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Molecular Design of a Novel Dendrimer Porphyrin for Supramolecular Fullerene/ Dendrimer Hybridization

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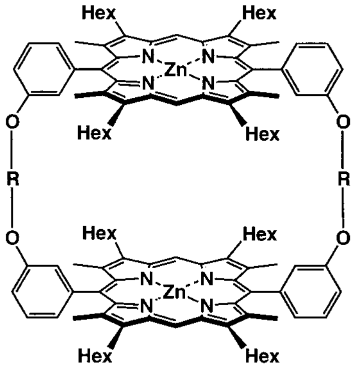
Molecular devices consisting of fullerenes have attracted great attention. However, the low processability of such carbon nanoclusters often limits their possible applications. On the other hand, one of the important approaches to overcoming this problem is the hybridization of fullerenes with polymeric materials,[1] which may also offer a possibility of tuning the electronic properties of fullerenes. Along this line, incorporation of fullerenes into dendritic macromolecules is expected to provide interesting models of fullerene/polymer hybrids, where each fullerene molecule is surrounded by a well-defined polymeric matrix in nanoscopic scale. From this point of view, several covalent and noncovalent approaches have been reported.[2,3] The covalent approach may be promising for the construction of well-defined fullerene/dendrimer hybrids,[2] in which however a partial destruction of the electronic conjugation of fullerenes is inevitable. On the other hand, the noncovalent (supramolecular) approach does not have such a disadvantage, but the reported examples[3] suffer a problem associated with a very weak interaction between fullerenes and dendrimers.

Recently, we have found that a face-to-face cyclic dimer of a zinc porphyrin having flexible hexamethylene spacers (**1**) forms a highly stable 1:1 inclusion complex with C_{60} in an induced-fit fashion, whereas its synthetic precursor with rigid diacetylenic spacers (**2**) hardly interacts with C_{60} (Table 1).[4] We report herein molecular design of novel dendritic macromolecules bearing a cyclic porphyrin dimer at the focal point ($\mathbf{3}_{\mathrm{L}n}$), which form stable supramolecular fullerene/dendrimer hybrids (Figure 1) in a well-defined fashion. Poly(benzyl ether) dendrimers $\mathbf{3}_{\mathrm{L}n}$ carrying two dendritic wedges of three and four aromatic layers (L*n*, *n* = 3, 4) were synthesized according to Scheme 1. 3,5-Dibromophenol,[5] protected by a *tert*-butyldiphenylsilyl group, was reacted with 3-ethynylbenzaldehyde[6] to afford the corresponding dialdehyde **4** (71%), which was further reacted with a Fréchet-type poly(benzyl ether) dendron bromide[7] (L*n*Br; *n* [number of the aromatic layers] = 3, 4) in the presence of KF/18-crown-6 ether to give dendritic dialdehyde $\mathbf{5}_{\mathrm{L}n}$ (71% for *n* = 3; 68% for *n* = 4).[8] Finally, $\mathbf{5}_{\mathrm{L}n}$ was condensed with dipyrrolylmethane[9] under acidic conditions for 3 h, and the reaction mixture was stirred in the presence of *p*-chloranil[10] and then subjected to column chromatography on silica gel with $CHCl_3/Et_2O$ (90/10 v/v) as eluent to isolate a reddish-purple porphyrin fraction. On preparative size-exclusion chromatography with $CHCl_3$ as eluent, this fraction was further separated into three fractions. According to MALDI−TOF−MS and ^{1}H NMR analyses,[11] the third fraction was found to correspond to cyclic dimer $\mathbf{3}_{\mathrm{L}n}$ (14% for *n* = 3; 13% for *n* = 4), while the first and second fractions contained cyclic tetramer (<1%) and trimer (~2%), respectively. The high selectivity for the formation of $\mathbf{3}_{\mathrm{L}n}$ is attributable to a large steric effect of the dendritic wedges, since use of a nondendritic dialdehyde bearing a cetyl group for the reaction resulted in a poor yield of cyclo-oligomeric porphyrins (<1%) with little preference to the cyclic dimer. Similarly, use a dendritic dialdehyde with a lower generation number ($\mathbf{5}_{\mathrm{L2}}$) resulted in the formation of a highly insoluble mixture of oligomeric porphyrins in low yield.

Table 1. Binding Constants (K_{assoc}) of Cyclodimeric Porphyrin Receptors with C_{60} (C_{70}) in Toluene at 25 °C

	receptors			
	1[a]	**2**[a]	$\mathbf{3}_{\mathrm{L3}}$	$\mathbf{3}_{\mathrm{L4}}$
K_{assoc}/M^{-1}	6.7×10^5	~0	1.7×10^4 (1.8×10^5)	1.5×10^4 (2.3×10^5)

[a] In benzene at 25 °C.



1: R = $(CH_2)_6$
2: R = $CH_2C{\equiv}C{-}C{\equiv}CCH_2$

In contrast with receptor **1** having flexible spacers, $\mathbf{3}_{\mathrm{L}n}$ has a limited freedom of conformational change at the binding site due to a high rigidity of the diethynylbenzene spacers. However, from a computer-aided CPK model study on $\mathbf{3}_{\mathrm{L}n}$, the distance between the mean planes of the two facing porphyrin units was estimated to be about 12 Å, which is likely suitable for the inclusion of fullerenes. Similarly to our previous report,[4] a toluene solution of $\mathbf{3}_{\mathrm{L}n}$, upon titration with C_{60}, showed a marked color change, where a bathochromic shift was observed for the Soret absorption band from 409 to 412 nm with isosbestic points at 382 and 415.5 nm.[12] Such a spectral change profile was even more explicit when C_{70} was mixed with $\mathbf{3}_{\mathrm{L}n}$.[12,13] Electrospray ionization mass spectrometry (ESI−MS) of a NaCl-saturated THF/MeOH (97/3 v/v) solution of a mixture of $\mathbf{3}_{\mathrm{L3}}$ and C_{70} showed two peaks centered at *m*/*z* 3159.3 and 3998.3, which correspond to Na^+ adducts of $\mathbf{3}_{\mathrm{L3}}$ uncomplexed

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[⊥] Responsible for ESI-MS spectrometry.

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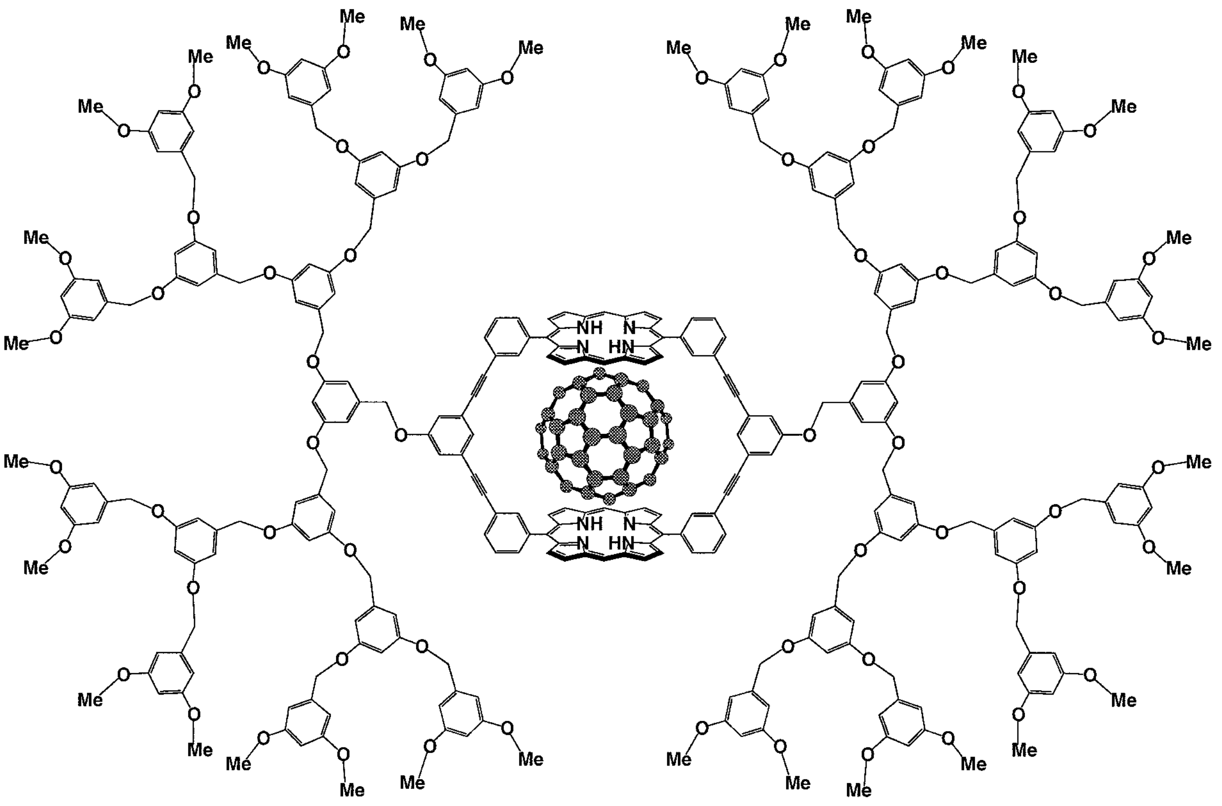
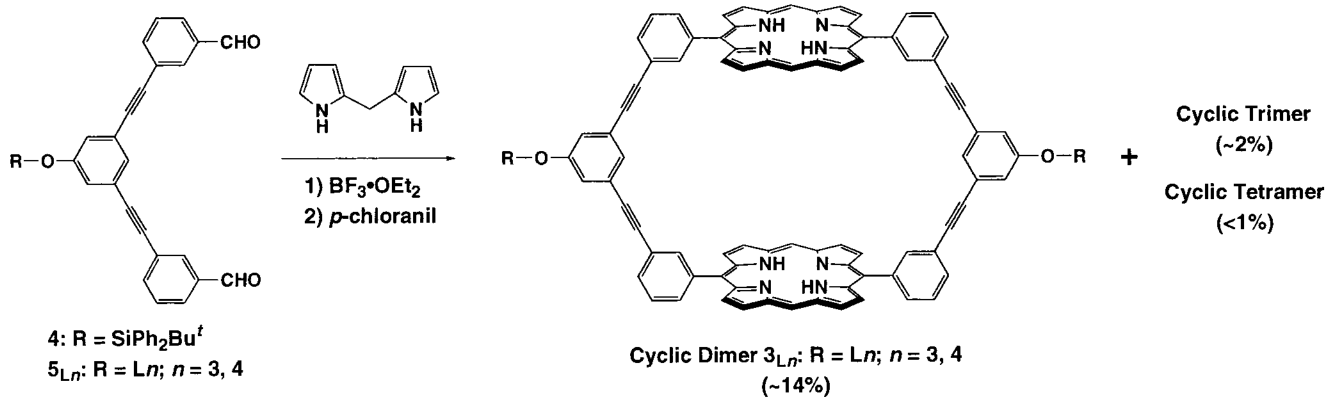


Figure 1. Schematic representation of a supramolecular hybrid of $\mathbf{3}_{\mathrm{L4}}$ with C_{60}.

Scheme 1. Synthetic Route to Dendrimer Porphyrins $\mathbf{3}_{\mathrm{L}n}$



(calculated 3158.2) and complexed with one molecule of C_{70} (calculated 3999.2), respectively.[12,14] The association constants (K_{assoc}) of $\mathbf{3}_{\mathrm{L3}}$ for fullerenes in toluene at 25 °C, as determined from the spectroscopic titration monitored at the Soret absorption band (409 nm), were 1.7×10^4 and 1.8×10^5 M^{-1} for C_{60} and C_{70}, respectively (Table 1). On the other hand, the one-generation larger $\mathbf{3}_{\mathrm{L4}}$, under the same conditions, showed almost comparable K_{assoc} values for C_{60} (1.5×10^4 M^{-1}) and C_{70} (2.3×10^5 M^{-1}), indicating a negligibly small effect of the dendritic wedges on the inclusion of fullerenes. It should be also noted here that the K_{assoc} values of $\mathbf{3}_{\mathrm{L}n}$ for C_{70} are almost one-order of magnitude larger than those for C_{60}. Since the redox properties of C_{70} are not much different from those of C_{60},[15] this trend may suggest a possible advantage of C_{70} with a larger contact area for the interaction with the cyclodimeric porphyrin cavity at the focal point of $\mathbf{3}_{\mathrm{L}n}$. In contrast with $\mathbf{3}_{\mathrm{L}n}$, a monomeric porphyrin reference ($\mathbf{6}_{\mathrm{L4}}$), prepared by a F^--mediated coupling of 5,15-bis(4′-*tert*-butyldiphenylsiloxyphenyl)porphyrin with dendron bromide L4Br, showed a negligibly small spectral change upon titration with C_{60} under similar conditions, and gave no peaks corresponding to the inclusion complexes with fullerenes in an ESI−MS spectrometry.[12]

$\mathbf{3}_{\mathrm{L}n}$ serves as a fluorosensor for fullerenes in various solvents. Upon excitation of the Soret absorption band at 409 nm in toluene, $\mathbf{3}_{\mathrm{L4}}$ emitted fluorescences at 635.5 and 700 nm. On the other hand, when C_{60} was added to the solution, the fluorescences from $\mathbf{3}_{\mathrm{L4}}$ were obviously quenched. Plots of the relative fluorescence intensity (I_0/I) vs [C_{60}] showed a linear correlation, which gave a Stern−Volmer constant (K_{SV}) of 1.4×10^4 M^{-1} (Figure 2b). The K_{SV} value in CH_2Cl_2 (1.0×10^4 M^{-1}, Figure 2c) was comparable to that in toluene, while in 1,2-dichlorobenzene, a good solvent for fullerenes, the K_{SV} value was only as small as 0.3×10^4 M^{-1} (Figure 2d). Of also interest is a much higher K_{SV} value observed in THF (4.3×10^4 M^{-1}, Figure 2a), where C_{60} alone is only sparingly soluble.

Poly(benzyl ether) dendrimers are miscible with a variety of commodity polymers. When a mixture of C_{60} (14

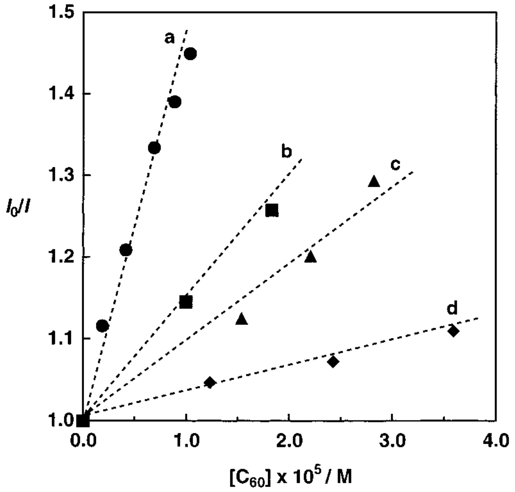


Figure 2. Stern–Volmer plots upon fluorescence titration of $\mathbf{3}_{L4}$ ($(1.2-1.5) \times 10^{-7}$ M) with C_{60} in THF (a), toluene (b), CH_2Cl_2 (c), and 1,2-dichlorobenzene (d) at 25 °C, excited at an isosbestic point in the Soret region.

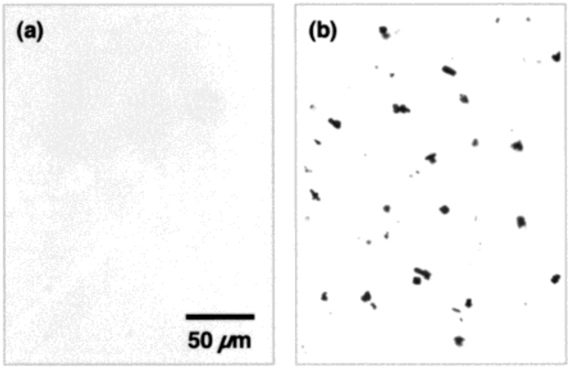


Figure 3. Optical microscope images of poly(methyl methacrylate)/C_{60} films cast from $CHCl_3$ in the presence (a) and absence of $\mathbf{3}_{L4}$ (b).

μg, 0.02 μmol) and poly(methyl methacrylate) (10 mg), in the presence of an equimolar amount of $\mathbf{3}_{L4}$ with respect to C_{60}, was cast from a $CHCl_3$ solution (145 μL), a reddish yellow, homogeneous film was obtained, in which no conglomerates of C_{60} were observed by optical microscopy (Figure 3a). In sharp contrast, without $\mathbf{3}_{L4}$ (Figure 3b) or using $\mathbf{6}_{L4}$ in place of $\mathbf{3}_{L4}$ under otherwise identical conditions to the above, formation of a heterogeneous film containing heavily aggregated C_{60} domains resulted. Therefore, $\mathbf{3}_{Ln}$ serves to solublize fullerenes into polymeric matrices where fullerenes alone are insoluble.

In conclusion, we have developed novel dendritic macromolecules ($\mathbf{3}_{Ln}$), which form highly stable supramolecular hybrids with fullerenes (Figure 1) in a well-defined fashion by virtue of the strong interaction at the focal-point cyclodimeric porphyrin cavity. The observed association constants are nearly two-order of magnitude larger than those with dendritic host molecules reported to date.[3] Application of $\mathbf{3}_{Ln}$ to the fabrication of photo- and electroactive polymeric materials of molecularly dispersed fullerenes is one of the subjects worthy of further investigation.

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Supporting Information Available: Figures showing results of absorption spectroscopic titrations and ESI–MS spectrometry. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) $\mathbf{3}_{L3}$. ^1H NMR (270 MHz, $CDCl_3$): 10.17 (s, 4H, *meso*), 9.26 (d, 8H, pyrrole-β-H), 8.94 (d, 8H, pyrrole-β-H), 8.20 (m, 8H, C_6H_4), 7.94 (d, 4H, C_6H_4), 7.75 (t, 4H, C_6H_4), 7.28 (solvent overlapped, 6H, C_6H_3), 6.80 (d, 4H, *o*-H in inner C_6H_3), 6.77 (d, 8H, *o*-H in middle C_6H_3), 6.64 (m, 22H, *p*-H in inner C_6H_3 and *p*-H in middle C_6H_3 and *o*-H in $C_6H_3(OMe)_2$), 6.45 (t, 8H, *p*-H in $C_6H_3(OMe)_2$), 5.17 (s, 4H, inner $Ar-CH_2-OAr'$), 5.09 (s, 8H, middle $Ar-CH_2-OAr'$), 5.06 (s, 16H, outer $Ar-CH_2-OAr'$), 3.82 (s, 48H, $Ar(OMe)_2$), −3.43 (s, 4H, NH). MALDI–TOF–MS: *m*/*z* calculated for M^+ ($C_{198}H_{164}N_8O_{30}$), 3135; found, 3135. UV–vis ($CHCl_3$): λ_{max} (log ϵ) 407 (5.88), 503 (4.52), 538 (3.99), 575 (4.03), 630 (3.48). $\mathbf{3}_{L4}$. ^1H NMR (270 MHz, CD_2Cl_2): 10.14 (s, 4H, *meso*), 9.25 (d, 8H, pyrrole-β-H), 8.90 (d, 8H, pyrrole-β-H), 8.19 (m, 8H, C_6H_4), 7.93 (d, 4H, C_6H_4), 7.73 (t, 4H, C_6H_4), 7.26 (d, 4H, C_6H_3), 7.17 (t, 2H, C_6H_3), 6.79 (d, 4H, *o*-H in inner C_6H_3), 6.75 (d, 8H, *o*-H in middle C_6H_3), 6.71 (d, 16H, *o*-H in middle C_6H_3), 6.66–6.55 (m, 46H, *p*-H in inner C_6H_3, *p*-H in middle C_6H_3 and *o*-H in $C_6H_3(OMe)_2$), 6.36 (t, 16H, *p*-H in $C_6H_3(OMe)_2$), 5.15 (s, 4H, inner $Ar-CH_2-OAr'$), 5.08 (s, 8H, middle $Ar-CH_2-OAr'$), 5.04 (s, 16H, middle $Ar-CH_2-OAr'$), 4.96 (s, 32H, outer $Ar-CH_2-OAr'$), 3.72 (s, 96H, $Ar(OMe)_2$), −3.55 (s, 4H, NH). MALDI–TOF–MS: *m*/*z* calcd for $[M+H]^+$ ($C_{326}H_{293}N_8O_{62}$), 5313; found, 5313. UV–vis ($CHCl_3$): λ_{max} (log ϵ) 407.5 (5.89), 504 (4.53), 538.5 (4.01), 576 (4.04), 631 (3.47).

(12) See Supporting Information.

(13) Chemical shift changes of selected ^1H NMR signals upon mixing of $\mathbf{3}_{L4}$ with C_{70} (1:1) in CD_2Cl_2 at 25 °C: δ 10.14→10.00 (meso-H), 9.25→9.16, 8.90→8.80 (pyrrole-β-H), −3.55→−3.83 (NH).

(14) ESI–MS spectrometry was carried out by a JEOL Type JMS-700T with a four-sector (BEBE) tandem mass spectrometer. Conditions: Needle volt, 2.0 kV; current, 300–700 nA; acceleration volt, 5.0 kV; resolution, 1000; chamber temperature, 250 °C; flow rate, 8 μL min^{-1}.

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