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Octakis(3-azidopropyl)octasilsesquioxane: A Versatile Nanobuilding Block for the Efficient Preparation of Highly Functionalized Cube-Octameric Polyhedral Oligosilsesquioxane Frameworks Through Click Assembly

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This work is dedicated to the memory of Professor Antonio Gómez-Sánchez

Abstract: A one-step synthesis of octakis(3-azidopropyl)octasilsesquioxane from commercially available octakis(3-aminopropyl)octasilsesquioxane has been developed through a highly efficient diazo-transfer reaction under very mild conditions. Nonaflyl azide is shown to be a safer, cheaper, and more efficient reagent for this transformation than the better known and generally used diazo-transfer reagent triflyl azide. Octakis(3-azidopropyl)octasilsesquioxane is an excellent nanobuilding block that can be readily octafunctionalized with a range of terminal alkynes by copper(I)-catalyzed 1,3-dipolar azide–alkyne cycloaddition to provide new functional nanocages, maintaining a perfect 3D cubic symmetry. The mildness, simplicity, and efficiency of this approach have been demonstrated in the preparation of a glyco-polyhedral oligosilsesquioxane (POSS) conjugate and a BODIPY–POSS cluster (BODIPY = boron dipyrromethene).

Keywords: azides · carbohydrates · click chemistry · dyes/pigments · silsesquioxanes

Introduction

Fully condensed polyhedral oligosilsesquioxanes (POSS) are unique nanometer-sized hybrid inorganic–organic materials of chemical composition $(RSiO_{1.5})_n$, which can be readily synthesized by hydrolytic condensation of trifunctional organosilicon monomers $RSiX_3$ (R = organic group; X = halogen or alkoxide group).[1] Due to their rigid inorganic core, POSS are endowed with considerable chemical and thermal stability. Although this family of compounds has been known for more than 60 years,[2] until the past decade, the majority of commonly available POSS derivatives lacked sufficient functionality for most chemical applications. The discovery of new spontaneous self-assembly reactions[3–5] that provide ready access to a variety of novel POSS frameworks, the development of general and efficient methodologies for the synthetic manipulation of their pendant organic groups (see below), and the recent commercial availability of a wide range of simple monomers on a multigram scale[6] have contributed to the fast development of POSS chemistry in the last decades. Applications in areas as diverse as polymers, composite materials, dendrimers, optical materials, liquid crystals, drug carriers, metal catalysts, and cosmetics have been described over the past several years, especially in the patent literature.[7] The most promising POSS monomers are the highly symmetrical and topologically ideal cube-octameric frameworks (T_8), of general formula type $(RSiO_{1.5})_8$. Among these, octahydridooctasilsesquioxane (**1**),[8–10] the simplest T_8 compound, together with octavinyloctasilsesquioxane (**2**),[5,11,12] octaphenyloctasilsesquioxane (**3**),[3,5,13] octakis(3-chloropropyl)octasilsesquioxane (**4**),[14–18] and octakis(3-aminopropyl)octasilsesquioxane (**5**)[19–22] have been the most useful precursors to a variety of T_8 products. Key to all potential uses of these POSS basic monomers is the ease with which their pendant organic functionality can be altered in a controlled and highly efficient way to produce new molecules suitable for further functionalization. Since these T_8 molecules contain eight points for functionalization and partial transformation produces complex mixtures of products that are generally difficult to separate, it is critical that the reaction chosen for this task proceeds in a very efficient way. A relatively wide range of derivatization

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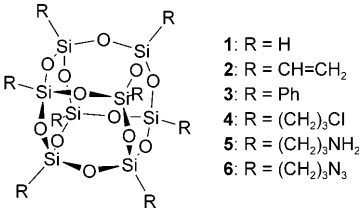
reactions are suited for this purpose, although care must be taken to avoid strongly acidic, basic, or oxidizing environments that can compromise the stability of the POSS cage. Transition metal-catalyzed reactions such as hydrosilylation,[14,–19–29] olefin cross-metathesis,[28,30–32] and Heck,[28,33–37] Suzuki,[28,36] or Sonogashira[28,36] couplings; acylation[21,38–41] and Michael addition[21,42] reactions of amines; electrophilic aromatic substitution reactions;[36,43–47] nucleophilic substitution of halogen;[14,17,48–50] and radical addition of thiols[51,52] or R_2PH[53–55] to olefins, have been used for this purpose with great success. Surprisingly, the copper(I)-catalyzed 1,3-dipolar Huisgen cycloaddition of azides to alkynes (CuAAC),[56–58] a paradigmatic example of a "click reaction",[59] which is a robust and reliable method for the efficient functionalization of a wide variety of molecules under mild conditions, has been scarcely used in POSS chemistry because of the lack of appropriately functionalized POSS derivatives.[60]



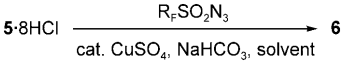
1: R = H
2: R = CH=CH$_2$
3: R = Ph
4: R = (CH$_2$)$_3$Cl
5: R = (CH$_2$)$_3$NH$_2$
6: R = (CH$_2$)$_3$N$_3$

Herein, we report the synthesis of the new octaazide-POSS **6** with a perfect 3D cubic symmetry, and an initial screening of reaction conditions for its octafunctionalization with a variety of alkynes through CuAAC reaction. To examine the scope and utility of this methodology for the preparation of new functional materials, we have undertaken the assembly of a multivalent POSS glycoconjugate[61] and a POSS–fluorophore cluster.[62] Synthetic multivalent glycoconjugates are interesting constructs for the study of carbohydrate–protein recognition processes and have a number of other potential practical applications, including the prevention of early adhesion of pathogens to host epithelial cells, the neutralization of viruses and toxins, the preparation of vaccines, and carbohydrate-guided targeted drug delivery.[64–66] On the other hand, multimeric fluorescent molecules have been used as chemosensors for H^+ or metal ions, biological probes, optical brighteners, light-harvesting devices, or as potential compounds for organic light-emitting diodes.[67,68]

Results and Discussion

We prepared compound **6** from the corresponding octaamino-POSS **5** by using an efficient diazo-transfer reaction. Compound **5** is commercially available as its octahydrochloride salt[6] and can be easily obtained in multigram quantities from an inexpensive organosilicon precursor.[19,20,38] We examined two different diazo-transfer reagents for the synthesis of **6**: trifluoromethanesulfonyl (triflyl) azide, which has often been used for the preparation of organic azides from the corresponding primary amines, mostly in carbohydrate chemistry;[69–71] and nonafluorobutanesulfonyl (nonaflyl) azide,[72,73] which at the onset of our work had never been used before for the synthesis of organic azides.[74] Triflyl azide is potentially explosive, it has a relatively poor shelf life and it must be prepared just before use from triflic anhydride and sodium azide as a solution in dichloromethane[69,75] or toluene.[76] In contrast, nonaflyl azide is stable at room temperature, can be safely distilled and kept as a neat reagent at 4 °C for later use without decomposition, and is easily obtained from the much cheaper and readily available nonaflyl fluoride.[72,73] In an initial screening of reaction conditions (Table 1), we identified two

Table 1. Synthesis of **6** from **5**·8HCl by diazo-transfer reaction.[a]



Entry	R_F	Solvent (v/v ratio)	Yield[b] [%]
1[c]	CF_3	toluene/MeOH/H_2O (7.8:11:0.2)	17–20
2	CF_3	toluene/MeOH/H_2O (7.8:11:0.2)	28–30
3	CF_3	toluene/EtOH/H_2O (7.8:11:0.2)	50–54
4	CF_3	toluene/*i*PrOH/H_2O (7.8:11:0.2)	55
5	CF_3	toluene/*t*BuOH/H_2O (7.8:11:0.2)	42
6	$CF_3(CF_2)_3$	Et_2O/EtOH/H_2O (1:3:1)	60–73

[a] Reaction conditions: **5**·8HCl (1 mol equiv), $R_FSO_2N_3$ ($R_F = CF_3$, ca. 36 mol equiv; $R_F = (CF_2)_3CF_3$, 24 mol equiv), $CuSO_4 \cdot 5H_2O$ (0.5 mol equiv), $NaHCO_3$ (32 mol equiv), RT, 16 h. [b] Yield of pure product after chromatography. [c] Compound **5** was added to the reaction as a solution in MeOH (prepared by stirring a suspension of **5**·8HCl in this solvent with an excess of Amberlite IRA-400/OH at 0 °C).

factors that were critical to obtain an optimal yield of **6**. The first is the procedure employed for the required neutralization of **5**·8HCl to the free amine, which is known to be difficult to accomplish without compromising the Si/O framework.[21] In situ neutralization by incorporation of an excess of an aqueous solution of $NaHCO_3$ in the diazo-transfer reaction (Table 1, entries 2–6) afforded better yields than the previously described[21] pretreatment of **5**·8HCl with Amberlite IRA-400/OH resin in methanol (Table 1, entry 1). The second factor affecting the yield is the reaction solvent. Homogenous solvent mixtures containing water, a simple alcohol, and an apolar organic solvent were needed to solubilize all reaction components. Toluene was used as the apolar organic solvent in the case of triflyl azide (Table 1, entries 1–5),[76] whereas diethyl ether was required to dissolve the nonaflyl reagent (Table 1, entry 6). Mixtures containing ethanol or isopropanol as the alcohol component afforded the best yields (Table 1, entries 3, 4, and 6). In gram-scale preparations of **6**, the order of addition of reagents was also of importance. When $NaHCO_3$ was added to an aqueous solution of **5**·8HCl and $CuSO_4 \cdot H_2O$, a blue precipitate appeared, which was probably formed from a mixture of Cu^{II} complexes of **5**. Under these conditions, yields usually halved due to the persistent heterogeneous nature of the reaction. Precipitation can be largely avoided by adding $NaHCO_3$ last

and in small portions under very efficient stirring. Eventually, nonaflyl azide proved to be the reagent of choice for this transformation, both for its higher efficiency and for its much lower cost. Under the optimized conditions (Table 1, entry 6), compound **6** was obtained in gram amounts as a viscous liquid in 60–73% yield after chromatographic purification, which accounts for an excellent yield per amino group (>94%) in the diazo-transfer reaction. The structure of **6** was unambiguously confirmed from its high-resolution mass spectrometry and FTIR and NMR spectroscopy data (Figure 1). Thus, a strong IR band at 2099 cm^{-1} (characteristic of the azide group), a single set of resonances in the ^{1}H and ^{13}C NMR spectra, and a narrow singlet resonance in the ^{29}Si NMR spectrum revealed the perfect 3D cubic symmetry of this compound.

Very recently, Ge et al.[60c] have described a different synthesis of **6** through nucleophilic substitution reaction of octakis(3-chloropropyl)octasilsesquioxane (**4**) with NaN_3. However, comparison of the reported spectral data[77] with those measured under the same conditions for our sample of **6** (see Figure 1 and the Experimental Section), revealed some significant differences. First, Ge et al. observed a considerable broadening of the ^{1}H NMR signals, as opposed to the well-resolved multiplets observed in our case (Figure 1c).

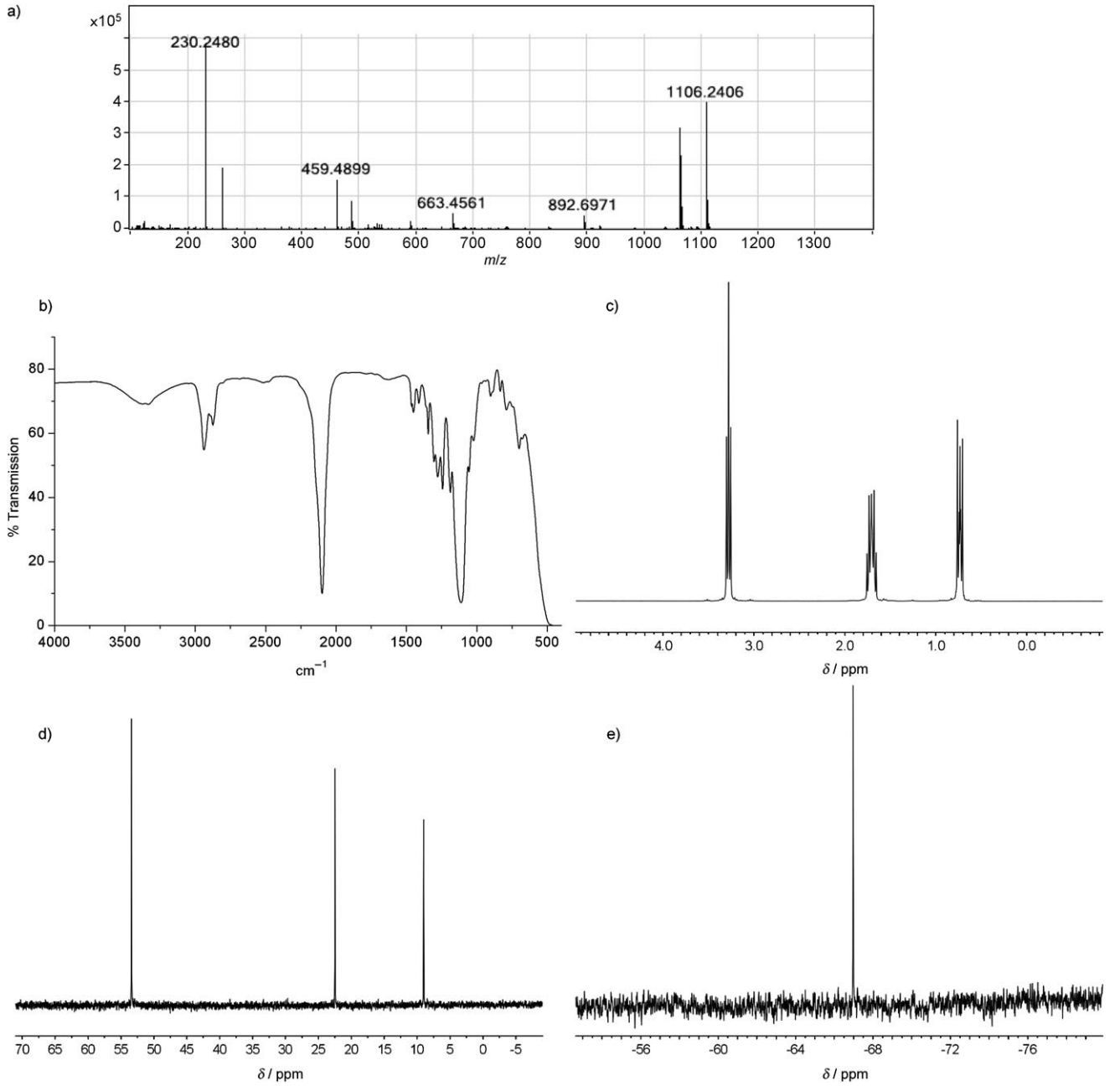
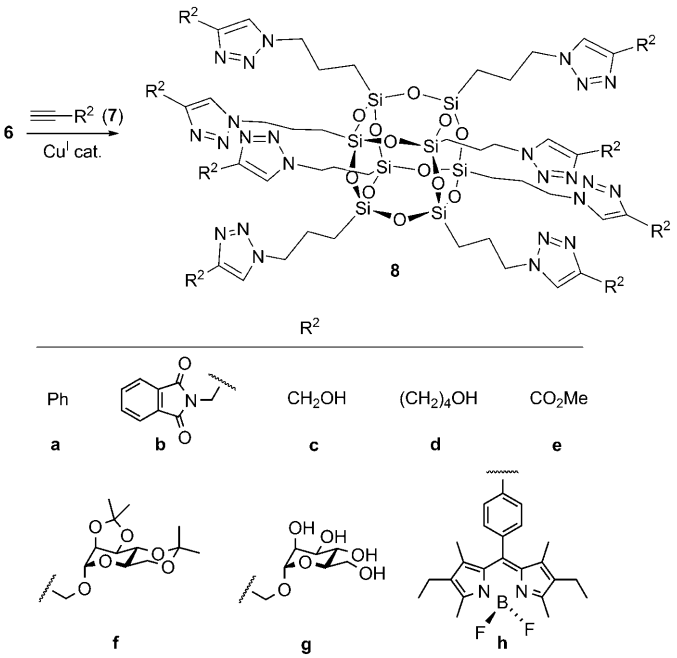


Figure 1. a) ESIMS (H_2O/MeOH containing 0.1% HCO_2NH_4): 1106.2406 $[M+NH_4]^+$, 1061.2084 $[(M-N_2)+H]^+$; b) FTIR (thin film); c) ^{1}H NMR spectrum ($CDCl_3$) of **6**; d) ^{13}C NMR spectrum ($CDCl_3$) of **6**; and e) ^{29}Si NMR spectrum ($CDCl_3$) of **6**.

Second, the ^{13}C and ^{29}Si NMR signals of the Si-CH_2 moiety (the most sensitive to cage structure modifications) for our sample of **6** were observed at $\delta = 9.0$ and -67.0 ppm, respectively. Ge et al reported that for their product, these signals were shifted approximately 1 ppm downfield (^{13}C NMR signals) and 2 ppm upfield (^{29}Si NMR signals) compared with our data. Moreover, since the authors did not report any mass spectral data for **6**, the identity of their compound could not be unambiguously ascertained. Most likely, these substantial spectral differences are a consequence of a structural divergence between the products prepared by the two routes. Given the known propensity of POSS cages to suffer cleavage and rearrangement upon attack by a nucleophile,[78] it is probable that the azide anion has caused cage expansion (to T_{10} and T_{12}) or even degradation to a mixture of oligomers under the harsh thermal conditions (DMF, 120 °C, 2 d) employed by the authors in the substitution reaction. In fact, in an interesting study of cage rearrangements of silsesquioxanes that included **4**, Marsmann and Rikowski[78] observed that the rearrangement of T_8 to T_{10} results in an upfield shift (approximately 2 ppm) of the ^{29}Si NMR resonance, which is precisely the same shift that was observed between the sample of **6** prepared by diazo-transfer reaction (this work) and the data reported by Ge et al. for the product obtained through nucleophilic substitution.[79]

Since azides are potentially explosive,[80] we evaluated the safety profile of **6** by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).[81] This study showed that a slow thermal decomposition of compound **6** started at 237 °C, which is well above the temperature required to perform the thermal cycloadditions (see below), and no characteristics of explosive behavior were observed. A weight loss of only about 27 % occurred, in approximately the same temperature range as the DSC exotherm. Thus, gram quantities of **6** can be safely prepared and stored for later use without any special precautions.

With an optimized procedure for the efficient gram-scale preparation of **6** in hand, we next studied its octafunctionalization with simple alkynes through CuAAC (Scheme 1). By



Scheme 1. Synthesis of octatriazolyl-POSS compounds **8** by CuAAC reaction of **6** with terminal alkynes.

using phenyl acetylene (**7a**) as a model, different copper catalysts and solvent systems were assayed for the synthesis of the corresponding product **8a** (Table 2, entries 1–4). Although all reaction conditions examined afforded excellent yields of **8a** with complete regioselectivity by using a 5 % molar copper catalyst with respect to alkyne, reaction times varied widely. Slow reactions were observed when the cycloaddition was performed at room temperature under homogeneous conditions in toluene using the soluble catalysts $(EtO)_3P{\cdot}CuI$[82] or the recently described [CuCl(IPr)][83,84] (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) and [Cu($C18_6$tren)]Br[85,86] ($C18_6$tren = tris(2-dioctadecylaminoethyl)amine) in the presence of base (Table 2, entries 1–

Table 2. Synthesis of **8a–h** from **6** by CuAAC reaction.

Entry	Alkyne	Catalyst	Base	Solvent (v/v ratio)	T[a] [°C]	t [h]	Product	Yield [%]
1	**7a**	$(EtO)_3P{\cdot}CuI$	iPr$_2$NEt	toluene	25	70	**8a**	90
2	**7a**	[CuCl(IPr)]	iPr$_2$NEt	toluene	25	48	**8a**	90
3	**7a**	[Cu($C18_6$tren)]Br	iPr$_2$NEt	toluene	25	20	**8a**	92
4	**7a**	$CuSO_4{\cdot}5H_2O$/sodium ascorbate	none	CH_2Cl_2/H_2O (1:1)	25	1	**8a**	96
5	**7b**	$CuSO_4{\cdot}5H_2O$/sodium ascorbate	none	CH_2Cl_2/H_2O (1:1)	25	18	**8b**	61
6	**7b**	[Cu($C18_6$tren)]Br	iPr$_2$NEt	toluene	80 (MW)	3	**8b**	89
7	**7c**	[Cu($C18_6$tren)]Br	iPr$_2$NEt	toluene	80 (MW)	3	**8c**	67
8	**7c**	[Cu($C18_6$tren)]Br	iPr$_2$NEt	THF/H_2O (2:1)	25	24	**8c**	77
9	**7d**	[Cu($C18_6$tren)]Br	iPr$_2$NEt	toluene	80 (MW)	3	**8d**	71
10	**7d**	[Cu($C18_6$tren)]Br	iPr$_2$NEt	THF/H_2O (2:1)	25	24	**8d**	80
11	**7e**	[Cu($C18_6$tren)]Br	iPr$_2$NEt	toluene	80 (MW)	3	**8e**	88
12	**7f**	$(EtO)_3P{\cdot}CuI$	iPr$_2$NEt	toluene	80 (MW)	9	**8f**	63
13	**7f**	[Cu($C18_6$tren)]Br	iPr$_2$NEt	toluene	80 (MW)	3	**8f**	78
14	**7f**	$CuSO_4{\cdot}5H_2O$/sodium ascorbate	none	CH_2Cl_2/H_2O (1:1)	25	2	**8f**	85
15	**7h**	$CuSO_4{\cdot}5H_2O$/sodium ascorbate	none	CH_2Cl_2/H_2O (1:1)	25	4.5	**8h**	70

[a] MW indicates that the reaction was conducted by microwave heating.

3), with reaction times diminishing in this same order. However, the fastest reaction and the highest yield (96% isolated yield, which represents >99% per azide group) was obtained with the $CuSO_4 \cdot H_2O$/sodium ascorbate precatalyst system[58] by using a biphasic CH_2Cl_2/water solvent mixture[87] at room temperature (Table 2, entry 4). The study was extended to other simple alkynes **7b–e** and the process was found to tolerate a broad range of functional groups and reaction conditions, affording the corresponding octatriazolyl-POSS products **8b--e** regioselectively and in good yield (the lowest yield was 61%, which represents 94% per azide group). In those cases for which the optimal room temperature conditions using the $CuSO_4 \cdot H_2O$/sodium ascorbate system resulted in sluggish reactions (Table 2, entry 5), the soluble copper(I) catalysts performed very efficiently under microwave heating in homogenous conditions, with greatly reduced reaction times (Table 2, entries 6, 7, 9, 11–13). The hexane-soluble [Cu(C18$_6$tren)]Br catalyst is particularly attractive in the case of hydrophilic alkynes (Table 2, entries 7–10), allowing a straightforward workup of the crude reaction mixture by a simple hexane/MeOH liquid–liquid extraction, which completely removed the copper catalyst in the hexane fraction, affording the pure product in the MeOH fraction, free from copper impurities. Moreover, this was the most efficient of the three soluble copper(I) catalysts tested. As already observed for their precursor **6**, all new octatriazolyl-POSS products **8** prepared in this work showed a single set of signals in ^{1}H and ^{13}C NMR spectra, and one singlet in the ^{29}Si NMR spectrum,[88] as expected for a perfect 3D cubic molecular symmetry. The narrow range of chemical shifts observed for the ^{29}Si NMR signal ($\delta = -66.6$ to -67.4 ppm), which is known to be very sensitive to cage rearrangements,[78] provided additional proof of the conserved cubic cage structure of all these new POSS derivatives.

Armed with the required methodology for the synthesis of **6** and its efficient derivatization with simple alkynes by CuAAC reaction, we proceeded to apply it to the preparation of more complex functional nanoplatforms. The assembly of a multivalent POSS glycoconjugate[61] (**8g**) and a POSS-fluorophore cluster[62] (**8h**) were selected for this study. Glyco-POSS **8f** was readily assembled from **6** by CuAAC reaction with acetal-protected propargyl α-D-mannopyranoside **7f**[89] under homogenous or biphasic conditions (Table 2, entries 12–14). As observed with the simple alkynes, the best yield was obtained with $CuSO_4 \cdot 5H_2O$/sodium ascorbate in a CH_2Cl_2/H_2O mixture at room temperature (Table 2, entry 14). Deprotection of **8f** under mildly acidic conditions by treatment with trifluoroacetic acid in THF/H_2O (4:1) at room temperature proceeded without affecting the stability of the POSS cage, to afford **8g** in 90% isolated yield. Likewise, reaction of **6** with the ethynylphenyl-functionalized boron dipyrromethene (BODIPY) fluorescent dye **7h**,[90,91] using $CuSO_4 \cdot 5H_2O$/sodium ascorbate in CH_2Cl_2/H_2O, provided the fluorophore cluster **8h** in very good yield (Table 2, entry 15). The kinetics and thermodynamics of the complexation reaction of **8g** and other similarly prepared glyco-POSS compounds with model lectins and the photophysical properties of fluorophore cluster **8h** are currently being evaluated in collaboration with other groups and will be reported in due course.

Conclusion

We have developed a one-step synthesis of **6** from commercially available **5** by a highly efficient diazo-transfer reaction under very mild conditions. We have found that nonaflyl azide is a safer, cheaper, and more efficient diazo-transfer reagent than the more well known and commonly used triflyl azide. Compound **6**, with eight azide groups, is an excellent nanobuilding block that can be efficiently and regioselectively octafunctionalized with a diversity of simple and complex terminal alkynes through CuAAC reaction under very mild conditions to provide new functional nanocages **8** in high yield, maintaining a perfect 3D cubic symmetry. A screening of different CuAAC reaction conditions revealed that both the $CuSO_4 \cdot 5H_2O$/sodium ascorbate precatalyst system in aqueous solvents at room temperature and the recently described [Cu(C18$_6$tren)]Br catalyst in organic solvents under microwave irradiation provided the best yields and shortest reaction times. The mildness, simplicity, efficiency, and versatility of this approach have been demonstrated in the preparation of a glyco-POSS conjugate and a BODIPY–POSS cluster. We believe that this methodology opens ample possibilities for the efficient and controlled assembly of new hybrid organic/inorganic nanomaterials with a high degree of symmetry and with carefully tailored functional properties.

Experimental Section

General: All melting points were measured with a Reicher Jung Thermovar micro-melting apparatus. Infrared (FTIR) spectra were measured as KBr pellets or oils between KBr plates by using a Perkin–Elmer Spectrum One spectrophotometer and data are reported in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER AMX-300 (300 and 75 MHz, respectively), a Varian INOVA 300 (300 and 75 MHz, respectively), a Varian INOVA 400 (400 and 100 MHz, respectively), or a Varian UNITY 500 (500 and 125 MHz, respectively) spectrometer. ^{29}Si NMR spectra were measured on a Varian INOVA 400 spectrometer (79.5 MHz). Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual peaks of the deuterated solvent used, or to internal tetramethylsilane. Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet and/or multiple resonances, br = broad), integration, coupling constants in hertz (Hz), and assignment. ^{1}H and ^{13}C NMR assignments are based on DQ-COSY, HSQC, and HMBC correlation experiments. TLC was performed with Merck Silica Gel 60 F254 plates. Chromatograms were visualized by using UV light and/or treatment with a solution of ammonium molybdate (50 g) and cerium(IV) sulfate (1 g) in 5% aqueous H_2SO_4 (1 L), followed by charring on a hot plate. For detection of azides, the chromatograms were first dipped in a 1% (w/v) solution of Ph_3P in EtOAc, dried at RT, then dipped in a 1% or 5% (w/v) solution of ninhydrin in 95% aqueous EtOH, and finally charred on a hot plate.[92] Column chromatography was performed with Merck silica gel, grade 60, 230–400 mesh. Mass spectra were recorded on a MALDI Voy-

ager-DE PRO time-of-flight (TOF) spectrometer (Applied Biosystems), using a 2,5-dihydroxybenzoic acid matrix, or in an Agilent/HP 1100 LC/MSD spectrometer using ESI or APCI sources. High-resolution mass spectra were recorded on an Agilent 6520 Q-TOF instrument with a ESI source. Elemental analyses were determined by using a Heraus CHN-O analyser. Anhydrous solvents were prepared according to standard methods by distillation over drying agents or elution through a Pure Solv column drying system,[93] obtained from Innovative Technology, Inc. All other solvents were of HPLC grade and were used as provided. All reactions were carried out with magnetic stirring and, if air or moisture sensitive, in oven-dried glassware under argon. Microwave irradiation experiments were performed with a single-mode Discover System from CEM Corporation, using standard Pyrex tubes (10 or 35 mL capacity) sealed with a rubber cap. The copper(I) catalysts $(EtO)_3P{\cdot}CuI$,[94] [CuCl(IPr)] (IPr = *N*,*N*′-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[95] and [Cu($C18_6$tren)]Br[85] ($C18_6$tren = tris(2-dioctadecylaminoethyl)amine) were prepared following described procedures.

Octakis(3-azidopropyl)octasilsesquioxane (6)

Method A: With triflyl azide: a) Synthesis of a solution of triflyl azide in toluene:[76] Toluene (2.6 mL) was added to a solution of sodium azide (1.06 g, 16.32 mmol) in water (2.6 mL), and the mixture was cooled to 0 °C. Triflic anhydride (1.4 mL, 8.16 mmol) was then added dropwise with vigorous stirring (30 min addition time) and the stirring was continued for 2 h at 10 °C. A saturated aqueous solution of $NaHCO_3$ was added dropwise until gas evolution had ceased, and the two phases were separated. The aqueous layer was extracted with toluene (2×2.6 mL). The combined organic layers containing trifyl azide were used in the subsequent diazo-transfer reaction. *b) Diazo-transfer reaction*: The previously prepared stock solution of triflyl azide (7.8 mL), then *i*PrOH (11 mL) were added sequentially to a solution of **5**·8HCl[21] (200 mg, 0.22 mmol), $NaHCO_3$ (592 mg, 7.04 mmol), and $CuSO_4{\cdot}5H_2O$ (4 mg, 0.34 mmol) in water (0.2 mL) at 0 °C. After vigorously stirring the resulting homogeneous mixture at RT for 12 h, the mixture was concentrated under reduced pressure, and the crude product was partitioned between EtOAc (25 mL) and a saturated aqueous solution of ethylenediaminetetraacetic acid (EDTA, 15 mL). The phases were separated, the aqueous solution was extracted with EtOAc (3×10 mL), the combined organic layers were washed with brine, dried (Na_2SO_4), and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc 15:1) to obtain **6** as a colorless viscous oil (130 mg, 54 %). When this reaction was run with 1.0–2.0 g of starting octaamino-POSS **5**, the yield dropped to 30–32 %.

Method B: With nonaflyl azide: a) Synthesis of nonaflyl azide:[73] Nonafluorobutanesulfonyl fluoride (20 mL, 111 mmol) was added to a solution of NaN_3 (8.0 g, 123 mmol) in MeOH (220 mL). After stirring at 20 °C for 12 h, the mixture was poured onto ice–water. If a stable emulsion was formed, which was broken by filtration through a layer of Na_2SO_4 to give two layers. The colorless oily layer of nonafluorobutanesulfonyl azide was separated, dried over Na_2SO_4, and used without further purification for the diazo-transfer reaction (22 g, 60 %). The pure reagent can be kept at 4 °C for several weeks without decomposition. *b) Diazo-transfer reaction*: EtOH (90 mL), a solution of nonafluorobutanesulfonyl azide (13.30 g, 40.9 mmol) in Et_2O (30 mL), a solution of $CuSO_4{\cdot}5H_2O$ (213 mg, 0.852 mmol) in water (2 mL), and a solution of $NaHCO_3$ (4.58 g, 54.6 mmol) in water (26 mL) were added sequentially to a solution of **5**·8HCl[21] (2.0 g, 1.70 mmol) in water (2 mL) at 0 °C. The reaction mixture was vigorously stirred at 0 °C for 1 h, and at RT for 24 h. The mixture was concentrated under reduced pressure, CH_2Cl_2 (150 mL) was added, and the resultant solution was washed with a saturated aqueous solution of $NaHCO_3$ (4×100 mL) to remove the nonafluorobutanesulfonamide. The organic layer was separated, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane/EtOAc 15:1) to afford **6** as a colorless viscous oil (1.250 g, 67 %). R_f = 0.6 (silica gel, hexane/EtOAc 5:1), IR (film): ν = 2939, 2875, 2099 (s; N_3), 1304, 1278, 1243, 1188, 1111 (s), 699 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.46–1.00 (m, 16H; $SiCH_2$), 1.42–1.99 (m, 16H; $SiCH_2CH_2$), 3.28 ppm (t, 16H, J = 6.9 Hz; $SiCH_2CH_2CH_2N_3$); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 9.0 ($SiCH_2$), 22.5 ($SiCH_2CH_2$), 53.4 ppm ($SiCH_2CH_2CH_2N_3$); ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = −67.0 ppm; MS (API-ESI): *m*/*z* (%): 1112 [M+Na^+]; HRMS (ESI): *m*/*z* calcd for $C_{24}H_{52}N_{25}O_{12}Si_8$: 1106.2381 [*M*+$NH_4^+$]; found: 1106.2396.

Octakis[3-(4′-phenyl-1′*H*-1′,2′,3′-triazol-1′-yl)propyl]octasilsesquioxane (8a)

Method A: $(EtO)_3P{\cdot}CuI$ (3 mg, 0.008 mmol) and *i*Pr_2NEt (66 μL, 0.378 mmol) were added to a solution of **6** (20 mg, 0.018 mmol) and phenylacetylene (20 μL, 0.182 mmol) in toluene (1 mL) under argon. After stirring for 70 h at RT, the solvent was removed under reduced pressure, the crude product was dissolved in CH_2Cl_2, and the product was precipitated with Et_2O to afford **8a** (30 mg, 90 %) as a white powder.

Method B: [CuCl(IPr)] (3 mg, 0.009 mmol) and *i*Pr_2NEt (66 μL, 0.378 mmol) were added to a solution of **6** (20 mg, 0.018 mmol) and phenylacetylene (20 μL, 0.182 mmol) in toluene (1 mL) under argon. After stirring for 48 h at RT, the solvent was removed under reduced pressure, the crude product was dissolved in CH_2Cl_2, and the product was precipitated with Et_2O to afford **8a** (30 mg, 90 %) as a white powder.

Method C: [Cu($C18_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr_2NEt (66 μL, 0.378 mmol) were added to a solution of **6** (20 mg, 0.018 mmol) and phenylacetylene (20 μL, 0.182 mmol) in toluene (1 mL) under argon. After stirring for 20 h at RT, the solvent was removed under reduced pressure, the crude product was dissolved in CH_2Cl_2, and the product was precipitated with Et_2O to afford **8a** (31 mg, 92 %) as a white powder.

Method D: A solution of $CuSO_4{\cdot}5H_2O$ (2.5 mg, 0.010 mmol) and sodium ascorbate (9 mg, 0.045 mmol) in water (0.5 mL) were added to a solution of **6** (20 mg, 0.018 mmol) and phenylacetylene (20 μL, 0.182 mmol) in CH_2Cl_2 (0.5 mL). After stirring for 1 h at RT, a saturated aqueous solution of EDTA (1 mL) was added, the mixture was vigorously stirred for 30 min, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed under reduced pressure, the crude product was dissolved in CH_2Cl_2, and the product was precipitated with Et_2O to afford **8a** (33 mg, 96 %) as a white powder. M.p. (Et_2O) 207–209 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.61–0.65 (m, 16H; $SiCH_2$), 2.00–2.04 (m, 16H; $SiCH_2CH_2$), 4.35 (t, 16H, J = 6.7 Hz; $SiCH_2CH_2CH_2N_3$), 7.26–7.38 (m, 24H; Ar), 7.82 (d, 16H, J = 7.4 Hz; Ar), 7.95 ppm (s, 8H; 1,2,3-triazole); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.8 ($SiCH_2$), 24.7 ($SiCH_2CH_2$), 52.4 ($SiCH_2CH_2CH_2N_3$), 120.4 (*C*H; 1,2,3-triazole), 125.8 (2*C*H; Ph), 128.3 (*C*H; Ph), 129.0 (2*C*H; Ph), 130.8 (C; Ph), 148.1 ppm (C, 1,2,3-triazole); ^{29}Si NMR (79.5 MHz, $CDCl_3$): δ = −67.2 ppm; HRMS (ESI): *m*/*z* calcd for $C_{88}H_{97}N_{22}O_{12}Si_8$: 1905.5872 [*M*+$H^+$]; found: 1905.5816.

Octakis[(3-(4′-((1″,3″-dioxoisoindolin-2″-yl)methyl)-1′*H*-1′,2′,3′-triazol-1′-yl)propyl)]octasilsesquioxane (8b)

Method C: [Cu($C18_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr_2NEt (66 μL, 0.378 mmol) were added to a solution of **6** (20 mg, 0.018 mmol) and *N*-propargylphthalimide (33 mg, 0.178 mmol) in toluene (1 mL) under argon. After heating for 3 h at 80 °C under microwave irradiation, a white precipitate was formed. The reaction mixture was dissolved in MeOH and the product was precipitated with $CHCl_3$ to afford **8b** as a white powder (34.2 mg, 74 %).

Method D: A solution of $CuSO_4{\cdot}5H_2O$ (2.5 mg, 0.010 mmol) and sodium ascorbate (9 mg, 0.045 mmol) in water (1 mL) were added to a solution of **6** (20 mg, 0.018 mmol) and *N*-propargylphthalimide (33 mg, 0.178 mmol) in CH_2Cl_2 (1 mL). After stirring for 18 h at RT, a saturated aqueous solution of EDTA (1 mL) was added, the mixture was vigorously stirred for 30 min, the phases were separated, and the aqueous layer was extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were dried over Na_2SO_4, the solvent was removed under reduced pressure, the crude product was dissolved in MeOH, and the product was precipitated with $CHCl_3$ to afford **8b** as a white powder (28 mg, 61 %). M.p. ($CHCl_3$) 163–166 °C; ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 0.46–0.50 (m, 16H; $SiCH_2$), 1.74–1.78 (m, 16H; $SiCH_2CH_2$), 4.21 (t, 16H, J = 6.7 Hz; $SiCH_2CH_2CH_2$), 7.77–7.83 (m, 32H; Ar), 8.03 ppm (s, 8H; 1,2,3-triazole); ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 7.9 ($SiCH_2$), 23.3 ($SiCH_2CH_2$), 32.9 (CH_2N-phthalimido), 51.2 ($SiCH_2CH_2CH_2$), 123.1 (*C*H, 1,2,3-triazole; 2*C*H; phthalimido), 131.5 (2*C*; phthalimido), 134.4 (2*C*H; phthalimido),

142.2 (*C*; 1,2,3-triazole), 167.2 ppm (*C*=O; phthalimido); ^{29}Si NMR (79.5 MHz, [D$_6$]DMSO): $\delta = -66.6$ ppm; HRMS (ESI): *m/z* calcd for $C_{112}H_{105}N_{32}O_{28}Si_8$: 2569.5930 [$M$+H$^+$]; found: 2569.5841.

Octakis[(3-(4′-(hydroxymethyl)-1′*H*-1′,2′,3′-triazol-1′-yl)propyl)]octasilsesquioxane (8c)

Method C: [Cu(C18$_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 μL, 0.378 mmol) were added to a solution of **6** (20 mg, 0.018 mmol) and propargyl alcohol (11 μL, 0.189 mmol) in toluene (1.0 mL) under argon. After heating for 3 h at 80 °C under microwave irradiation, a white precipitate was formed. The precipitate was dissolved in MeOH (2 mL), the solution was extracted with hexane (3×3 mL), and the methanol layer was concentrated under reduced pressure to afford **8c** as a colorless oil (18.5 mg, 67 %). Using THF/H$_2$O (2:1) instead of toluene in this procedure gave **8c** in 77 % yield, after stirring the reaction for 25 h at RT. ^{1}H NMR (400 MHz, CD$_3$OD): $\delta = 0.59$–0.63 (m, 16H; SiCH_2), 1.92–1.98 (m, 16H; SiCH$_2$CH_2), 4.39 (t, 16H, $J = 6.8$ Hz; SiCH$_2$CH$_2$CH_2), 4.69 (s, 16H; CH_2OH), 7.93 ppm (s, 8H; 1,2,3-triazole); ^{13}C NMR (100 MHz, CD$_3$OD): $\delta = 9.5$ (Si*C*H$_2$), 25.2 (SiCH$_2$*C*H$_2$), 53.4 (SiCH$_2$CH$_2$*C*H$_2$), 56.6 (*C*H$_2$OH), 124.5 (*C*H; 1,2,3-triazole), 149.2 ppm (*C*; 1,2,3-triazole); HRMS (ESI): *m/z* calcd for $C_{48}H_{81}N_{24}O_{20}Si_8$: 1537.4213 [$M$+H$^+$]; found: 1537.4253.

Octakis[3-(4′-(4″-hydroxybutyl)-1′*H*-1′,2′,3′-triazol-1′-yl]propyl)silsesquioxane (8d)

Method C: [Cu(C18$_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 μL, 0.378 mmol) were added to a solution of **6** (20 mg, 0.018 mmol) and 5-hexyn-1-ol (21 μL, 0.190 mmol) in toluene (1 mL), under argon. After heating for 3 h at 80 °C under microwave irradiation, a white precipitate was formed. The precipitate was dissolved in MeOH (2 mL), the solution was extracted with hexane (3×5 mL), and the methanol layer was concentrated under reduced pressure to afford **8d** (24 mg, 71 %) as a colorless oil. Using THF/H$_2$O (2:1) instead of toluene in this procedure gave **8d** in 80 % yield after stirring the reaction for 25 h at RT. ^{1}H NMR (400 MHz, [D$_6$]DMSO): $\delta = 0.45$ (brs, 16H; SiCH_2), 1.39–1.47 (m, 16H; CH$_2$CH$_2$CH_2CH$_2$OH), 1.53–1.63 (m, 16H; CH$_2$CH_2CH$_2$CH$_2$OH), 1.75 (brs, 16H; SiCH$_2$CH_2), 2.55–2.60 (m, 16H; CH_2CH$_2$CH$_2$CH$_2$OH), 3.37 (brs, 16H; CH$_2$CH$_2$CH$_2$CH_2OH), 4.22 (brs, 16H; SiCH$_2$CH$_2$CH_2), 4.39 (brs, 16H; CH$_2$CH$_2$CH$_2$CH$_2$O*H*), 7.79 ppm (s, 8H; 1,2,3-triazole); ^{13}C NMR (100 MHz, [D$_6$]DMSO): $\delta = 9.2$ (Si*C*H$_2$; data obtained from the HSQC spectrum), 24.1 (SiCH$_2$*C*H$_2$), 25.5 (*C*H$_2$CH$_2$CH$_2$CH$_2$OH), 26.3 (CH$_2$*C*H$_2$CH$_2$CH$_2$OH), 32.7 (CH$_2$CH$_2$*C*H$_2$CH$_2$OH), 51.7 (SiCH$_2$CH$_2$*C*H$_2$), 61.1 (CH$_2$CH$_2$CH$_2$*C*H$_2$OH), 122.3 (*C*H; 1,2,3-triazole), 147.6 ppm (*C*; 1,2,3-triazole); HRMS (ESI): *m/z* calcd for $C_{72}H_{129}N_{24}O_{20}Si_8$: 1873.7969 [$M$+H$^+$]; found: 1873.7951.

Octakis[3-(4′-(methoxycarbonyl)-1′*H*-1′,2′,3′-triazol-1′-yl)propyl]octasilsesquioxane (8e)

Method C: [Cu(C18$_6$tren)]Br (17 mg, 0.009 mmol) and *i*Pr$_2$NEt (66 μL, 0.378 mmol) were added to a solution of **6** (20 mg, 0.018 mmol) and methyl propiolate (16 μL, 0.180 mmol) in toluene (1 mL) under argon. After heating for 8 h at 80 °C under microwave irradiation, a white precipitate was formed. The reaction mixture was dissolved in MeOH and the product was precipitated by addition of CHCl$_3$ to afford **8e** (28 mg, 88 %) as a white powder. M.p. (CHCl$_3$) 125–127 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.54$–0.59 (m, 16H; SiCH_2), 1.97–2.02 (m, 16H; SiCH$_2$CH_2), 3.93 (s, 24H; COOCH_3), 4.42 (t, 16H, $J = 6.7$ Hz; SiCH$_2$CH$_2$CH_2), 8.24 ppm (s, 8H; 1,2,3-triazole); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 8.3$ (Si*C*H$_2$), 23.7 (SiCH$_2$*C*H$_2$), 52.2 (SiCH$_2$CH$_2$*C*H$_2$), 52.4 (COO*C*H$_3$), 127.9 (*C*H; 1,2,3-triazole), 139.8 (*C*; 1,2,3-triazole), 161.1 ppm (*C*OOCH$_3$); ^{29}Si NMR (79.5 MHz, CDCl$_3$) $\delta = -67.4$ ppm; HRMS (ESI): *m/z* calcd for $C_{56}H_{81}N_{24}O_{28}Si_8$: 1761.3806 [$M$+H$^+$]; found: 1761.3796.

Octakis{3-[4′-((2″,3″,4″,6″-di-*O*-isopropylidene-α-D-mannopyranos-1″-yl)-methyl)-1′*H*-1′,2′,3′-triazol-1′-yl]propyl}octasilsesquioxane (8f)

Method A: (EtO)$_3$P·CuI (5 mg, 0.014 mmol) and *i*Pr$_2$NEt (91 μL, 0.522 mmol) were added to a solution of **6** (35 mg, 0.032 mmol) and **7f**[89] (86 mg, 0.288 mmol) in THF (1 mL) under argon. After stirring for 9 h at 80 °C under microwave irradiation, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH 10:1) to afford **8f** as a white powder (70 mg, 63 %).

Method C: [Cu(C18$_6$tren)]Br (43 mg, 0.024 mmol) and *i*Pr$_2$NEt (135 μL, 0.775 mmol) were added to a solution of **6** (51 mg, 0.047 mmol) and **7f**[89] (144 mg, 0.483 mmol) in toluene (5 mL) under argon. After stirring for 8 h at 80 °C under microwave irradiation, a white precipitate was formed. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH 10:1) to afford **8f** as a white powder (127 mg, 78 %).

Method D: A solution of CuSO$_4$·5H$_2$O (2.5 mg, 0.010 mmol) and sodium ascorbate (9 mg, 0.045 mmol) in water (0.5 mL) was added to a solution of **6** (20 mg, 0.018 mmol) and **7f**[89] (53 mg, 0.178 mmol) in CH$_2$Cl$_2$ (0.5 mL). After stirring for 2 h at RT, a saturated aqueous solution of EDTA (1 mL) was added, the mixture was vigorously stirred for 30 min, the phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (2×2 mL). The organic layers were combined, dried over Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (CH$_2$Cl$_2$/MeOH 10:1) to afford **8f** as a white powder (53 mg, 85 %). M.p. (CH$_2$Cl$_2$) 118–122 °C; ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.57$–0.61 (m, 16H; Si-CH_2CH$_2$CH$_2$), 1.25 (s, 24H; C(CH$_3$)$_2$), 1.34 (s, 24H; C(CH$_3$)$_2$), 1.45 (s, 24H; C(CH$_3$)$_2$), 1.47 (s, 24H; C(CH$_3$)$_2$), 1.92–2.03 (m, 16H; SiCH$_2$CH_2CH$_2$), 3.51–3.60 (m, 8H; H-5″), 3.66–3.67 (m, 8H; H-4″), 3.70 (t, 8H, $J = 10.5$ Hz; H-6a″), 3.82 (dd, 8H, $J = 5.6$, 10.5 Hz; H-6b″), 4.05 (dd, 8H, $J = 5.4$, 7.8 Hz; H-3″), 4.11 (d, 8H, $J = 5.4$ Hz; H-2″), 4.27 (t, 16H, $J = 7.1$ Hz; SiCH$_2$CH$_2$CH_2), 4.60 (d, 8H, $J = 12.2$ Hz; CH_2O-C-1″), 4.77 (d, 8H, $J = 12.2$ Hz; CH_2O-C-1″), 5.09 (s, 1H; H-1″), 7.72 ppm (s, 8H; CH of 1,2,3-triazole); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 8.9$ (Si*C*H$_2$CH$_2$CH$_2$), 19.0 (C(*C*H$_3$)$_2$), 24.2 (SiCH$_2$*C*H$_2$CH$_2$), 26.4 (C(*C*H$_3$)$_2$), 28.4 (C(*C*H$_3$)$_2$), 29.3 (C(*C*H$_3$)$_2$), 52.4 (SiCH$_2$CH$_2$*C*H$_2$), 60.5 (*C*H$_2$O-C-1″), 61.8 (C-5″), 62.2 (C-6″), 72.8 (C-4″), 75.0 (C-3″), 76.1 (C-2″), 97.2 (C-1″), 99.9 (*C*(CH$_3$)$_2$), 109.7 (*C*(CH$_3$)$_2$), 123.6 (CH of 1,2,3-triazole), 143.9 ppm (C of 1,2,3-triazole); ^{29}Si NMR (79.5 MHz, CDCl$_3$): $\delta = -67.3$ ppm; MS (MALDI-TOF; 2,5-dihydroxybenzoic acid matrix): *m/z*: 3496 [M+Na$^+$]; HRMS (ESI): *m/z* calcd for $C_{144}H_{226}N_{24}O_{60}Si_8$: 1737.6762 [($M$+2H)$^{2+}$]; found: 1737.6858.

Octakis{3-[4′-((α-D-mannopyranos-1′-yl)methyl)-1′*H*-1′,2′,3′-triazol-1′-yl]-propyl}octasilsesquioxane (8g): Trifluoroacetic acid (25 μL, 0.324 mmol) was added to a solution of **8f** (54 mg, 0.015 mmol) in THF/H$_2$O (4:1) (2 mL). After stirring for 3 h at RT, compound **8g** was isolated as a white precipitate (38 mg, 90 %), m. p. (H$_2$O) 112–116 °C; ^{1}H NMR (500 MHz, D$_2$O): $\delta = 0.32$–0.44 (m, 16H; Si-CH_2CH$_2$CH$_2$), 1.74–1.78 (m, 16H; SiCH$_2$CH_2CH$_2$), 3.47–3.78 (m, 48H; H-2″, H-3″, H-4″, H-5″, H-6a″, and H-6b″), 4.14–4.30 (m, 16H; SiCH$_2$CH$_2$CH_2), 4.61–4.68 (m, 16H; CH_2CCH), 4.80 (s, 8H; H-1″), 7.90 ppm (brs, 8H; 1,2,3-triazole); ^{13}C NMR (125 MHz, [D$_6$]DMSO): $\delta = 10.7$ (Si*C*H$_2$CH$_2$CH$_2$; data obtained from HSQC spectrum), 25.2 (SiCH$_2$*C*H$_2$CH$_2$), 53.46 (SiCH$_2$CH$_2$*C*H2), 61.0 (O*C*H$_2$-triazole), 62.3 (C-6″), 68.1 (C-4″), 71.4 (C-2″), 71.9 (C-3″), 74.5 (C-5″), 100.7 (C-1″), 126.4 (CH in triazole), 145.0 ppm (C in triazole); MS (MALDI-TOF, 2,5-dihydroxybenxoic acid matrix): *m/z*: 2855 [M+Na]$^+$; HRMS (ESI): *m/z*: calcd for $C_{97}H_{161}N_{23}NaO_{60}Si_8$: 2855.8258 [$M$+Na]$^+$; found: 2855.8253.

Octakis(3-{4′-[4″-(2‴,8‴-diethyl-5‴,5‴-difluoro-1‴,3‴,7‴,9‴-tetramethyl-dipyrrolo[1‴,2‴c:2‴,1‴f][1‴,3‴,2‴]diazaborinin-4‴-ium-5‴-uid-10‴-yl)-phenyl]-1′*H*-1′,2′,3′-triazol-1′-yl}propyl)octasilsesquioxane (8h)

Method D: A solution of CuSO$_4$·5H$_2$O (2.5 mg, 0.010 mmol) and sodium ascorbate (9 mg, 0.045 mmol) in water (0.6 mL) was added to a solution of **6** (20 mg, 0.018 mmol) and **8h**[90] (72 mg, 0,178 mmol) in CH$_2$Cl$_2$ (0.9 mL). After stirring for 4.5 h at RT, a saturated aqueous solution of EDTA (1 mL) was added, the mixture was vigorously stirred for 30 min, the phases were separated, and the aqueous layer was extracted with CH$_2$Cl$_2$ (2×3 mL). The organic layers were combined, dried over Na$_2$SO$_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (hexane/EtOAc 5:1) to afford **8h** as a red powder (54 mg, 70 %). M.p. (CH$_2$Cl$_2$) 290 °C (decomposition); ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 0.68$–0.75 (m, 16H; Si-CH_2CH$_2$CH$_2$), 0.93 (t, 48H, $J = 7.4$ Hz; 16×(CH_3CH$_2$), 1.30 (s, 48H; 16×CH_3-C), 2.13–2.18 (m, 16H; SiCH$_2$CH_2CH$_2$), 2.25 (q, 32H, $J = 7.4$ Hz; 16×CH_2CH$_3$), 2.51 (s, 48H; 16×CH_3-C), 4.46 (t, 16H, $J = 6.9$ Hz; SiCH$_2$CH$_2$CH_2), 7.32 (d, 16H, $J = 8.2$ Hz; 2×C*H* Ar), 8.01 (d, 16H, J=

8.2; 2×C*H* Ar), 8.15 ppm (s, 8H; 1,2,3-triazole); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 8.7$ ($SiCH_2CH_2CH_2$), 11.9 (CH_3), 12.5 (CH_3), 14.6 (CH_3-CH_2), 17.0 (CH_3-CH_2), 24.1 ($SiCH_2CH_2CH_2$), 52.4 ($SiCH_2CH_2CH_2$), 120.7 (CH in 1,2,3-triazole), 126.1 (Ph), 129.0 (Ph), 130.1, 131.2, 133.1, 135.8, 137.9, 139.2 (C in 1,2,3-triazole), 147.1, 154.0 ppm; ^{29}Si NMR (79.5 MHz, $CDCl_3$) $\delta = -67.1$ ppm; MS (MALDI-TOF, 2,5-dihydroxybenzoic acid matrix): m/z: 4304 $[M-F]^+$.

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