Pergamon

Tetrahedron Letters 40 (1999) 6945–6948

TETRAHEDRON
LETTERS

Dendrimers can act as a host for [60]fullerene

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Received 4 June 1999; revised 7 July 1999; accepted 9 July 1999

Abstract

Fréchet-type dendrimers with a phloroglucinol core or a tetraphenylporphyrin core (Aida's dendrimers) were synthesized. Spectroscopic examination revealed that [60]fullerene is bound to the interior space of these dendrimers. The findings indicate that one can regard the dendrimers as novel host compounds bearing a large interior cavity. © 1999 Elsevier Science Ltd. All rights reserved.

Host·guest chemistry has been a central concern in the field of molecular recognition for the last several decades. A characteristic feature common to hosts is to preserve a 'cavity' within the molecular structure, by which molecular recognition is achieved through the size selectivity process. In this context, it is quite convenient for us to estimate the guest selectivity for such hosts that have the homologous series of cavity size. The host molecules such as cyclodextrins, crown ethers, calix[*n*]arenes, etc., all satisfy this requirement. Meanwhile, the developmental investigation on the novel application of dendrimers has been of recent concern. The dendrimer has a spherical structure featuring a densely-packed exterior and a largely-meshed interior. It thus occurred to us that if the densely-packed exterior can firmly maintain the space in a largely-meshed interior, it may act as a 'cavity' to accept guest molecules. However, since the 'cavity' is considerably large, only moderately large guests would fill the interior space. In fact, Meijer et al.[1] recently found that Rose Bengal is bound to poly(propyleneimine)-type dendrimers, but it is not yet clarified what is the major driving-force for this inclusion. We considered that [60]fullerene might be able to fill this large space, because: (i) a [60]fullerene derivative can act as an efficient inhibitor for HIV-1 protease because it can fill the large hydrophobic space present in the active site; (ii) the large calix[*n*]arene cavities[2] can be filled by [60]fullerene with the aid of the π–π interaction and/or the solvophobic interaction;[3–7] and (iii) judging from the CPK molecular models, Fréchet's dendrimers[8] can provide the space size comparable with [60]fullerene and have a number of resorcinyl ether groups to enjoy the π–π interaction with [60]fullerene. In this communication, we report a novel finding that in toluene solvent dendrimers **1–3** with a phloroglucinol core and **4–6** with a tetraphenylporphyrin core (Aida's dendrimers)[9] can bind [60]fullerene into the interior space.

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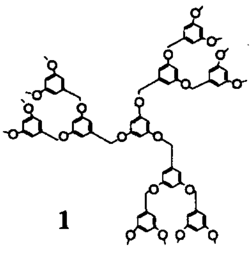
PII: S0040-4039(99)01362-3



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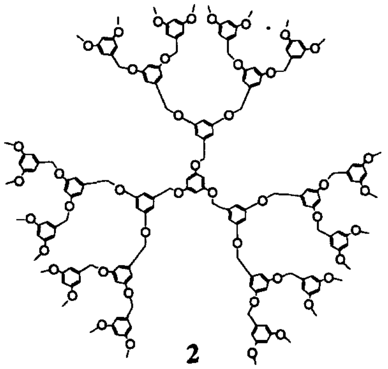

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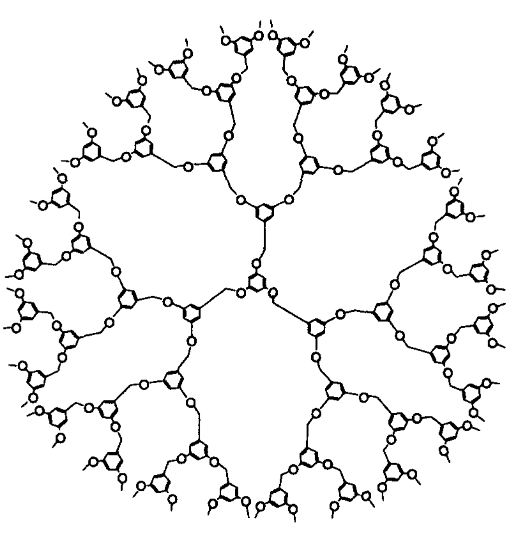

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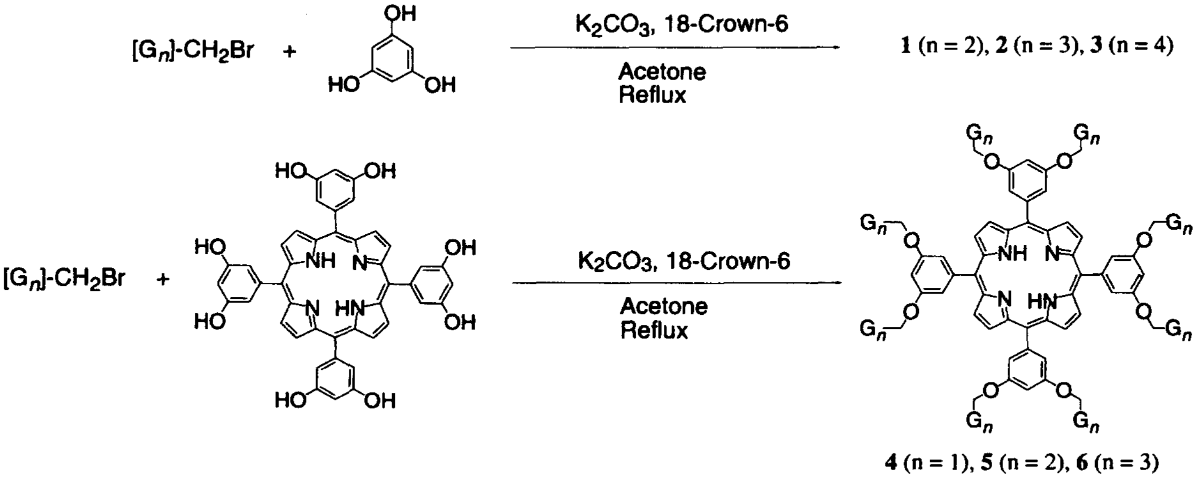
Compounds **1**–**3** were synthesized as shown in Scheme 1. We utilized Fréchet's convergent approach method for the synthesis of dendritic parts.[8] Coupling of 3 equiv. of dendritic parts ([G$_n$]–CH$_2$Br) with phloroglucinol was performed in refluxing acetone in the presence of K_2CO_3 and 18-crown-6 to afford dendrimers **1**–**3** in 60–70% yields. Dendrimers **1**–**3** were identified by ^{1}H NMR and mass [TOF–MS (dithranol, NaClO$_4$): **1**, *m*/*z* 1450 (M+Na$^+$); **2**, *m*/*z* 3053 (M+Na$^+$); **3**, *m*/*z* 6354 (M+Na$^+$)] spectral evidence and elemental analyses. Dendrimers **4**–**6** with a tetraphenyl porphyrin core were synthesized according to the Aida's method.[9]



Scheme 1.

The absorption spectra of [60]fullerene were measured in toluene at 25°C as a function of **3** concentration (Fig. 1(a)). As already seen in inclusion of [60]fullerene into calix[*n*]arenes,[3–7] the absorption band at around 440 nm increased with increasing **3** concentration. As shown in Fig. 1(b), a plot of A_{440} vs. [**3**] showed a saturation dependence. Although it was difficult to estimate the stoichiometry

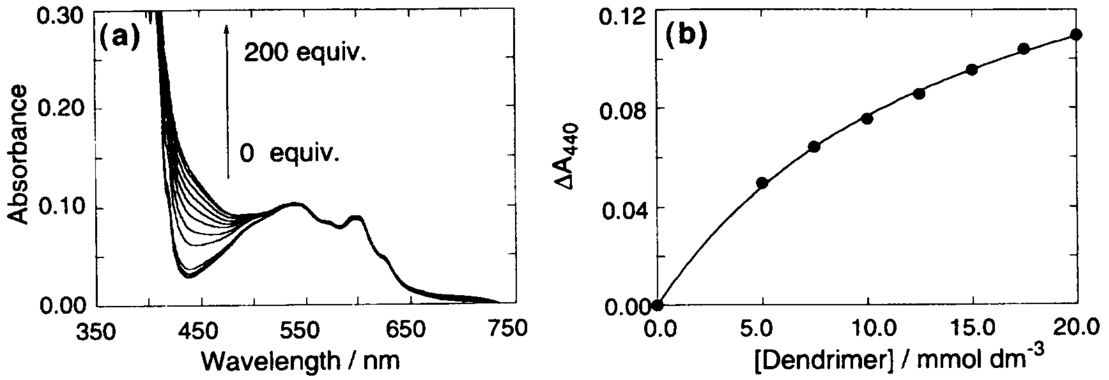


Figure 1. (a) Absorption spectral change of [60]fullerene in the presence of dendrimer **3** in toluene at 25°C; (b) Plots of ΔA_{440} vs. [**3**]

between [60]fullerene and **3** by the conventional methods, the present measurement condition ([[60]fullerene]=0.10 mmol dm^{-3}<[**3**]=0.10~20 mmol dm^{-3}) would allow us to assume the 1:1 stoichiometry for the [60]fullerene·**3** complex. The association constant (K_{ass}) was estimated to be 68±4 dm^3 mol^{-1}.[10] According to the similar spectroscopic method, we estimated the K_{ass} values for **1** and **2** to be 5±2 dm^3 mol^{-1} and 12±1 dm^3 mol^{-1}, respectively. On the other hand, the spectral change was scarcely observed for either tri-*O*-methylphloroglucinol or tri-*O*-benzylphloroglucinol. The difference implies that the dendritic structure is indispensable for inclusion of [60]fullerene.

Where does [60]fullerene reside in **1**–**3** dendrimers? The NMR spectral data would be helpful to answer this question. The ^1H NMR spectra changed significantly by the addition of [60]fullerene, but the shift could not be estimated precisely because of the serious peak overlap. Hence, we utilized ^{13}C NMR spectroscopy. In toluene-d_8 at 25°C, the ^{13}C-enriched (10–15%) [60]fullerene peak appeared at 143.200 ppm: in the presence of an equimolar amount of **3** (2.0 mmol dm^{-3}), the peak did not give a separate one but just shifted to 143.197 ppm. The chemical shift change was further enlarged at −60°C (from 143.232 ppm to 142.942 ppm in the presence of **3**). The 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**. As shown in Fig. 2, other peaks in **3** were also shifted but the largest shift was observed for the phloroglucinol carbons. The result suggests that [60]fullerene resides in the space present around the phloroglucinol moiety. The similar trend in the chemical shift change was also observed for the complexation with **1** and **2**, but the magnitude was smaller than that in **3**.

Unambiguous evidence for the binding of [60]fullerene to the core space was obtained from the absorption spectroscopic measurements using **4**–**6**.[9] It is known that [60]fullerene interacts with free-base porphyrins to reduce the absorbance of the Soret band.[11] The Soret band (λ_{max} 424.0 nm in toluene at 25°C) in **4**, **5**, and **6** (0.025 mmol dm^{-3}) decreased by 94.1%, 89.4%, and 90.2%, respectively, in the presence of [60]fullerene (0.250 mmol dm^{-3}). The finding also supports the view that [60]fullerene is bound to the core space around the tetraphenylporphyrin moiety.

In conclusion, the present study reports for the first time that Fréchet-type dendrimers can act as a host molecule to include [60]fullerene. Since conventional fused aromatics such as pyrene, anthracene, etc., were not included in these dendrimers in the measurable concentration, we believe that this phenomenon is not only due to the simple π–π interaction but also due to the fill-up effect of the core space which eventually stabilize the higher-order dendrimer conformation. In this context, the dendrimer can exert the 'hole-size selectivity' characteristic of general host molecules.

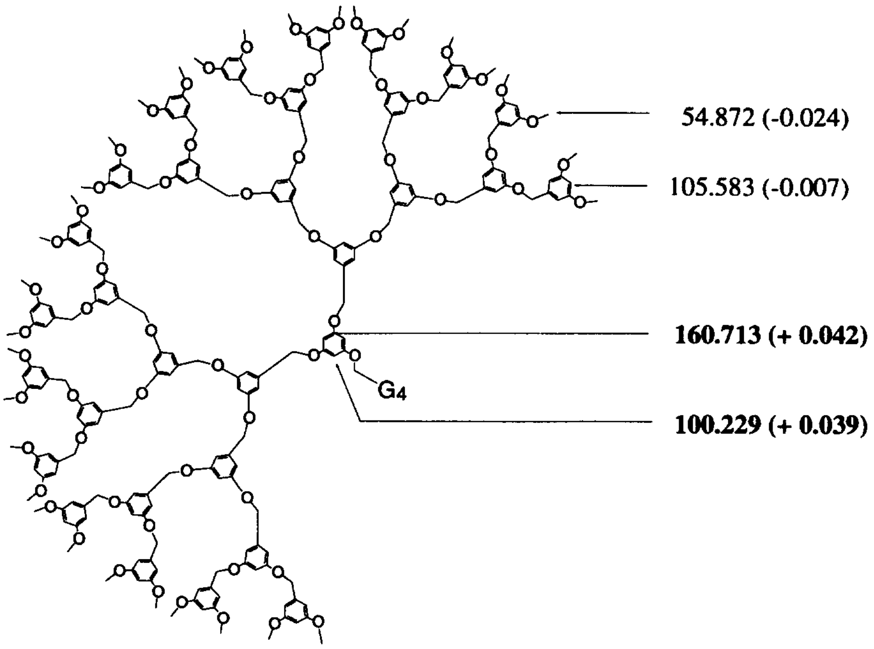


Figure 2. Chemical shift changes of dendrimer **3** in the presence of [60]fullerene. The numbers indicate the chemical shift: 150 MHz, toluene-d_8, 25°C. [**3**]=[60]fullerene=2.0 mmol dm^{-3}. The numbers in parentheses denote the shift from uncomplexed 3 (+ to lower magnetic field, –to higher magnetic field)

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