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The Dendritic Box: Shape-Selective Liberation of Encapsulated Guests

Johan F. G. A. Jansen and E. W. Meijer*

Laboratory of Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven The Netherlands

Ellen M. de Brabander-van den Berg DSM Research, P.O. Box 18, 6160 MD Geleen The Netherlands

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The possibilities for encapsulating guest molecules in dendritic hosts were proposed by Maciejewski1 in 1982 and discussed as the main application of dendrimers ever since.2 Despite the fact that dendrimers and hyperbranched polymers are subjects of intensive research,3 examples of guest encapsulations are limited to an organic guest dissolved in the interior of a dendrimer. Fréchet et al. were able to solubilize pyrene in water employing a water-soluble dendrimer,4 while Tomalia et al. have demonstrated by means of NMR relaxation measurements that organic molecules like aspirin can penetrate into the interior of a polyamidoamine (PAMAM) dendrimer.5 However, both examples are based on dynamic processes, and the guests can easily diffuse in or out of the dendrimer host, depending on the equilibrium conditions.

Recently we demonstrated that it is possible to physically lock (imprison or encapsulate) guest molecules in a monomolecular dendritic container with a diameter of approximate 5 nm, the so-called dendritic box.6 These dendritic boxes (Scheme 1) are constructed from a flexible poly(propylene imine) dendrimer with 64 amine end groups7 and an L-phenylalanine derivative. In solution, this 64-L-Phe box possesses a highly dense hydrogen-bonded shell with solid-state character, as has been demonstrated with 13C-NMR relaxation data8 and chiroptical studies.9 Guest molecules are captured within the internal cavities of these boxes by constructing the dense shell in their presence.6 In this Communication, we report on our preliminary results concerning the shape-selective liberation of guests from these dendritic boxes. The basic principle of a selective liberation is shown in Figure 1. Initially, the liberation principle has been demonstrated with the 64-L-Phe box (Scheme 1), as we have previously demonstrated that this box is the most ideal molecular container obtained so far.

In a first example, we encapsulated Bengal Rose (1) and p-nitrobenzoic acid (2) together in a dendritic box. Exhaustive dialysis with acetone/water (cellulose 24 Å, seven times, 5% water in acetone) is used to remove the adhered or excess guest. Next, the shell is partially perforated, yielding a modified dendritic box in which only the larger guest is entrapped and from which the smaller guest is liberated. Subsequent removal of the shell liberates the larger guests, and the starting poly(propylene imine) dendrimer is recovered.

Figure 1. Schematic presentation of the principle of encapsulation and shape-selective liberation. First, two guests that differ in size are encapsulated in the box, and dialysis is used to remove adhered and excess guest. Next, the shell is partially perforated, yielding a modified dendritic box in which only the larger guest is entrapped and from which the smaller guest is liberated. Subsequent removal of the shell liberates the larger guests, and the starting poly(propylene imine) dendrimer is recovered.

Scheme 1
After encapsulation of four molecules of 1 and 8-10 molecules of 2 per box, hydrolysis of the tBOC groups with formic acid (95% HCOOH, 16 h) is performed. Subsequent dialysis (5% water in acetone) of the reaction mixture yields a perforated dendritic box in which only the four molecules of 1 are entrapped, whereas all the 2 is dissolved in the acetone/water mixture.  

Bengal Rose (1) cannot be liberated from the perforated box, even with the addition of hydrochloric acid (12 N). However, hydrolysis of the outer shell using 12 N HCl under reflux for 2 h liberates 1 after dialysis (100% water), and starting poly(propylene imine) dendrimer is recovered in 50–70% yield.

To improve the detection of the concentration of different guests encapsulated into the box, we used an EPR probe together with a UV–vis probe in the next set of experiments. 2,2,3,4,5,5-Hexamethyl-3-imidazoliumyloxy methyl sulfate free radical 3 has been employed as the small guest, whereas the dyes Bengal Rose (1), Rhodamine B (4), and New Coccine (5) have been used as the large guests (Table 1). Table 1 clearly shows that after removal of the N-tBOC protecting group with formic acid EPR probe, 3 is liberated completely as no EPR resonance is detected in the dendrimer after dialysis.  

In all these cases, no significant difference in the UV–vis spectrum for the dendrimer with the dense shell and the partially perforated shell was detected.

Although a large number of experimental results clearly point to the presence of a supramolecular and ordered arrangement of (the larger) guests in the dendritic box, the nature of the encapsulation is not of direct importance for the shape-selective liberation presented here. Even a model in which a statistical distribution of dissolved guests is assumed can be used.

The liberated guests are characterized by UV–vis spectroscopy; identical spectra are observed for virgin and liberated dyes. The perforated and recovered poly(propylene imine) dendrimers are characterized by NMR spectroscopy and HPLC.

The load differences observed are within the error of detection; if possible, clathrate formation of solvent is taken into account.

Supplementary Material Available: Synthesis and characterization of the dendritic box, and procedures for the encapsulation and stepwise liberation of guests (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.