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Organic Nanotubes

A New Route to Organic Nanotubes from Porphyrin Dendrimers[**]

Yoonkyung Kim, Michael F. Mayer, and
Steven C. Zimmerman[*]

The controlled synthesis of discrete nanostructures is an exciting challenge that remains the cornerstone of the bottom-up approach. In this regard, considerable effort has been directed toward nanotubes. Within the last decade, numerous reports have described the synthesis and properties of carbon (single-walled and multi-walled nanotubes (SWNTs and MWNTs, respectively)),[1] inorganic,[2] and non-fullerene organic nanotubes.[3] In particular, organic nanotubes have been synthesized from oligopeptides,[4] oligosaccharides,[5] block copolymers,[6] and a variety of other organic building blocks.[7] Many of these nanotubes, however, are formed as noncovalent assemblies and are, thus, stable only under specific conditions. Herein we report a core–shell approach[8] to covalent organic nanotubes by molding dendritic building blocks around an oligoporphyrin core.

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[*] Prof. S. C. Zimmerman, Y. Kim, Dr. M. F. Mayer
Department of Chemistry
University of Illinois at Urbana-Champaign
600 S. Mathews Avenue, Urbana, IL 61801 (USA)
Fax: (+1) 217-244-9919
E-mail: sczimmer@uiuc.edu

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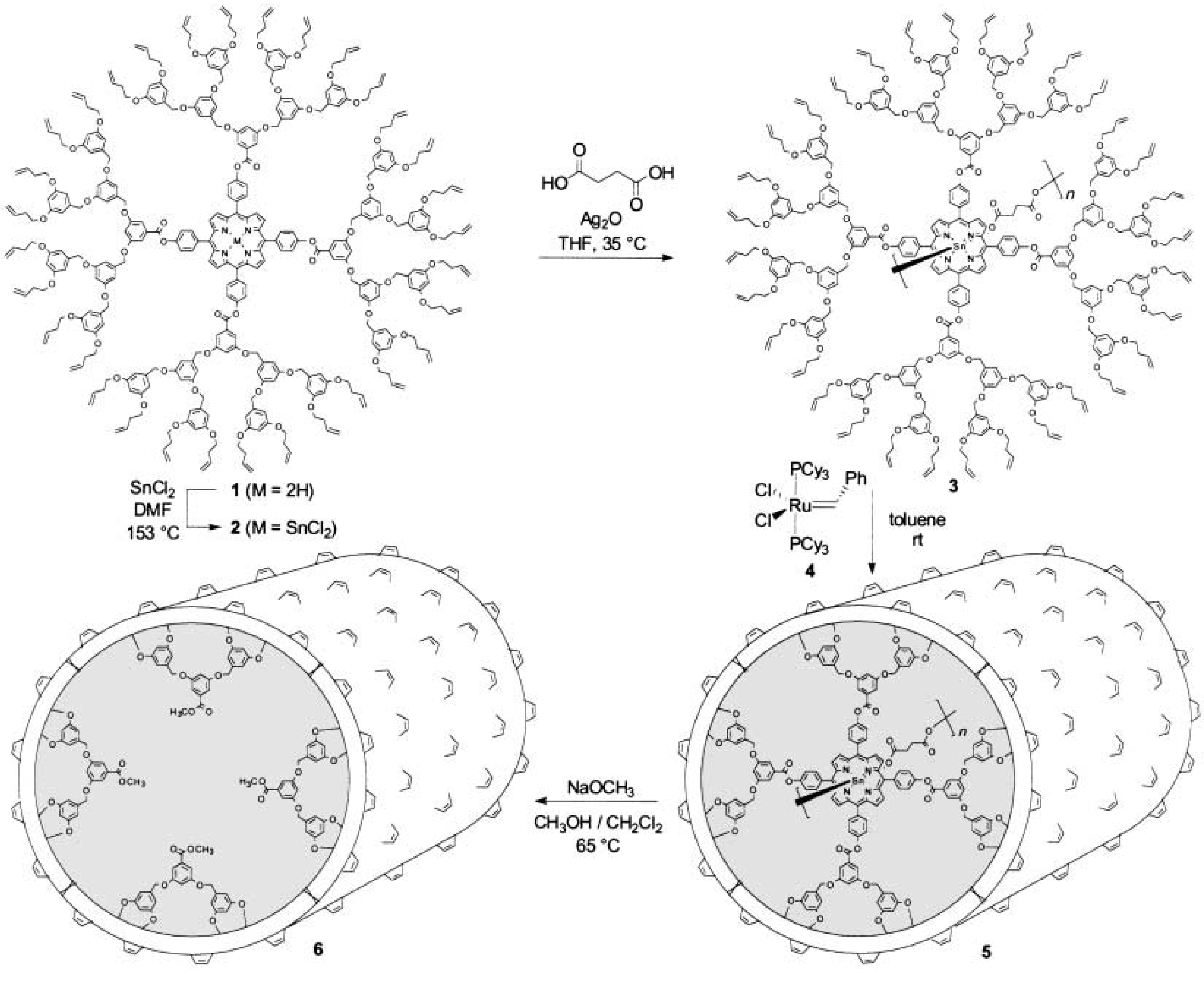
The specific method involves three key steps: 1) formation of a coordination polymer from a dendritic metalloporphyrin containing multiple alkene end groups,[9] 2) extensive cross-linking of the dendrons by a ring-closing metathesis (RCM) reaction,[10] and 3) cleavage of the focal point linkages (dendron-to-porphyrin) to remove the oligomerized core.[11] The synthesis began with porphyrin dendrimer **1**,[12,13] which was treated with tin(II) chloride (by using the DMF method[14]) to produce tin(IV) porphyrin complex **2** (Scheme 1). The metalation was quantitative, but was accompanied by a small amount of cleavage of the porphyrin dendron ester, thus resulting in a 95% yield. Analytically pure **2** was obtained after size-exclusion chromatography (SEC). The oligomerization of **2** was carried out in a concentrated THF solution with excess Ag_2O and using one equivalent of succinic acid as the bridging bidentate ligand. The reaction was monitored by analytical SEC and UV/Vis spectroscopy. As the reaction progressed, the Soret band of the tin porphyrin shifted from 430 to 420 nm and the SEC analysis showed significant peak broadening along with a shift to shorter retention time; the leading edge of the broadened peak corresponded to the size exclusion limit of the column (Figure 1). Key to the success of this oligomerization was the gradual concentration of the reaction mixture by slow evaporation of the solvent over the course of the reaction. After filtration, the crude product **3** was characterized and used directly in the next step.

The oligomerized product **3** was sufficiently soluble and stable in common organic solvents to allow characterization by ^{1}H NMR spectroscopy and SEC. The ^{1}H NMR spectrum of **3** showed significant peak broadening relative to that of **2**.[12] A broad peak at $\delta = -3.3$ ppm was observed and assigned to the methylene groups of the axially bridging succinate ligand. Analysis of **3** by SEC was carried out in toluene with molecular-weight (M_W) calibration performed both with conventional polystyrene (PS) and dendrimer standards.[16] Although dendrimers are considered more appropriate size standards, the current calibration used just three compounds and considerable extrapolation was required for the high-molecular-weight oligomeric porphyrins. The two sets of standards, PS and dendrimers, gave average M_W values of 23000 and 72600 Da for **3**, roughly corresponding to a



Scheme 1. The synthetic route to organic nanotubes.[15]

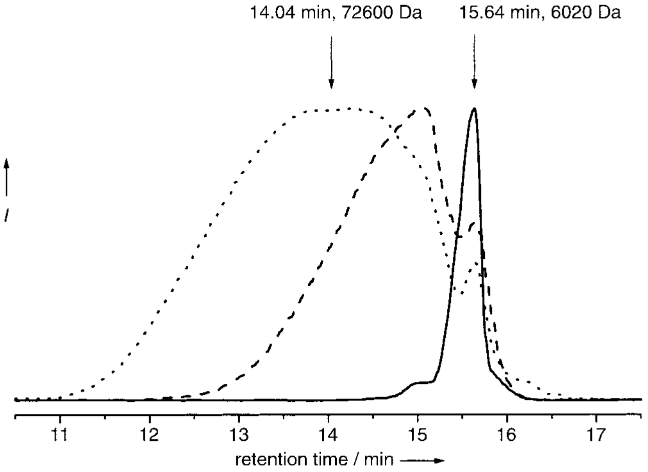


Figure 1. SEC traces (toluene, UV detector at 289 nm) obtained on a double Waters Styragel HR 4E column (M_W range is 50–100000 Da) from an oligomerization to form **3**, reaction time: 4 h: ——, 29 h: -----, and 45 h: •••••. Each plot was normalized according to the peak maximum. Peak picking was done at the maximum and the center of the bandwidth at the half-height for traces —— and •••••, respectively. Molecular weights were estimated by calibration with dendrimer standards.

tetramer and dodecamer, respectively (Figure 1 and Table 1). These values likely set the limits on the size of **3**. Peaks corresponding to oligomer **3** were not observed by MALDI-TOF-MS, instead peaks for the monomer (**3**, $n = 1$) and a tin porphyrin dendrimer adduct of the matrix, 2-([4-hydroxyphenyl)azo]benzoic acid (HABA) were present.[12]

Computer modeling studies on hexameric **3** were performed to show the approximate dimensions of a small oligomer and the possibility of cross-linking the alkene groups between monomers (Figure 2). The model suggests a Sn to Sn distance (terminal units) of about 4.5 nm and a dendron focal point to focal point (*trans*) distance of about 1.5 nm. The alkene moieties of dendrons attached to the same and adjacent porphyrin units are proximate, which suggests that extensive interdendron cross-linking would be feasible along porphyrin oligomer **3**. The potential for interoligomer cross-linking was estimated by performing RCM reactions of **2** at 10^{-5} and 10^{-4} M with 15 mol% of the Grubbs ruthenium catalyst **4**[10] per alkene group. Analysis of the cross-linked products by SEC showed that the intramolecularly cross-linked product (**7**) was the major product and that the amount of dimer formed from **2** was 11% at 10^{-5} M and 37% at 10^{-4} M, which is consistent with previous studies.[17]

Oligomer **3** was cross-linked immediately after work-up because the molecular weight of **3**, as determined by SEC, was found to decrease over time.[12] The homoallyl groups of oligomer **3** were metathesized by using the same procedure as described for **2** at a concentration of 10^{-5} M in the monomeric unit. With a degree of polymerization (DP) between four and twelve, the actual molar concentration of oligomer **3** should be well below 10^{-5} M, thus ensuring much less than 10% interoligomer cross-linking.

The RCM reaction was monitored by MALDI-TOF-MS and conducted until the highest peak for the monomer (namely, **5**, $n = 1$) corresponded to a product with 15 out of 16 possible cross-links. In addition to monomer, the MALDI-MS of **5** contained a distribution of broad peaks (Figure 3a) roughly separated by the mass of the monomeric unit. The detection of oligomers with molecular weights over 100000 Da (DP $\geq$ 18) was not possible as these peaks were too broad. Peak broadening was also observed in the ^{1}H NMR spectrum of **5**.[12] An upfield shift for the methine peak of the alkene moieties from 5.74 to 5.49 ppm was observed, which is diagnostic of conversion of a terminal alkene into an internal alkene.[17c]

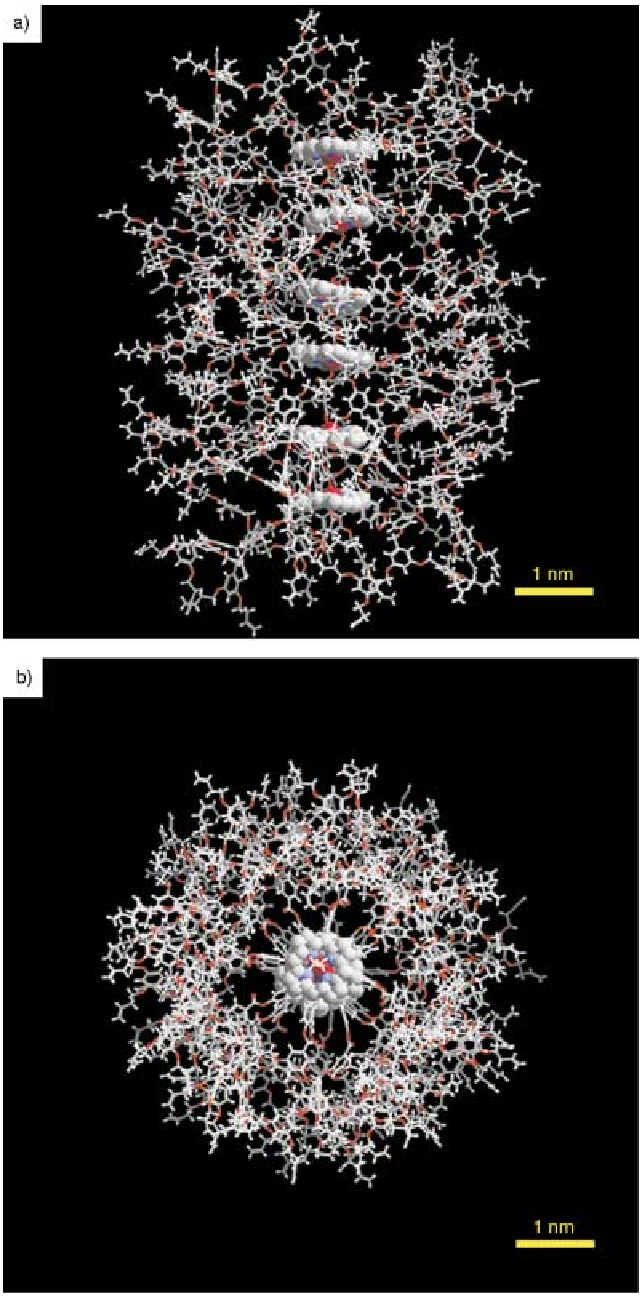


Figure 2. Computer-generated structure of **3** (a hexameric tin–porphyrin dendrimer bridged by succinate ligands). Energy minimization of the hexamer was performed by using the modeling program Cerius^2 (MSI, Inc.) and its Dreiding force field. a) Side view; b) top view.

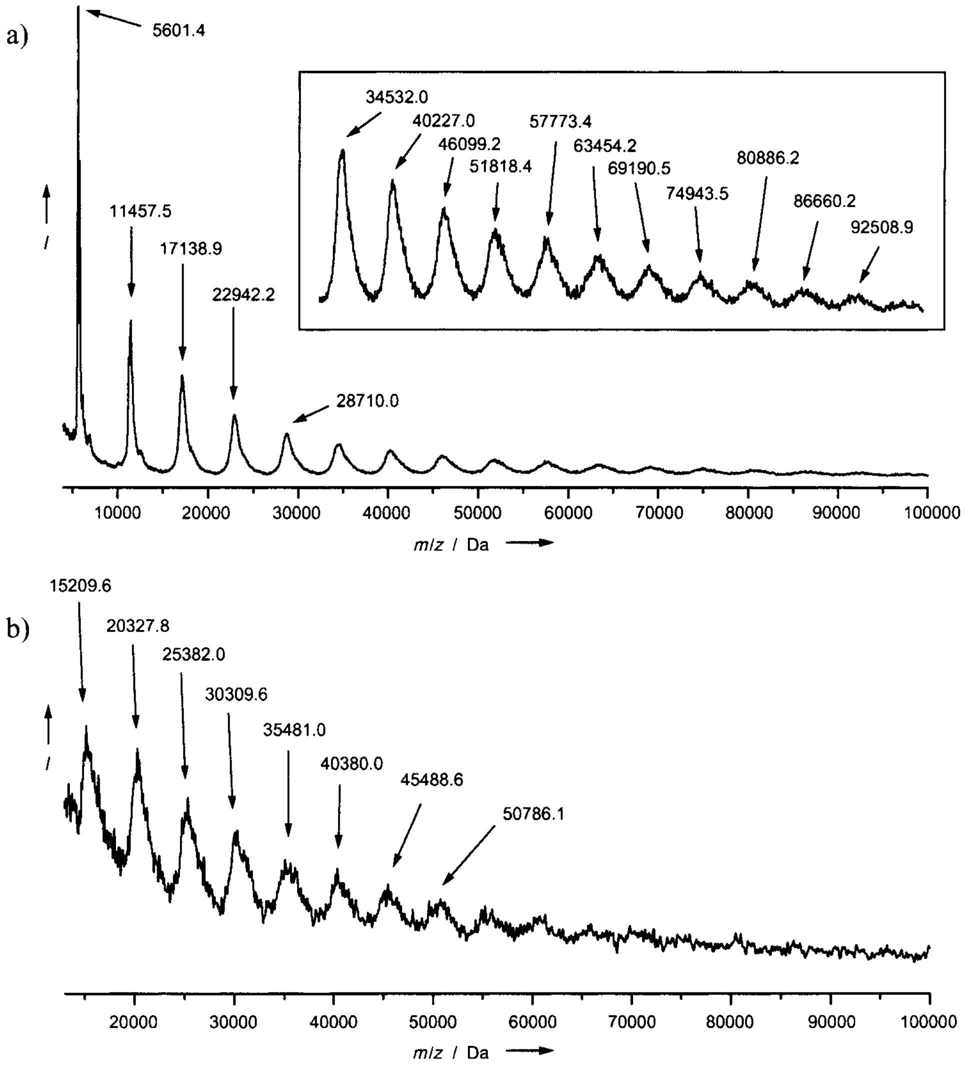


Figure 3. MALDI-MS spectra of a) **5** (the inset shows the expanded region for *m/z* 32000–100000 Da) and b) **6**. The *m/z* values were assigned at the center of the bandwidth at the half-height for each broad peak. The spectrum of **6** was obtained using a column fraction from preparative SEC containing oligomers of trimer and higher.

Table 1: Comparison of molecular weights calculated by SEC in toluene or NMP, using PS and dendrimer standards (DS).

Cmpd	Theoretical M_w[a]	Toluene[b] PS[d,e]	Toluene[b] DS[d]	NMP[c] PS[d,e] M_n[f]	NMP[c] PS[d,e] M_w[g]	NMP[c] PS[d,e] PDI[h]	NMP[c] DS[d]
2	6073	6020	5840	14200	15900	1.12	6130
3	*n*(6118)	23000	72600	N/A	N/A	N/A	N/A
5	*n*(5669)	N/A	N/A	35000	83800	2.40	30500
6[i]	*n*(4886)	N/A	N/A	32000	124000	3.88	39700
7[j]	5624	4260	3040	12500	13600	1.09	3950

[a] The theoretical molecular weights for oligomers **3**, **5**, and **6** are shown in terms of the monomeric unit (*n* = integer). The theoretical molecular weights for **5**, **6**, and **7** correspond to fully cross-linked compounds. [b] UV detector at 289 nm. [c] Refractive index detector. [d] Calculated on the basis of the center of the bandwidth at the half-height of the broad peak for **3**, **5**, and **6**. For details see ref. [12]. [e] Estimated with a conventional PS calibration. [f] Number-average molar mass. [g] Weight-average molar mass. [h] Polydispersity index. [i] SEC data for **6** were obtained by using combined preparative SEC column fractions composed of trimer and higher oligomers. [j] Compound **7** is the intramolecular cross-linked product of the RCM reaction of **2**.

Compound **5** was not fully soluble in either toluene or THF so its SEC analysis (Figure 4) was performed in 1-methyl-2-pyrrolidinone (NMP). The molecular weights determined with PS standards (35000 Da) and dendrimer standards (30500 Da) agreed well in this solvent, and suggested that oligomer **5** corresponded, on average, to a pentamer. However, similarly cross-linked dendrimers are significantly more compact than their precursors and, thus, their molecular weights determined by SEC are typically underestimated by 20–30% (for example, see **7** versus **2** in Table 1 and ref. [17]). As such, **5** may be somewhat longer than a pentamer.

In the final step of the synthetic route, the internal oligoporphyrin core of **5** was removed through a transesterification reac-

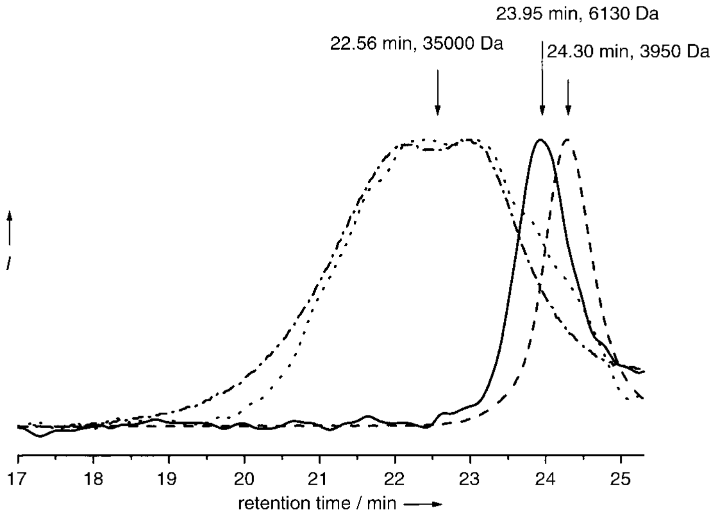


Figure 4. SEC traces (NMP, RI detector) of **2** (——), **7** (-----), **5** (•••••), and **6** (–•–•). SEC was performed on a triple PLgel 10 μm MIXED-B LS column (M_W range 500–10000000 Da) from Polymer Laboratories. Each plot was normalized according to the peak maximum. Peaks were picked at the maxima for **2** and **7**, and at an arbitrary value at the approximate center of the broad regions for **5** and **6**. Molecular weights were estimated by calibration with dendrimer standards. The trace of **6** was obtained using a column fraction from preparative SEC containing oligomers of trimer and higher.

tion. The resultant cored compound **6** was relatively soluble in organic solvents, thus enabling purification and partial fractionation by SEC. A portion of reaction mixture was eluted with THF through a preparative SEC column and two widely separated major bands were observed. A first light-green band was collected in several fractions. Analytical SEC of these fractions showed that **6** was not only separated from the core but also partially fractionated by length. Each column fraction was analyzed by MALDI-TOF-MS and only the fractions containing trimer and higher were combined for further analysis. The mass spectra show a straightforward relationship in the M_W differences between **5** and **6** for each oligomer (Figure 3), with an average loss of 734 Da per monomeric unit after removal of the core.[12] This value is in reasonable agreement with the calculated effective loss of mass of a core per monomer (783 Da). Mass balance of the combined fractions (trimer and higher) was 56% of all the fractions containing cross-linked dendritic structures.

The second preparative SEC band was dark turquoise and showed an intense Soret band at 435 nm, which is consistent with a monomeric Sn(IV) porphyrin. Interestingly, **6** had a similar UV/Vis spectrum to that of the cleaved porphyrin core (**8**), but the absorbance intensity of **6** was much lower at 425 nm (Soret band) than at 289 nm (aromatic absorption). This observation indicated that a minor amount of porphyrin remained—probably the result of incomplete transesterification or a small amount of encapsulation by either noncovalent or mechanical means. Oligomeric **6** (trimer and higher) was analyzed by SEC in NMP (Table 1). An M_n value of 35 kDa was obtained, which corresponds to a heptamer. However, as described above for **5** the actual oligomer length may be somewhat longer.[18]

Additional structural information is needed to determine whether the hollow channel collapses or remains open. Nonetheless, the route to non-fullerene organic nanotubes described herein features significant potential versatility. For example, the thickness of the tube wall may be modulated by choice of the generation of the dendron while the diameter of the inner tube may be controlled by adoption of suitably sized cores. Additionally, the functionality on the outer tube can be selected by use of appropriate dendron precursors. In a similar way, the functionality on the inner tube can be controlled by both the linking functionality and type of cleavage reaction employed. Although this route does not feature significant control over the length of the nanotube, fractionation of the product by SEC does allow particular distributions to be isolated. In closing, we have demonstrated a new application for our recently disclosed method of dendrimer coring.[17]

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[15] The illustrations of **5** and **6** represent mixtures of the oligomers where many combinations of intramolecular cross-links are possible; they are not meant to suggest a single product.

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[18] Transmission electron microscopy was performed on **5** and **6** but mainly resulted in images of aggregates with sizes that were dependent on the method of sample preparation.[12]

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