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A Highly Directional Fourfold Hydrogen-Bonding Motif for Supramolecular Structures through Self-Assembly of Fullerodendrimers

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Dedicated to Professor David I. Schuster on the occasion of his 70th birthday

Abstract: Supramolecular dendrimers resulting from the dimerization of fullerene-functionalized dendrons through a quadruple hydrogen-bonding motif were prepared. The synthetic strategy is based on the esterification of a *tert*-butoxycarbonyl (Boc)-protected 2-ureido-4-[1*H*]pyrimidinone precursor possessing an alcohol function with fullerodendrons bearing a carboxylic acid unit at the focal point. Subsequent acidic treatment to cleave the protecting group and reaction of the resulting amine with octylisocyanate affords the targeted compounds. As demonstrated by the results of MALDI-TOF mass spectrometry and ^{1}H NMR spectroscopy, both of the 2-ureido-4-[1H]pyrimidinone derivatives form self-assembled dimers spontaneously through hydrogen-bonding interactions, thus leading to supramolecular structures containing two or ten fullerene moieties.

Keywords: aggregation · dendrimers · fullerenes · hydrogen bonds · self-assembly

Introduction

Since the pioneering work of Vögtle in the late 1970s,[1] the synthetic concept based on repetitive growth with branching units has been investigated extensively, and has lead to a wide range of core-shell macromolecular structures, now recognized as *dendrimers*.[2] In recent years, the rapid advances in dendrimer synthetic chemistry have focussed on the creation of functional systems, with increased attention being given to potential applications.[3] Among the large number of molecular subunits used for dendrimer chemistry, C_{60} has proven to be a versatile building block and fullerene-functionalized dendrimers, that is, *fullerodendrimers*,[4] have generated significant research activities in the past few years.[5] In particular, the peculiar physical properties of fullerene derivatives make fullerodendrimers attractive candidates for a variety of interesting features in supramolecular chemistry and materials science.[6]

C_{60} itself is a convenient core for dendrimer chemistry[5a] and the functionalization of C_{60} with a controlled number of dendrons improves dramatically the solubility of the fullerenes.[7] Furthermore, variable degrees of addition within the fullerene core are possible and its almost spherical shape leads to globular systems even with low-generation dendrons.[8] On the other hand, specific advantages are gained by the encapsulation of a fullerene moiety in the middle of a dendritic structure.[9] The shielding effect resulting from the presence of the surrounding shell has been useful in optimizing the optical limiting properties of C_{60} derivatives,[10] to obtain amphiphilic derivatives with good spreading characteristics,[11] or to prepare fullerene-containing liquid-crystalline materials.[12] The use of the fullerene sphere as a photoactive core unit has also been reported.[9] In particular, the

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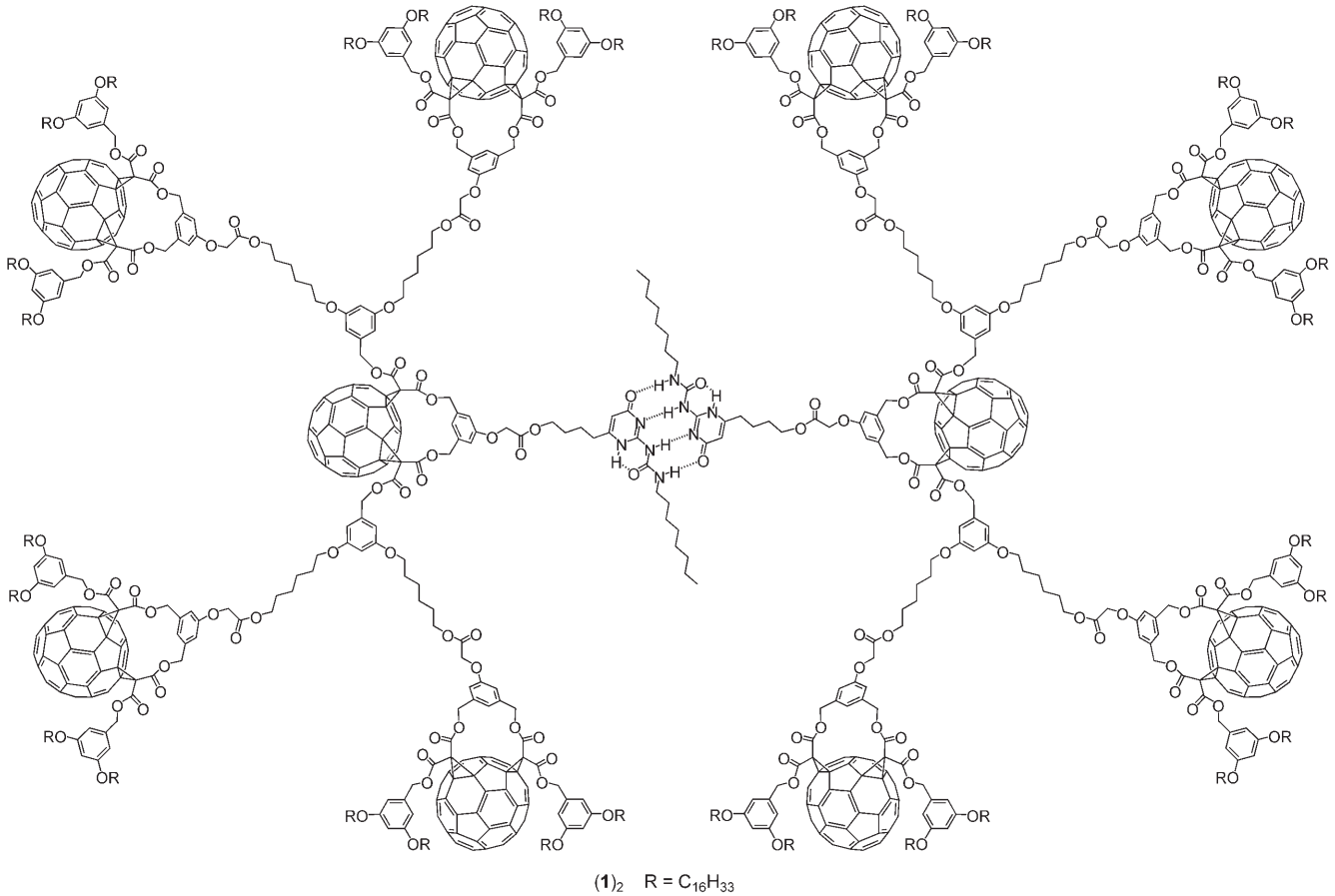
special photophysical properties of C_{60} have been used to evidence dendritic shielding effects[13] and to prepare dendrimer-based light-harvesting systems.[14] Although the main part of the fullerene-containing dendrimers reported so far have been prepared with a C_{60} core, dendritic structures with fullerene units at their surface or with C_{60} spheres in the dendritic branches have been scarcely considered. This is due mainly to the difficulties associated with the synthesis of fullerene-rich molecules.[5] Indeed, the two major problems for the preparation of such dendrimers are the low solubility of C_{60} and its chemical reactivity, which limit the range of reactions that can be used for the synthesis of branched structures bearing multiple C_{60} units.

Over the past years, we have developed a research program for the synthesis of dendrons substituted with fullerene moieties.[15] These fullerodendrons have intriguing properties and are interesting building blocks for the preparation of monodisperse fullerene-rich macromolecules.[16] However, the synthesis of such covalent fullerodendrimers remains difficult and often involves several steps, thus limiting their accessibility and, therefore, their application. This prompted us to explore the assembly of the fullerene-containing components by using supramolecular interactions rather than covalent chemistry.[17] This strategy appears particularly attractive as the range of systems that can be investigated is not limited severely by the synthetic route. Here, we report the preparation of supramolecular dendrimer $(\mathbf{1})_2$ (Figure 1), which results from the dimerization of a fullerene-functionalized dendron through a quadruple hydrogen-bonding motif. The latter self-complementary arrays of four hydrogen bonds developed originally by Meijer et al.[18] affords remarkably stable dimers with high association constants in apolar organic solvents ($K_a > 10^7\,\mathrm{M}^{-1}$ in $CHCl_3$).[19] A large variety of supramolecular architectures based on these hydrogen-bonding interactions of 2-ureido-4-[1*H*]pyrimidinone subunits have already been described. They include self-assembled supramolecular polymers,[20] calixarene dimers,[21] noncovalent C_{60}-dimers,[22] fullerene-containing supramolecular polymers[23] as well as noncovalent fullerene-based donor–acceptor dyads.[24] However, to the best of our knowledge, no bulky and flexible dendritic structures representing a challenge for this fourfold hydrogen-bonding motif have been reported. Furthermore, the self-assembly of dendritic macromolecules through hydrogen-bonding interactions[25] is particularly well-suited for the preparation of fullerene-rich molecules. Indeed, the synthesis itself is restricted to the preparation of dendrons, and self-aggregation leads to the dendritic structure. This avoids tedious final synthetic steps with precursors incorporating potentially reactive functional groups, such as C_{60}.

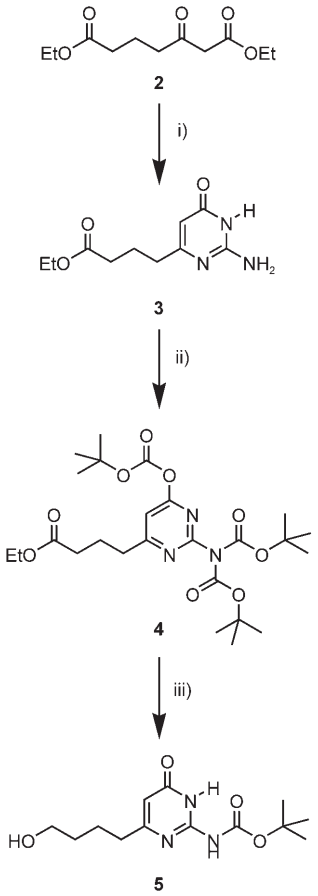


$(\mathbf{1})_2$ R = $C_{16}H_{33}$

Figure 1. Self-assembled fullerodendrimer dimer $(\mathbf{1})_2$.

Results and Discussion

The synthetic route envisaged for the preparation of supramolecular dimer $(\mathbf{1})_2$ relies upon esterification of a 2-ureido-4-[1H]pyrimidinone precursor (**5**) bearing an alcohol function with a fullerodendron possessing a carboxylic acid group at the focal point. To this end, precursor **5** was prepared in three steps from diethyl 3-oxoheptanedioate (**2**) (Scheme 1). Reaction of **2** with guanidinium carbonate in refluxing ethanol gave the ester-terminated aminopyrimidinone **3** in 51% yield. Treatment of **3** with an excess of di-*tert*-butyl dicarbonate (Boc_2O) in THF at 40°C for two days, in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine (DMAP), yielded the triply *tert*-butoxycarbonyl (Boc)-protected derivative **4**. Reduction of the ester function in **4** by treatment with diisobutylaluminum hydride (DIBAL-H) in CH_2Cl_2 at −78°C provokes, simultaneously, the cleavage of two Boc protecting groups, affording the [1*H*]pyrimidin-4-one derivative **5** with a residual Boc-protected amine function in position 2 and a 4-hydroxybutyl chain in position 6.

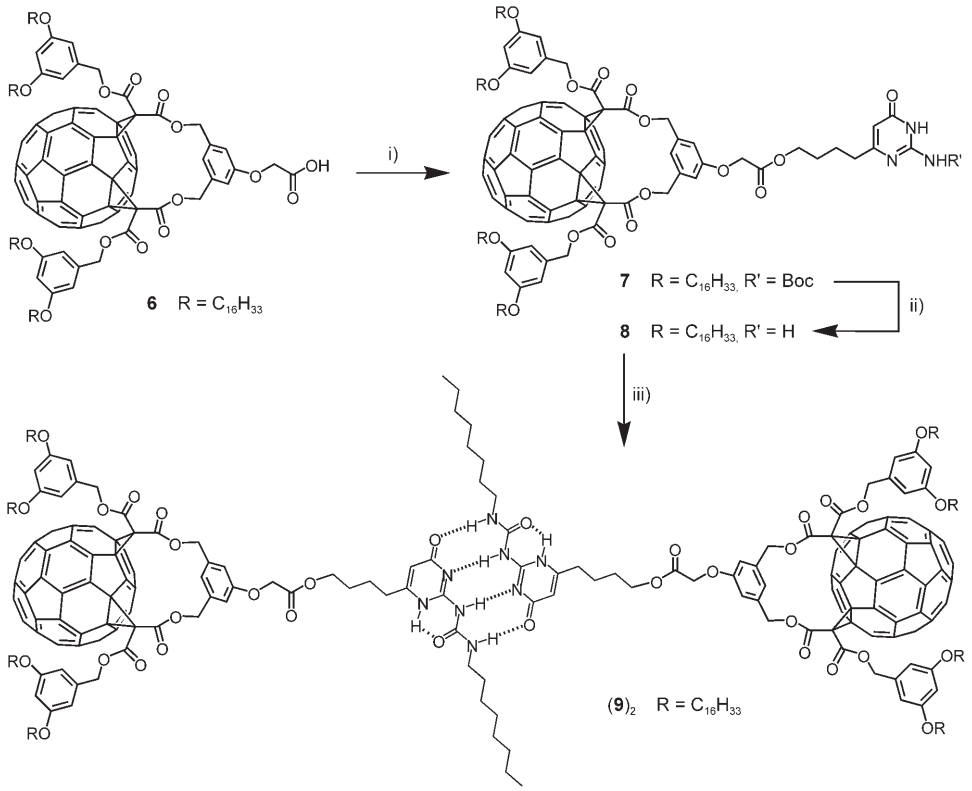


Scheme 1. Reagents and conditions: (i) guanidinium carbonate, EtOH, reflux (51%); (ii) Boc_2O, Et_3N, DMAP cat., THF, 40°C (47%); (iii) DIBAL-H, CH_2Cl_2, −78°C (56%).

The synthesis of supramolecular fullerodendrimer dimer $(\mathbf{1})_2$ began from a first generation derivative bearing only one fullerene moiety (Scheme 2). The C_s symmetrical fullerene bis-adduct precursor **6** was obtained in eleven steps according to a procedure reported previously.[26] Esterification of carboxylic acid **6** with alcohol **5** by using *N*,*N*′-dicyclohexylcarbodiimide (DCC), DMAP, and 1-hydroxybenzotriazole (HOBt) gave **7** in good yields. However, due to difficulties encountered during its purification, the isolated yield was quite low (30%). In fact, partial cleavage of the Boc protecting group of the amine function in **7** occurred during column chromatography on silica gel. To prevent this problem, modified purification conditions were employed for compound **7**. Indeed, we found that gel permeation chromatography was an efficient tool for obtaining **7** in a pure form without significant loss of material. At the end of the esterification reaction, the crude mixture was filtered, evaporated, and purified by employing gel permeation chromatography, giving **7** in 58% yield. Subsequent treatment with an excess of trifluoroacetic acid (TFA) afforded the amine **8** in a good yield. Finally, reaction of **8** with octylisocyanate in the presence of triethylamine gave the supramolecular fullerene dimer $(\mathbf{9})_2$ in 48% yield.

The synthesis of compound **1** is depicted in Scheme 3. Dendron **10** containing five fullerene units was prepared according to a procedure described recently.[26] DCC-mediated esterification of **10** with **5** in CH_2Cl_2 afforded the dendritic Boc-protected amine **11**. The crude product was purified by performing preparative size exclusion chromatography to prevent any problems arising from the partial cleavage of the Boc protecting group. Treatment of **11** with an excess of TFA in CH_2Cl_2 followed by column chromatography gave compound **12** as a glassy, orange product in 52% overall yield. Reaction of the free amine with octylisocyanate in toluene at 40°C in the presence of triethylamine gave the targeted dendritic 2-ureido-4-[1H]pyrimidinone functionalized fullerene derivative **1**.

Owing to the presence of the four hexadecyloxy substituents per peripheral fullerene subunit, compounds **1** and **9** are highly soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, toluene, or THF, and spectroscopic characterization was easily achieved. Both **1** and **9** were also characterized in the gas phase by using (MALDI-TOF) mass spectrometry, which, because its mild ionization process prevents high levels of fragmentations, is a well-suited tool for characterizing such high-molecular-weight compounds.[13c] Even if the mass spectrum of **9** is dominated by the ion peak corresponding to the monomer at *m*/*z* 2564.7 (*m*/*z* calculated for $C_{171}H_{181}N_4O_{17}=2564.3$), the molecular ion peak of the dimer $(\mathbf{9})_2$ was also detected at *m*/*z* 5126.0 (*m*/*z* calculated for $C_{342}H_{361}N_8O_{34}=5127.6$). Similarly, the MALDI-TOF mass spectrum of fullerodendrimer **1** is characterized by two peaks corresponding to the supramolecular dimer $(\mathbf{1})_2$ at *m*/*z* 21932 ($[2M^+ + H]^+$, *m*/*z* calculated for $C_{1494}H_{1401}N_8O_{154}=21932.1$) and to the monomer at *m*/*z* 10964 ($[M^+ + H]$, *m*/*z* calculated for $C_{747}H_{701}N_4O_{77}=10966.5$). As seen for **9**, the mass spectrum of **1** is dominat-



Scheme 2. Reagents and conditions: i) **5**, DCC, DMAP, HOBt, CH_2Cl_2, 0°C to RT (58%); ii) TFA, CH_2Cl_2, RT (89%); iii) octylisocyanate, Et_3N, toluene, 40°C (48%).

ed largely by the ion peak corresponding to the monomer subunit, and the relative intensity of the signal attributed to the supramolecular dimer is quite low (5%). Finally, no peaks corresponding to defected dendrons were observed in the MALDI-TOF mass spectra of **1**, thus providing clear evidence for its monodispersity.

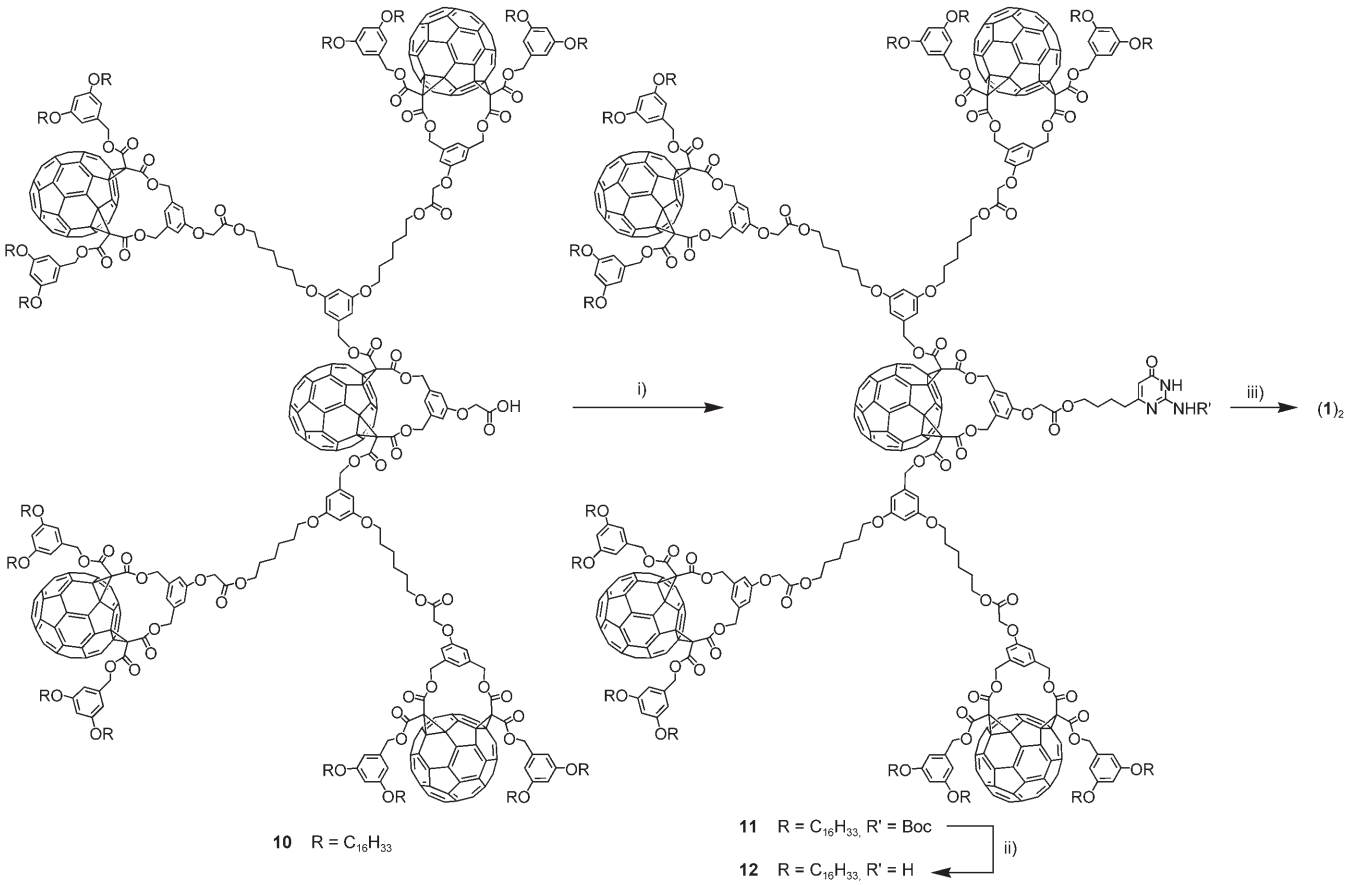
Definitive evidence for the dimer structure of **1** and **9** came from the results of ^{1}H NMR measurements conducted in $CDCl_3$. In both cases, signals corresponding to a single compound are detected. The spectrum of **9** shows the characteristic features of C_s symmetrical 1,3-phenylenebis-(methylene)-tethered fullerene *cis*-2-bis-adducts.[11b,16b] Effectively, in addition to the signals arising from the 3,5-didodecyloxybenzyl units, an AB quartet is observed for the diastereotopic benzyl CH_2 group and an AX_2 system for the aromatic protons of the 1,3,5-trisubstituted bridging phenyl ring. The signals corresponding to the central unit were also observed clearly. Importantly, large downfield shifts were found for the protons of the hydrogen-bonding motif. The signals of the urea NH protons are observed at $\delta = 11.81$ and 10.06 ppm and the intramolecularly chelated pyrimidinone NH at $\delta = 13.23$ ppm. This observation is fully consistent with four donor–donor–acceptor–acceptor (DDAA) hydrogen bonds in the supramolecular fullerene–dimer system. As shown in Figure 2, the ^{1}H NMR spectrum of **1** recorded in $CDCl_3$ also displays the characteristic signals for the hydrogen-bonding protons ($\delta = 11.86$ and 10.12 ppm for urea NH protons and $\delta = 13.25$ ppm for the pyrimidinone NH), thus providing conclusive evidence for the dimeric structure in solution.

Conclusion

We have demonstrated that strong self-assembled dimers based on 2-ureido-4-[1*H*]pyrimidinone can be formed efficiently even from highly crowded fullerodendrons. The synthetic strategy is based on the esterification of a Boc-protected 2-ureido-4-[1*H*]pyrimidinone precursor possessing an alcohol function with a carboxylic acid bearing the functional unit. Subsequent acidic treatment to cleave the protecting group and reaction of the resulting amine with octylisocyanate gave the final targeted compound. By following this synthetic route, it was possible to prepare new 2-ureido-4-[1*H*]pyrimidinone derivatives substituted by one or five fullerene subunits. As demonstrated by the results of MALDI-TOF mass spectrometry and ^{1}H NMR spectroscopy, both compounds form self-assembled dimers spontaneously through hydrogen-bonding interactions, thus leading to supramolecular structures containing two or ten fullerene moieties. The highly directional fourfold hydrogen-bonding motif based on 2-ureido-4-[1*H*]pyrimidinone is, therefore, well suited for stable, dimeric dendritic assembly, and the results described in this paper pave the way for the expeditious and efficient construction of new stable, noncovalent dendritic supramolecular arrays. Through the choice of suitable molecular components, new supramolecular architectures displaying interesting properties, such as photoinduced intercomponent processes, can be envisaged.

Experimental Section

General: Reagents and solvents purchased were of reagent grade and were used without further purification. Compounds **6** and **10** were prepared according to procedures described previously.[26] All reactions were performed by using standard glassware under an argon atmosphere. Solvents were distilled prior to use. Evaporation and concentration were conducted at water aspirator pressure and by drying in a vacuum at 10^{-2} Torr. Column chromatography was performed by using silica gel 60, 230–400 mesh (Merck). Thin layer chromatography (TLC) was performed by using glass sheets coated with silica gel 60 F_{254} (Merck), fol-



Scheme 3. Reagents and conditions: i) **5**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to RT (70 %); ii) TFA, CH_2Cl_2, RT (75 %); iii) octylisocyanate, Et_3N, toluene, 40 °C (87 %).

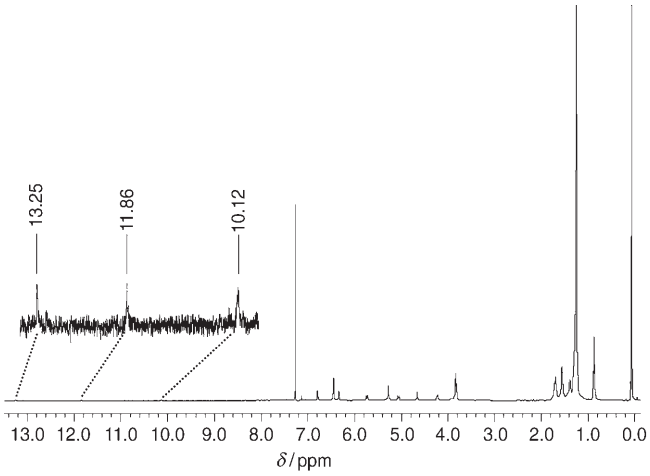


Figure 2. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of fullerodendrimer dimer $(\mathbf{1})_2$ highlighting the hydrogen-bonding protons.

lowed by visualization with UV light. Melting points were measured by using an Electrothermal Digital Melting Point apparatus and are uncorrected. UV/Vis spectra [λ_{max} in nm (ε)] were measured by using a Hitachi U-3000 spectrophotometer. IR spectra (cm^{-1}) were measured by using an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded by using Bruker AC 200 (200 MHz), Avance 300 (300 MHz), or AM 500 (500 MHz) spectrometers, with solvent peaks as reference. ESI-mass spectra (low and high resolution) were performed by using a Waters LCT Premier spectrometer. FAB-mass spectra were recorded by using a ZA HF instrument with *m*-nitrobenzyl alcohol (NBA) as matrix. MALDI-TOF mass spectra were recorded by using a Bruker BIFLEX instrument with 1,8,9-trihydroxyanthracene (dithranol) as matrix.

Compound 3: A suspension of **2** (2 mL, 8.01 mmol) and guanidinium carbonate (772 mg, 4.01 mmol) in dry ethanol (30 mL) was refluxed overnight. The mixture was concentrated to about 10 mL, cooled to 4 °C, and the resulting precipitate was filtered and washed with cold ethanol to yield **3** (919 mg, 51 %) as a white solid. M.p. 146–148 °C; ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.47 (brs, 3H), 5.36 (s, 1H), 4.04 (q, ^3J(H,H) = 7 Hz, 2H), 2.27 (quint, ^3J(H,H) = 8 Hz, 4H), 1.79 (quint, ^3J(H,H) = 8 Hz, 2H), 1.17 ppm (t, ^3J(H,H) = 7 Hz, 3H); ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 174.8, 163.7, 173.1, 156.2, 100.4, 60.2, 33.5, 33.4, 23.3, 14.6 ppm; MS (ESI): *m*/*z*: 226.1 [M^++H]; HRMS: *m*/*z* calcd for $C_{10}H_{16}N_3O_3$ [M^++H]: 226.1192; found: 226.1188.

Compound 4: A mixture of **3** (637 mg, 2.83 mmol), Boc_2O (2.60 g, 11.89 mmol), triethylamine (0.6 mL, 4.25 mmol), and a catalytic amount of DMAP in THF (20 mL) was stirred at 40 °C for two days. The solvent was evaporated and the residue was purified by column chromatography on silica gel (hexanes/EtOAc, 5:2), yielding **4** (694 mg, 47 %) as a pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.94 (s, 1H), 4.12 (q, ^3J(H,H) = 7 Hz, 2H), 2.83 (t, ^3J(H,H) = 8 Hz, 2H), 2.35 (t, ^3J(H,H) = 8 Hz, 2H), 2.05 (quint, ^3J(H,H) = 8 Hz, 2H), 1.54 (s, 9H), 1.41 (s, 18H), 1.23 ppm (t, ^3J(H,H) = 7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.6, 172.8, 166.0, 158.1, 150.1, 148.9, 108.5, 85.1, 83.3, 60.4, 36.5, 33.2, 27.7, 27.5, 23.5, 14.2 ppm; MS (ESI): *m*/*z*: 526.3 [M^++H], 426.2 [M^++H−Boc], 326.2 [M^++H−2Boc], 226.1 [M^++H−3Boc]; HRMS: *m*/*z* calcd for $C_{25}H_{40}N_3O_9$ [M^++H]: 526.2765; found: 526.2753.

Compound 5: A solution of DIBAL-H (1 M in CH_2Cl_2, 6.6 mL, 6.60 mmol) was added dropwise to a solution of **4** (694 mg, 1.32 mmol) in

dry CH_2Cl_2 (6 mL) at −78 °C under argon. The reaction mixture was stirred at −78 °C for 5 h and then allowed to warm to room temperature overnight. The mixture was diluted with CH_2Cl_2, washed with sat. aq. NH_4Cl and brine, dried ($MgSO_4$), and the solvent was evaporated. Purification by column chromatography on silica gel (hexanes/EtOAc, 7:3) gave **5** (208 mg, 56%) as a pale green oil. The final product is a mixture of ~25% enol and ~75% keto (as determined by NMR analysis); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 5.90 (s, 1H), 5.60 (s, 1H; enol), 3.62 (t, ^3J(H,H) = 8 Hz, 2H), 2.44 (m, 2H), 1.67 (m, 2H), 1.58 (m, 2H), 1.50 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.2, 168.6, 161.8, 155.9, 152.8, 152.7, 150.1, 106.7, 100.2, 84.3, 62.2, 60.4, 36.7, 32.0, 31.8, 29.7, 28.1, 28.0, 24.4, 24.2 ppm; MS (ESI): *m/z*: 284.1 [M^++H]; HRMS: *m/z* calcd for $C_{13}H_{22}N_3O_4$ [M^++H]: 284.1610; found: 284.1620.

General procedure for the preparation of carbamates 7 and 11: DCC (2.2 equiv) was added to a stirred solution of **5** (1 equiv), the appropriate fullerene derivative (**6** or **10**, 1 equiv), HOBt (0.1 equiv), and DMAP (0.5 equiv) in CH_2Cl_2 at 0 °C. After 1 h, the mixture was allowed to warm slowly to room temperature, then stirred at room temperature for 24 h, the arising solid was filtered off and the solvent was evaporated. The crude product was then purified as outlined in the following text.

Compound 7: Prepared from **6** (212 mg, 0.095 mmol) and purified by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **7** (138 mg, 58%) as a glassy, orange product; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.16 (brs, 1H), 6.80 (brs, 2H), 6.47 (d, ^4J(H,H) = 2 Hz, 4H), 6.36 (t, ^4J(H,H) = 2 Hz, 2H), 5.93 (s, 1H), 5.76 (d, ^2J(H,H) = 13 Hz, 2H), 5.30 (s, 4H), 5.06 (d, ^2J(H,H) = 13 Hz, 2H), 4.68 (s, 2H), 4.26 (brt, 2H), 3.85 (t, ^3J(H,H) = 6 Hz, 8H), 2.43 (brt, 2H), 1.70 (m, 12H), 1.53 (s, 9H), 1.27 (m, 104H), 0.89 ppm (t, ^3J(H,H) = 6 Hz, 12H); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 168.6, 168.1, 162.6, 161.6, 160.4, 157.8, 152.4, 149.7, 148.6, 147.4, 147.3, 146.0, 145.7, 145.6, 145.3, 145.2, 145.0, 144.9, 144.6, 144.3, 144.2, 144.0, 143.7, 143.6, 143.2, 142.7, 142.3, 141.12, 141.06, 140.0, 138.4, 137.8, 136.5, 136.1, 135.8, 134.4, 116.2, 112.6, 107.1, 106.9, 101.6, 84.4, 70.6, 68.7, 68.1, 67.1, 66.8, 65.5, 65.1, 49.0, 36.6, 31.9, 29.7, 29.7, 29.5, 29.4, 29.3, 28.0, 27.9, 28.1, 24.0, 22.7, 14.2 ppm; IR (KBr): $\tilde{\nu}$ = 1748 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (112000), 438 (3100), 463 nm (2500 mol^{-1} m^3 cm^{-1}); MS (FAB): *m/z*: 2508.3 [M^++H]; elemental analysis calcd (%) for $C_{167}H_{171}N_3O_{18}$ (2508.1): C 79.97, H 6.87, N 1.68; found: C 79.79, H 6.98, N 1.70.

Compound 11: Prepared from **10** (300 mg, 0.028 mmol) and purified by gel permeation chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **11** (138 mg, 70%) as a glassy, orange-red product; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.10 (m, 5H), 6.79 (s, 8H), 6.71 (s, 2H), 6.44 (m, 20H), 6.33 (m, 6H), 5.73 (d, ^2J(H,H) = 13 Hz, 10H), 5.91 (s, 1H), 5.29 (s, 20H), 5.04 (d, ^2J(H,H) = 13 Hz, 10H), 4.65 (s 10H), 4.23 (m, 10H), 3.82 (t, ^3J(H,H) = 7 Hz, 40H), 2.38 (m, 2H), 1.71 (m, 50H), 1.20 (m, 451H), 0.89 ppm (t, ^3J(H,H) = 7 Hz, 48H).

General procedure for the preparation of amines 8 and 12: The appropriate Boc-protected derivative (**7** or **11**) was dissolved in a mixture of CH_2Cl_2 (10 mL) and TFA (6 mL). The resulting solution was stirred at room temperature for 3 h, then washed successively with 10% aq. $NaHCO_3$ and water, dried ($MgSO_4$), and the solvent was evaporated. The crude product was then purified as outlined in the following text.

Compound 8: Prepared from **7** (135 mg, 0.054 mmol) and washed with MeOH and Et_2O to give **8** (118 mg, 89%) as a glassy, orange-red product; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.12 (brs, 1H), 6.78 (brs, 2H), 6.44 (d, ^4J(H,H) = 2 Hz, 4H), 6.34 (t, ^4J(H,H) = 2 Hz, 2H), 5.74 (d, ^2J(H,H) = 13 Hz, 2H), 5.59 (s, 1H), 5.28 (s, 4H), 5.03 (d, ^2J(H,H) = 13 Hz, 2H), 4.66 (s, 2H), 4.23 (brt, ^3J(H,H) = 6 Hz, 2H), 3.82 (t, ^3J(H,H) = 7 Hz, 8H), 2.36 (brt, 2H), 1.70 (m, 12H), 1.44–1.16 (m, 104H), 0.87 ppm (t, ^3J(H,H) = 7 Hz, 12H); IR (KBr): $\tilde{\nu}$ = 1748 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (119000), 437 (3400), 464 nm (3200 mol^{-1} m^3 cm^{-1}); MS (FAB): *m/z*: 2408.8 [M^++H].

Compound 12: Prepared from **11** (138 mg, 0.013 mmol) and purified by column chromatography on silica gel (CH_2Cl_2/MeOH, 98:2 to 95:5) to give **12** (103 mg, 75%) as a glassy, dark orange product; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 (s, 4H), 7.01 (s, 1H), 6.78 (s, 8H), 6.70 (s, 2H), 6.44 (m, 20H), 6.33 (m, 6H), 5.74 (d, ^2J(H,H) = 13 Hz, 2H), 5.73 (d, ^2J(H,H) = 13 Hz, 8H), 5.59 (s, 1H), 5.29 (s, 20H), 5.05 (d, ^2J(H,H) = 13 Hz, 8H), 5.03 (d, ^2J(H,H) = 13 Hz, 2H), 4.65 (s 10H), 4.23 (t, ^3J(H,H) = 7 Hz, 10H), 3.82 (t, ^3J(H,H) = 7 Hz, 40H), 2.26 (m, 2H), 1.71 (m, 50H), 1.20 (m, 442H), 0.88 ppm (t, ^3J(H,H) = 7 Hz, 48H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 168.7, 162.7, 162.6, 160.5, 158.0, 148.7, 147.5, 147.4, 146.1, 145.8, 145.6, 145.4, 145.2, 145.0, 145.0, 144.7, 144.4, 144.2, 144.0, 143.8, 143.6, 143.2, 142.8, 142.3, 141.2, 141.1, 140.1, 138.5, 137.9, 136.6, 136.1, 135.8, 134.4, 129.1, 127.3, 116.1, 112.6, 107.3, 101.8, 71.3, 70.7, 68.8, 68.2, 67.9, 67.2, 66.9, 65.6, 65.5, 53.4, 49.1, 32.0, 29.8, 29.7, 29.5, 29.4, 29.4, 29.2, 28.6, 28.1, 26.2, 25.9, 25.7, 25.0, 22.8, 14.2 ppm; IR (KBr): $\tilde{\nu}$ = 1749 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (560000), 437 (18300), 465 nm (17900 mol^{-1} m^3 cm^{-1}); MS (MALDI-TOF): *m/z*: 10812.7 [M^++H]; elemental analysis calcd (%) for $C_{738}H_{683}N_3O_{76}$ (10810.3): C 82.00, H 6.37, N 0.39; found: C 81.79, H 6.52, N 0.41.

General procedure for the preparation of compounds 1 and 9: Triethylamine (60 equiv) and octylisocyanate (7 equiv) were added to a solution of the appropriate amine (**8** or **12**) in dry toluene (1 mL), and the mixture was heated at 40 °C overnight. The solvent was evaporated and the crude product was dissolved in $CHCl_3$. The organic phase was washed with brine, dried ($MgSO_4$), and the solvent was evaporated. Purification was performed as outlined in the following text.

Compound 9: Prepared from **8** (24 mg, 0.010 mmol) and purified by column chromatography on silica gel (hexanes/EtOAc, 7:2 to EtOAc) to give **9** (12 mg, 48%) as a glassy, dark orange product; ^{1}H NMR (500 MHz, $CHCl_3$): δ = 13.23 (brs, 2H), 11.81 (brs, 2H), 10.06 (brs, 2H), 7.12 (s, 2H), 6.78 (s, 4H), 6.43 (d, ^4J(H,H) = 2 Hz, 4H), 6.32 (t, ^4J(H,H) = 2 Hz, 2H), 5.79 (s, 2H), 5.71 (d, ^2J(H,H) = 13 Hz, 4H), 5.25 (s, 8H), 5.04 (d, ^2J(H,H) = 13 Hz, 4H), 4.67 (s, 4H), 4.23 (t, ^3J(H,H) = 6 Hz, 4H), 3.81 (t, ^3J(H,H) = 6 Hz, 16H), 3.19 (q, ^3J(H,H) = 8 Hz, 4H), 2.47 (t, ^3J(H,H) = 7 Hz, 4H), 1.27 (m, 108H), 0.89 ppm (t, ^3J(H,H) = 6 Hz, 24H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 260 (256000), 438 (7200), 463 nm (6800 mol^{-1} m^3 cm^{-1}); MS (MALDI-TOF): *m/z*: 5126.0 [2M^++H] 2564.7 [M^++H]; HRMS: *m/z* calcd for $C_{171}H_{181}N_4O_{17}$ [M^++H]: 2564.2834; found: 2564.4042.

Compound 1: Prepared from **12** (45 mg, 0.004 mmol) and purified by precipitation with cold MeOH to give **1** (38 mg, 87%) as a dark orange-brown solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ = 13.25 (brs, 2H), 11.86 (brs, 2H), 10.12 (brs, 2H), 7.12 (s, 10H), 6.78 (s, 16H), 6.70 (s, 4H), 6.45 (m, 40H), 6.35 (m, 20H), 5.74 (d, ^2J(H,H) = 13 Hz, 20H), 5.59 (s, 2H), 5.29 (s, 40H), 5.05 (d, ^2J(H,H) = 13 Hz, 20H), 4.65 (s, 20H), 4.23 (m, 20H), 3.82 (m, 80H), 2.26 (m, 4H), 1.71 (m, 100H), 1.48–1.20 (m, 896H), 0.88 ppm (t, ^3J(H,H) = 7 Hz, 102H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 261 (980000), 437 (35300), 464 nm (33200 mol^{-1} m^3 cm^{-1}); MS (MALDI-TOF): *m/z*: 21932 [2M^++H], 10964 [M^++H].

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