

A Route to Redox-active Nanoparticle-cored Dendrimers: Post-encapsulation of Ferrocene

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Redox-active nanoparticle-cored dendrimers were synthesized by a stepwise reaction, in which synthesis of functionalized nanoparticles was followed by organic reactions to build dendritic architecture around a nanoparticle core. Incorporation of redox molecules on the surface of nanoparticles resulted in the formation of a redox-active nanoparticle-cored dendrimer.

Significant progress has been made in research involving the use of dendritic frameworks to surround functional core molecules.^{1–6} Dendritic encapsulation of a functional molecule provides a site isolation which mimics principles from biomaterials because dendritic scaffolds can provide the segregation of external and internal functionality.^{1–3} The current approaches of dendritic encapsulation are mostly based on building dendritic frameworks to surround active core using iterative reaction sequence.^{1,3} Our new strategy provides an alternative way to core-functionalized dendrimers (Scheme 1), which the nanoparticle core in nanoparticle-cored dendrimers (NCDs)^{7–11} acts as a template for redox molecules. Incorporation of electroactive compounds on the surface of nanoparticles in dendritic architecture should provide an opportunity to tune their electrochemical properties.¹¹

We have synthesized NCDs by an approach in which the synthesis of 11-mercaptoundecanoic acid functionalized monolayer-protected clusters (MUA MPCs)^{12–14} was followed by adding dendrons on MUA MPCs [$\approx\text{Au}_{201}(\text{SC6})_{28}-(\text{SC10COOH})_{43}$].¹⁵

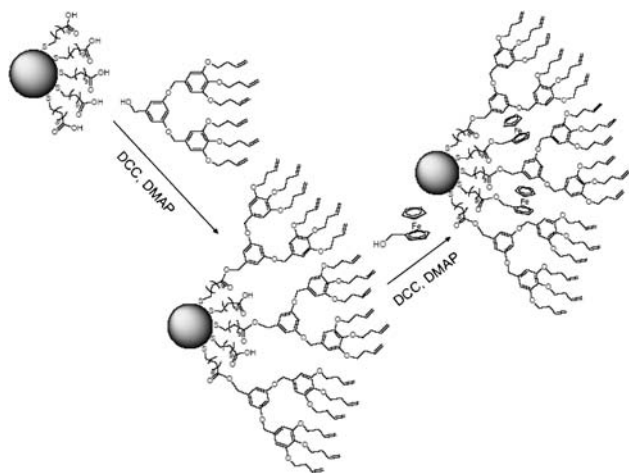
Hydroxy-functionalized “Fréchet-type” dendrons were synthesized by the modification of the previously published method.² Briefly, the synthesis started with Mitsunobu coupling reaction of methyl 3,4,5-trihydroxybenzoate with homoallyl

alcohol. Reduction of these ester-functionalized dendrons using lithium aluminum hydride (LAH) generated the hydroxy-functionalized “Fréchet-type” dendron ([G1]-OH). For the synthesis of [G2]-OH, the Mitsunobu coupling reaction of methyl 3,5-dihydroxybenzoate with [G1]-OH followed by LAH reduction were performed.¹⁵

The convergent synthesis of NCDs was accomplished by the ester coupling reaction of MUA MPCs with excess hydroxy-functionalized “Fréchet-type” dendrons ([G2]-OH) in the presence of ester coupling reagents (1,3-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP)).¹⁴ This synthetic approach provided an access to functionalized NCDs, which contained multiple reactive functional groups (COOH) inside dendritic wedges even after the coupling of dendrons. The unreacted COOH groups were resulted from steric repulsion of dendrons during the synthesis of NCDs. The incorporation of redox labels in NCDs was achieved by a simple coupling reaction of ferrocene methanol with the remaining COOH groups inside dendritic wedges of NCDs ([G2] NCDs).¹⁵

The appearance of a new band at ca. 1735 cm^{-1} in FT-IR spectroscopy after the reaction indicated a formation of ester bonds due to successful coupling reaction between 11-mercaptoundecanoic acids and [G2]-OH. IR spectrum of [G2] NCDs synthesized by convergent method also showed C=C and aromatic stretching bands at ca. 1660 and ca. 1600 cm^{-1} , respectively (Figure 1).

This was a clear evidence for the attachment of hydroxy-functionalized dendrons by the coupling reaction. The presence of the carbonyl band at ca. 1710 cm^{-1} even after the reaction suggested that the [G2] NCDs still contained unreacted COOH functional groups in the monolayer. This was due to the steric repulsion of incoming dendrons by the dendrons attached to the clusters. After additional ester coupling reaction between [G2] NCDs and ferrocene methanol, the IR spectrum of the NCD-encapsulated ferrocene (Fc@NCDs) showed an increase in the intensity of a band at 1735 cm^{-1} in addition to the strong



Scheme 1. Synthesis of nanoparticle-cored dendrimers encapsulated ferrocene.

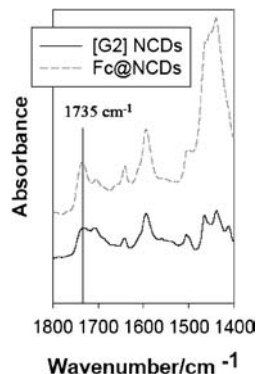


Figure 1. IR spectra of [G2] NCDs and Fc@NCDs.

band around 1450 cm^{-1} indicating the presence of cyclopentadienyl groups.

The ^1H NMR spectrum of [G2]-OH showed the signals for aromatic protons (6.45–6.65 ppm, 7H), $-\text{CH}_2\text{CH}=\text{CH}_2$ (5.80–6.00 ppm, 6H), $-\text{CH}_2\text{CH}=\text{CH}_2$ (5.00–5.20 ppm, 12H), $-\text{ArCH}_2\text{OArCH}_2\text{OH}$ (4.92 ppm, 4H), $-\text{ArOCH}_2\text{OH}$ (4.64 ppm, 2H), $-\text{ArOCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ (3.90–4.10 ppm, 12H), $-\text{CH}_2\text{CH}=\text{CH}_2$ (2.40–2.60 ppm, 12H). Compared to the NMR spectrum of [G2]-OH, the spectrum of [G2] NCDs showed the signals for all these protons with a few different features. Due to the coupling reaction of [G2]-OH and MUA MPCs, the signals for ArCH_2OH shifted further downfield from 4.64 to 4.86 ppm. The signals for CH_2CO_2^- were also observed at 2.32 ppm. The signals for CH_2 (1.20–1.40 ppm) and CH_3 (0.80–0.90 ppm) were shown in the spectrum due to the presence of MUA and hexanethiolate ligands on the cluster surface. The results also showed the same peak-broadening effect, as do monolayers of alkanethiolate-protected nanoparticles generated from alkanethiols. This peak-broadening effect clearly suggested that [G2]-OH was reacted with MUA MPCs and bonded onto the surface of nanoparticles. The NMR spectrum of Fc@NCDs showed additional broad bands at ca. 4.10 ppm, which corresponded to the signals from cyclopentadienyl groups. No additional sharp resonances corresponding to free ferrocene methanol were seen.¹⁵

The increased organic fractions (42.43% from 25.95%) were also observed by thermogravimetric analysis (TGA). The quantitative analysis using TGA data suggested that ca. 14 COOH groups (out of ca. 43) on MUA MPCs have been reacted with [G2]-OH dendrons. This analysis was in agreement with IR results, showing the existence of unreacted COOH groups in the interior of [G2] NCDs. This result suggested that the produced [G2] NCDs has an average molecular formula of $\text{Au}_{201}(\text{SC}_6)_{28}(\text{SC}_{10}\text{COOH})_{29}(\text{SC}_{10}\text{COO}[\text{G2}])_{14}$. The reaction of ferrocene methanol with [G2] NCDs resulted in the incorporation of ca. 15 ferrocene units per each nanoparticle based on

the relative absorbance of two carbonyl bands at ca. 1735 and ca. 1710 cm^{-1} in IR spectra (Figure 1).

Cyclic voltammetry was employed to compare electrochemical behaviors of ferrocene methanol and Fc@NCDs (Figure 2). Both ferrocene methanol and Fc@NCDs exhibited well-defined voltammetric peaks corresponding to ferrocenyl groups. From the voltammogram of ferrocene methanol, it could be seen that there was a pair of voltammetric waves with a peak splitting of 233 mV at 100 mV/s indicating quasi-reversible electron-transfer processes. Interestingly, the peak splitting was found to be 112 mV at 100 mV/s for Fc@NCDs , which was only half of that for ferrocene methanol. This might be due to either multi-electron transfer or adsorption of the particles to the electrode.

In summary, NCDs and redox-active NCDs were synthesized by a stepwise reaction, in which synthesis of functionalized nanoparticles was followed by organic reactions to build dendritic architecture and to incorporate redox molecules on the surface of nanoparticles. The preparation of redox-active NCDs using new methods represents an important advance to the control and preparation of new organized nanostructures. Synthesis of redox-active NCDs with distinct generations and functional moieties will be attempted for the structural control at the nanoscopic level. The detailed electrochemical properties of various redox-active NCDs will be also studied in the near future.

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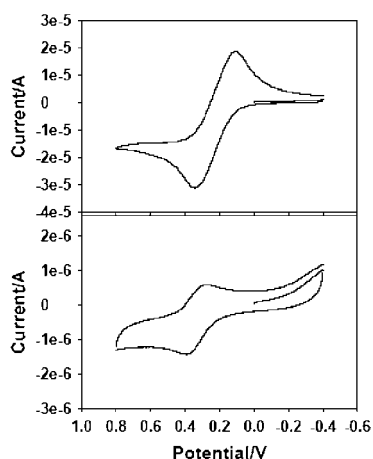


Figure 2. Cyclic voltammogram of (a) ferrocene methanol and (b) Fc@NCDs in CH_2Cl_2 . A Pt electrode was used as the working electrode, a Ag QR wire was used as the quasi reference electrode, and the counter electrode was a Pt wire. The solution was deaerated for at least 10 min with nitrogen before data acquisition and blanketed with a nitrogen atmosphere during the experiment. (scan rate = 100 mV/s).