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Toward Self-Assembling Dendrimers: Metal Complexation Induces the Assembly of Hyperbranched Structures

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Abstract: A novel 1,10-phenanthroline ligand, symmetrically substituted at the 3,8-positions with branched multifunctional groups, is self-assembled into dendritic structures upon metal complexation. Copyright © 1996 Elsevier Science Ltd

Dendrimers are hyperbranched, highly-ordered oligomeric structures that emerge from a single polyfunctional core. Their size, shape and topology, as well as flexibility and surface functionalities, are controlled at the molecular level.[1] This new family of molecules presents challenging problems in polymer physics and chemistry, and displays novel properties.[2] Dendritic compounds have been predicted to replace a range of existing materials in a variety of applications--including adhesives, drug delivery systems and catalyst carriers--and have been proposed as building blocks for nanostructured materials.[3]

Dendrimers are currently synthesized by convergent- and divergent-growth approaches; both require elaborate chemistry and multi-step procedures.[1,4] An attractive alternative approach that may overcome some of these lengthy procedures would be to self-assemble simpler hyperbranched building blocks into dendritic structures.[5] Here we propose to use metal ion coordination to nucleate such dendritic assemblies. The approach is illustrated in Figure 1: a 1,10-phenanthroline ligand, symmetrically substituted at the 3,8-positions with branched multifunctional groups (**1**), is expected to self-assemble into dendritic-like structures upon metal complexation.[6] In this way, the polyfunctional core is replaced by a coordinated metal ion and the pre-made dendrons are assembled to generate a globular dendritic structure. The symmetry and the fractal characteristics of the resulting structures are governed by the coordination number and geometry of the selected metal ion, as well as by the degree of branching of the disubstituted phenanthroline ligand. Depending on the metal ion selected, the resulting dendritic structure may be kinetically labile or kinetically inert. In this communication, we describe the synthesis of a novel branched 1,10-phenanthroline ligand and its complexation with transition metal ions to generate tetrahedral and octahedral hyperbranched assemblies.

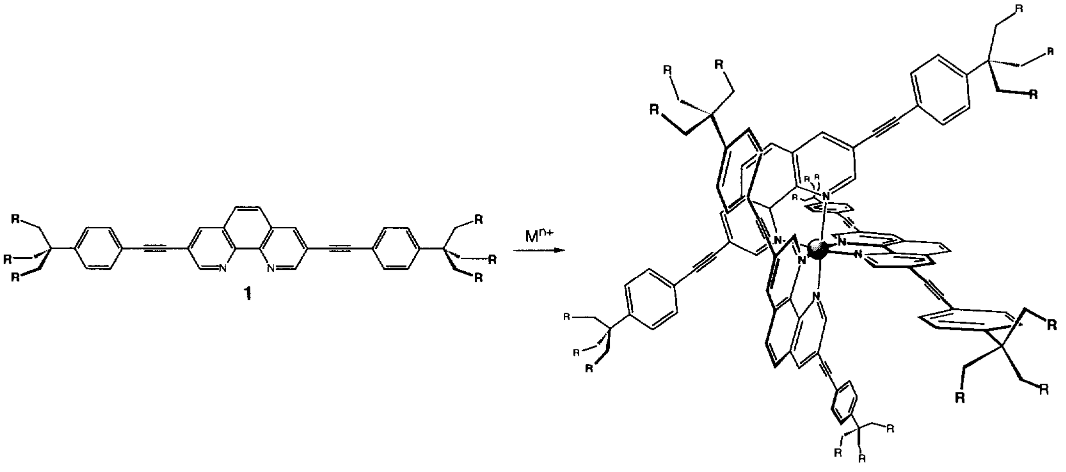
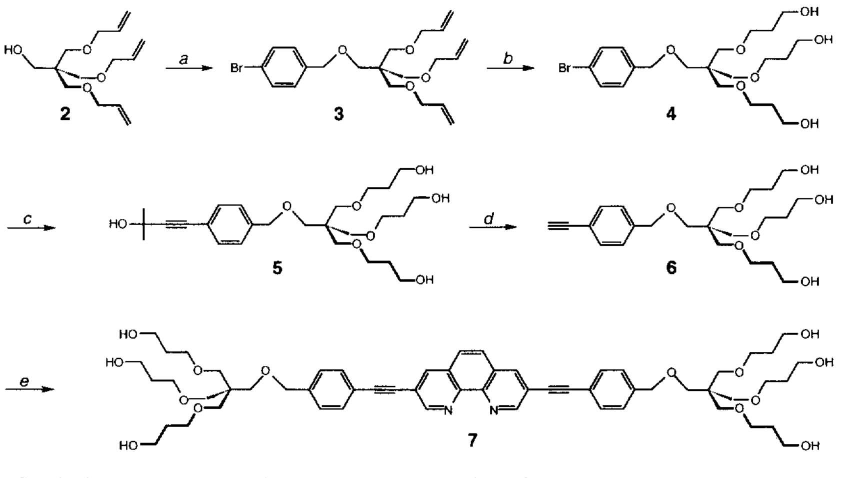


Figure 1. A schematic illustration of the general strategy for the self-assembly of dendritic structures. A 1,10-phenanthroline ligand **1**, symmetrically substituted at the 3 and 8 positions with branched multifunctional groups, is self-assembled into octahedral dendritic structures upon metal complexation. Note that other geometries are accessible by selecting different metal ions and that R itself can be a branched structure.

The synthesis of the first generation branched ligand is illustrated in Scheme 1. The commercially available pentaerythritol triallyl ether **2** is treated with 4-bromobenzyl bromide to afford **3**. Hydroboration with 9-BBN, followed by an oxidative work-up, gives the triol **4**. Palladium-mediated cross-coupling of **4** with 2-methyl-3-butyn-2-ol provides the protected alkyne **5**. Base-catalyzed deprotection affords the alkyne-triol **6** that is cross-coupled to 3,8-dibromo-1,10-phenanthroline[7,8] to furnish ligand **7** in an overall 35% yield.[9]



Scheme 1. Synthetic route to the core ligand **7**. *Reagents and conditions*: (*a*) NaH, 4-$BrC_6H_4CH_2Br$, DMF, 25°C, 24 h, 91%; (*b*) (i) 9-BBN, THF, 25°C, (ii) NaOH, H_2O_2, 78%; (*c*) $HC{\equiv}CC(OH)Me_2$, (dppf)$PdCl_2$, CuI, pyrrolidine, reflux, 48 h, 81%; (*d*) NaOH, toluene, reflux, 40 min, 79%; (*e*) 3,8-dibromo-1,10-phenanthroline, $(Ph_3P)_2PdCl_2$, CuI, MeOH, Et_3N, sonication, 3 h, 76%.

The dumbbell-shaped ligand **7** possesses a rigid 3,8-bis(phenylethynyl)-1,10-phenanthroline core and two flexible tripodal hydroxyether end-groups. Assembling ligand **7** around an octahedral metal ion is expected to furnish a globular structure with 18 surface hydroxyl groups and a diameter of *ca.* 40Å. Such a first-generation self-assembled structure would correspond to a second/third generation starburst dendrimer with respect to the number of surface groups, and to a fourth/fifth generation in terms of size.[1a]

Complexation of ligand **7** with 0.5 equivalent of $(CH_3CN)_4Cu^+PF_6^-$ in acetonitrile at room temperature afforded the tetrahedral $[Cu(\mathbf{7})_2]^+PF_6^-$ in 81% yield.[10] Comparison of the electronic absorption of the complex to that of ligand **7** indicated that the π–π^* transitions of the conjugated 1,10-phenanthroline ligand remain largely unchanged upon metal complexation. A metal to ligand charge transfer (MLCT) band, typical to tetrahedral $[Cu(polypyridyl)_2]^+$ complexes, appears at 464 nm (ε 2×10^3 $M^{-1}cm^{-1}$). Electrospray ionization- and FAB-mass spectrometry of the red-brown solid gave a molecular peak at m/z 2114. The isotopic distribution of the observed peak matched the calculated pattern for the desired product confirming the assembly of two phenanthrolinic dendrons around a Cu^+ center.

Treating a methanolic solution of ligand **7** with 0.33 equivalent of aqueous $FeSO_4.7H_2O$ followed by adding excess KPF_6 gave a red-purple solution of the octahedral $[Fe(\mathbf{7})_3]^{2+}(PF_6^-)_2$.[10] The UV-Vis spectrum of the complex showed minor shifts of the π–π^* transitions--compared to that of the free ligand--and the appearance of a typical MLCT band at 536 nm (ε 2.3×10^3 $M^{-1}cm^{-1}$). Electrospray ionization mass spectrometry of the complex showed a doubly charged ion at m/z 1566 (Figure 2). The isotopic distribution of this ion matched the theoretical pattern calculated for $[Fe(\mathbf{7})_3]^{2+}$, thus verifying the formation of an assembly containing 18 hydroxyl groups that surround an octahedral Fe^{2+} center.

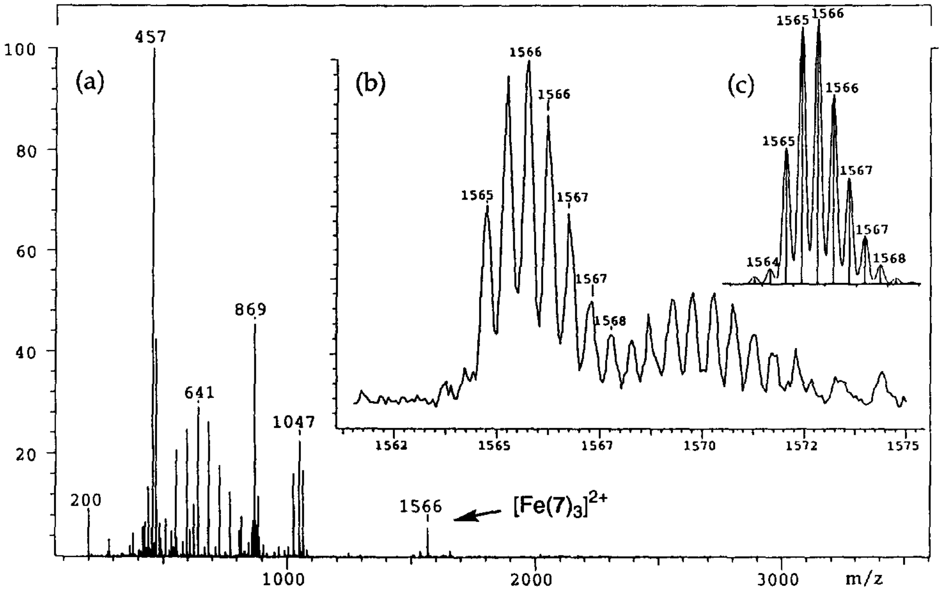


Figure 2. (a) ESI-MS of $[Fe(\mathbf{7})_3]^{2+}(PF_6^-)_2$. (b) Expansion of the doubly charged peak at m/z 1566 corresponding to the $[Fe(\mathbf{7})_3]^{2+}$ ion. (c) Calculated pattern for $[C_{174}FeH_{228}N_6O_{42}]^{2+}$.

Our results demonstrate that hyperbranched structures can be self-assembled around metal ions as the structural core. This non-covalent approach to the assembly of dendritic structures possesses certain unique features: (a) morphologies that are not easily accessible from polyfunctional organic compounds can be assembled by taking advantage of metal ions with high coordination numbers; (b) various geometrical arrangements can be obtained from the same building block depending on the metal ion selected. Experiments exploring the assembly of dendritic structures with different functional groups on their exterior, with higher generations and with other metal ions as the nucleating cores, are underway in our laboratory.

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9. Spectral data for ligand **7**: FAB MS 1048 $[MNa]^+$; ^1H NMR (CD_3OD, 323°K) δ 9.05 (s, 2H, H2,9 phen), 8.38 (s, 2H, H4,7 phen), 7.85 (s, 2H, H5,6 phen), 7.54 (d, *J*=7.8 Hz, 4H, Ph), 7.35 (d, *J*=7.8 Hz, 4H, Ph), 4.49 (s, 4H, $PhCH_2O$), 3.64 (t, *J*=6.3 Hz, 12H, CH_2OH), 3.54 (dd, *J*=6.3, 5.9 Hz, 12H, OCH_2CH_2), 3.48 (s, 4H, OCH_2C), 3.43 (s, 12H, OCH_2-C), 1.76 (m, 12H, $CH_2CH_2CH_2OH$); ^{13}C NMR (CD_3OD) δ 152.5, 144.4, 141.5, 139.4, 132.8, 129.4, 128.4, 128.1, 122.4, 121.1, 106.9, 95.1, 86.8, 73.8, 70.9, 69.6, 60.4, 46.4, 33.7; IR (film) ν_{max} 3367 cm^{-1} (OH), 2210 cm^{-1} ($C\equiv C$), 1095 cm^{-1} (C–O); UV (CH_3OH) λ_{max} 286 nm (ε 5.2×10^4), 348 nm (ε 5.8×10^4), 360 nm (ε 5.4×10^4).
10. $[Cu(\mathbf{7})_2]^+PF_6^-$ was purified by column chromatography on neutral aluminum oxide (5-10% $MeOH/CH_2Cl_2$). $[Fe(\mathbf{7})_3]^{2+}(PF_6^-)_2$ was not stable to column chromatography and has been used as obtained without further purification. The dendritic complexes showed spectroscopic data (UV-VIS, IR, NMR and MS) consistent with the assigned structures.

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