

An octa-cationic core-shell dendrimer as a molecular template for the assembly of anionic fullerene derivatives

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Abstract—An assembly comprising the non-covalent binding of eight mono-anionic fullerene subunits to a polyaryl ether dendrimer with an octa-cationic tetra[bis(benzylammonium)aryl]silane core has been prepared via a straightforward anion exchange reaction. The assembled octa-fullero-dendrimer has been characterized by NMR and UV–vis spectroscopy and its molecular weight determined by size-exclusion chromatography coupled with low angle light scattering (LALLS) techniques.

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In the past decade, the synthesis of fullerene-functionalized dendrimers, so-called *fullero-dendrimers*, has been actively explored.¹ In particular the application of a mono-disperse, highly branched dendritic shell around a fullerene core offers several interesting advantages such as improved solubility and isolation of the C₆₀ moiety from external contacts.² The latter shielding effect has been found useful for the optimization of the optical limiting properties of C₆₀ derivatives.³ It has also been shown that the encapsulation of a fullerene moiety in the middle of a dendritic structure is an effective strategy to obtain amphiphilic derivatives with good spreading characteristics⁴ or to prepare fullerene-containing liquid crystalline materials.⁵ Furthermore, the highly-branched molecular structure of a dendritic framework allows for the multiplication of fullerene entities at the inner branches or at the periphery.⁶

Fullero-dendrimers bearing multiple C₆₀ units at the surface could be applied as antenna for light-harvesting or as a fullerene-rich material for the preparation of plastic solar cells.¹ The synthesis of these covalent ful-

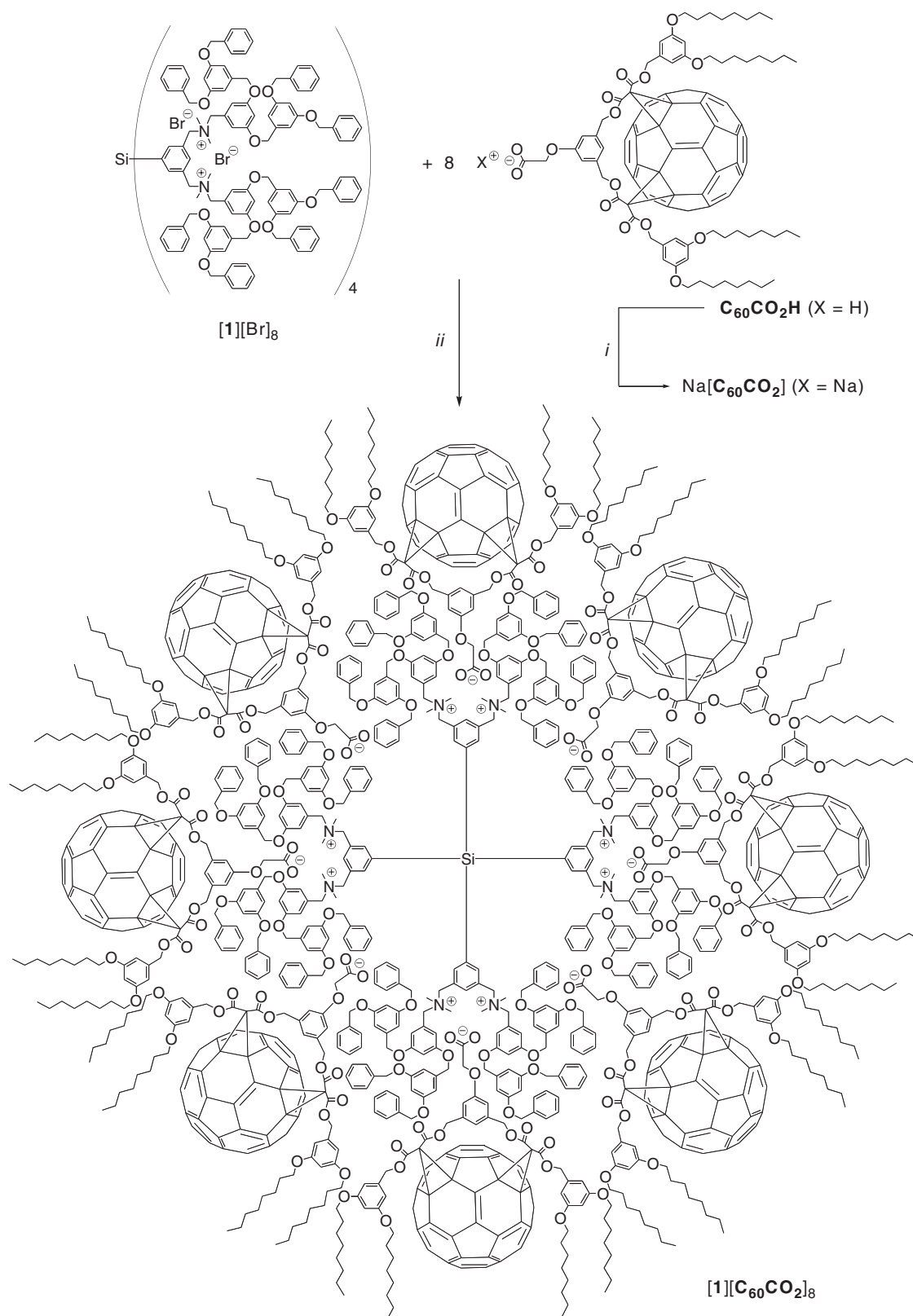
lero-dendrimers remains, however, difficult and often requires a large number of synthetic steps thus limiting both their accessibility and applicability.⁶ In this light, the non-covalent binding of fullerene entities to a dendritic scaffold could be a better alternative to the common covalent synthesis of fullero-dendrimers. Whereas a few examples of dendrimers capable of forming 1:1 host–guest complexes with C₆₀ or fullerene derivatives have already been described,⁷ the simultaneous non-covalent binding of a *multiple* number of fullerene units to a single dendrimer has so far remained unexplored.

Herein, we report the synthesis and characterization of an octa-fullero-dendrimer, which consists of a core-shell dendrimer with an ionic tetra[bis(benzylammonium)aryl]silane core that non-covalently binds to eight anionic fullerene entities. In previous studies, such ionic dendrimers were successfully applied as host molecules for the non-covalent binding of a wide variety of organic and inorganic functional molecules,⁸ among which a catalytically active palladium(II) complex was a key example.⁹ We established that the number of anionic functional molecules accommodated by these dendrimers is pre-defined by the number of cationic sites (eight in the present example) in the core of the dendrimer.

In order to study the number of fullerene units that could be attached non-covalently to dendrimer [1]Br₈ (Scheme 1), we selected a C₆₀ derivative bearing a

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Scheme 1. Synthesis of a self-assembled octa-fullero dendrimer. Reagents and conditions: (i) NaOH, H₂O, CH₂Cl₂ (quantitative); (ii) CH₂Cl₂, H₂O (67%).

carboxylate subunit that could serve as an anionic anchoring point to the octa-cationic core $[1]^{8+}$. This compound, denoted $Na[C_{60}CO_2]$, was prepared by reaction of the corresponding carboxylic acid $C_{60}CO_2H$ with

NaOH in CH₂Cl₂.^{10,11} The anionic fullerene derivative $[C_{60}CO_2]^-$ was then attached to the octa-cationic dendritic backbone via a straightforward anion exchange reaction of $[1]Br_8$ with $Na[C_{60}CO_2]$.¹²

Purification by preparative gel permeation chromatography (Bio-Beads SX-1, CH_2Cl_2) to remove the low molecular weight impurities then afforded $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$ as an orange glassy product in 67% yield. The assembly $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$ was characterized by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectrum of a solution of $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$ in CDCl_3 , the diagnostic signals of both $[\mathbf{1}]^{8+}$ and $[\text{C}_{60}\text{CO}_2]^-$ can clearly be observed (Fig. 1). Furthermore, specific peak integrals show that the octa-cationic dendritic moiety $[\mathbf{1}]^{8+}$ and the anions $[\text{C}_{60}\text{CO}_2]^-$ are present in a 1:8 molar ratio. Broadening of the signals was observed for $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$. The singlet resonance of the OCH_2 protons of the octyloxy chains of the $[\text{C}_{60}\text{CO}_2]^-$ guests (Scheme 1) was split, on binding, into two sets of triplets at 3.66 and 3.83 ppm with an 1:4.3 integral ratio while the multiplets were also broadened. These observations point to reduced mobility of the anionic guest molecules assembled onto the octa-cationic dendritic structure.^{13,14}

The UV-absorption spectrum of a solution of $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$ in CH_2Cl_2 showed characteristic absorption features, which could be ascribed to the fullerene units as well as a band diagnostic for the cationic dendri-

mer. In fact, the UV-absorption spectrum of $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$ matched the spectral profile of a 1:8 molar mixture of authentic $[\mathbf{1}]\text{Br}_8$ and the *t*-butyl ester, $\text{C}_{60}\text{CO}_2t\text{-Bu}$ of the $[\text{C}_{60}\text{CO}_2]^-$ anion, which is unable to self-assemble. The similarity of these spectra indicated that there were no significant ground state interactions between the respective chromophores in the supramolecular complex $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$. The luminescence properties of solutions of $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$ in CH_2Cl_2 were also investigated and compared with the behavior of an isoabsorbing model mixture of authentic $[\mathbf{1}]\text{Br}_8$ and $\text{C}_{60}\text{CO}_2t\text{-Bu}$. Upon excitation of the latter model mixture in the UV-region, where the main part of the light is absorbed by the dendritic wedges of the octa-cationic moiety $[\mathbf{1}]^{8+}$, the characteristic emission of the polybenzyl aryl ether dendritic wedges was observed. In contrast, complete quenching of this emission of $[\mathbf{1}]^{8+}$ was observed in $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$, which suggests that upon excitation, intramolecular energy transfer occurs from the lowest singlet excited state of the Fréchet-type dendritic branch to the low lying fullerene singlet excited state. The latter observation provides further evidence for the association of $[\mathbf{1}]^{8+}$ and $[\text{C}_{60}\text{CO}_2]^-$.

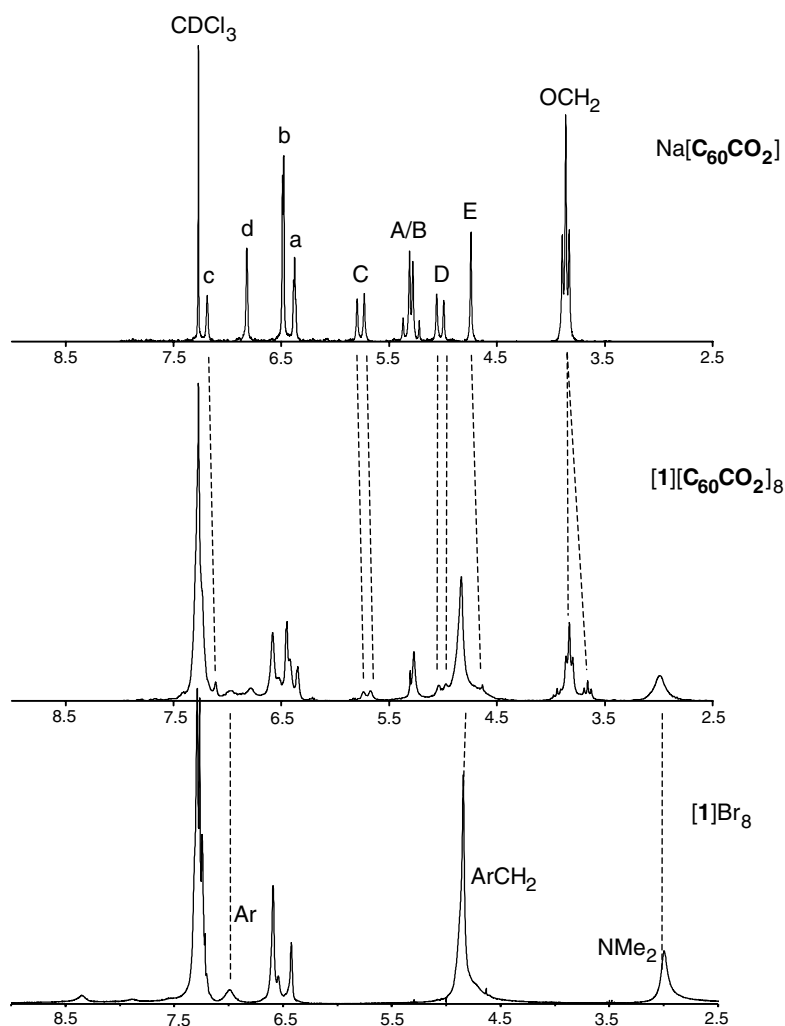


Figure 1. ^1H NMR spectra (300 MHz, CDCl_3) of $\text{Na}[\text{C}_{60}\text{CO}_2]$ (top), $[\mathbf{1}][\text{C}_{60}\text{CO}_2]_8$ (middle), and $[\mathbf{1}]\text{Br}_8$ (bottom).

In order to establish the molecular weight of the host–guest assembly, gel permeation chromatography coupled to a low angle laser light scattering (GPC/LALLS) instrument was performed using THF as eluent.¹⁴ The chromatogram displayed three peaks. The first corresponded to a mass of 21780 g/mol ($M_w/M_n = 1.27$) and was identified as the 1:8 host–guest octa-fullero-dendrimer assembly $[1][C_{60}CO_2]_8$ (calculated M_w : 20960.05 g/mol). The molecular weights associated to the two additional peaks were higher: 38,670 ($M_w/M_n = 1.04$) and 94,070 g/mol ($M_w/M_n = 1.02$), respectively. To these fractions were attributed superstructures consisting of aggregated assemblies derived from $[1][C_{60}CO_2]_8$. Such behavior is commonly observed during the GPC analysis of poly-ionic macromolecules when an organic solvent is used as eluent. Importantly, no peaks corresponding to compounds with a molecular weight lower than $[1][C_{60}CO_2]_8$ were detected, which further substantiates the formation of a stoichiometric assembly between octa-cationic $[1]^{8+}$ and eight $[C_{60}CO_2]^-$ anions.

In conclusion, we have demonstrated the use of an octa-cationic dendrimer as a molecular template for the non-covalent binding of eight anionic fullerene subunits in a straightforward manner. To the best of our knowledge, this is the first example of a non-covalent fullero-dendrimer bearing a *multiple* number of C_{60} units. An exciting aspect of the non-covalent approach described above is its flexibility toward assembling and de-assembling of functional groups. Future work will be directed toward the simultaneous incorporation of both anionic fullerene units and complementary anionic donor units to core-shell dendrimers similar to $[1]^{8+}$, which may lead to the preparation of unprecedented photoactive molecular devices.

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- Procedure*: A solution of dendrimer $[1]Br_8$ (24.5 mg, 3.4 μ mol, 1 equiv) and a slight excess of $Na[C_{60}CO_2]$ (51 mg, 27.9 μ mol 8.2 equiv) in CH_2Cl_2 (20 mL) was stirred for 3 h, after which the mixture was extensively washed with water to extract NaBr and then evaporated to dryness.
- The structural aspects and binding properties of poly-ionic core-shell dendrimers have been studied in detail, see: van de Coevering, R.; Bruijninx, P. C. A.; Lutz, M.; Spek, A. L.; Klein Gebbink, R. J. M.; van Koten, G., in preparation; Similar decoalescence behavior was also observed for the OCH_2 protons of poly-ionic dendrimers with an outer shell of dodecyl groups upon formation of structurally congested host–guest assemblies, see: van de Coevering, R.; Bruijninx, P. C. A.; van Walree, C. A.; Klein Gebbink, R. J. M.; van Koten, G., in preparation.
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