

DEVELOPMENT OF A FUNCTIONAL DENDRITIC MONOMER AND APPLICATION TO SOPHISTICATED LIGHT HARVESTING SYSTEMS

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Introduction

In recent years, dendrimers² have shown great promise as macromolecules capable of sophisticated functions, such as encapsulation of active core functionalities,³ arrangement of complementary donor and acceptor chromophores for light harvesting systems,⁴ and stabilization of reactive transition states for catalysis.⁵ Many of these functions are based on a combination of properties unique to the dendritic architecture: monodispersity, a large number of peripheral functionalizable groups surrounding a single core unit, and globular shape.

Despite these successes, the complexity of dendritic structures available *via* well known synthetic methods is limited. Traditional dendrimer syntheses are compatible with a broad range of core functionality and allow the periphery to be uniformly decorated with another functional group. However, the ability to incorporate a diverse array of functionality along the dendrimer backbone, which would allow the synthesis of more sophisticated systems (Figure 1), remains challenging.

In order to facilitate the preparation of the next generation of functional dendrimers, we set out to design and synthesize a new branched monomer, which allows the modular incorporation of functional groups at each generation of growth. Here we describe our recent success in the monomer synthesis, and development of suitable conditions required for sequential generation growth and deprotection. Most importantly, the modularity of our synthetic route will allow the use of this functional monomer for a wide variety of applications, including multiple chromophore energy harvesting.

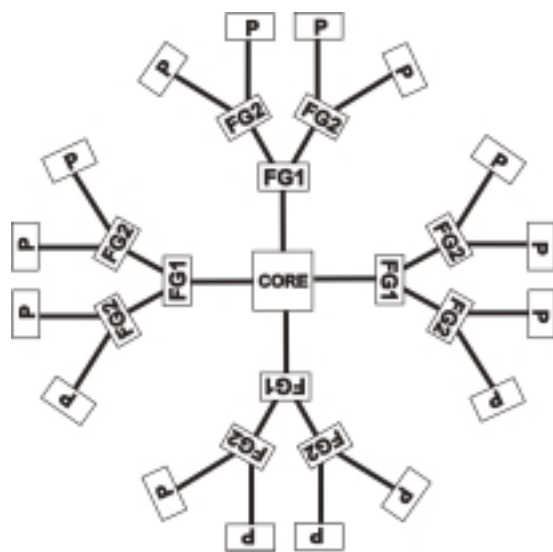


Figure 1. Illustration of dendritic architectures arising from a functional AB₂ monomer (FG1, FG2 = functional groups; P = peripheral group).

Results and Discussion

The functional monomer **3** was synthesized from commercially available tris(hydroxymethyl)methylamine hydrochloride (TRIS HCl). Two of the three hydroxyl groups were protected as the corresponding acetone using dimethoxypropane under acidic conditions. The functional group is then incorporated *via* an amide linkage under mild carbodiimide coupling conditions, taking advantage of the greater nucleophilicity of the amine as compared to the alcohol. Finally, a carboxylic acid handle for growth from polyol cores was introduced using the ring opening of succinic anhydride

(Figure 2). The first functional monomer was synthesized employing coumarin-3-carboxylic acid, previously used as a suitable donor chromophore in Förster Resonance Energy Transfer (FRET) to a tetraphenylporphyrin based acceptor, as the functional group.⁶ It should be pointed out that this approach is extremely versatile in nature and hence, any functional carboxylic acid could be introduced at this stage and later be incorporated into the dendrimer framework.

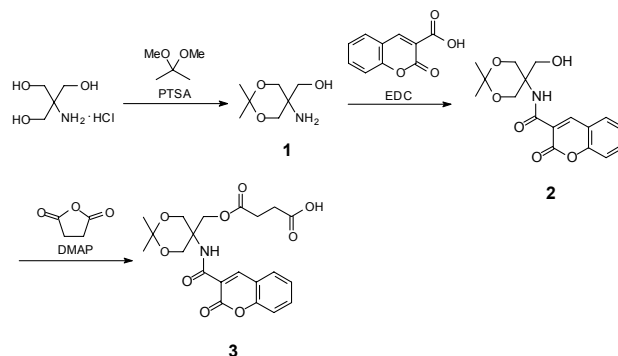


Figure 2. Synthesis of the functional dendritic monomer.

Conditions for esterification of the monomer with cores containing multiple hydroxyl groups were developed. The monomer reacts with tris(hydroxymethyl)ethane under standard carbodiimide coupling conditions using catalytic amounts of DMAP and dimethylaminopyridinium *p*-toluenesulfonate (DPTS).⁷ In order to facilitate purification of the product from urea byproducts, a solid supported carbodiimide was used in the coupling reaction. Deprotection of the peripheral acetone protecting groups under standard aqueous acidic conditions resulted in partial hydrolysis of the polyester dendritic backbone. However, successful deprotection was accomplished using catalytic amounts of ammonium cerium nitrate (Figure 3).

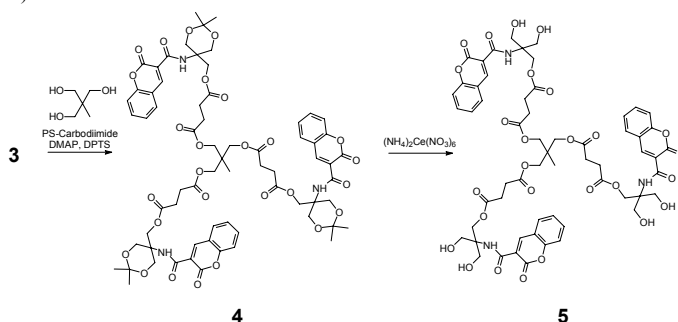


Figure 3. Synthesis and deprotection of a first generation coumarin functionalized dendrimer.

These findings constitute the basis for a successful implementation of functional monomer **3** in the synthesis of dendrimers carrying different functionalities in their interior layers. Such investigations are currently in progress in our laboratories and aim at the design of improved light harvesting molecules for catalysis, photovoltaics, and sensing.

References

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- (2) Newkome, G. R.; Moorefield, C. N.; Vögtle, F. *Dendrimers and Dendrons: Concepts, Syntheses, Applications*. VCH, Weinheim, **2001**.
- (3) Fréchet, J. M. J.; Tomalia, D. A. *Dendrimers and Other Dendritic Polymers*. Wiley, New York, **2002**.
- (4) Hecht, S.; Fréchet, J. M. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 74.
- (5) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, 1701.