Supramolecular chemistry for the self-assembly of fullerene-rich dendrimers†‡

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Owing to their peculiar electronic properties, fullerene derivatives are attractive building blocks for dendrimer chemistry. Whereas 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 barely considered. This is mainly associated with the difficulties related to the synthesis of fullerene-rich molecules. As a part of this research, the self-assembly of fullerene-containing components using supramolecular interactions rather than covalent chemistry has recently generated significant research efforts. These results are summarized in the present account to illustrate the current state-of-the-art of fullerene chemistry for the development of new dendritic materials.

Introduction

In recent years, the rapid advances in dendrimer synthetic chemistry have moved towards the creation of functional systems with increased attention to potential applications.[1] 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, *i.e. fullerodendrimers*,[2] have generated significant research activities in recent years.[3,4] 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.[5] C_{60} itself is a convenient core for dendrimer chemistry[3] and the functionalization of C_{60} with a controlled number of dendrons dramatically improves the solubility of the fullerenes.[6] 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.[7] On the other hand, specific advantages are brought about by the encapsulation of a fullerene moiety in the middle of a dendritic structure.[8] The shielding effect resulting from the presence of the surrounding shell has been found to be useful in optimizing the optical limiting properties

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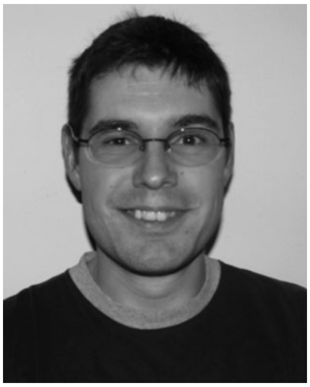

François Cardinali was born in France in 1978 and received his master in Chemical Engineering from the European School of Chemistry, Polymer Science and Materials Science (ECPM) of Strasbourg, France, in 2001. After completing his PhD under the supervision of Dr Jean-François Nierengarten in 2005, he joined the group of Nicola Armaroli at the Institute of Organic Synthesis and Photoreactivity of the Italian National Research Council (ISOF-CNR) in Bologna, Italy, working on lanthanide complexes for lighting applications.

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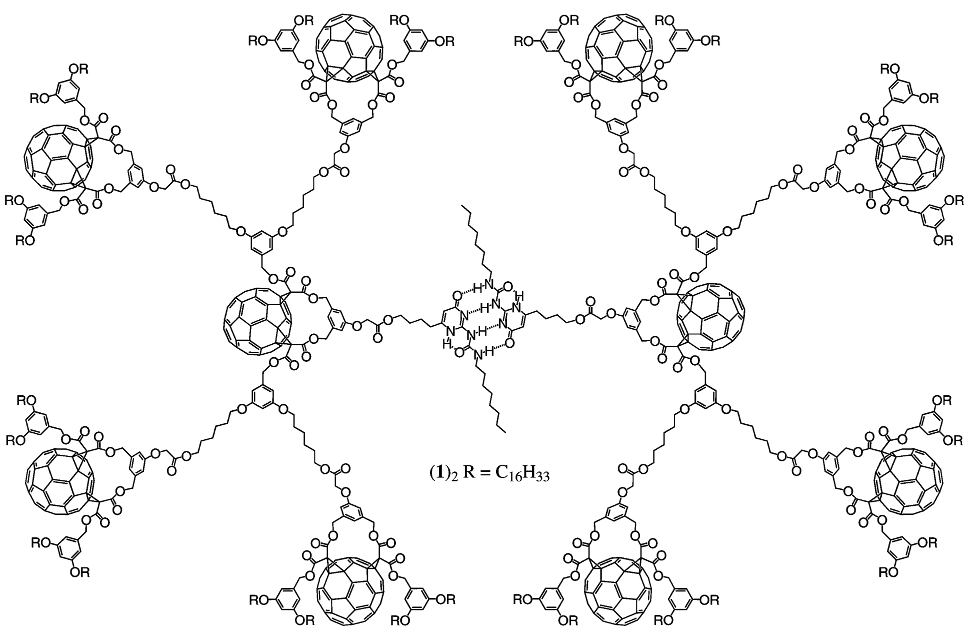


Fig. 1 Supramolecular dendrimer $(\mathbf{1})_2$ resulting from the dimerization of a fullerene-functionalized dendron by a quadruple hydrogen bonding motif.

of C_{60} derivatives,[9] in obtaining amphiphilic derivatives with good spreading characteristics,[10] or in preparing fullerene-containing liquid crystalline materials.[11] The use of the fullerene sphere as a photoactive core unit has also been reported.[12] In particular, the special photophysical properties of C_{60} have been used to evidence dendritic shielding effects[13] and to prepare dendrimer-based light-harvesting systems.[14] Whereas 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 barely considered. This is mainly associated with the difficulties related to the synthesis of fullerene-rich molecules.[4] Indeed, the two major problems for the preparation of such dendrimers are the low solubility of C_{60} and its chemical reactivity limiting 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 are interesting building blocks for the preparation of monodisperse fullerene-rich macromolecules with intriguing properties. This specific aspect of fullerene-containing dendritic systems has been summarized in a recent review article[4] and will not be discussed in the present account in which the most recent developments on the self-assembly of fullerene-rich nanostructures will be presented.

Jean-François Nierengarten was born in France in 1966. He studied Biochemistry and Chemistry at the Université Louis Pasteur of Strasbourg, France, and received his doctoral degree under the supervision of Jean-Pierre Sauvage and Christiane Dietrich-Buchecker in Strasbourg in 1994. After postdoctoral work with François Diederich at the ETH-Zürich, Switzerland, during 1994–1996, he returned to Strasbourg as a CNRS researcher. In 2005, he moved to the Laboratoire de Chimie de Coordination (LCC) in Toulouse where he is head of the Groupe de Chimie des Fullerènes et des Systèmes Conjugués. He has been awarded the bronze medal of the CNRS in 2001 and the SFC-ACROS prize from the Organic Chemistry Division of the French Chemical Society in 2004. His research interests range from covalent chemistry of fullerenes to dendrimers and π-conjugated systems with unusual electronic and optical properties.

H-Bonding for the self-assembly of fullerene-rich dendrimers

We have recently shown that the self-assembly of dendritic macromolecules using hydrogen-bonding interactions is particularly well-suited for the preparation of fullerene-rich molecules.[16] Indeed, the synthesis itself is restricted to the preparation of dendrons and self-aggregation leads to a dendritic superstructure thus avoiding tedious final synthetic steps with precursors incorporating potentially reactive functional groups such as C_{60}.[17] The supramolecular dendrimer $(\mathbf{1})_2$ thus obtained (Fig. 1) results from the dimerization of a fullerene-functionalized dendron by a quadruple hydrogen bonding motif.[16] The latter self-complementary arrays of four hydrogen bonds originally developed by Meijer *et al.*[18] leads to remarkably stable dimers with high association constants in apolar organic solvents ($K_a > 10^7\ M^{-1}$ in $CHCl_3$)[19] and is a perfect tool for the self-assembly of dendritic branches.[20]

Owing to the presence of the four hexadecyloxy substituents per peripheral fullerene subunit, compound $(\mathbf{1})_2$ is highly soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, toluene, or THF, and spectroscopic characterization has been easily achieved. Dendrimer $(\mathbf{1})_2$ has been also characterized in

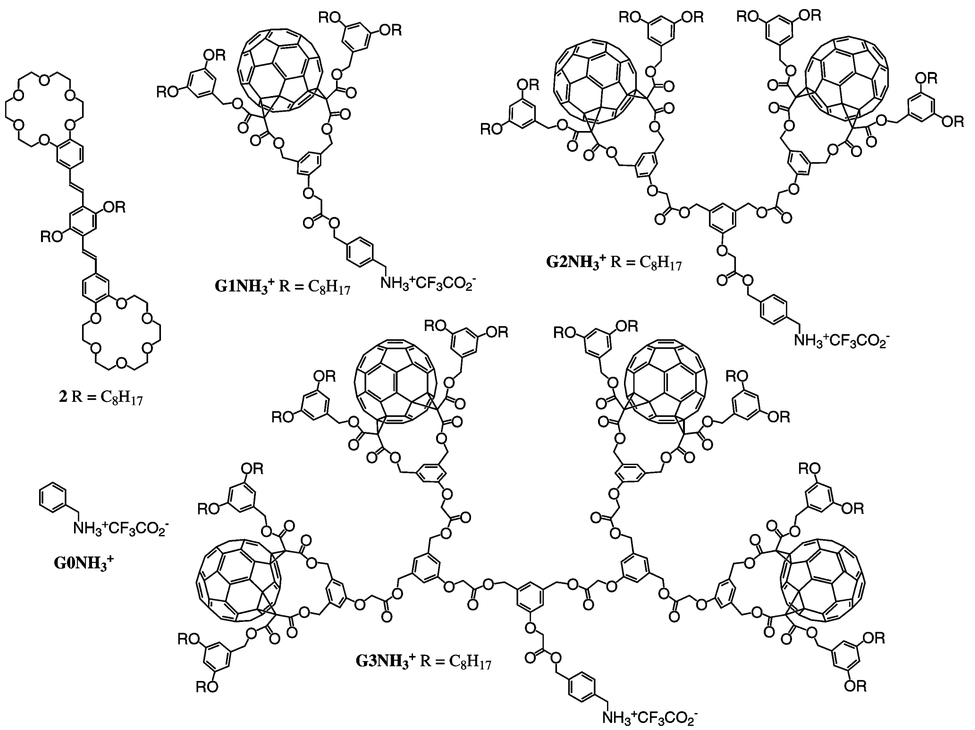


Fig. 2 Compounds **G(0–3)NH$_3$$^+$** and bis-crown ether **2**.

the gas phase by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry. The mass spectrum is characterized by two peaks corresponding to the supramolecular dimer (**1**)$_2$ at m/z = 21932 ([2M + H]$^+$, m/z = 21932.1 calculated for $C_{1494}H_{1401}N_8O_{154}$) and to the monomer at m/z = 10964 ([M + H]$^+$, calculated for $C_{747}H_{701}N_4O_{77}$: 10966.5). The spectrum of **1** is largely dominated by the ion peak corresponding to the monomeric subunit and the relative intensity of the signal attributed to the supramolecular dimer is quite low (5%). It can also be pointed out that no peaks corresponding to defective dendrons are observed in the MALDI-TOF mass spectrum of (**1**)$_2$, thus providing clear evidence for its monodispersity. Definitive evidence for the dimeric structure came from ^{1}H NMR measurements in $CDCl_3$. Importantly, large downfield shifts have been found for the protons of the hydrogen bonding motif. The signals of the urea NH have been observed at 11.86 and 10.12 ppm and the intramolecularly chelated pyrimidone NH at 13.25 ppm. This observation is fully consistent with four donor–donor–acceptor–acceptor (DDAA) hydrogen bonds in the supramolecular dendritic dimeric system.

Having shown that the construction of dendrimers containing multiple C_{60} subunits by non-covalent interactions is successful, the next challenges are to comprehensively investigate the self-assembly of such large supermolecules and to prepare fullerene-rich nanostructures with new properties. With this idea in mind, we have investigated the self-assembly of fullerene-functionalized dendritic branches **G(1–3)NH$_3$$^+$** bearing an ammonium function at the focal point on the fluorescent ditopic crown ether receptor **2** (Fig. 2).[21] The resulting 2 : 1 supramolecular complexes are multicomponent photoactive devices in which the emission of the central ditopic receptor is dramatically quenched by the peripheral fullerene units (Fig. 3).[22] This new property resulting from the association of the different molecular subunits allowed us to investigate in detail the self-assembly process.

The complexation between the fullerodendrons **G(1–3)NH$_3$$^+$** and **2** has been investigated in CH_2Cl_2 by UV/Vis and fluorescence binding studies. For comparison purposes, binding studies have been also performed with a reference unsubstituted benzylammonium guest (**G0NH$_3$$^+$**). The processing of the titration data led to the determination of two binding constants defined by equilibria (1) and (2); the binding constants deduced from the experimental data are summarized in Table 1.

$$\mathbf{2} + \mathbf{G}n\mathbf{NH_3^+} \xrightleftharpoons{K_1} [(\mathbf{2})\cdot(\mathbf{G}n\mathbf{NH_3^+})] \qquad (1)$$

$$K_1 = \frac{[(\mathbf{2})\cdot(\mathbf{G}n\mathbf{NH_3^+})]}{[(\mathbf{2})] \times [(\mathbf{G}n\mathbf{NH_3^+})]}$$

$$[(\mathbf{2})\cdot(\mathbf{G}n\mathbf{NH_3^+})] + \mathbf{G}n\mathbf{NH_3^+} \xrightleftharpoons{K_2} [(\mathbf{2})\cdot(\mathbf{G}n\mathbf{NH_3^+})_2] \qquad (2)$$

$$K_2 = \frac{[(\mathbf{2})\cdot(\mathbf{G}n\mathbf{NH_3^+})_2]}{[(\mathbf{G}n\mathbf{NH_3^+})] \times [(\mathbf{2})\cdot(\mathbf{G}n\mathbf{NH_3^+})]}$$

Several key points can be deduced from the results reported in Table 1. Interestingly, a strong stabilization of about one to two orders of magnitude is observed, when the log K_1 values are compared to those generally reported in the literature for complexes formed between crown ether derivatives and various ammonium cations.[23] The log K_1 values for the binding of fullerodendrons **G(1–3)NH$_3$$^+$** to **2** are also about one order of

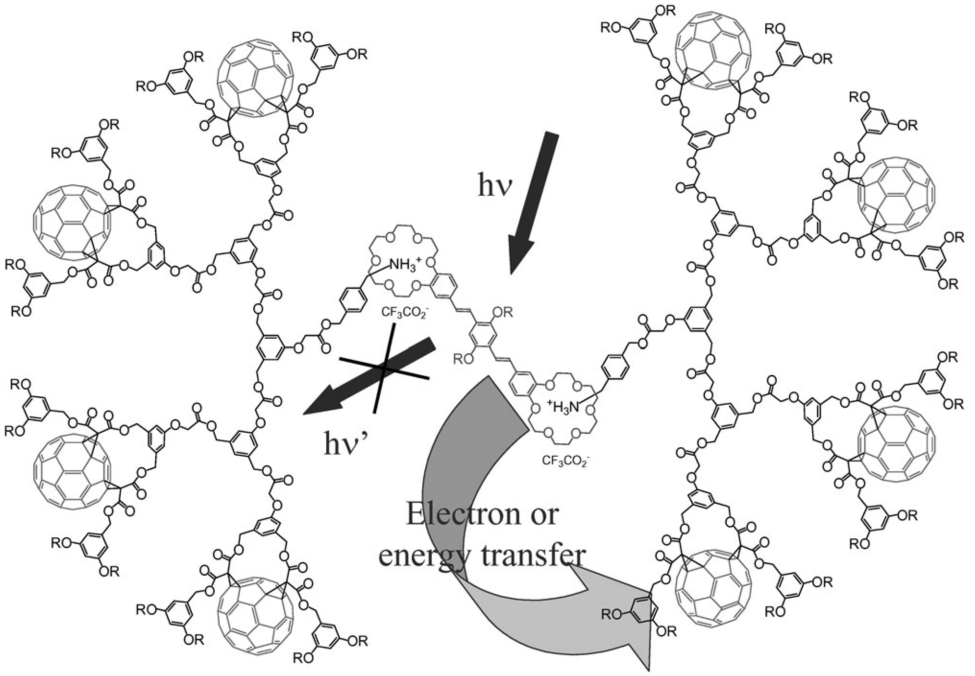


Fig. 3 Schematic representation of supramolecular complex [($\mathbf{G3NH_3^+}$)$_2$ · (**2**)]. Upon selective excitation of the ditopic receptor, its emission is dramatically quenched by the peripheral fullerene units.

magnitude higher than that of the simple benzylammonium guest $\mathbf{G0NH_3^+}$. Moreover, it is noteworthy that the log K_1 values slightly increase with the size of the branches. A sum of secondary weak intramolecular interactions such as π–π stacking and hydrophobic interactions within the supramolecular structures resulting from the association of **2** with $\mathbf{G(1–3)NH_3^+}$ must be at the origin of this stronger coordination. As far as the 2 : 1 non-covalent arrays are concerned, the K_2/K_1 ratio provides a criterion to quantify the interactions between the two identical and independent binding sites.[24a] For the binding of $\mathbf{G(1–3)NH_3^+}$ to **2**, the K_2/K_1 values summarized in Table 1 are significantly larger than 0.25 which is the value expected for a statistical model[24a] and clearly indicates positive intramolecular interactions in the 2 : 1 associates [($\mathbf{G(1–3)NH_3^+}$)$_2$ · (**2**)]. It can be added here that the averaged number of occupied sites of **2** calculated from Scatchard[24b] or Hill[24c] plots is close to 1 for $\mathbf{G0NH_3^+}$ and significantly higher than 1 for $\mathbf{G(1–3)NH_3^+}$ (**G1**: 1.59, **G2**: 1.72, and **G3**: 1.75), thus providing further evidence for the marked positive cooperative effect deduced from the binding constant analysis. The observed cooperativity may be ascribed to strong intramolecular fullerene–fullerene interactions between the two $\mathbf{G(1–3)NH_3^+}$ guests within [($\mathbf{G(1–3)NH_3^+}$)$_2$ · (**2**)]. This hypothesis is also supported by the absence of any positive interactions for the 2 : 1 complex obtained from **2** and the ammonium derivative $\mathbf{G0NH_3^+}$ lacking the fullerene subunits for which the K_2/K_1 ratio ≈ 0.08(0.12). Finally, it is also important to highlight that the K_2/K_1 ratio is significantly increased when the size of the dendritic branches is increased. In other words, the cooperative effect is more and more effective when the number of C_{60} units is increased. This positive dendritic effect further

Table 1 Stability constants determined by UV/Vis and luminescence binding studies[a]

	2		
	Log K_1	Log K_2	K_2/K_1
$\mathbf{G0NH_3^+}$	4.5(9)[b]	3.4(1.8)[b]	0.08(0.12)
	Nd[c]	Nd[c]	
$\mathbf{G1NH_3^+}$	5.6(8)[b]	6.5(2)[b]	
	5.0(1)[c]	5.6(1)[c]	4.0(1.2)
$\mathbf{G2NH_3^+}$	5.8(6)[b]	6.7(8)[b]	
	5.33(1)[c]	6.3(1)[c]	9(3)
$\mathbf{G3NH_3^+}$	Nd[b]	log β_2 = 12.6(9)[b]	
	5.28(7)[c]	6.48(7)[c]	16(4)

[a] All the measurements have been carried out in CH_2Cl_2 at 25 ± 0.2 °C. The errors correspond to standard deviations given as 3σ. Nd (not determined). [b] Determined from the UV-visible absorption titration. [c] Determined from the indirect luminescence titration.

confirms that intramolecular fullerene–fullerene interactions must be at the origin of the observed cooperative effect. These results show that the size of dendritic building blocks does not constitute a severe limitation for the self-assembly of large dendritic architectures. Furthermore, it appears that the stability of the highest generation supramolecular ensemble is increased due to the increased number of possible secondary interactions within the self-assembled structure.

Metal-directed self-assembly of fullerene-rich dendrimers

The use of metal coordination is perhaps the most highly developed method for the directed assembly of dendritic superstructures.[25] Most often, the metal center forms the core of the supramolecular dendrimer, with dendrons that have ligating groups at the focal point being coordinated around a single, central metal ion.[26] This strategy was used for the assembly of fullerene-rich dendrimers.[27] Specifically, dendrimers **(L0–3)$_2$Cu** with a bis(1,10-phenanthroline)copper(I) core and fullerene π chromophores at the periphery have been prepared by treatment of the corresponding ligands **L0–3** (1 equiv.) with $Cu(CH_3CN)_4\cdot BF_4$ (0.6 equiv.) in CH_2Cl_2–CH_3CN (2 : 1) at room temperature (Fig. 4). **(L1–3)$_2$Cu** were thus formed in good yields; however, due to difficulties encountered during their purification, the isolated yields were low [56% for **(L1)$_2$Cu**, 35% for **(L2)$_2$Cu** and 33% for **(L3)$_2$Cu**]. In contrast to model compound **L0**, the coordination of the ligands **L1–3** to the copper(I) cation could not be easily observed by apparition of the metal-to-ligand charge transfer (MLCT) band characteristic of bis(2,9-dialkyl-1,10-phenanthroline)copper(I) derivatives at *ca.* 450 nm[28] since it is masked by the fullerene absorption in this region. However, the ^{1}H-NMR spectra of **(L1–3)$_2$Cu** provide good evidence for their formation. Effectively, the methylene group directly attached to the phenanthroline core observed at *ca.* 3.2 ppm in the ligands **L1–3** is shifted to *ca.* 2.6 ppm in the corresponding complexes **(L1–3)$_2$Cu**. This particular behavior, also evidenced for model complex **(L0)$_2$Cu**, is highly specific for such copper(I) complexes[29] and is the result of the ring current effect of one phenanthroline subunit on the 2,9-substituents of the second one in the complex.

The electrochemical properties of **(L0–3)$_2$Cu** have been investigated by both steady-state voltammetry (SSV) and cyclic voltammetry (CV) in CH_2Cl_2 + 0.1 M Bu_4NPF_6 on a glassy C-electrode.[30] Compounds **(L1–3)$_2$Cu** show the characteristic behavior previously reported for fullerene bis-adducts with a *cis-2* addition pattern.[31] Whereas the first reduction, which occurs at −1.07 V *vs.* Fc/Fc^+, is reversible, the second reduction observed at *ca.* −1.4 V is irreversible. It has actually been shown that the second electron transfer in *cis-2* derivatives is followed by a chemical reaction.[31] It can also be noted that all the peripheral fullerene subunits behave as independent redox centers in all the compounds. The Cu^I/Cu^{II} oxidation potential in **(L1)$_2$Cu** remains unchanged when compared to model compound **(L0)$_2$Cu** showing that there is no particular intramolecular electronic communication between the central copper(I) complex and the four surrounding fullerene units in **(L1)$_2$Cu**. The amplitude of the fullerene-centered reduction is expected to be four times larger than that of the Cu-centered oxidation. Interestingly, however, the amplitude of the oxidation peak in **(L1)$_2$Cu** is smaller than expected. This suggests that the bulky fullerene units around the Cu center partially prevent its approach to the electrode surface and, as a result, the oxidation of the central core is slow.[32] Consistent with this, the electrochemical oxidation of the Cu site could no longer be observed in dendrimers of the highest generations **(L2)$_2$Cu** and **(L3)$_2$Cu** under the same experimental conditions. The central electroactive site appears to be totally inaccessible since it is isolated by the bulkier surrounding dendritic structures.

In good agreement with the electrochemical data, the absorption spectra of all the dendrimers **(L1–3)$_2$Cu** coincide with the sum of the corresponding component units, showing no appreciable ground state electronic interactions among them. The increasing number of fullerene units around the Cu(I)-complexed core implies a more and more extended shielding of the central core from the incident light, especially in the ultraviolet spectral region. With regard to this, it is worth noting that the molar extinction coefficient of **(L3)$_2$Cu** at 258 nm almost reaches a respectable value of 1.5×10^6 M^{-1} cm^{-1}, probably one of the highest ever found for soluble supermolecules, thus allowing a limit of detection below 1 ppm in CH_2Cl_2 solution. Upon selective excitation of the peripheral units at 600 nm, fullerene fluorescence is observed for all dendrimers **(L1–3)$_2$Cu**; the corresponding emission quantum yields and excited state lifetimes are identical, within experimental error, to those of the corresponding dendritic subunits. Despite the fact that selective excitation of the $[Cu(phen)_2]^+$-type central core is not possible, clear evidence of the luminescence quenching of such a moiety has been obtained. For instance by exciting **(L1)$_2$Cu** at 456 nm, although the light partition is about 34% (core) and 66% (fullerenes), the MLCT emission of the central core is dramatically quenched. Analogous patterns are shown by **(L2–3)$_2$Cu**, although the light partition is less favorable for the central core because of the above mentioned shielding effect. In order to rationalize the observed photophysics of the dendrimers an energy level diagram reporting all the low-lying electronic levels can be drawn (Fig. 5), *i.e.* the lowest singlet ($^1C_{60}$) and triplet ($^3C_{60}$) centered on the peripheral fullerene fragments and the lowest MLCT excited state of the Cu(I)-complexed central core (^{MLCT}Cu). The energy values were obtained from corrected luminescence band maxima at 77 K or, when not available as in the case of $^3C_{60}$, from theoretical calculations. It is noteworthy that a new low-energy electronic level is made available in the supramolecular array, namely the charge separated state Cu^+–C_{60}^- located at 1.68 eV, as deduced from the electrochemical data. In principle, the quenching of the MLCT excited state (positioned at 1.85 eV) can occur *via* two pathways: (i) energy transfer to the fullerene centered singlet $^1C_{60}$ (ΔG = −0.10 eV) or to the fullerene centered triplet $^3C_{60}$ (ΔG = −0.45 eV); (ii) electron transfer to the charge separated state (ΔG = −0.17 eV). It is believed that electron transfer [process (ii)] is not the prevailing phenomenon for at least two reasons: (a) it does not take place from $^1C_{60}$ (no quenching of the fluorescence of the fullerene moiety is observed), although a similar thermodynamic driving force (ΔG = −0.07 eV) would be involved; (b) the quenching of the central core occurs

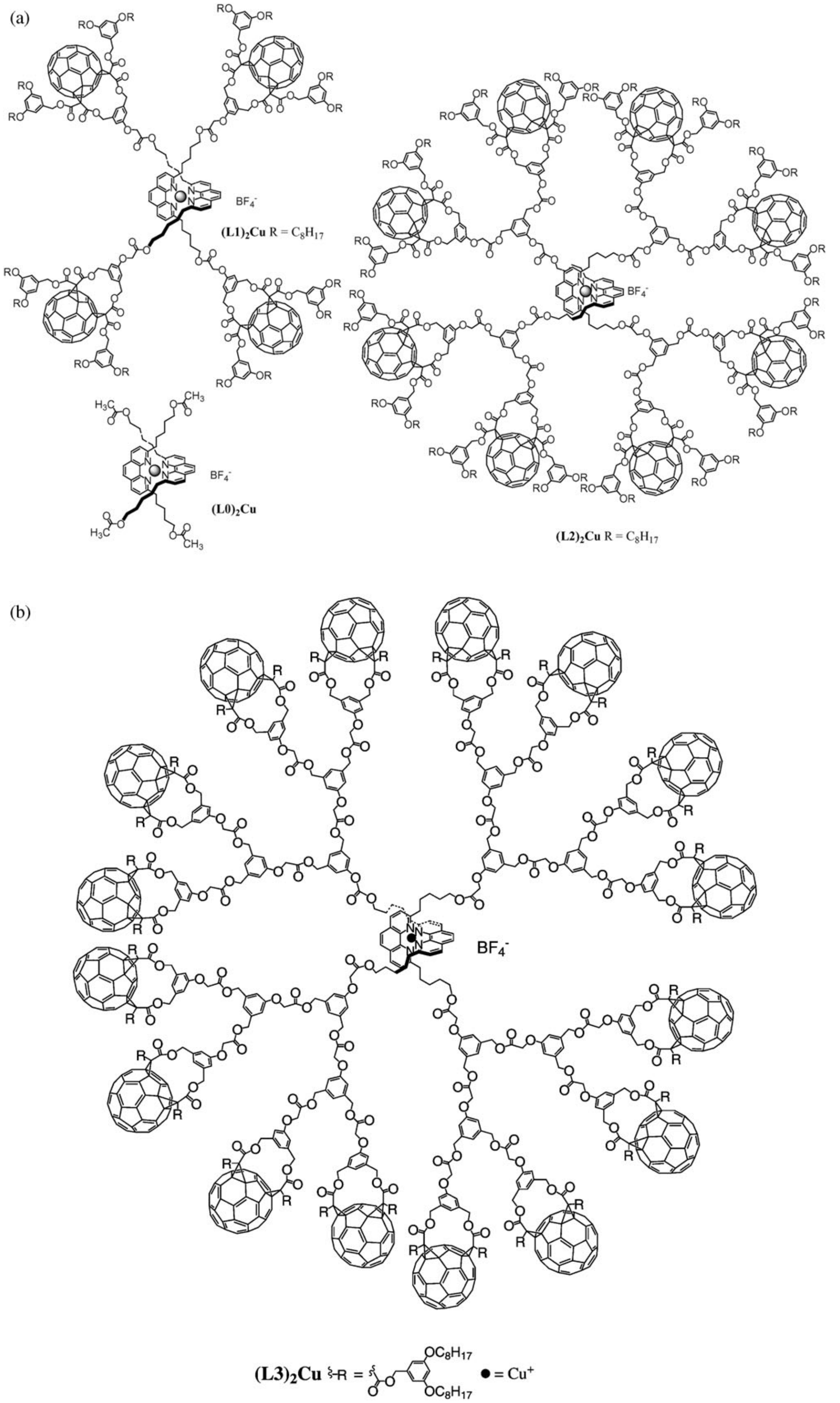


Fig. 4 (a) Model compound **$(L0)_2Cu$** and metallodendrimers **$(L1)_2Cu$** and **$(L2)_2Cu$**. (b) Metallodendrimer **$(L3)_2Cu$**.

also at 77 K, but electron-transfer in a rigid matrix is usually blocked if not exothermic by at least 0.6–0.7 eV (in this case $\Delta G = -0.17$ eV, Fig. 5).

From the electronic properties of **$(L0–3)_2Cu$**, one can conclude that the Cu(I) central core is buried in a *dendritic black box*. For the two largest fullerodendrimers, the central

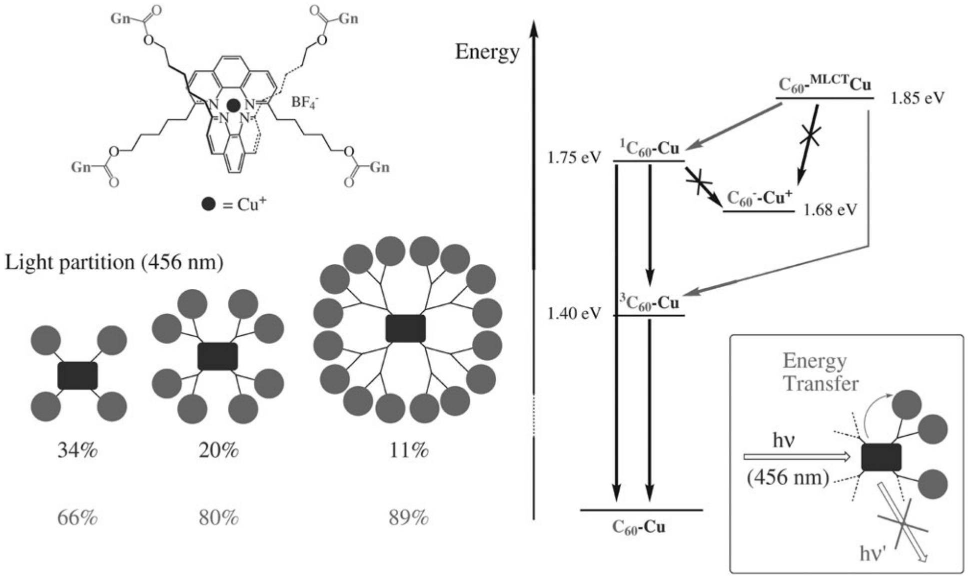
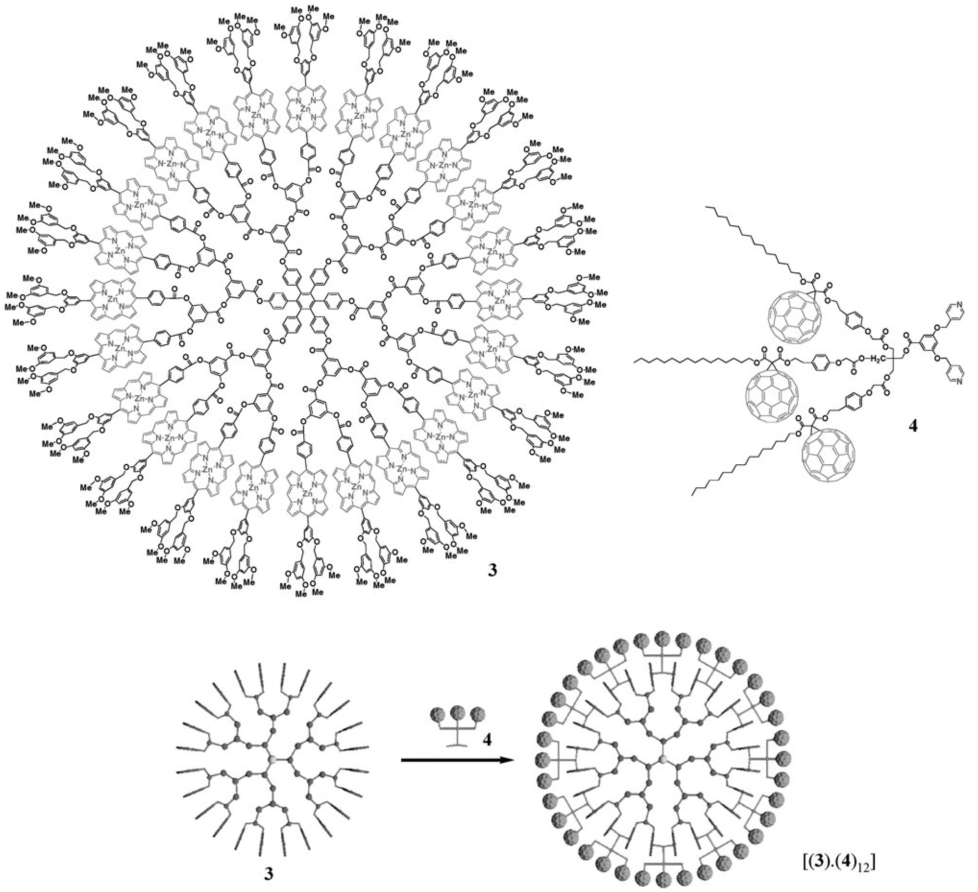


Fig. 5 Energy-level diagram describing the excited state deactivation pathways and the intercomponent energy transfer processes in dendrimers **(L1–3)$_2$Cu**, in CH$_2$Cl$_2$ solution. The light partition upon excitation at 456 nm reveals that the increasing number of fullerene units around the Cu(I)-complex implies a more and more extended shielding of the central core from the incident light.

copper(I) core appears inaccessible to external contacts as shown by the electrochemical investigations. Furthermore, due to the increasing number of surrounding fullerene subunits in **(L1)$_2$Cu** to **(L3)$_2$Cu**, there is less and less light available for the core and the small portion of light energy able to excite the central Cu(I) complex is returned to the external fullerenes by energy transfer.

Aida and co-workers have reported the preparation of fullerene-rich dendritic structures resulting from the apical coordination of C$_{60}$ derivatives bearing pyridyl moieties to



3

4

3

4

[(3).(4)$_{12}$]

Fig. 6 Compounds **3** and **4** and schematic representation of the self-assembly process leading to the fullerene-rich dendrimer [(**3**) · (**4**)$_{12}$].

dendritic molecules appended with multiple Zn(II) porphyrin units.[33] For example, compound **3** bound **4** strongly to form stable [(**3**)·(**4**)$_{12}$] (Fig. 6). Upon titration with **4** in $CHCl_3$ at 25 °C, **3** displayed a large spectral change in the Soret and Q-bands, characteristic of the axial coordination of zinc porphyrins, with a clear saturation profile at a molar ratio **4** : **3** exceeding 12 : 1. The average binding affinity (*K*), as estimated by simply assuming a one-to-one coordination between the individual zinc porphyrin and pyridine units, is $1.2 \times 10^6\ M^{-1}$. This value is more than 2 orders of magnitude greater than association constants reported for monodentate coordination between zinc porphyrins and pyridine derivatives.[34] The sizeable increase of stability can be ascribed to the simultaneous coordination of two Zn centers of **3** by the two pyridine moieties of **4**. Similar increases in association constants have been reported for supramolecular systems resulting from the axial coordination of a bis-Zn(II) porphyrinic receptor to substrates bearing two pyridine subunits.[35]

Supramolecular assembly [(**3**)·(**4**)$_{12}$] combining C_{60} units and porphyrin moieties[36] is also a photochemical molecular device. Indeed, the photophysical properties of this system have been studied in detail and an almost quantitative intramolecular photoinduced electron transfer from the photoexcited porphyrins to the C_{60} units has been evidenced by means of steady-state emission spectroscopy and nanosecond flash photolysis measurements. Excited-state dynamic studies have been carried out to investigate both charge-separation and charge-recombination events in [(**3**)·(**4**)$_{12}$]. The charge-separation rate constants (k_{CS}) and the charge-recombination rate constants (k_{CR}) have been thus deduced. Importantly, the k_{CS}/k_{CR} ratio for [(**3**)·(**4**)$_{12}$] is more than an order of magnitude greater than those reported for precedent

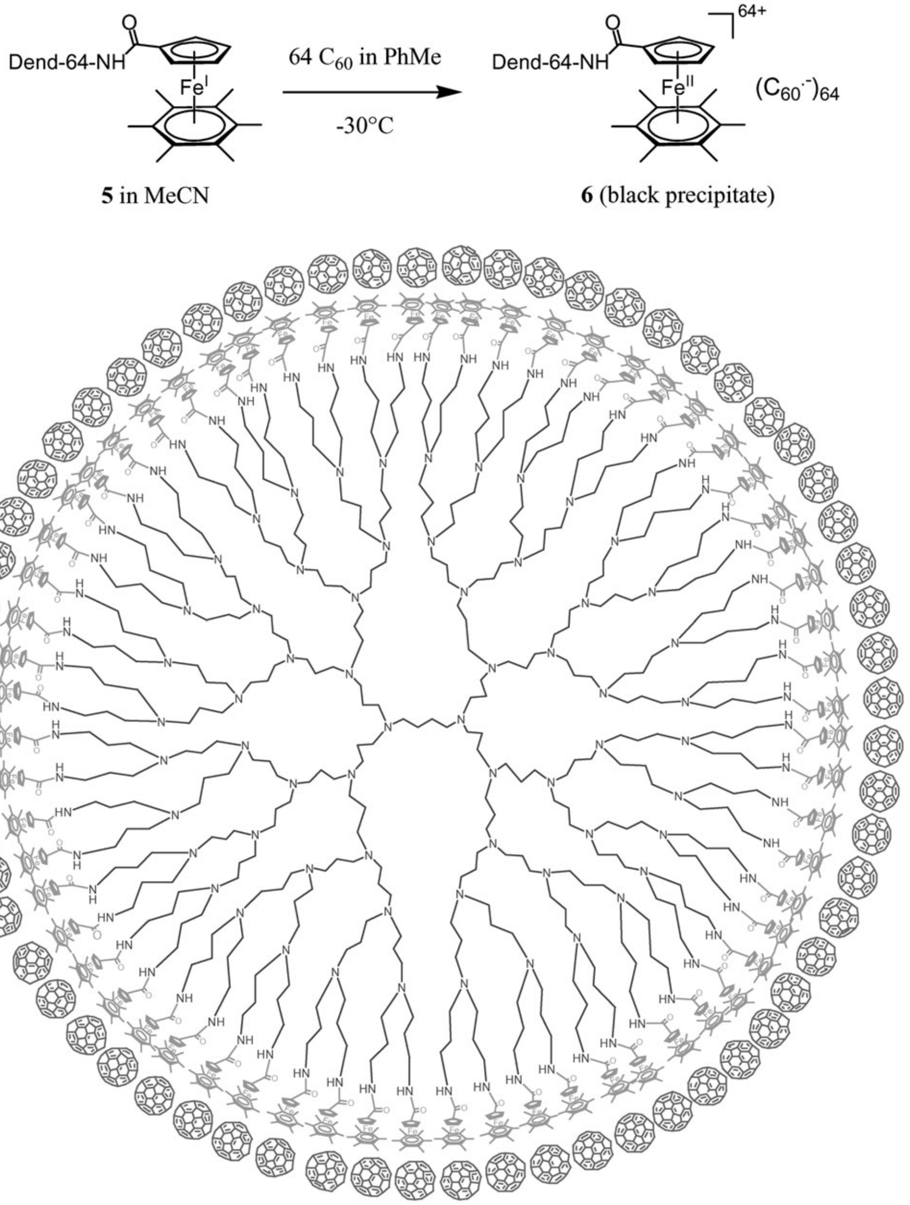


Fig. 7 Dendrimer **6** resulting from the reaction of **5** (1 equiv.) with C_{60} (64 equiv.) in MeCN–C_6H_5Me at −30 °C.

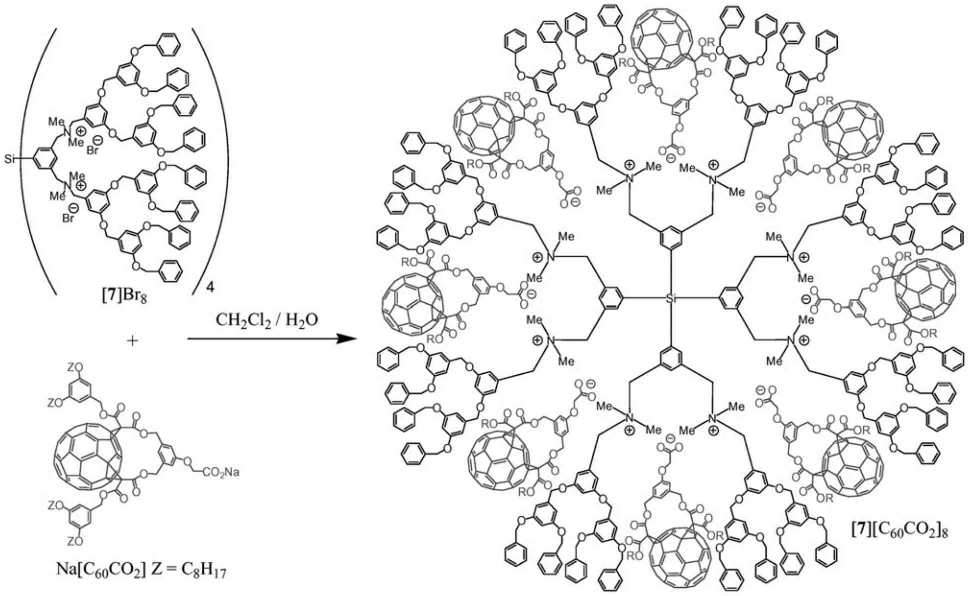


Fig. 8 Anion exchange reaction of **[7]**Br$_8$ with Na**[8]** leading to the fullerene-rich dendrimer **[7][8]**$_8$.

porphyrin–fullerene supramolecular dyads and triads.[37] It is obvious that a larger number of the fullerene units in [(**3**)·(**4**)$_{12}$] can enhance the probability of electron transfer from the zinc porphyrin units. However, in addition to this, one can also presume that an efficient energy migration along the densely packed Zn(II) porphyrin array[38] may enhance the opportunity for this electron transfer.

Ionic interactions for the self-assembly of fullerene-rich dendrimers

C$_{60}$ itself and simple fullerene derivatives have also been assembled on dendritic templates by using purely electrostatic interactions. For example, Astruc and co-workers have taken advantage of the electrochemical properties of C$_{60}$ to assemble a fullerene-rich supramolecular dendritic structure.[39] When a toluene solution of C$_{60}$ (64 equiv.) was added to an acetonitrile solution of the 64-Fe(I) dendrimer **5** (1 equiv.), a black precipitate of **6** was obtained (Fig. 7). Tentative extraction of this precipitate with toluene yielded a colorless solution, thus indicating that no C$_{60}$ was present. The Mössbauer spectrum of this black solid **6** is a clean quadrupole doublet whose parameters at 77 K are consistent with the presence of an Fe(II) sandwich complex. Its EPR spectrum recorded at 298 K shows the characteristic feature observed for a model compound obtained from the reaction of C$_{60}$ with the 19-electron complex [Fe(I)Cp(η^6-C$_6$Me$_6$)].[40] It can thus be concluded that C$_{60}$ has been reduced to its monoanion, as designed for a process that is exergonic by 0.9 eV. The peripheral cationic Fe(II) units with their C$_{60}{}^-$ counteranion being very large, are most likely located at the dendrimer periphery, presumably with rather tight ion pairs although the number of fullerene layers and overall molecular size are unknown.

Another system based on electrostatic interactions has been reported by van Koten and co-workers.[41] A core–shell dendrimer with a cationic tetrakis[bis(benzylammonium)aryl] silane core has been used as a template for the assembly of fullerene–carboxylate derivatives *via* a straightforward anion exchange reaction of **[7]**Br$_8$ with Na**[8]** (Fig. 8).[42] In contrast to dendrimer **6**, the supramolecular fullerene-rich assembly **[7][8]**$_8$ thus prepared is soluble in common organic solvents and its spectroscopic characterization could be easily achieved. In the ^{1}H NMR spectrum of a solution of **[7][8]**$_8$ in CDCl$_3$, the diagnostic signals of both **[7]**$^{8+}$ and **[8]**$^-$ can clearly be observed. Furthermore, specific peak integrals show that the octa-cationic dendritic moiety **[7]**$^{8+}$ and the anions **[8]**$^-$ are present in a 1 to 8 molar ratio.

The UV-absorption spectrum of a solution of **[7][8]**$_8$ in CH$_2$Cl$_2$ shows characteristic absorption features which can be ascribed to the fullerene units as well as a band diagnostic for the cationic dendrimer. Actually, the UV-absorption spectrum of **[7][8]**$_8$ matches the spectral profile of a 1 to 8 molar mixture of authentic **[7]**Br$_8$ and the *tert*-butyl ester, **8**–^{t}Bu of the **[8]**$^-$ anion, which is unable to self-assemble. The similarity of these spectra indicates that there are no significant ground state interactions between the respective chromophores in the supramolecular complex **[7][8]**$_8$. The luminescence properties of solutions of **[7][8]**$_8$ in CH$_2$Cl$_2$ were also investigated and compared to the behavior of an isoabsorbing model mixture of authentic **[7]**Br$_8$ and **8**–^{t}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 **[7]**$^{8+}$, the characteristic emission of the polybenzyl aryl ether dendritic wedges is observed. In contrast, complete quenching of this emission of **[7]**$^{8+}$ is observed in **[7][8]**$_8$, 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 **[7]**$^{8+}$ and **[8]**$^-$. 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 one corresponds to a mass of 21 780 g mol^{-1} (M_w/M_n = 1.27), which was identified as the 1 : 8 host–guest octa-fullerodendrimer assembly **[7][8]**$_8$ (calculated M_w: 20 960.05 g mol^{-1}). The molecular weights associated with the two additional peaks are higher: 38 670 (M_w/M_n = 1.04) and 94 070 g mol^{-1} (M_w/M_n = 1.02), respectively. These fractions are attributed to superstructures consisting of aggregated assemblies derived from **[7][8]**$_8$. Such a 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 **[7][8]**$_8$ were detected, which further substantiates the formation of a stoichiometric assembly between octa-cationic **[7]**$^{8+}$ and eight **[8]**$^-$ anions.

Conclusions and outlook

The preparation of covalent fullerene-rich dendrimers is difficult and involves a high number of synthetic steps thus limiting their accessibility and therefore their applications.[4] The recent results on the self-assembly of fullerene-containing components by using supramolecular interactions rather than covalent bonds clearly demonstrate that this strategy is an attractive alternative for their preparation. Indeed, fullerene-rich derivatives are thus easier to produce and the range of systems that can be prepared is not severely limited by the synthetic route. In this way, in-depth investigations of their properties are possible and one can really start to envisage the use of fullerene-rich materials for specific applications. Despite some remarkable recent achievements, it is clear that the examples discussed herein represent only the first steps towards the design of fullerene-rich molecular assemblies which can display functionality at the macroscopic level. More research in this area is clearly needed to fully explore the possibilities offered by these materials, for example, in nanotechnology or in photovoltaics.

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