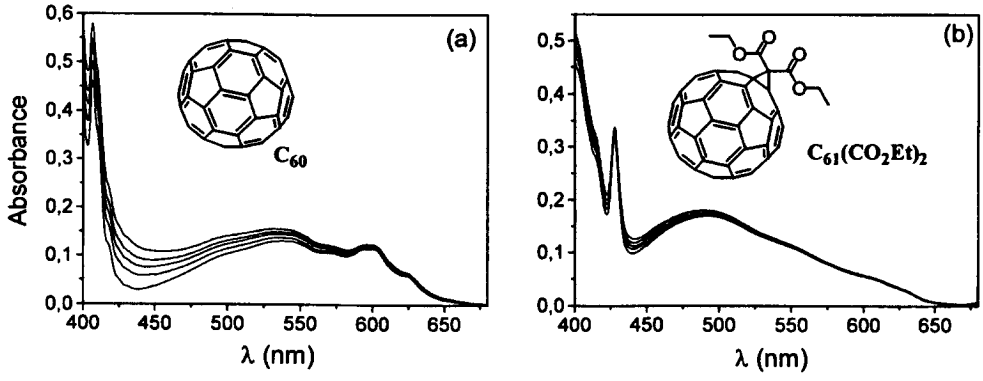

Figure 2. (a) Absorption spectra of C_{60} in the presence of CTV(G3)$_3$ (from the bottom: 0, 8, 16, 24 and 40 equiv.) in C_6H_6 at 298 K. (b) Absorption spectra of $C_{61}(CO_2Et)_2$ in the presence of CTV(G3)$_3$ (from the bottom: 0, 11, 22, 33 and 55 equiv.) in C_6H_6 at 298 K

refluxing acetone under vigorous stirring for 48 hours afforded CTV(G0–3)$_3$ in 68 to 77% yield. All of the spectroscopic studies and elemental analysis results were consistent with the proposed molecular structures.[11]

The formation of host–guest complexes in CH_2Cl_2 or C_6H_6 solutions between C_{60} or $C_{61}(CO_2Et)_2$ and CTV(G0–3)$_3$ was evidenced by the continuous changes observed in the UV–vis spectra by successive additions of the host to the fullerene solutions (Fig. 2). A similar effect is observed for the four CTV derivatives CTV(G0–3)$_3$ in both CH_2Cl_2 and C_6H_6. The observed spectral changes are similar to those previously described by addition of other CTV derivatives to fullerene solutions.[7c]

Job's plot provided evidence for 1:1 complex formation in solution. The association constants (K_a) for the binding of C_{60} and $C_{61}(CO_2Et)_2$ to CTV(G0-3)$_3$ were determined by standard UV–vis titrations[6i] in CH_2Cl_2 and C_6H_6 at 298 K. The results are summarized in Table 1.

The K_a values are similar for both C_{60} and $C_{61}(CO_2Et)_2$ and there is no significant difference in the complexation behavior in CH_2Cl_2 and C_6H_6. The CTV recognition site at the center of the dendrimers remains available and effective for all generations. Noteworthy, no significant changes in the UV–vis spectra could be observed by successive additions of the dendrons G1–3 to fullerene solutions, suggested that the dendritic branches alone are not able to bind the fullerene. Therefore the guest is likely to

Table 1
Association constants K_a ($dm^3\ mol^{-1}$) from UV–vis binding titrations for 1:1 complexes of C_{60} and $C_{61}(CO_2Et)_2$ to CTV(G0-3)$_3$ in CH_2Cl_2 and C_6H_6 at 298 K[a]

	C_{60}		$C_{61}(CO_2Et)_2$	
	CH_2Cl_2	C_6H_6	CH_2Cl_2	C_6H_6
CTV(G0)$_3$	85±20	%[b]	90±30	%[b]
CTV(G1)$_3$	120±20	115±15	130±20	110±30
CTV(G2)$_3$	200±10	190±20	190±20	180±20
CTV(G3)$_3$	340±20	345±20	300±30	290±30

[a] The association constants K_a have been determined by monitoring the variations of absorbance at different wavelengths in the 430-445 nm region where the strongest spectral changes are observed. Identical results within the error range in duplicate and triplicate runs were obtained, and average values are reported. [b]Not determined due to the poor solubility of **CTV(G0)$_3$** in C_6H_6.

be located in the CTV cavity and nonspecific incorporation into the dendritic shell are negligible. Interestingly, in both solvents and for both substrates, the K_a values are significantly increased as the generation number of the dendritic substituents is increased. This effect could be tentatively ascribed to possible additional π–π interactions between the polyaryl ether dendrons and the fullerene guest. The number of aromatic rings increases in parallel with the generation number of the dendrons, therefore more and more π–π interactions become available, and the diffusion of the guest out of the dendrimer is somewhat slowed down when the generation number increases. As a result, the K_a value increases when the surrounding dendrons become larger. Further investigations aiming at understanding the nature of the host–guest interactions are now underway in our laboratories.

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11. Selected spectroscopic data for CTV(G0)$_3$: ^{1}H NMR ($CDCl_3$, 200 MHz): 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). Anal. calcd for $C_{45}H_{42}O_6$: C 79.62, H 6.24; found: C 79.60, H 6.27. For CTV(G1)$_3$: ^{1}H NMR ($CDCl_3$, 200 MHz): 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). Anal. calcd for $C_{87}H_{78}O_{12}$: C 79.43, H 5.98; found: C 79.33, H 6.04. For CTV(G2)$_3$: ^{1}H NMR ($CDCl_3$, 200 MHz): 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). Anal. calcd for $C_{171}H_{150}O_{24}$: C 79.33, H 5.84; found: C 79.17, H 5.80. For CTV(G3)$_3$: ^{1}H NMR ($CDCl_3$, 200 MHz): 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). Anal. calcd for $C_{339}H_{294}O_{48}$: C 79.28, H 5.77; found: C 79.04, H 5.99.