Syntheses and Phase-Transfer Properties of Dendritic Nanocarriers That Contain Perfluorinated Shell Structures

Abel Garcia-Bernabé,[a] Michael Krämer,[b] Bèla Olàh,[b] and Rainer Haag*[a]

Abstract: Perfect dendrimers that contain perfluorinated shells have recently attracted attention because they have been shown to encapsulate polar molecules in supercritical CO_2 and catalytically active metal nanoparticles in perfluorinated solvents. Moreover, they can then be easily separated after reaction from the biphasic organic/fluorous system. In this paper several dendritic architectures that contain perfluorinated shells were derived by covalent modification of glycerol dendrimers ([G0.5]–[G3.5]), hyperbranched polyglycerol, and polyethyleneimine. These core-shell architectures show interesting physicochemical properties. For example, they are soluble in fluorinated solvents, they are able to transport different guest molecules, and they display thermomorphic behavior. The transport capacity of these molecular nanocarriers increases significantly when amino groups are present in the core. Certain functionalized polyethyleneimines that contain perfluorinated shells show high transport capacities (up to 3 dye molecules per nanocarrier) in perfluorinated solvents. Moreover, these perfluoro-functionalized dendritic polyethyleneimines can act as templates that stabilize nanoparticles; for example, encapsulation and subsequent chemical reduction of Ag^I ions. Silver nanoparticles with a narrow size distribution (3.9 ± 1 nm) have been prepared and characterized by transmission electron microscopy. Furthermore, it has been demonstrated that the encapsulated guest molecules remain accessible to small molecules after transport into the fluorous phase. Therefore, dendritic nanocarriers that contain perfluorinated shells are currently being investigated as polar environments in nonpolar reaction media such as fluorous phases and supercritical CO_2, in particular, for application in homogenous catalysis.

Keywords: dendrimers · fluorous biphasic catalysis · host–guest systems · hyperbranched polymers · supramolecular chemistry

Introduction

In this paper we describe simple and efficient approaches to dendritic core-shell architectures that contain covalently linked perfluorinated shells. These molecular nanocarriers provide polar environments in nonpolar reaction media, and some candidates show interesting phase-transfer behavior with respect to polar molecules in the fluorous phase.

Dendritic core-shell architectures have attracted increased interest because of their ability to act as unimolecular nanocarriers for catalysts, drugs, and other guest molecules.[1,2] More recently, such nanostructures have also been used to generate polar environments within alternative reaction media such as fluorous phases and supercritical carbon dioxide ($scCO_2$). The advantage of these alternative reaction media is the simple workup, which allows products to be easily recovered and catalysts to be recycled.[3] As a result of their chemical inertness, perfluorinated compounds are also considered to be environmentally friendly.

Fréchet and DeSimone reported the first example of a molecular nanocarrier based on a perfect polyamine dendrimer with a covalently bonded perfluorinated shell.[4] More recently, Crooks et al. prepared dendrimer-encapsulated metal nanoparticles in the fluorous phase by electrostatic attachment of perfluorocarboxylic groups to a poly(amidoamine) (PAMAM) dendrimer.[5] In both cases, the defined core-shell architecture and a pronounced polarity gradient of the dendrimer seem to play an important role in their solubility and transport behavior. Many examples of dendrimer-encapsulated guest molecules have been reported,[2] some of which have been metal nanoparticles (e.g. Cu, Pt, Ag, Au, and Pd), and in some cases, their applications towards homogenous catalysis has been demonstrated.[6] These nanoparticles can be prepared by chemical reduction of the corresponding encapsulated metallic cations. For example, a poly(amidoamine) (PAMAM) dendrimer with an ionically

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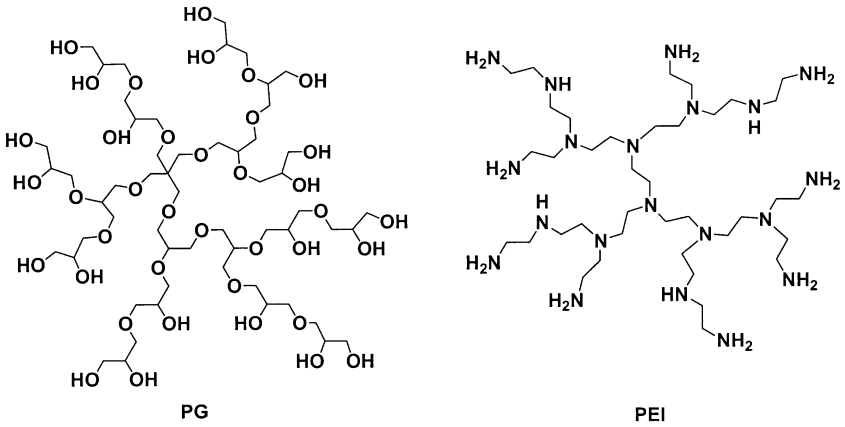
bonded fluorous shell was used to stabilize Pd nanoparticles in the fluorous phase, and this was then applied in C–C bond forming reactions.[5] However, in some cases (i.e. in polar solvents) these electrostatic complexes can be unstable. Therefore, our approach was based on preparing covalently linked perfluorinated shells that give rise to an easily accessible and highly branched polymer scaffold.

The dendrimer topology allows a clear differentiation between the interior branching scaffold (the core) and the end groups in the periphery (the shell). For many applications the difficult accessibility of dendrimers through costly multistep syntheses represents a major problem.[7] Hyperbranched polymers that can be obtained in one reaction step from the polymerization of AB_m or latent AB_m monomers are currently being considered as possible alternatives.[8] In contrast to the perfectly branched glycerol dendrimers (degree of branching $(DB) = 100\,\%$),[9] hyperbranched polyglycerol (PG)[10] and hyperbranched polyethyleneimine (PEI)[8a,11] (Scheme 1) are randomly branched,



Scheme 1. Hyperbranched polyglycerol (PG) and polyethyleneimine (PEI). The depicted structures contain 25–40 % linear functional groups and 30–40 % terminal groups, and represent only small idealized fragments of the large polymer cores.

but still have well-defined dendritic structures with a *DB* of 60 to 75 %. They are prepared in a one-step process, are readily available on a large scale, and have relatively low polydispersities (≤ 2).[8a,11,12] Upon selective functionalization of these hyperbranched polymers special environments are created in the core of these dendritic architectures.[13] These can then act as molecular nanocarriers[14] to encapsulate and transport polar guests (e.g. drugs, dyes, metal salts).

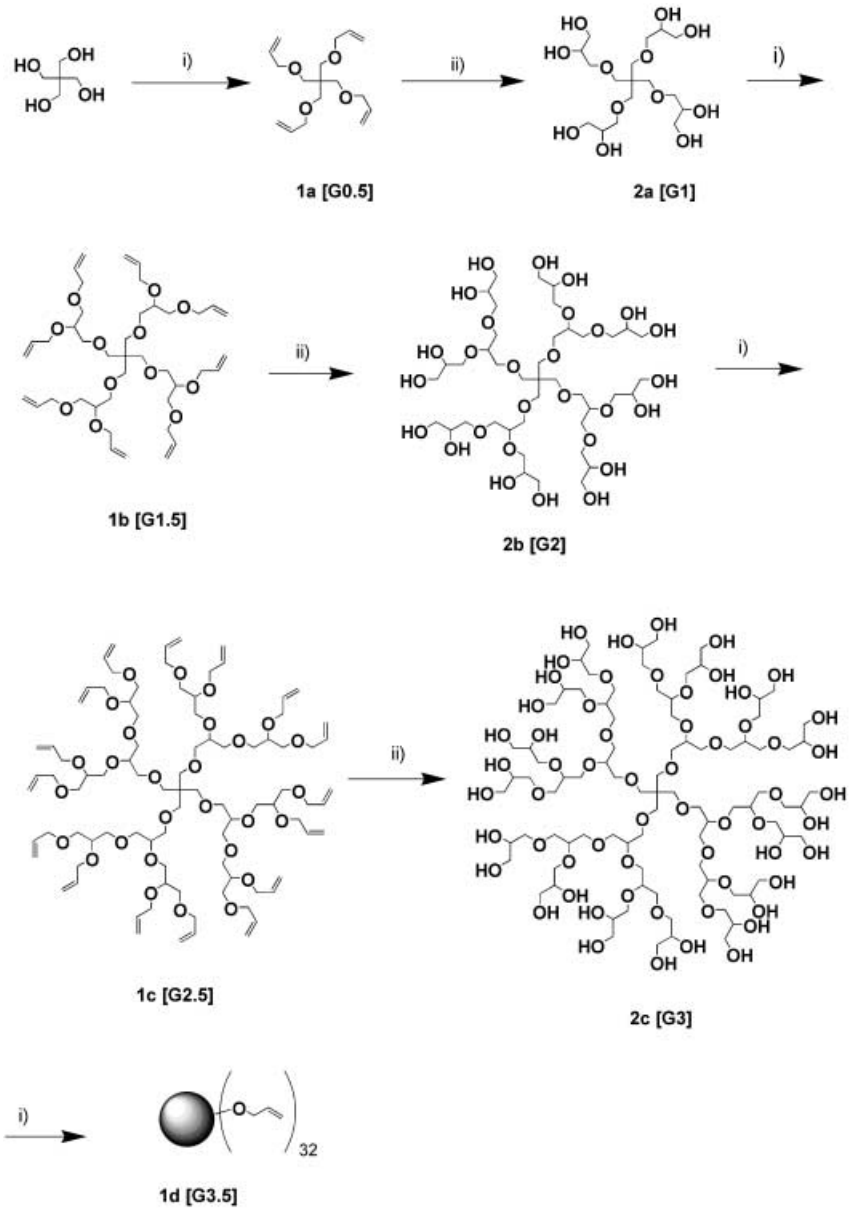
Here we describe an efficient approach to access novel dendritic architectures that contain perfluorinated shells through covalent modification of perfect glycerol dendrimers, hyperbranched polyglycerol (PG), and hyperbranched polyethyleneimine (PEI). These core-shell architectures that contain perfluorinated shells are soluble in several fluorous solvents and can transport ions, polar guest molecules, and metal nanoparticles. In addition, some of these molecular nanocarriers have been applied in phase-transfer reactions, for example, between aqueous and fluorous phases.

Results and Discussion

Synthesis of glycerol dendrimers: To generate the molecular nanocarriers **3a–d**, three generations of the four-armed glycerol dendrimers **2a–c**, which give rise to a more dense central core architecture, were prepared. For this purpose, a reaction sequence similar to the one we recently developed for three-armed glycerol dendrimers and pseudo-dendrimers was utilized (Scheme 2).[9] The synthesis is based on a simple iterative two-step protocol that involves allylation of an alcohol and subsequent catalytic dihydroxylation of the allylic double bond. Under phase-transfer conditions, the allylation reproducibly affords high yields of the product even when polyols are employed.[15] Catalytic dihydroxylation of the double bond with osmium tetroxide and *N*-methyl morpholine-*N*-oxide (NMO) as co-oxidant[16] completes the sequence and leads to the formation of new glycerol units on every available alcohol functionality (Scheme 2). As previously reported for a three-armed trimethylolpropane core, both transformations can be carried out in aqueous phase and are suitable for a wide range of core molecules.[9] The use of a four-armed core molecule gave rise to high conversions (> 90 %) but lower isolated yields (60–80 % per sequence) of the glycerol dendrimers **2a–c**. This might be the result of steric crowding and cross-linking of the allylated intermediates **1a–d**.

Dendritic polyglycerols that contain perfluorinated shells: Four glycerol dendrimers with perfluorinated shells **3a–d** were obtained by free-radical addition of tridecafluorooctane-1-thiol to the perallylated intermediates **1a–d**; this afforded the thioether linkages with high conversions (> 95 %, Scheme 3). Also, various other hyperbranched polyglycerols ($DB \approx 60\,\%$)[10] of different molecular weights were functionalized with a perfluorinated shell (**5a–d**) using the same synthetic strategy, but the sequence began with the perallylated hyperbranched polyglycerols **4a–d**.[9] The degree of functionalization in these cases was 83–94 %.[17] All the dendritic polyglycerols[18] with perfluorinated shells (**3b–d, 5a–d**), apart from [G0.5] (**3a**), are soluble in perfluorinated solvents such as perfluorobenzene, perfluorohexane (FC-72), and perfluoro-2-butyltetrahydrofuran (FC-75), as well as in partially fluorinated solvents such as trifluorotoluene (Table 1). However, good solubility at room temperature was only observed in perfluorobenzene, trifluorotoluene, and FC-72.

Unexpectedly, the transport capacity of the dendritic polyglycerols **3** and **5** was very poor, and seemed to be independent of the core size (see below, Table 2). Only dendritic



Scheme 2. Synthesis of perfect glycerol dendrimers up to generation 3.5 using a four-arm core. The first step involves allylation of the OH groups with allyl chloride (**1a–d:** G0.5, G1.5, G2.5, G3.5) under phase-transfer conditions followed by dihydroxylation of the double bonds with catalytic amounts of OsO_4 and NMO as co-oxidant (**2a–c:** G1, G2, G3): i) Bu_4NBr, NaOH, allyl chloride, toluene/water, 24 h, 50 °C; ii) OsO_4 (cat.), NMO, acetone/water/*tert*-butanol, 20 h, 25 °C.

polyglycerol **5d**, which contains an amine group in the core,[10b] was able to transport polar guest molecules, but its transport capacity was still low in comparison to alkyl-modified hyperbranched polyglycerols.[13a,g]

Dendritic polyethyleneimines that contain perfluorinated shells: As it appeared that amine groups in the dendritic structure increased the transport capacity of the resulting dendrimer, we synthesized three dendritic architectures based on hyperbranched polyamine core structures that contain perfluorinated shells (**6**, **7**, and **9**, Scheme 4). Hyperbranched polyethyleneimines (PEI, Scheme 1) are commercially available polymers with a *DB* in the range of 65 to 75 %.[11] To generate a dendritic polyamine with perfluorinated shells, PEI was modified by alkylation (**6**) and amidation (**7**), as well as by amidation and subsequent thiol addition approach (**9**). The reaction conditions for these transformations were problematic because of the extreme polarity difference between the polar PEI core and the perfluorinated reactant. As a result, the solvent had to be carefully chosen or omitted. Alkylation of PEI with heptadecafluoro-10-iododecane to give the amphiphilic polyamine **6** was performed in acetonitrile under reflux for 15 h using potassium carbonate as base (Scheme 4). Unfortunately, even though an excess of the alkylating agent was used, conversion of the available amino groups was only 29 % (according to elemental analysis). Amidation of PEI to give the polyamide **7** was performed in bulk at 140 °C using heptadecafluoroundecanoic acid and a nitrogen stream to remove the water formed during the reaction (Scheme 3). In this case, according to elemental analysis, conversion was about 56 %. To generate the amphiphilic molecular nanocarriers **9**, PEI first underwent amidation with 10-undecenoic acid to give the polyalkenyl derivative **8** with a conversion of 67 % (according to ^{1}H NMR spectroscopy). Subsequently, to elongate the alkyl chains and obtain a less pronounced polarity gradient, the terminal double bonds of the intermediate **8** were reacted with a tridecafluorooctane-1-thiol reagent using the same protocol as described for **3** and **5** (Scheme 4). In this case, as observed by ^{1}H NMR spectroscopy, conversion of the double bonds into thioethers was quantitative.

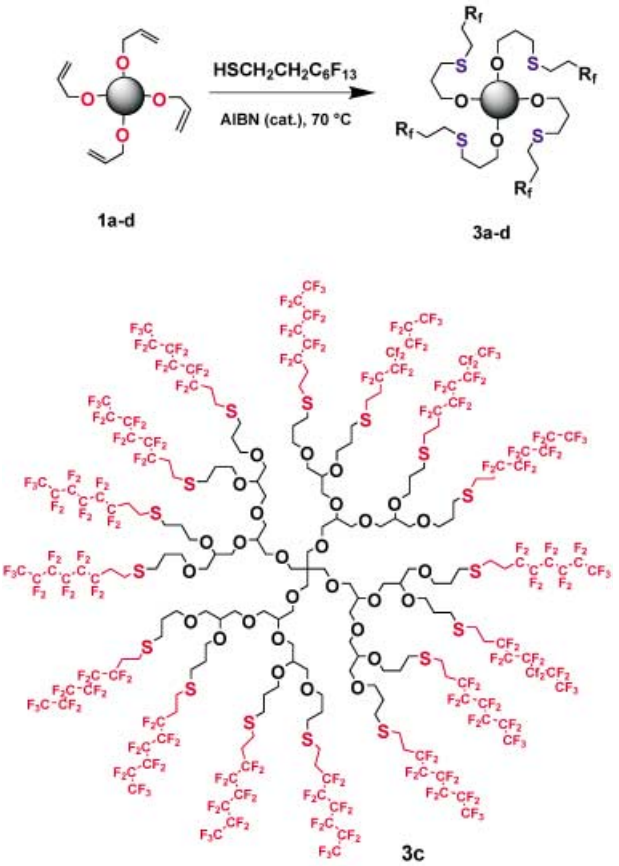
All the dendritic architectures that contained perfluorinated shells were subsequently evaluated for their solubility in perfluorinated solvents, phase-transfer behavior, and thermal properties.

Solubility and thermomorphic behavior: The solubility of dendritic architectures is highly dependent on the structural features of the shell. For many applications, partial (40–

Table 1. Degree of functionalization and solubility of dendritic architectures that contain perfluorinated shells.[a]

Sample	Generation [M_n]	Degree of functionalization [%]	Shell structure	Trifluorotoluene	Perfluorobenzene	FC-72	FC-75	$CHCl_3$
3a	G0.5	>98	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	40 °C	X	n.s.	n.s.	X
3b	G1.5	>98	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	X	X	rflx	X	rflx
3c	G2.5	>98	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	X	X	rflx	rflx	rflx
3d	G3.5	>98	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	X	X	X	rflx	rflx
5a	2000	92[b]	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	X	X	X	rflx	n.s.
5b	5000	85[b]	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	X	X	X	rflx	rflx
5c	15000	83[b]	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	X	X	X	rflx	rflx
5d	4500[c]	94[b]	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	X	X	n.s.	rflx	rflx
6	4500	29[d]	$(CH_2)_2(CF_2)_7CF_3$	X	n.s.	n.s.	n.s.	n.s.
7	4500	56[d]	$CO(CH_2)_2(CF_2)_7CF_3$	X	X	rflx	43 °C	n.s.
9	4500	67[b]	$CO(CH_2)_{10}S(CH_2)_2(CF_2)_7CF_3$	X	X	n.s.	65 °C	X

[a] X = soluble at 20 °C, rflx = soluble at reflux, n.s. = not soluble. [b] From ^1H NMR measurements. [c] PG-core contains a stearylamine starter. [d] By elemental analysis.



Scheme 3. Synthesis of glycerol dendrimers with perfluorinated shells **3a–d**. The double bonds of the allyl ether dendrimers **1a–d** were functionalized with perfluorinated alkenethiols (e.g. [G2.5] dendrimer **3c**).

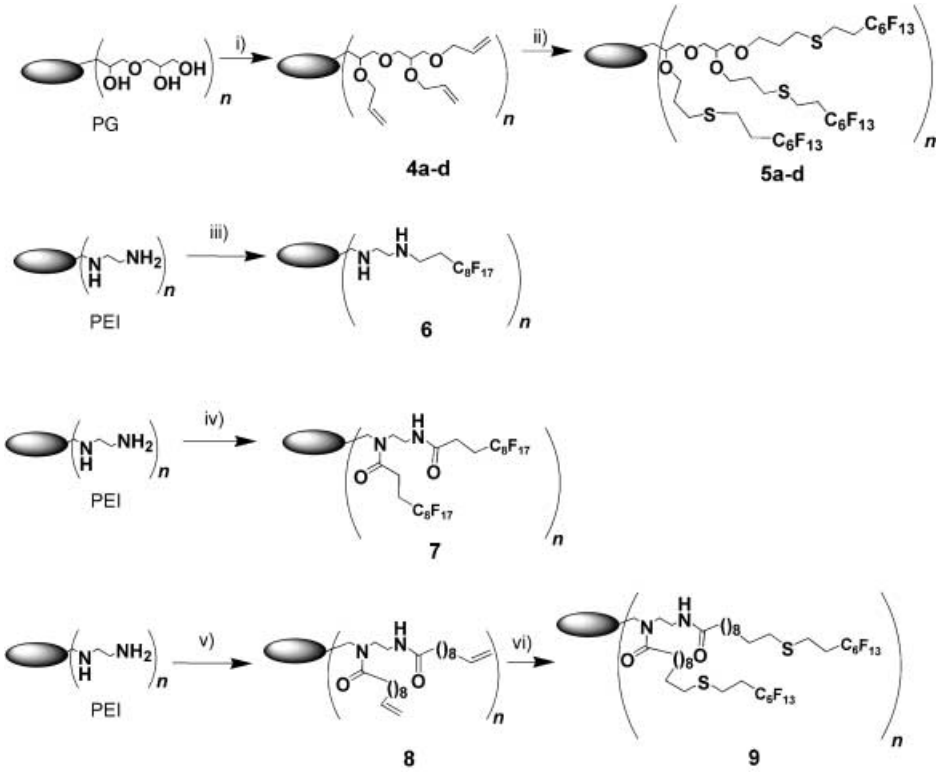
60%) shell modification is sufficient to adjust the polarity and solubility with respect to specific solvents. Although the dendritic polyethers **3** and **5** show high solubilities in most perfluorinated solvents (Table 1), the dendritic polyamines **7** and **9**, which contain a degree of functionalization higher than 50%, are only soluble in α,α,α-trifluorotoluene and perfluorobenzene. To dissolve the least functionalized polyamine **6** in trifluorotoluene, the mixture has to be heated up to 80 °C (accelerated by ultrasound), whereas compound **9** dissolves readily in hexafluorobenzene or trifluorotoluene. Even though both partially fluorinated amides **7** and **9** are insoluble in the perfluorinated solvent FC-75 at room temperature, they become soluble in FC-75 at higher temperatures (43 and 65 °C, respectively). In contrast, polymer **6** is only slightly soluble even at the boiling point of FC-75 (99–107 °C) (see Table 1); this can be attributed to compound **6** only having a relatively low fluorine content (29%).

Nanocarriers **7** and **9** have been observed to encapsulate polar bromophenol blue dye in the pure perfluorinated solvent FC-75 at elevated temperatures (Figure 1), even

Figure 1. Thermomorphic behavior of dendritic nanocarrier **9** in FC-75 in the presence of encapsulated bromphenol blue: left, 70 °C (clear solution); and right, 20 °C (suspension).

though bromophenol blue is not itself soluble in FC-75 at these temperatures. This reversible thermomorphic[19] behavior at about 60 °C has possible application in biphasic catalysis, whereby the guest could be separated from its molecular transporter by simple precipitation (Figure 1).[3]

Phase-transfer behavior of dendritic polyamines that contain perfluorinated shells: The phase-transfer behavior of the dendritic nanocarriers that contain perfluorinated shells was studied for different guest molecules. The respective amphiphilic dendritic polymer was dissolved in trifluorotoluene, perfluorobenzene, or FC-75, and the solution was then treated with a polar guest dissolved in aqueous solution. We observed significantly higher transport capacities (see below) for these amphiphilic PEIs in comparison to PGs that contain perfluorinated shells (cf. Table 2). For example, the polar dye bromophenol blue can be encapsulated and transported within the polyamine based architectures in hexafluorobenzene or a 1:2 mixture of trifluorotoluene/FC-75



Scheme 4. Synthesis of dendritic architectures **5**, **6**, **7**, and **9** starting from hyperbranched PG and PEI (cf. Scheme 1). In compounds **4d** and **5d** the core contains a stearylamine starter: i) Bu_4NBr, NaOH, allyl chloride, toluene/water, 24 h, 50 °C; ii) $HSCH_2CH_2(CF_2)_5CF_3$, AIBN, 22 h, 70 °C; iii) $ICH_2CH_2(CF_2)_7CF_3$, K_2CO_3, CH_3CN, 15 h, reflux; iv) $HOOCCH_2CH_2(CF_2)_7CF_3$, 4 h, 140 °C; v) $CH_2CH(CH_2)_8COOH$, 20 h, 120 °C; vi) $HSCH_2CH_2(CF_2)_5CF_3$, AIBN, 16 h, 100 °C.

Table 2. Transport capacities of congo red dye at 20 °C in dendritic nanocarriers that contain perfluorinated shells.

Polymer	Degree of functionalization [%]	Shell structure	Number of encapsulated dye molecules[a]		
			hexafluorobenzene	trifluorotoluene	$CHCl_3$
3a	100	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	n.d.	< 0.01	< 0.01
3b	100	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	n.d.	< 0.01	n.s.
3c	100	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	n.d.	< 0.01	n.s.
3d	100	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	n.d.	< 0.01	n.s.
5a	92	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	n.d.	< 0.01	n.s.
5b	85	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	n.d.	< 0.01	n.s.
5c	83	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	n.d.	< 0.01	n.s.
5d	94	$(CH_2)_3S(CH_2)_2(CF_2)_5CF_3$	n.d.	0.01[b]	n.s.
6	29	$(CH_2)_2(CF_2)_7CF_3$	n.s.	0.05 ± 0.01	n.s.
7	56	$CO(CH_2)_2(CF_2)_7CF_3$	0.5 ± 0.1	1.0 ± 0.3	n.s.
9	67	$CO(CH_2)_{10}S(CH_2)_2(CF_2)_7CF_3$	3.0 ± 0.8	0.13 ± 0.03	0.25 ± 0.06

[a] n.d. = not determined, n.s. = not soluble. [b] PG-core contains a stearylamine starter.

(Figure 2). The polar amine groups situated within the core of nanocarrier **9** provide a polar microenvironment that allows efficient complexation and transport (see below). Furthermore, the color of the encapsulated pH-indicator dye changed from blue to yellow after addition of acid to the aqueous phase (pH 1), and returned to blue after addition of base. This clearly demonstrates that the encapsulated guest molecule is still accessible to small molecules (i.e. acid/base) upon encapsulation, and that complete phase transfer occurs from the aqueous to the fluorous phase. Similar results have been observed for the dendritic nanocarrier **7**.

Transport capacity of dendritic structures that contain perfluorinated shells: To quantify the transport capacities of the perfluorinated nanocarriers (**3**, **5**, **6**, **7**, and **9**) an aliquot of each dendrimer was dissolved in trifluorotoluene, hexafluorobenzene, or chloroform, and this was then saturated with an excess of congo red. The UV/Vis absorption spectrum of the encapsulated congo red dye in solution was then measured as previously described.[13a,g] Saturation of the fluorinated phase was achieved by adding solid congo red dye to the solution. On the basis that the concentration of the respective dendritic polymer in the perfluorous solution is known, and that the extinction coefficient for both the encapsulated dye and the dye dissolved in water can be assumed to be similar, one can calculate the number of encapsulated guest molecules for each dendritic nanocarrier by using a calibration curve (Table 2).[15] It is noteworthy that the transport capacities of these perfluorinated core-shell architectures were found to be lower than the maximum transport capacity we recently observed for selectively modified PGs[13a] and PEIs,[13b] which contained longer alkyl chains. This again demonstrates that a strong polarity gradient and a relatively thick shell (1–2 nm) are necessary for high transport capacity. In addition, a degree

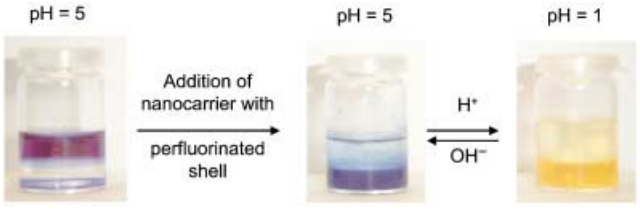


Figure 2. Encapsulation of bromophenol blue by compound **9** in aqueous and trifluorotoluene/FC-75 (1:2) solutions. The first picture depicts that the dye is soluble in water (pH 5). In the second photo, the bromphenol blue is encapsulated within the dendritic nanocarrier **9** at pH 5. Upon addition of acid (pH 1), a color change is observed as a result of the encapsulated dye undergoing an acid–base reaction. The reaction is reversible upon addition of base.

of functionalization of about 50% seems to be optimum for efficient transport. We have also observed a significant solvent dependence in these encapsulation experiments (see Table 2). A significant increase in transport capacity was observed for the dendritic polyamide **9** when the solvent was changed from trifluorotoluene to hexafluorobenzene. This might be the result of the alkyl–perfluoroalkyl shell undertaking a different orientation in each respective solvent.

Two factors that seem to play an important role in the mechanism of encapsulation are: 1) the flexibility and orientation of both the shell and core at the interface of the two phases (aqueous and perfluorous phase); and 2) the strong interaction of the polar guest (e.g. anionic dyes) with the polar groups in the core of the dendritic architecture. The flexibility and orientation of the perfluorinated shells are determined by the degree of functionalization, the degree of branching, and the polarity gradient between the core and the shell. The low transport capacities observed for PGs **3** and **5** can be attributed to the weak interactions that arise between the polar (anionic) guests and the polyether polyol core, whereas the higher transport capacities of PEIs **7** and **9** arise because of the strong interactions between the anionic species and the amino groups in the core of the dendritic architecture.

Encapsulation of metal salts and nanoparticle formation: Silver cations have been encapsulated in PEIs that contain perfluorinated shells because dendritic polyamines have good ligand properties. The encapsulated silver cations were then reduced with an excess of sodium triacetoxyborohydride according to a previously described procedure.[13b] Upon reduction of the encapsulated silver salt an orange-brown color was observed (455 nm); this indicated the formation of silver nanoparticles. The transmission-electron microscopy (TEM) image (Figure 3) of encapsulated silver

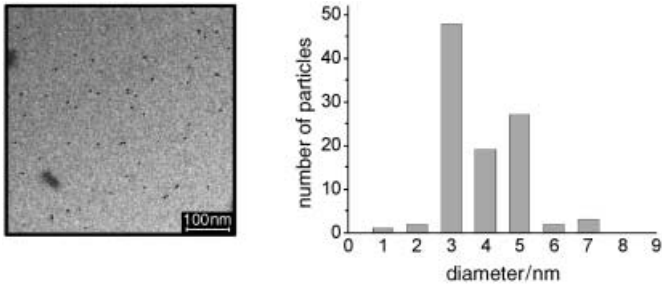


Figure 3. TEM image and particle size distribution of silver nanoparticles encapsulated in nanocarrier **9**. The bar in the TEM image is equivalent to 100 nm.

nanoparticles reveals that the nanoparticles formed are spherical and have a narrow distribution. For dendrimer **9**, the silver particles obtained had diameters of 3.9 ± 1 nm (Figure 3). This demonstrates that dendritic polyamines that contain perfluorinated shells can act as templates and stabilizers[13b,d] for silver nanoparticles even in the fluorous phase. Moreover, this effect can then be used either in the preparation of catalytically active nanoparticles[6,13f] or in bacteriostatic applications.[13d]

Thermal behavior of dendritic architectures that contain perfluorinated shells: The interesting properties observed in solution for dendritic architectures that contain fluorinated shells raised the question whether as bulk materials they possess ordered phases. The thermal behavior of the dendritic architectures was studied by differential scanning calorimetry (DSC) to obtain insight into their bulk structures. The results are summarized in Table 3, and a typical DSC diagram of polyamide **7** is shown in Figure 4. While the PG-based systems displayed none, or in the case of **5a–c**, only very small glass transitions, the PEI cores that contained perfluorinated shells showed glass transitions in the range of −10 to 14 °C. In contrast to the results obtained for perfluorinated carbosilane dendrimers,[20] liquid crystalline behavior could not be detected for either core polymer type (PG or PEI).

Table 3. Glass transition temperatures T_g and melting temperatures for perfluorinated PEI. T_g values were obtained by extrapolation to a heating rate of 0 °C min^{-1}.

Polymer	T_g [°C]	T_m [°C]
3a	–	68
3b	–	47
3c	–	71
3d	–	52
5a	23[a]	41
5b	21[a]	48
5c	26[a]	50
5d	–	−14[b]
6	−10	150
7	14	75
9	−3[a]	80

[a] Weak T_g at a heating rate of 36 °C min^{-1}. [b] PG-core contains a stearylamine starter.

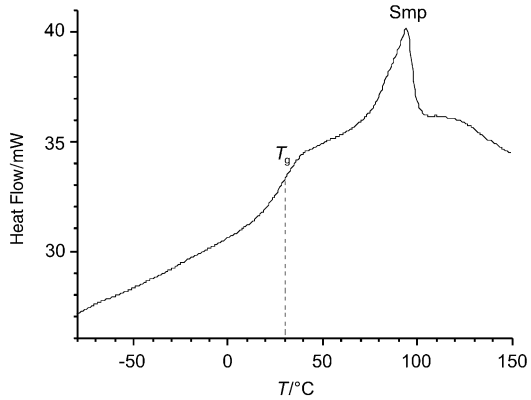


Figure 4. DSC diagram of PEI–perfluoroamide **7**. Heating rate was 36 °C min^{-1}.

Conclusion

To study the physicochemical properties of molecular nanocarriers that have extremly nonpolar peripheries, we synthesized a number of novel dendritic architectures that contain covalently linked perfluorinated shells from glycerol den-

drimers [G0-G3], commercially available hyperbranched polyglycerols (PG), and polyethyleneimines (PEI). While perfluorinated PGs are soluble in many perfluorinated solvents, perfluorinated PEIs are soluble only in some perfluorinated solvents such as hexafluorobenzene or hot FC-75. These amphiphilic core-shell architectures are able to provide polar environments in very nonpolar reaction media such as fluorous phases. Phase-transfer behavior between an aqueous/fluorous phase interface was demonstrated by the encapsulation and transport of polar molecules (e.g. dyes and metal salts) into the fluorous phase. It is noteworthy that high transport capacities were only observed for the dendritic PEIs that contained perfluorinated shells, while poor transport was detected for the corresponding PG-based systems independent of their core size. The different transport behavior observed clearly depends on the guest molecule and the core of the dendritic architecture undergoing different interactions. We also demonstrated that the encapsulated guest molecules remain accessible to small molecules after transport into the fluorous phase. As a result, this behavior can be used for the generation of polar nanoreactors in very nonpolar reaction media such as fluorous phases and supercritical CO_2. In some cases (e.g. **9**) a thermomorphic behavior was also observed. This was important because it would allow the host–guest system to be separated from the perfluorinated solvent by precipitation at room temperature. Evaluation of these molecular nanocarriers as homogeneous supports for catalysts is currently in progress.

Experimental Section

Materials: Hyperbranched polyglycerol was prepared as previously described by using bis(2,3-dihydroxypropyl)stearylamine and pentaerythritol as initiators.[10b] Polyethyleneimine was obtained from BASF. Perfluorinated reagents and solvents were obtained from 3M. Perfluorobenzene, α,α,α-trifluorotoluene, and hexaflourobenzene were purchased from Aldrich. 2,2′-Azobisisobutyronitrile (AIBN) was purchased from Fluka. Sodium hydroxide, potassium carbonate, and all other solvents were purchased from Merck. Allyl chloride was received from Solvay. All reagents and solvents were used without any further purification.

General procedure for the synthesis of dendritic polyglycerols by allylation (1a–d, 4a–d): **CAUTION**: Allyl chloride is toxic. Allyl chloride (162.8 mL, 2 mol) was added to a solution of tetrahydroxymethylmethane (13.6 g, 0.4 mol OH groups), tetrabutylammonium bromide (TBAB) as phase-transfer catalyst, and NaOH (80 g, 2 mol) in distilled water (80 mL), and the reaction mixture was then stirred for 24 h at 50 °C. After the addition of toluene (400 mL), the organic phase was separated, dried over $MgSO_4$, filtered,and concentrated under vacuum. The crude product was further purified by column chromatography (silica gel, petroleum ether/ethyl acetate 10:1 to 1:1) to give a colorless oil. In some cases the product had a tendency to slowly polymerize (especially at higher generations). For long-term storage, it was necessary to keep the allyl ether product under an inert atmosphere at −20 °C.

Characterization data

[G0.5] Tetraallyl ether 1a: 19.5 g (66 %). The spectroscopic data were in good agreement with those reported in the literature.[15]

[G1.5] Allyl ether dendrimer 1b: ($M(C_{41}H_{68}O_{12})=752\ g\,mol^{-1}$): 6.3 g (78 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=3.30$–3.50 (m, OCH_2), 3.61 (t, OCH_2), 3.96 (d, $OCH_2CH{=}C$), 4.08 (d, $OCH_2CH{=}C$), 5.10 (t, $CH_2{=}C$), 5.22 (d, $CH_2{=}C$), 5.84 ppm (m, $CH_2{=}CHCH_2$); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta=45.6$ ($C(CH_2)_4$), 70.2 (OCH_2), 70.5 (OCH_2), 71.3 (OCH_2), 71.7 (OCH_2), 72.3 (OCH_2), 116.5 ($CH_2{=}C$), 116.8 ($CH_2{=}C$), 134.8 ($CH_2{=}C$), 135.3 ppm ($CH_2{=}C$); MS (70 eV, EI): *m/z* (%): 81 (40), 421.1 (39), 639.5 (40), 753.5 (100) $[M+H]^+$.

[G2.5] Allyl ether dendrimer 1c: ($M(C_{89}H_{148}O_{28})=1664\ g\,mol^{-1}$): 4.7 g (63 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.82$ (TBAB traces), 1.22 (TBAB traces), 3.30–3.80 (m, OCH_2), 3.96 (d, $OCH_2CH{=}C$), 4.10 (d, $OCH_2CH{=}C$), 5.11 (m, $CH_2{=}C$), 5.21 (s, $CH_2{=}C$), 5.26 (s, $CH_2{=}C$), 5.85 ppm (m, $CH_2{=}CHCH_2$); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta=29.6$ (TBAB traces), 45.4 ($C(CH_2)_4$), 70.3 (OCH_2), 71.3 (OCH_2), 71.9 (OCH_2), 72.3 (OCH_2), 78.6 (OCH_2), 116.7 ($CH_2{=}C$), 134.7 ($CH_2{=}C$), 135.2 ppm ($CH_2{=}C$); MS (70 eV, EI): *m/z*: 1688.1, 1574, 1459.9, 855.5.

[G3.5] Allyl ether dendrimer 1d: ($M(C_{185}H_{308}O_{60})=3488\ g\,mol^{-1}$): 0.67 g (61 %). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=0.82$ (TBAB traces), 1.22 (TBAB traces), 3.20–3.70 (m, OCH_2), 3.95 (s, $OCH_2CH{=}C$), 4.10 (s, $OCH_2CH{=}C$), 5.11 (t, $CH_2{=}C$), 5.20 (s, $CH_2{=}C$), 5.26 (s, $CH_2{=}C$), 5.85 ppm (m, $CH_2{=}CHCH_2$); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta=29.6$ (TBAB traces), 45.4 ($C(CH_2)_4$), 70.4 (OCH_2), 71.3 (OCH_2), 71.7 (OCH_2), 72.0 (OCH_2), 72.2 (OCH_2), 72.6 (OCH_2), 77.4 (OCH_2), 78.7 (OCH_2), 78.9 (OCH_2), 116.6 ($CH_2{=}C$), 134.8 ($CH{=}C$), 135.3 ppm ($CH_2{=}C$); MS (70 eV, EI): *m/z*: 3493, 3378, 3264, 3149, 3035.

General procedure for the synthesis of dendritic polyglycerols by dihydroxylation (2a–c): **CAUTION**: Osmium tetroxide is toxic. A 4 % wt OsO_4 solution in water (2 mL) was added to a solution of the polyallyl ether (0.1 mol allyl equivalents) and *N*-methylmorpholine-*N*-oxide (14.8 g, 0.11 mol) in acetone (50 mL), distilled water (50 mL), and *tert*-butanol (10 mL). Initially, an exothermic reaction was observed and it was necessary at times to cool the reaction mixture in a water bath. The mixture was then stirred for 20 h at 25 °C. The volatile compounds were removed under vacuum, and the product was further purified by reverse-phase column chromatography (methanol) to give, after concentration, pale-yellow oils. The high molecular weight [G3] dendrimer **2c** was purified by dialysis in methanol using a benzylated cellulose membrane (MWCO 1000, Sigma).

Characterization data

[G1] Glycerol dendrimer 2a: ($M(C_{17}H_{36}O_{12})=432\ g\,mol^{-1}$): 9.1 g (103 %, product contained traces of NMO). ^{1}H NMR (300 MHz, D_2O): $\delta=2.79$ (s, COH), 3.38 (m, CH_2O), 3.53 (m, CH_2O), 3.76 ppm (quintuplet, CH_2O); ^{13}C NMR (300 MHz, D_2O): $\delta=47.5$ ($C(CH_2)_4$), 55.5 (CH_2O), 65.0 (CH_2O), 66.1 (CH_2O), 72.3 (CH_2O), 72.6 (CH_2O), 74.7 ppm (CH_2O); MS (70 eV, EI): *m/z*: 439.0.

[G2] Glycerol dendrimer 2b: ($M(C_{41}H_{84}O_{28})=1024\ g\,mol^{-1}$): 8.7 g (101 %, product contained traces of NMO). ^{1}H NMR (300 MHz, D_2O): $\delta=0.74$ (s, COH), 1.14 (s, COH), 3.30–3.90 ppm (m, CH_2O); ^{13}C NMR (300 MHz, D_2O): $\delta=12.0$, 20.7, 27.9, 43.3 ($C(CH_2)_4$), 60.7 (CH_2O), 68.1 (CH_2O), 68.4 (CH_2O), 68.7 (CH_2O), 70.2 (CH_2O), 76.0 ppm (CH_2O); MS (70 eV, EI): *m/z*: 593.7, 1030.6.

[G3] Glycerol dendrimer 2c: ($M(C_{89}H_{180}O_{60})=2208\ g\,mol^{-1}$): 1.9 g (68 %, after extensive dialysis). ^{1}H NMR (300 MHz, D_2O): $\delta=0.70$ (t, COH), 1.20 (q, COH), 1.50 (m, COH), 3.10 (s, CH_2O), 3.16 (s, CH_2O), 3.49 (m, CH_2O), 3.75 ppm (m, CH_2O); ^{13}C NMR (300 MHz, D_2O): $\delta=14.9$, 21.3, 25.2, 47.5 ($C(CH_2)_4$), 60.2 (CH_2O), 60.8 (CH_2O), 63.5 (CH_2O), 64.7 (CH_2O), 66.9 (CH_2O), 71.3 (CH_2O), 72.5 (CH_2O), 72.7 (CH_2O), 72.8 (CH_2O), 74.3 (CH_2O), 80.3 ppm (CH_2O); MS (70 eV, EI): *m/z*: 2099.4, 2173.5, 2247.5.

Synthesis of perfect glycerol dendrimers (3a–d) and dendritic polyglycerols (5a–d) with perfluorinated shells: A solution of the polyallyl ether **1a–d** or **4a–d** (0.1 mol allyl ether group equivalents) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane-1-thiol (0.5 mol) was stirred under reduced pressure (3 mbar) to remove oxygen from the solution. After heating to 70 °C, AIBN (2 mmol) was added under an atmosphere of nitrogen, and the reaction mixture was stirred for 2 h. After further addition of the same amount of AIBN, the mixture was stirred for another 20 h at 70 °C, and the solvent was then evaporated to yield a pale-yellow product. For higher generations (molecular weights), further purification was achieved by dialysis in trifluorotoluene.

Characterization data for perfect four-arm dendrimers with perfluorinated shells (3a–d)

[G0.5] Compound 3a: ($M(C_{49}H_{48}O_4S_4F_{52})=1816\ g\,mol^{-1}$): 1.3 g crude. ^{1}H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=1.78$ (quintuplet, $^3J_{H,H}=7$ and 6 Hz, 8H; $OCH_2CH_2CH_2S$), 2.28 (tt, $^3J_{H,F}=18$ and $^3J_{H,H}=9$ Hz, 8H;

$CH_2CH_2CF_2$), 2.50–2.70 (m, 16H; CH_2S), 3.35 (s, 8H; CCH_2O), 3.44 ppm (t, $^3J_{H,H}=6$ Hz, 4H; OCH_2CH_2); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=$ 22.6 (SCH_2), 29.1 (SCH_2), 29.8 ($CH_2CH_2CH_2$), 32.3 (t, $^1J_{F,C}=22$ Hz; CH_2CF_2), 40.3 ($C(CH_2)_4$), 45.8 (CH_2O), 69.6 (CH_2O), 110–120 ppm (m, CF_2); MS (70 eV, EI): *m/z*: 149, 421, 493, 521, 939, 958, 1140.

[G1.5] Compound 3b: ($M(C_{105}H_{108}O_{12}S_8F_{104})=3792$ g mol^{-1}): 1.4 g crude. ^1H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=1.80$ (m, 16H; $OCH_2CH_2CH_2S$), 2.29 (tt, $^3J_{H,F}=17$ and $^3J_{H,H}=9$ Hz, 16H; $CH_2CH_2CF_2$), 2.50–2.70 (m, 32H; CH_2S), 3.30–3.60 (m, 40H; CCH_2O), 3.65 ppm (tt, $^3J_{H,H}=6$ and 6 Hz, 4H; OCH); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=22.7$ ($CH_2CH_2CH_2$), 28.7 (SCH_2), 29.1 (SCH_2), 29.2 (SCH_2), 29.8 (SCH_2), 30.1 (SCH_2), 32.3 (t, $^1J_{F,C}=22$ Hz; CH_2CF_2), 46.0 ($C(CH_2)_4$), 68.9 (CH_2O), 69.9 (CH_2O), 70.6 (CH_2O), 71.8 (CH_2O), 72.1 (CH_2O), 78.5 (CH_2O), 115–125 ppm (m, CF_2); MS (70 eV, EI): *m/z*: 617.9, 1115.9, 1687.8, 2199.9, 2314.1, 2791.5, 3516.2.

[G2.5] Compound 3c: ($M(C_{217}H_{228}O_{28}S_{16}F_{208})=7744$ g mol^{-1}): 2.3 g (70.5%, after dialysis). ^1H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=1.84$ (m, 32H; $OCH_2CH_2CH_2S$,), 2.50 (tt, $^3J_{H,F}=18$ and $^3J_{H,H}=9$ Hz, 32H; $CH_2CH_2CF_2$), 2.80–2.90 (m, 64H; CH_2S), 3.40–3.80 ppm (m, 100H; CCH_2O); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=22.7$ ($CH_2CH_2CH_2$), 28.6 (SCH_2), 28.7 (SCH_2), 29.2 (SCH_2), 30.3 (SCH_2), 31.6 (SCH_2), 32.2 (t, $^1J_{F,C}=17$ Hz; CH_2CF_2,), 110–120 ppm (m, CF_2); MS (ESI): *m/z*: 617.9, 1114.0, 1578.0, 2056.0, 2359.1, 2375.1, 2399.2, 2878.7, 2894.7, 3404.4.

[G3.5] Compound 3d: ($M(C_{441}H_{468}O_{60}S_{32}F_{416})=15648$ g mol^{-1}): 0.50 g (57%, after dialysis). ^1H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=1.84$ (m, 64H; $OCH_2CH_2CH_2S$), 2.32 (m, 64H; $CH_2CH_2CF_2$), 2.60 (m, 128H; CH_2S), 3.30–3.90 ppm (m, 212H; CH_2O and CHO); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=22.7$ ($CH_2CH_2CH_2$), 29.2 (SCH_2), 29.8 (SCH_2), 30.1 (SCH_2), 32.23 (t, $^1J_{F,C}=22$ Hz; CH_2CF_2), 68.9 (CH_2O), 69 (CH_2O), 70.1 (CH_2O), 71.9 (CH_2O), 72.1 (CH_2O), 78.7 (CH_2O), 78.9 (CH_2O), 110–120 ppm (m, CF_2); MS (ESI): no reliable peak detection was possible.

Perallylated hyperbranched polyglycerols (4a–d)[9]

Compound 4a: (M_n(core) = 2000 g mol^{-1}): ^1H NMR (300 MHz, $CDCl_3$): $\delta=3.1$–3.6 (m, CH_2O, CHO), 3.78 (d, $CH_2CH{=}CH_2$, $^3J_{H,H=}4$ Hz), 3.92 (d, $^3J_{H,H}=4$ Hz, $CH_2CH{=}CH_2$), 4.93 (m, $CH{=}CH_2$), 5.02 (d, $^3J_{H,H}=2$ Hz, $CH{=}CH_2$), 5.08 (d, $^3J_{H,H}=2$ Hz, $CH{=}CH_2$), 5.70 ppm (m, $CH{=}CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=45.4$ (CCH_2) 70.2 (CH_2O), 71.2 (CH_2O), 71.6 (CH_2O), 72.2 (CH_2O), 77.3 (CH_2O), 77.6 (CH_2O), 78.6 (CH_2O), 78.8 (CH_2O), 116.5 ($CH_2{=}CH$), 116.6 ($CH_2{=}CH$), 116.7 ($CH_2{=}CH$), 134.7 ($CH_2{=}CH$), 134.8 ($CH_2{=}CH$), 135.2 ppm ($CH_2{=}CH$).

Hyperbranched polyglycerols that contain perfluorinated shells (5a–d)

Compound 5a: (M_n(core) = 2000 g mol^{-1}): 3.1 g crude. ^1H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=1.9$ (m, $OCH_2CH_2CH_2S$), 2.3 (m, $CH_2CH_2CF_2$), 2.7 (m, CH_2S), 3.3–3.9 ppm (m, CH_2O and CHO); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=22.5$ ($CH_2CH_2CH_2$), 28.4 (SCH_2), 29.1 (SCH_2), 29.7 (SCH_2), 30.1 (SCH_2), 31.5 (SCH_2), 31.7 (SCH_2), 31.9 (SCH_2), 32.6 (t, $^1J_{F,C}=23$ Hz; CH_2CF_2), 68.8 (CH_2O), 69.8 (CH_2O), 70.8 (CH_2O), 72.0 (CH_2O), 78.7 (CH_2O), 79.0 (CH_2O), 105–125 ppm (m, CF_2).

Compound 5b: (M_n(core) = 5000 g mol^{-1}): 9.5 g (73%, after dialysis). ^1H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=1.9$ (m, $OCH_2CH_2CH_2S$), 2.3 (m, $CH_2CH_2CF_2$), 2.7 (m, CH_2S), 3.3–3.9 ppm (m, CH_2O and CHO); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=22.5$ ($CH_2CH_2CH_2$), 28.4 (SCH_2), 29.1 (SCH_2), 29.8 (SCH_2), 30.1 (SCH_2), 31.7 (SCH_2), 32.3 (t, $^1J_{F,C}=22$ Hz; CH_2CF_2), 68.7 (CH_2O), 69.7 (CH_2O), 72.2 (CH_2O), 78.7 (CH_2O), 79.0 (CH_2O), 79.5 (CH_2O), 79.6 (CH_2O), 105–120 ppm (m, CF_2).

Compound 5c: (M_n(core) = 15000 g mol^{-1}): 7.1 g (41%, after dialysis). ^1H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=1.8$ (m, $OCH_2CH_2CH_2S$), 2.3 (m, $CH_2CH_2CF_2$), 2.6 (m, CH_2S), 3.3–3.9 ppm (m, CH_2O and CHO); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=22.6$ ($CH_2CH_2CH_2$), 28.6 (SCH_2), 29.1 (SCH_2), 29.7 (SCH_2), 30.1 (SCH_2), 31.8 (SCH_2), 32.2 (t, $^1J_{F,C}=23$ Hz; CH_2CF_2), 68.7 (CH_2O), 69.8 (CH_2O), 72.0 (CH_2O), 78.6 (CH_2O), 78.8 (CH_2O), 105–120ppm (m, CF_2).

Compound 5d: (Hyperbranched polyglycerol with a stearylamine starter group, M_n(core) = 4500 g mol^{-1}): 8.5 g (50%, after dialysis). ^1H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=1.44$ (m, $OCH_2CH_2CH_2S$), 2.03 (m, $CH_2CH_2CF_2$), 2.58 (m, CH_2S), 2.88 (CH_2O, CHO), 3.81 ppm (CH_2O and CHO); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=22.4$ ($CH_2CH_2CH_2$), 29.0 (SCH_2), 29.8 (SCH_2), 30.2 (SCH_2), 32.3 (SCH_2), 32.3 (t, $^3J_{F,C}=22$ Hz; CH_2CF_2), 40.3 (d, $^3J_{F,C}=21$ Hz, CH_2CF_2), 68.7 (CH_2O), 69.7 (CH_2O), 71.1 (CH_2O), 72.1 (CH_2O), 78.8 (CH_2O), 105–125 ppm (m, CF_2).

Synthesis of dendritic polyamines that contain perfluorinated shells

Synthesis of the partially fluorinated dendritic polyamine 6: A suspension of PEI (M_n(core) = 4500 g mol^{-1}, PD = 1.3, 0.5 g, 4 mmol of primary amino groups), 1,1,1,2,2,3,3,4,4,5,5,6,6,7,7,8,8-heptadecafluoro-10-iododecane (4.69 g, 8 mmol), and potassium carbonate (9 g, 65 mmol) in acetonitrile (200 mL) was heated to reflux for 15 h. The reaction mixture was then washed with water and methanol, and dried to give a brownish rubber-like material (0.94 g, 60% based on functionalization). An NMR spectrum could not be recorded because of the poor solubility of the product in perdeuterated or perfluorinated solvents. Elemental analysis found (%): C 35.05, H 3.83, N 8.13. Degree of functionalization from CHN-analysis: 29%.

Synthesis of the partially fluorinated dendritic polyamide 7: A mixture of PEI (M_n(core) = 4500 g mol^{-1}, PD = 1.3, 0.19 g, 1.5 mmol of primary amino groups) and 4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecanoic acid (1.5 g, 3 mmol) was heated at 140°C for 4 h under an atmosphere of argon. The reaction mixture was then dissolved in perfluorinated benzene (20 mL), filtered, Ionenaustauscher III (0.75 g, 4 mmol OH^- g^{-1}) (Merck) was added to the filtrate, and the resultant mixture was stirred for 3 h. The Ionenaustauscher III was removed by filtration and the solvent was evaporated under vacuum to give a brownish solid (1.57 g, 95% based on functionalization). ^1H NMR (300 MHz, $C_6F_6/CDCl_3$): $\delta=0.6$ (s), 1.0 (s), 1.3–4.0 ppm (m); ^{13}C NMR (75 MHz, $C_6F_6/CDCl_3$): $\delta=28$–60 (m, CH_2), 100–125 (m, CF_2), 172 ppm (s, C=O); elemental analysis found (%): C 34.83, H 3.12, N 4.57. Degree of functionalization from CHN-analysis: 56%.

Synthesis of the partially fluorinated dendritic polyalkylamide 9: A mixture of PEI (M_n(core) = 4500 g mol^{-1}, PD = 1.3, 3.57 g, 54.3 mmol of amino group) and 10-undecenoic acid (10 g, 54.3 mmol) was heated at 120°C for 20 h under an atmosphere of argon (stream). The crude amide **8** (11.4 g) was then used without further purification in the next step.

A mixture of polyethyleneimine alkenylamide **8** (11.4 g, 49 mmol of allyl ether groups) and 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctane-1-thiol (93.38 g, 246 mmol) was stirred under reduced pressure (3 mbar) to remove oxygen from the solution. The mixture was then heated to 100°C and AIBN (4 mmol) was added under an atmosphere of nitrogen. The reaction mixture was stirred for 8 h. After further addition of AIBN (8 mmol) the mixture was stirred for another 8 h at 100°C, and then the excess AIBN was deactivated by addition of butylhydroxytoluene. The polymer was purified by dialysis in chloroform using a benzoylated cellulose membrane (MWCO 1000, Sigma), and the solvent was evaporated to yield a yellow polymer (29.0 g, 90% over two steps based on functionalization). ^1H NMR ($CDCl_3$): $\delta=1.51$ (m, CH_2), 1.82 (m, CH_2CH_2S and $NCOCH_2$), 2.44 (m, CH_2S), 2.26 (m, NCH_2), 2.78 (m, NCH_2), 2.97 (m, NCH_2), 3.11 (m, NCH_2), 3.73 (m, NCH_2), 4.30 ppm (m, NCH_2); ^{13}C NMR ($CDCl_3$): $\delta=15.8$ (t, $J=5$ Hz; CH_2), 22.9 (t, $J=4$ Hz, CH_2), 23.7 (s, CH_2), 26.4 (s, CH_2), 28.8 (s, CH_2), 29.2 (s, CH_2), 29.7 (m, CH_2), 30.0 (m, CH_2), 31.9 (s, CH_2), 32.1 (s, CH_2), 32.4 (s, CH_2), 32.6 (s, CH_2), 32.7 (s, CH_2), 36.0 (s, CH_2), 36.3 (s, CH_2), 36.6 (s, CH_2), 37.0 (s, CH_2), 105–125 (m, CF_2), 180.0 ppm (s, CO). Degree of functionalization from ^1H NMR: 67%.

Determination of the number of encapsulated guest molecules: Solid congo red dye was added to a solution of the respective dendritic nanocarrier **3, 5, 6, 7,** or **9** (50 mg) in 5 mL of solvent (see Table 3) and the resultant mixture was stirred for two days. The suspension was filtered and the absorbance of the solution at 530 nm was measured. The concentration of congo red was determined from a calibration curve in water. The transport capacity *n* (number of encapsulated congo red molecules) was calculated by using Equation (1).

$$n=\frac{[\text{dye}]}{[\text{polymer}]} \quad (1)$$

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