

# Molecular-Size Nanocage for Catalysis: Shell Cross-Linked Carbamate Dendrimer Strategy

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## Introduction

The nanometer-size, hollow nanocages containing porous shells deserve much attention because they could encapsulate functional moieties inside and possess molecular-size selectivity through the hollow porous shell and isolation of core from its environment. Hence, their potential applications include nanoreactors for controlled chemical processes, catalysts and sensors development etc. The established method of forming shell cross-linked micellar (SCM) self-assemblies of surfactants (e.g. multiblock copolymers) cannot achieve encapsulation of designed molecular cores easily<sup>1,2</sup>. Here, the carbamate immolative dendritic strategy for the synthesis of a molecular-size nanocage will be presented.

A dendrimer has a highly regulated globular structure as well as nanoscale in size (<10 nm). Methods to synthesize dendrimers permit highly tunable design of the core, branching units, and surface functional groups for different applications. These physical and chemical properties of dendrimer permit preparation of well-defined nanocages encapsulating functional cores. However, the commercial dendrimers such as PAMAM and PPI are not readily degradable, which is necessary to form the core-shell structure. Instead, the dendrimer needs to be immolative. To achieve this, we have synthesized a spherical immolative carbamate dendrimer of 4<sup>th</sup> generation. The carbamate dendrimer was designed such that: 1) it is easy and fast to synthesize and purify; 2) surface functional groups (e.g. C=C) are readily tunable for shell cross-linking; and 3) the linkages between core and shell are selectively degradable for the generation of nanocage. Here, we present the result of the preparation of a nanocage (<10 nm) of such a core-shell structure and characterization of its physico-chemical properties as a potential catalytic material.

## Materials and Methods

The immolative carbamate dendrimer of 4<sup>th</sup> generation (G4) was prepared using a combination of divergent and convergent methods, by coupling G2 dendrons to a G2 core. 4-nitrophenyl chloroformate and 1,3-diamino-2-propanol were used to form carbamate linkages in dendron synthesis. A tetrahedral core was prepared by esterification of pentaerythritol with Boc-Gly-OH. The surface olefin groups of dendrimer could be modified by hydrosilylation with alkoxy silanes to form a siloxane network shell, or with silanes to form a carbosilane shell. Finally, degradation of the carbamate linkages would selectively form an excavated nanocage (Fig. 2). Dynamic light scattering (DLS) and semi-empirical equilibrium geometry calculation (AM1) were employed to estimate the size and molecular structure of dendrimers and nanocages.

## Results and Discussion

We have developed an efficient synthetic scheme that produces immolative carbamate dendron/dendrimer in a gram scale. Their chemical structures were confirmed by <sup>1</sup>H, <sup>13</sup>C NMR and MALDI-TOF mass spectroscopy. According to molecular simulation, G4 carbamate dendrimer is highly symmetrical and spherical in shape and about 4 nm in size, and the latter was confirmed by DLS. The surface olefin groups of the dendrimer were successfully modified into triethoxy silyl groups using the Karstedt catalyst. And the surface Si-OH groups generated after hydrolysis of the hydrosilylated dendrimer are dense enough for shell cross-linking. The siloxane shell network is accomplished by employing sol-gel chemistry (i.e., *hydrolysis and condensation*) under acid alcoholic solution with alkoxy siloxane as shell cross-linking agents. The remaining surface Si-OH groups are capped with trimethyl methoxysilane. As measured by DLS analysis (Fig. 1), the size of dendrimer increased from 4.3 to 5.6 nm after shell cross-linking and inter-particle condensation (agglomeration) was minimized under the condition used for this study. The shell cross linking process was monitored by <sup>1</sup>H and <sup>29</sup>Si NMR. Finally, the internal carbamate linkages between core and shell could be cleaved out of the shell to generate nanocage by trimethylsilyl iodide/methanol treating.

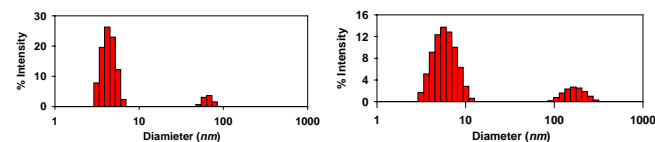


Fig. 1. DLS analysis of dendrimer (left) and shell cross-linked dendrimer (right).

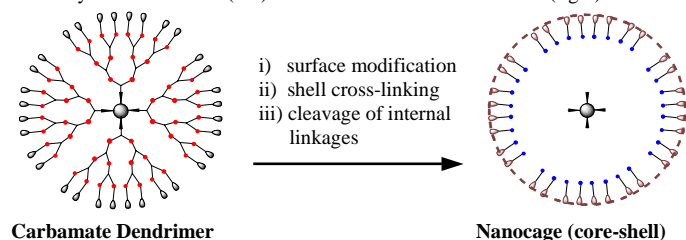


Fig. 2. Schematics for dendrimer directed synthesis of molecular-size nanocage

## Significance

A method is devised to synthesize molecular-size nanocages with a porous shell that could be used for catalysis in a confined environment and as nano-reactor for catalytic and preparative chemistry.

## References

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