

# Functionally Layered Dendrimers: A New Building Block and Its Application to the Synthesis of Multichromophoric Light-Harvesting Systems

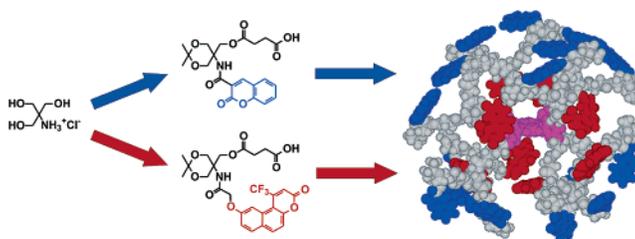
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## ABSTRACT



A divergent synthesis of internally functionalized dendrimers based on a modular functional monomer has been developed. This strategy was applied to the construction of a light-harvesting dendrimer containing one set of naphthopyranone dyes located at the interior and another set of coumarin chromophores located in the adjacent outer layer surrounding a porphyrin acceptor. Quantitative energy transfer from both donor pigments is observed, giving rise to exclusive emission from the porphyrin core over all excitation wavelengths.

In recent years, the special architecture of dendrimers<sup>1,2</sup> has been exploited in the design of functional macromolecules both capable of mimicking many natural phenomena,<sup>3</sup> such as site isolation,<sup>3–5</sup> catalysis,<sup>6–13</sup> and light-harvesting,<sup>13–18</sup> and useful in a variety of technological<sup>19–21</sup> or therapeutic<sup>22</sup> applications. Due to available synthetic protocols, functional groups have typically been incorporated at the core and/or

periphery of the dendrimer, with the backbone acting only as a passive scaffold separating these two domains. The difficult functionalization of the interior of the dendrimer<sup>23</sup> constitutes a serious obstacle to the full exploitation of the dendritic scaffold.<sup>24–28</sup> For example, internally functionalized layered structures are desirable to establish complex energy gradients<sup>25,26</sup> between core and periphery or to tailor specific properties of the dendritic interior.<sup>13,25</sup>

As a first example of the complex structures readily accessed via this synthetic approach, the sophisticated light-harvesting system **1** was synthesized containing two different types of donor chromophores in a layered arrangement

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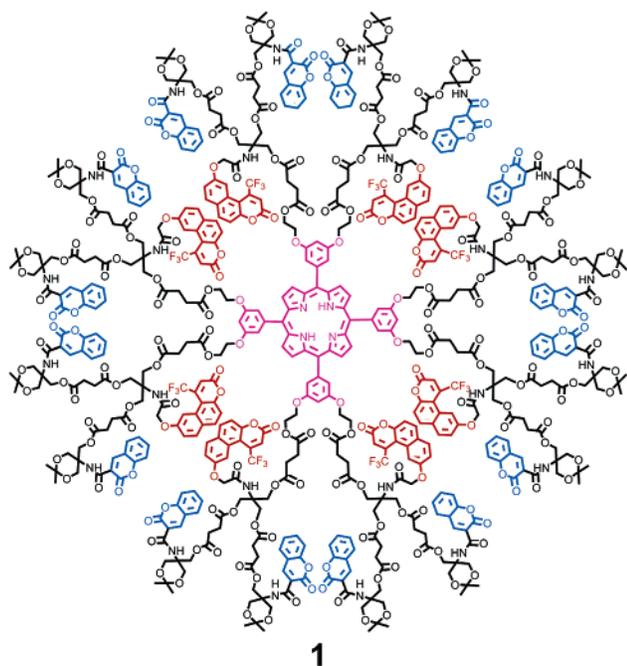
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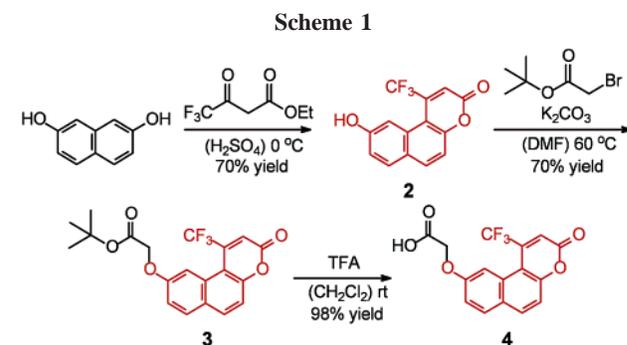
around a porphyrin core (Figure 1). The 25 chromophore



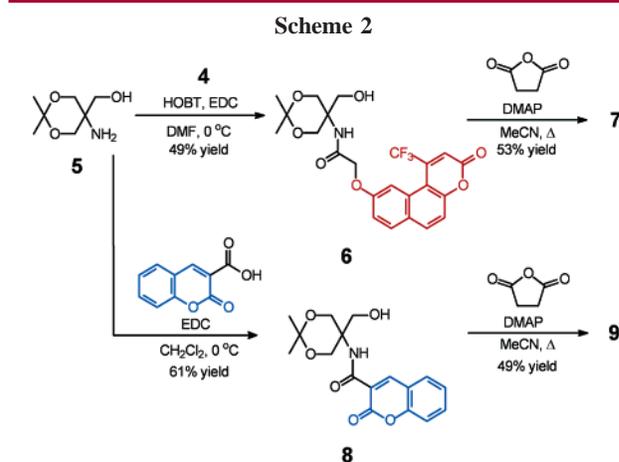
**Figure 1.** Internally functionalized dendrimer containing eight naphthopyranone and 16 coumarin-3-carboxylate donor chromophores.

assembly absorbs light over a broad range of the UV and visible spectrum and converts harvested photons into a single emission from the central porphyrin acceptor in the red region of the spectrum via fluorescence resonance energy transfer (FRET). Light-harvesting systems containing multiple accessory pigments mimic natural photosynthesis and offer potential technological advantages in a variety of photonic applications.<sup>3,14,15</sup> The target molecule **1** was synthesized via an iterative esterification/deprotection divergent growth procedure using two different functionalized monomers carrying the chosen donor chromophore at each branch point. Though other light-harvesting dendrimers containing multiple

types of donor chromophores have recently been reported,<sup>18,26,29</sup> our approach differs significantly as it is generally applicable to a broad range of functionality and avoids statistical monofunctionalization reactions in its synthesis. Donor chromophores were selected based on their emission characteristics, enabling efficient sensitization of the porphyrin absorption bands as well as the presence of a carboxylic acid functionality necessary for incorporation into the functional monomer synthesis. For the first donor chromophore, novel naphthopyranone dye **4** was targeted (Scheme 1) as it was expected that its absorbance and



emission bands would undergo a bathochromic shift relative to the coumarin derivative, thereby enhancing the absorption cross-section of the overall assembly while also leading to sensitization of the porphyrin Q-bands.<sup>30</sup> Indeed, this chromophore has an absorption maximum at 365 nm, to the red of the coumarin absorbance, and exhibits a broad emission from 425 to 625 nm with a maximum at 472 nm (vide supra). The dye was synthesized via a Peckmann condensation between 2,7-dihydroxynaphthalene and ethyl trifluoroacetate to exclusively afford the bent isomer upon crystallization from ethanol. A carboxylic acid group necessary for incorporation into the branched monomer was introduced by alkylation with *tert*-butyl bromoacetate followed by acid-catalyzed deprotection of the *tert*-butyl ester. The synthesis of **4** requires no chromatography and can be scaled up to



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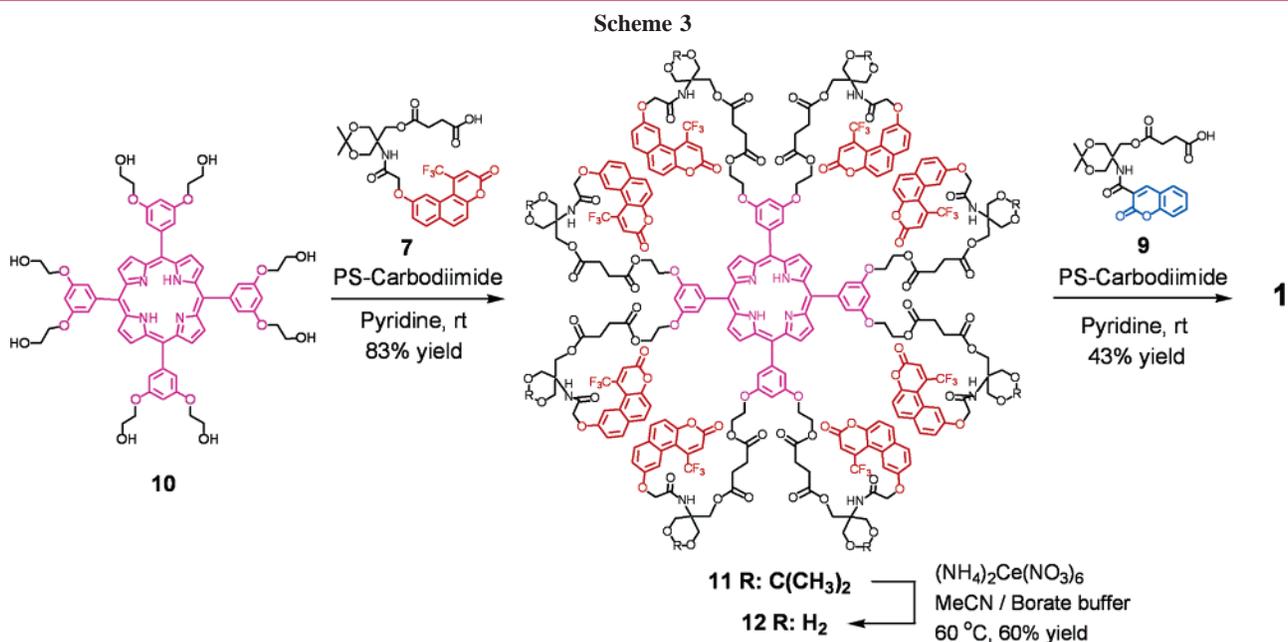
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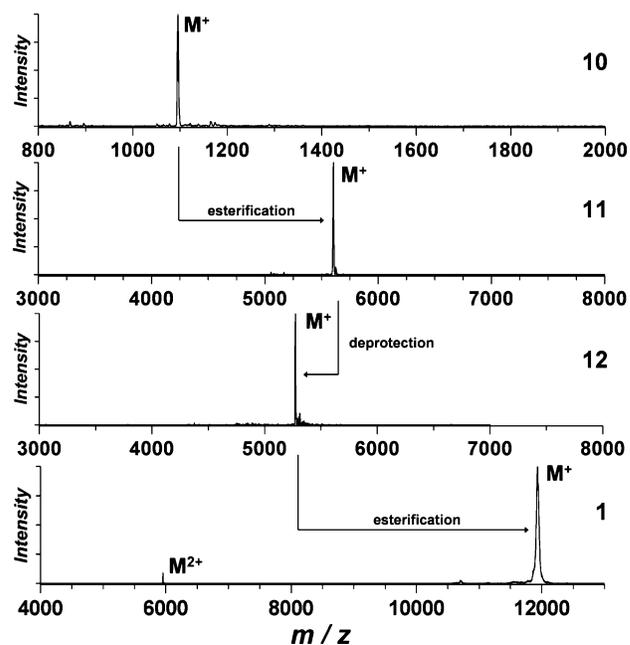
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produce multigram quantities of the dye. Commercially available coumarin-3-carboxylic acid was chosen as the first donor chromophore because it had already been shown to be an excellent sensitizer of the porphyrin Soret band.<sup>31,32</sup>

Once each donor chromophore had been selected, monomers bearing each dye were prepared (Scheme 2). Depending on the availability of the carboxylic acid being used, two different acylation procedures were developed. With readily available coumarin-3-carboxylate, equimolar amounts of **5**<sup>33</sup> and the carboxylic acid are mixed in the presence of EDC at 0 °C. In the case of more precious synthetic chromophores, such as **4**, an excess of the acetonide was used and HOBT was added to the mixture to enhance the selectivity for the formation of the monoacylated species. Following successful amide formation, the alcohol in each monomer was reacted with succinic anhydride to provide a carboxylic acid handle required for dendrimer growth. While TLC and NMR analyses of the crude reaction mixtures suggest that the reactions proceeded in good to excellent yields, the unoptimized yields reported here are only moderate due to difficulties in purification arising from the low solubility of the relatively polar synthetic intermediates.

With these monomers in hand, synthetic conditions for dendrimer growth and deprotection were developed (Scheme 3). The first generation dendrimer **11** was synthesized from an octahydroxyporphyrin **10** and **7** using a polystyrene-bound carbodiimide reagent<sup>34</sup> as the coupling agent in the presence of DMAP and dimethylaminopyridinium *p*-toluenesulfonate (DPTS).<sup>35</sup> The use of a resin-bound carbodiimide allowed



**Figure 2.** MALDI-TOF mass spectra of the porphyrin core (**10**), the G-1 acetonide protected dendrimer (**11**), the G-1 deprotected dendrimer (**12**), and the final target (**1**). The observed molecular weight of each compound in each spectrum corresponds to the expected value, and the monodispersity of the spectra indicates that each esterification and deprotection step proceeded to completion.

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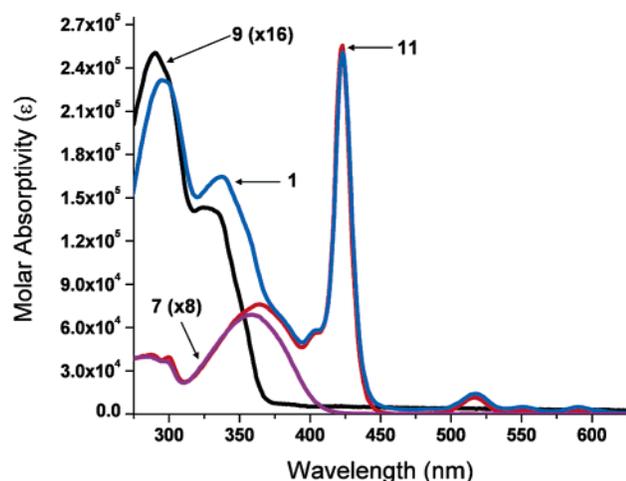
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the stoichiometric carbodiimide-derived byproducts to be removed by filtration, greatly simplifying the chromatographic purification of the dendrimers. Complete deprotection of all eight acetonide protecting groups of **11** could not be accomplished using aqueous acid without a small amount of hydrolysis of the polyester backbone. However, complete deprotection without degradation was achieved using a catalytic amount of ammonium nitrate (CAN) in an acetonitrile/borate buffer mixture at pH 7, modified from the procedure reported by Marko et al.<sup>36,37</sup> The deprotection provides the activated first generation compound **12** containing 16 hydroxyl groups that can serve as reactive sites for another iteration of the esterification procedure. The final target **1** was prepared under similar conditions as **11** by using coumarin monomer **9** in the coupling procedure. The purity of all compounds in this synthetic sequence was confirmed by NMR spectroscopy and by MALDI-TOF mass spectrometry (Figure 2), paying special attention to monitor each growth and deprotection step and for completion and for unwanted side reactions.

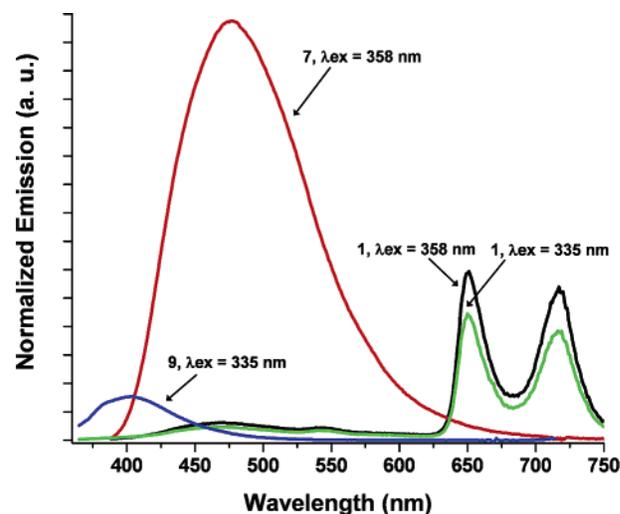
The absorption spectra of each of the multiple chromophore assemblies **1** and **11** (Figure 3) show peak shapes and



**Figure 3.** Absorbance spectra of the target and model compounds in THF at room temperature. The spectra of **7** and **9** are multiplied by appropriate factors to account for their dye composition relative to **1** and **11**. The spectra of **1** and **11** show the expected extinction coefficients and peak shapes based on the number and type of chromophores they contain.

molar absorptivities that represent linear additions of the absorption spectra of their component chromophores. This confirms the presence of all of the chromophores in each of the dendrimers and demonstrates that there is little ground-state interaction between the dyes.

The fluorescence spectra of **1** (Figure 4) taken at two excitation wavelengths corresponding to donor absorption are indicative of near quantitative energy transfer from each



**Figure 4.** Fluorescence spectra of **1**, **7**, and **9** in THF at room temperature. Fluorescence spectra of **7** and **9** are normalized to the absorbance of compound **1** at 358 and 335 nm, respectively. Emission from the coumarin and naphthopyranone moieties in **1** is quenched relative to that seen from the monomers in the absence of the porphyrin acceptor. Emission is, instead, observed from the porphyrin core.

of the two donor chromophores. When **1** is excited at 335 nm, virtually no coumarin emission is observed as compared to the emission of coumarin from an isoabsorbing solution of **9**. Instead, the characteristic porphyrin emission, with maxima at 651 and 717 nm, is observed. Extremely low levels of residual naphthopyranone emission are also observed, representing a slight deviation from quantitative energy transfer from naphthopyranone excited states generated by either direct excitation or FRET from the coumarin donors. When **1** is excited at 358 nm, corresponding to direct naphthopyranone excitation, the expected naphthopyranone absorption is quenched by 97%, and predominant emission from the porphyrin is seen, indicating efficient FRET from the naphthopyranone to the porphyrin.

With this modular synthetic approach to complex dendritic architectures allowing for precise control over interior functionality in hand, ongoing efforts in our laboratories are focused on improving photon collection of light-harvesting dendrimers<sup>3,31,32</sup> and subsequent conversion of the excited-state energy concentrated at the dendrimer core into chemical energy.<sup>12</sup> Such light-driven nanoreactors closely imitate the function of natural photosynthetic machinery.<sup>38</sup>

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**Supporting Information Available:** Experimental details and characterization data of all compounds (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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