

# Synthesis and Steady-State Photophysical Properties of Dye-Labeled Dendrimers Having Novel Oligothiophene Cores: A Comparative Study

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Novel chromophore-labeled dendrimers with penta- and heptathiophene cores and coumarin-2 chromophores at their periphery have been shown to be very efficient light-harvesting systems. Excitation of the peripheral coumarin-2 chromophores results in energy transfer to the oligothiophene cores as a result of the large overlap between the donor emission spectrum and the acceptor absorption spectrum, as well as the large transition dipole moments of the oligothiophenes. Although these core dyes have low fluorescence quantum yields, their emission intensity is significantly enhanced by the ability of the large light-harvesting dendron to funnel absorbed energy to the core. Because of the large Stokes shift of the oligothiophenes, the emission spectrum of the dendrimers was red-shifted by 200 nm from the excitation wavelength. Additionally, it was found that oligothiophene orientation—end functionalization vs central functionalization—did not have a significant effect on energy-transfer efficiency.

## Introduction

The interest in molecules and molecular assemblies capable of light harvesting and energy transfer has expanded greatly in recent years. Progress in the study of natural photosynthetic systems<sup>1</sup> has provided the impetus to design artificial light-harvesting assemblies based on a variety of architectures. For instance, numerous reports on organic,<sup>2</sup> organometallic,<sup>3</sup> supramolecular,<sup>4</sup> and polymeric<sup>5</sup> chromophore assemblies capable of acting as light-harvesting antennae have appeared in the literature. More recently, dendritic light-harvesting assemblies<sup>6</sup> have also attracted much attention. Several elegant systems in which light ab-

sorption is followed by nearly quantitative energy transfer through the dendritic backbone to a core chromophore have been described. However, many of these examples are limited in scope since the energy transfer is dependent on an inherent transport property that is unique to the dendritic backbone.

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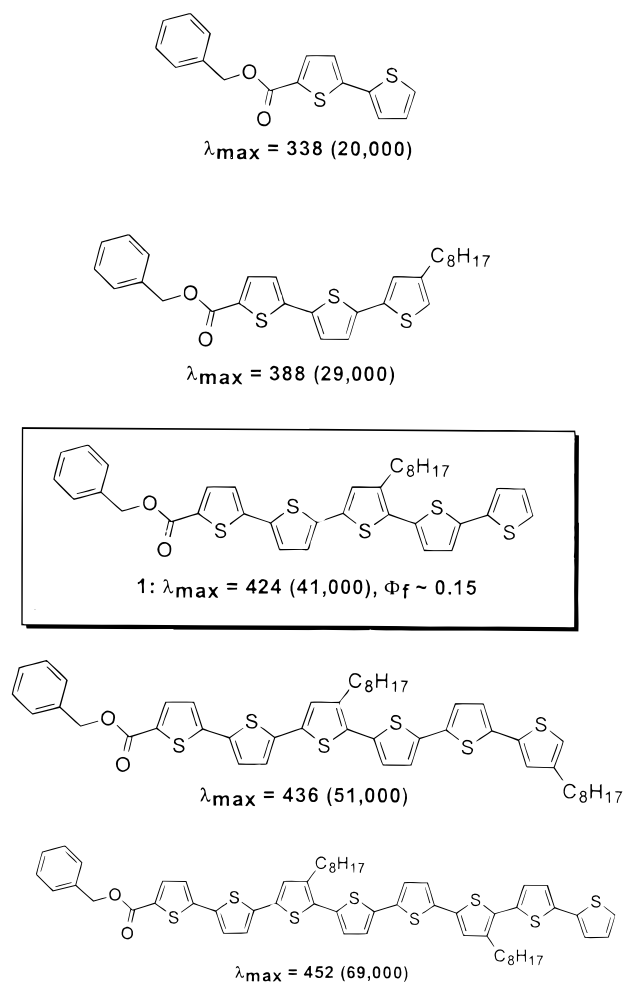
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Recently, our group has reported a highly efficient dendritic light-harvesting and energy-transfer system in which the dendrimer acts merely as a multifunctional scaffold and does not participate in the actual energy-transfer mechanism.<sup>7</sup> In this system, the dendrimer surface is functionalized with “donor” dyes that are capable of absorbing light and efficiently transferring the energy to a single “acceptor” dye tethered to the focal point of the dendrimer. This approach is fundamentally different from previous reports and provides unprecedented versatility such that additional features can be easily introduced by simply changing the various components of the dendrimer. Such versatility is important because application of these molecules in photonic devices would require the ability to control properties such as absorption/emission wavelength, fluorescence lifetime, fluorescence quantum yield, type of excitation energy including excitation by applied voltage rather than applied light, solubility, processability, and stability. To maintain high Förster energy-transfer efficiency in such devices, it is necessary to preserve a good spectral overlap between the emission spectrum of the donor dye and the absorption spectrum of the acceptor dye and to select moieties with high transition dipole moments.<sup>8</sup> Furthermore, the chromophores must contain additional functional groups that enable their attachment to the dendritic scaffold. Unfortunately, finding a suitable donor–acceptor pair can be difficult since the solubility properties of these highly conjugated molecules are not ideal. Additionally, modification of functional groups on the chromophores can often lead to undesired changes in the photophysical properties of the dyes.

Linear  $\alpha,\alpha$ -linked oligothiophenes are organic optoelectronic materials that can be easily tailored for a specific application.<sup>9</sup> For instance, by simply varying the length of the oligomer, the wavelength of absorbance and emission can be tuned. Furthermore, the thiophene moiety can be easily derivatized such that the inherent photophysical properties of the oligomer are maintained while simultaneously introducing points of attachment at various locations on the oligomer. For example, it is possible to derivatize the oligothiophene at either the  $\alpha$  or  $\beta$  positions of the thiophene rings. Herein, we demonstrate the versatility of our modular approach to light harvesting and energy transfer. We describe the synthesis of a series of oligothiophene “acceptor” dyes having functional handles at either the  $\alpha$  or  $\beta$  position and their successful incorporation into a dendritic



**Figure 1.** Structure and spectral properties of the  $\alpha$ -benzyl ester series of oligothiophenes ( $\text{CHCl}_3$ ,  $\text{M}^{-1} \text{cm}^{-1}$ ).

chromophore assembly. Convergent dendrimers of generation one through three (G1, G2, and G3) having coumarin-2 dyes at their periphery have been functionalized at the focal position with oligothiophene dyes. The versatility of these oligothiophenes can be easily appreciated since the desired spectral characteristics are obtained with two oligomers having different degrees of oligomerization and regio-chemical points of attachment. On the basis of steady-state fluorescence data, the oligothiophene acceptors proved to be highly efficient acceptors of energy initially absorbed by the peripheral coumarin-2 “donor” dyes and compare favorably to the wholly coumarin labeled materials we have reported previously.<sup>7</sup>

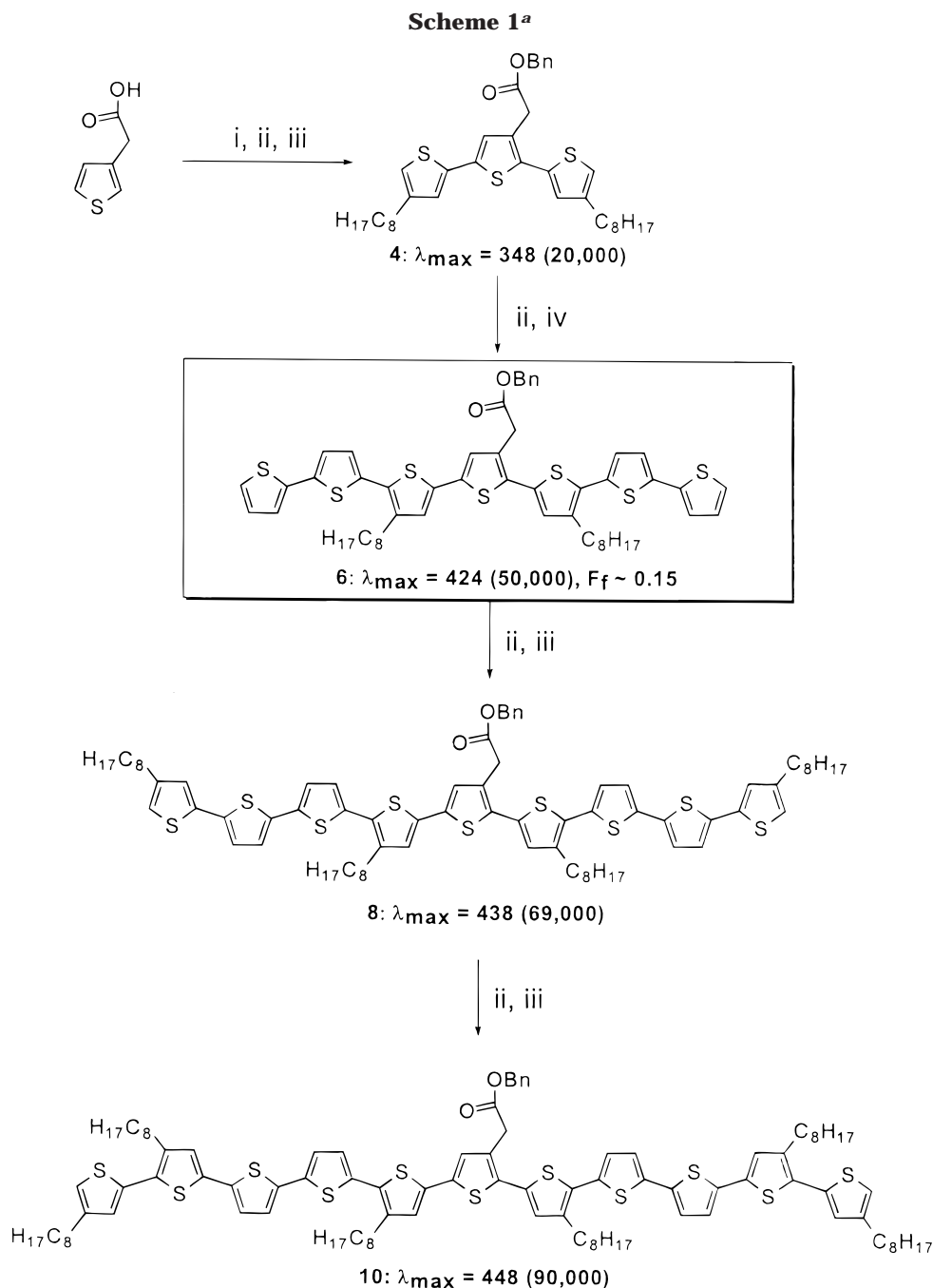
## Results and Discussion

**Molecular Design of Oligothiophenes for Light Harvesting.** When selecting a donor–acceptor pair, it is important to maximize the spectral overlap between the emission of the donor dye and the absorbance of the acceptor dye to enhance the probability of energy transfer. In our system, the chain ends of the dendrimer are functionalized with coumarin-2 dyes having a maximum emission wavelength ( $\lambda_{\text{em}}$ ) at  $\sim 420 \text{ nm}$ ,<sup>7</sup> hence a suitable acceptor would have a maximum absorption in the same spectral region. Figure 1 shows a series of  $\alpha$  benzyl ester functionalized oligothiophenes

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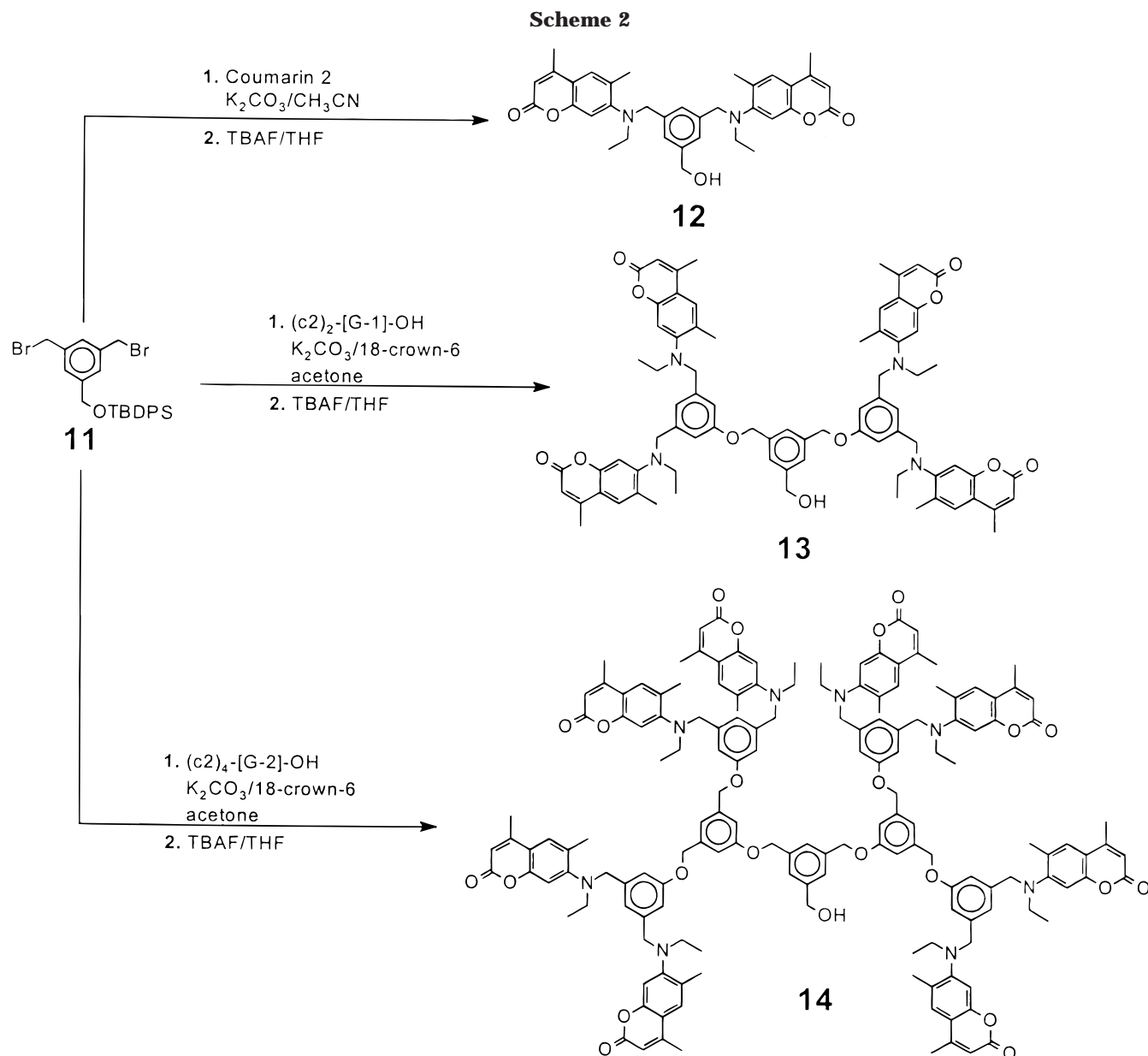


<sup>a</sup> (i) BnBr, K<sub>2</sub>CO<sub>3</sub>, 18-crown-6, THF, reflux. (ii) NBS, DMF, room temperature. (iii) 2-(Trimethylstannyl)-4-octylthiophene, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, DMF, 90 °C. (iv) 5-(Trimethylstannyl)-2,2'-bithiophene, Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, DMF, 90 °C. F<sub>f</sub> represents the quantum yield of fluorescence.

and reports their  $\lambda_{\max}$  of absorbance and extinction coefficient values. As expected, the absorbance maxima of these oligothiophenes shift bathochromically with higher degrees of oligomerization due to the extension in conjugation. Since the oligomer will be tethered to the dendrimer via an ester linkage, its spectral characteristics are not expected to be significantly affected by their attachment to the dendritic scaffold. Given that the  $\lambda_{\max}$  of the pentamer is 424 nm, a good match for the emission of the peripheral coumarin-2 laser dyes,<sup>7</sup> it makes an excellent candidate as an acceptor in our light-harvesting system.

As a comparison, we also explored the use of oligothiophenes having a point of attachment along the main chain of the oligomer (i.e., at the  $\beta$  position). Scheme 1

shows the preparation of such oligothiophenes, with a carboxylic acid functionality in the middle of the oligomer (vide infra) starting from 3-thiophene acetic acid. This bidirectional approach allows the preparation of lengthy oligomers in good yield in relatively few steps. As shown in Scheme 1, the  $\lambda_{\max}$  of heptamer **6** is 424 nm, thus making it also an ideal candidate to accept energy from the coumarin-2 laser dyes. Given that the carboxylate functionality is not conjugated with the oligothiophene backbone in the  $\beta$ -benzyl ester series, longer oligomers are needed to achieve the same conjugation length obtained in the  $\alpha$  series. Substitution is an additional parameter that can affect the conjugation and heptamer **6** has three  $\beta$ -substituents that decrease the conjugation due to steric interactions, thus



also contributing to the need for a lengthier oligomer in the  $\beta$  series to adjust the  $\lambda_{\max}$  accordingly.

**Synthesis of Oligothiophenes.** The synthesis of the  $\alpha$ -benzyl ester protected oligothiophene series (Figure 1) has been described elsewhere.<sup>10a</sup> The pentameric carboxylic acid analogue was obtained by saponification of the pentamer benzyl ester (**1**) with potassium hydroxide in a H<sub>2</sub>O/THF mixture followed by acidification with 1 M HCl (aq). The synthesis of the  $\beta$ -benzyl ester protected oligothiophene series depicted in Scheme 1 was accomplished using an iterative protocol of NBS bromination and Stille coupling reactions. Benzyl-3-thiopheneacetate **2** was prepared through reaction of 3-thiopheneacetic acid with benzyl bromide in the presence of potassium carbonate and 18-crown-6 (98%). Bromination of **2** with 2 equiv of NBS in DMF provided the monothiophene di-bromide **3** (86%). A Stille coupling

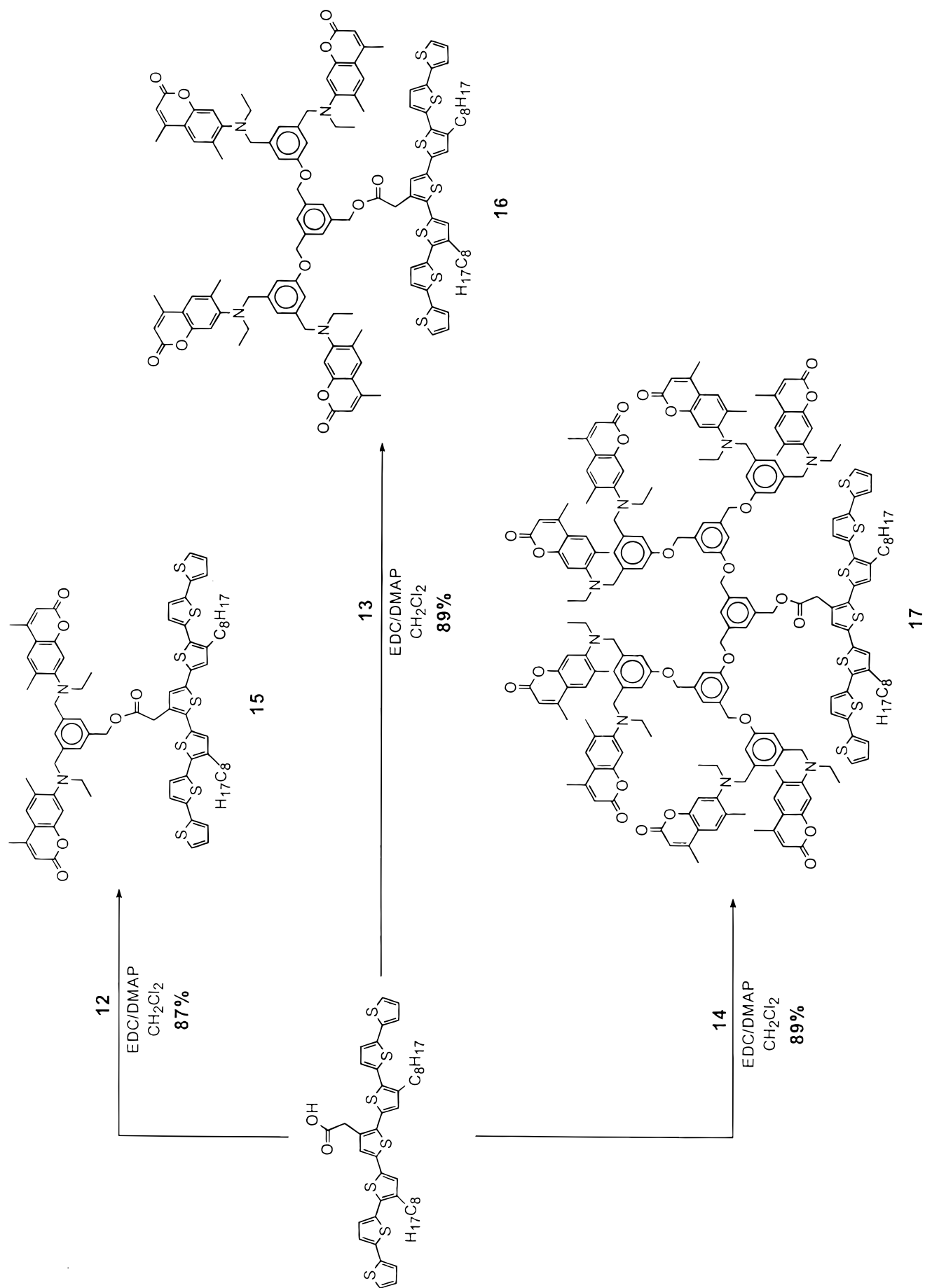
reaction between **3** and 2 equiv of 2-(trimethylstannyl)-4-octylthiophene<sup>10</sup> provided trimer **4** (77%). Bromination of **4** with 2 equiv of NBS in DMF yielded trimer dibromide **5** (95%). A subsequent Stille coupling between **5** and 2 equiv of 5-(trimethylstannyl)-2,2'-bithiophene<sup>11</sup> provided heptamer **6** (60%). Another iteration of the bromination and Stille coupling reactions with NBS and 2-(trimethylstannyl)-4-octylthiophene respectively provided nonamer **8** (71%) and undecamer **10** (84%). Heptamer **6** was converted to the carboxylic acid derivative by saponification with potassium hydroxide in a H<sub>2</sub>O/THF mixture followed by acidification with 1 M HCl (aq). All of the benzyl ester derivatives were found to be soluble in common organic solvents such as CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub>, and THF and were purified by column chromatography.

**Synthesis of Dendrimer-Oligomer Hybrids.** The preparation of the coumarin-2-functionalized dendrimers having a benzyl alcohol at the focal point was carried

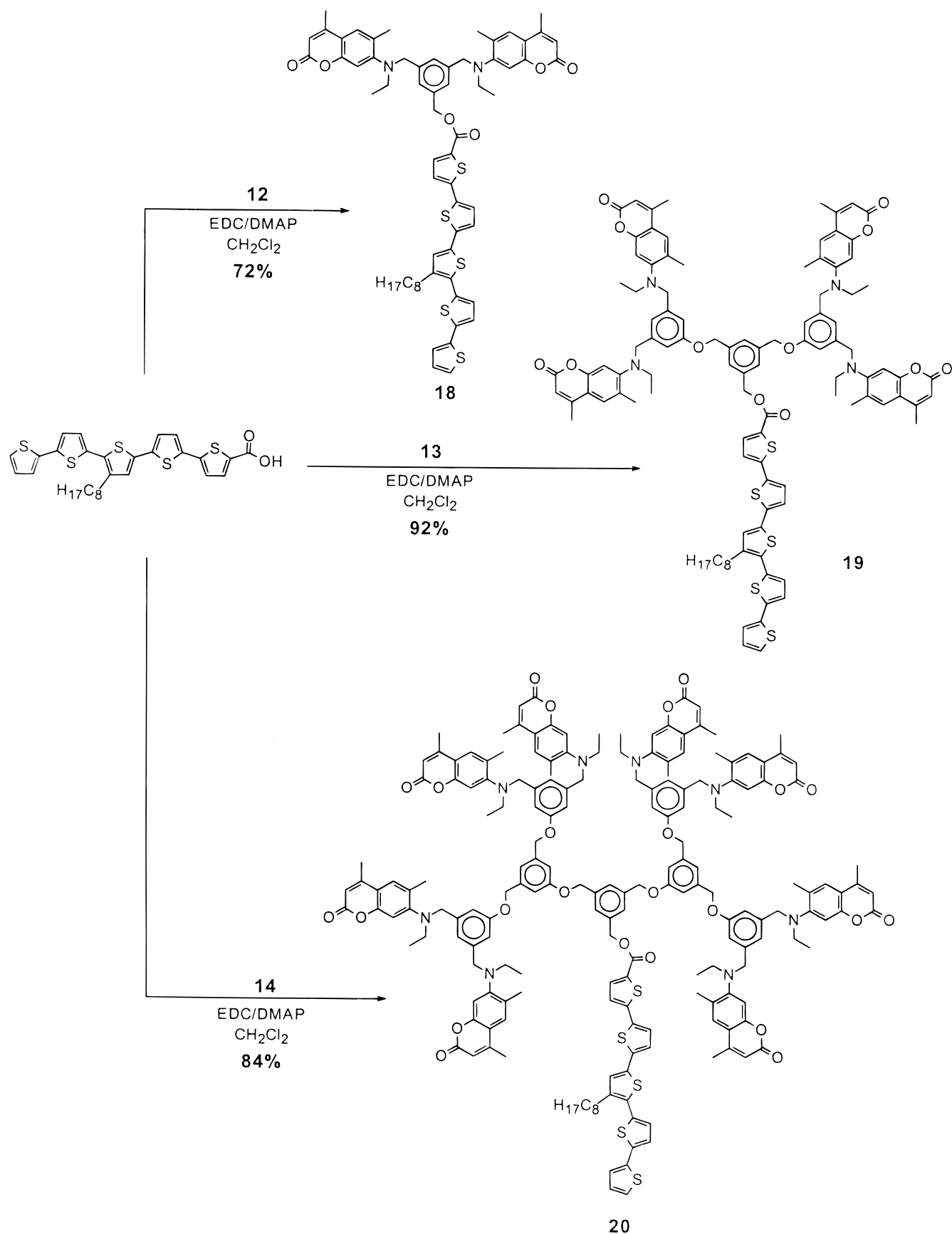
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Scheme 3

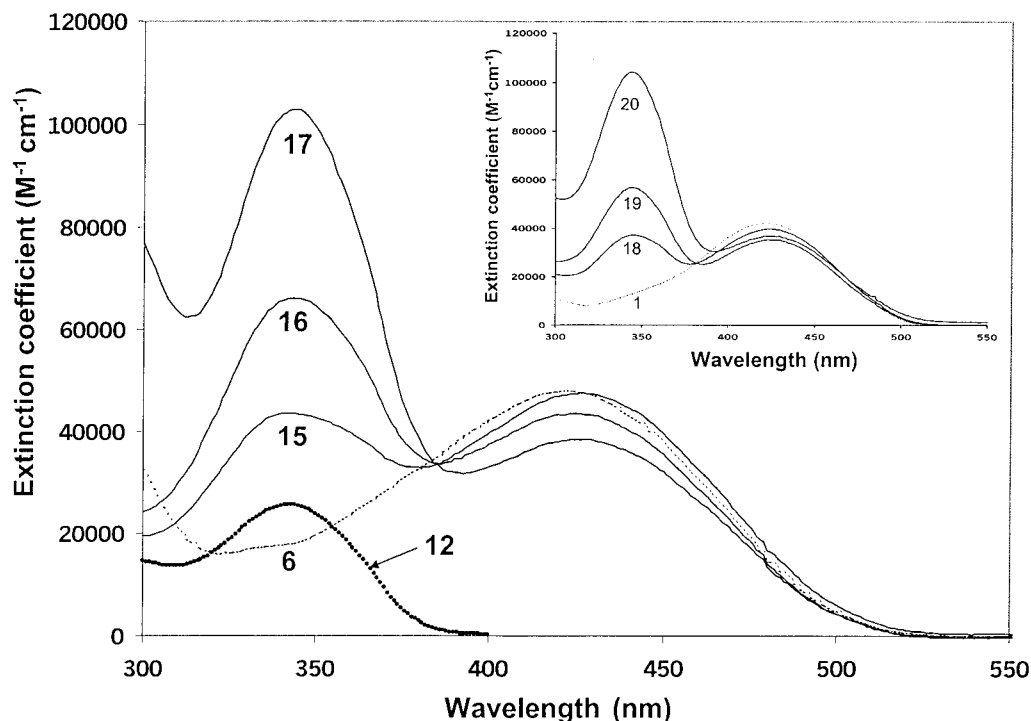


Scheme 4



out using the *tert*-butyldiphenylsilyl (TBDPS)-protected 5-hydroxymethyl-1,3-bis(bromomethyl)benzene<sup>7b</sup> **11** (Scheme 2). Synthesis of the G-1 dendron involved

reaction of 2 equiv of coumarin-2 with **11** in acetonitrile under reflux followed by deprotection with *tert*-butylammonium fluoride (TBAF). The G-2 and G-3 analogues



**Figure 2.** Absorption spectra of the three T-7 core dendrimer generations and both the acceptor model compound (dashed) and the donor model compound (dotted). Inset: Analogous spectra for the molecules having T-5 at the core.

were prepared via reaction of the previously described phenol core dendrons<sup>7</sup> (c2)<sub>2</sub>-[G-1]-OH and (c2)<sub>4</sub>-[G-2]-OH with **11** under phase transfer conditions, again followed by deprotection with TBAF (Scheme 2). Attachment of penta- and heptathiophene acid derivatives to the focal point of these deprotected dendrons was accomplished in high yield with the use of standard carbodiimide coupling conditions and by employing 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) and 4-(dimethylamino)pyridine (DMAP) (see Schemes 3 and 4).

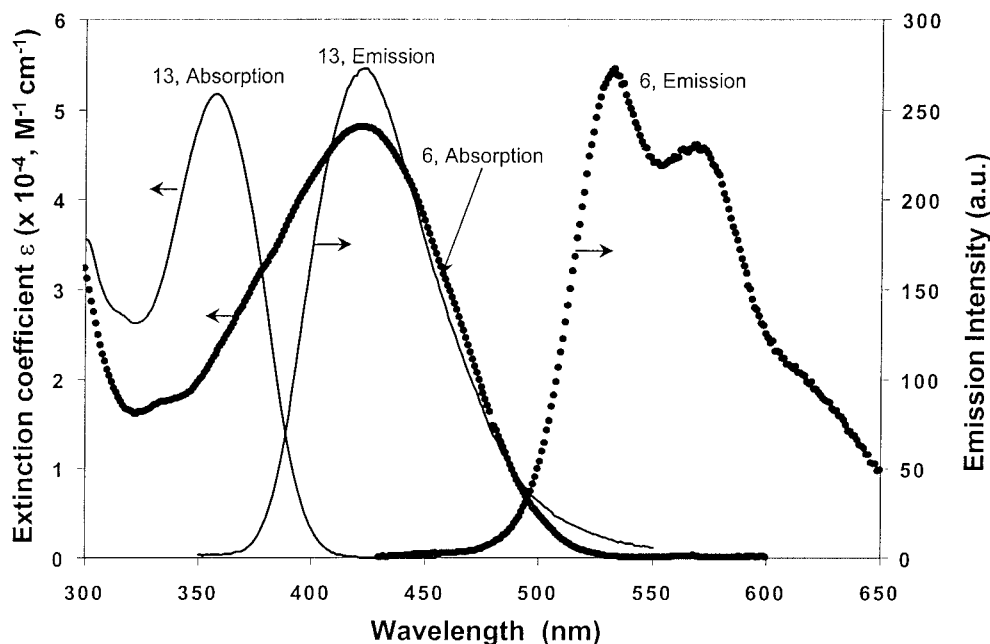
**UV Absorption Properties of Dendrimer–Oligothiophene Hybrids.** To deconvolute the spectral properties of the chromophore-labeled dendritic structures, it is first necessary to study the individual absorption properties of the donor and acceptor chromophores. Figure 2 illustrates the absorption properties of the model donor and acceptor fragments, along with the fully labeled dendrimers. First, it should be noted that the absorption spectrum of the oligothiophene core is very broad and that it overlaps significantly with that of the donor coumarins. Although this eliminates the ability to solely excite the donor dyes, the interference of the core is greatly diminished at higher dendrimer generations (*vide infra*). A comparison can also be made between the individual absorptions of the two model fragments to the absorption of the G-1 dendrimer. It is clear from this comparison that the absorption spectrum of the dendrimer corresponds to the sum of the individual absorptions of the two fragments, indicating that there are no deleterious ground-state interactions between the coumarins and the oligothiophene.

The overlaid absorption spectra for the G-1 to G-3 dendrimers are depicted in Figure 2. The absorption maxima ( $\lambda_{\max}$ ) and extinction coefficients ( $\epsilon$ ) for **15–20** along with those of the model acceptors **1** and **6** in

**Table 1. Absorption Maxima ( $\lambda_{\max}$ ) and Extinction Coefficients ( $\epsilon$ ) for the Dendrimers and Model Acceptor Compounds**

compound	$\lambda_{\max}$ ( $\epsilon$ )	
	donors	acceptors
<b>6</b>		423 (48 000)
<b>15</b>	341 (43 500)	426 (47 500)
<b>16</b>	343 (66 000)	426 (43 500)
<b>17</b>	344 (103 000)	425 (38 500)
<b>1</b>		422 (42 000)
<b>18</b>	345 (37 000)	423 (40 000)
<b>19</b>	344 (57 000)	423 (35 000)
<b>20</b>	344 (104 000)	423 (37 000)

toluene are given in Table 1. It can be seen that, as expected, the absorption of the peripheral coumarin chromophores doubles as the generation number increases. This indicates that with increasing generation, the molecule is capable of harvesting increasing amounts of light. Additionally, it can be clearly seen that, at higher generations, the absorption of the core at 350 nm becomes much less significant than the peripheral absorption. Neither spectral broadening nor spectral shifts of the donor absorption band with increasing generation were observed. However, the absorption band of the core heptathiophene (T7) was found to slightly decrease with increasing generation. The exact cause of this decrease is yet unknown, but it is possible to imagine that an increasing steric interaction would occur between the growing dendron and the relatively large core dye. Since only a slight spectral shift is observed for the oligothiophene, it may be surmised that conjugation length is not being significantly affected by the larger dendrons. Further evidence for this slight steric interaction arises from the analogous spectra of the pentathiophene (T5) core dendrimers (Figure 2, inset). In this series of molecules, the absorption band of the peripheral dyes is identical to the T7 dendrimers,



**Figure 3.** Overlaid absorption and emission spectra for the model donor (**12**) and acceptor (**6**) compounds.

but the absorption band of the core pentathiophene behaves differently. The monotonic decrease in absorption intensity is no longer present (the intensity in G-3 is higher than in G-2, but lower than G-1). It is expected that, in this series, the steric interactions between the dendron and the core are minimized since the core is end-functionalized and pointing away from the dendron.

#### Fluorescence Properties and Energy Transfer.

The overlaid absorption and emission spectra for the model donor and acceptor compounds are presented in Figure 3. From this figure, it can be seen that the overlap between the donor emission and acceptor absorption is extremely large, thus fulfilling one of the key requirements for Förster energy transfer. Additionally, it should be noted that the Stokes shift for the acceptor model compound is in excess of 100 nm. Such a large Stokes shift results from a significant conformational change that occurs upon excitation of the oligothiophene.<sup>12</sup> The excited state has been described as being quinoid-like, thus resulting in a planar conformation as opposed to the more twisted conformation in the ground state. As a result, the acceptor emission does not significantly overlap with that of the donor, thus eliminating the need for spectral subtraction. This not only simplifies the calculation of energy-transfer efficiency based on donor fluorescence quenching, but also increases its accuracy (*vide infra*).

Figure 4 illustrates the fluorescence emission spectra for the two dendrimer series in toluene, with excitation at 343 nm. Clearly, excitation of the peripheral donor coumarins results in emission emanating solely from the core oligothiophene as a result of highly efficient energy transfer. The lack of emission at 420 nm indicates that the donors have been completely quenched by the core acceptor. Additional evidence for energy transfer is

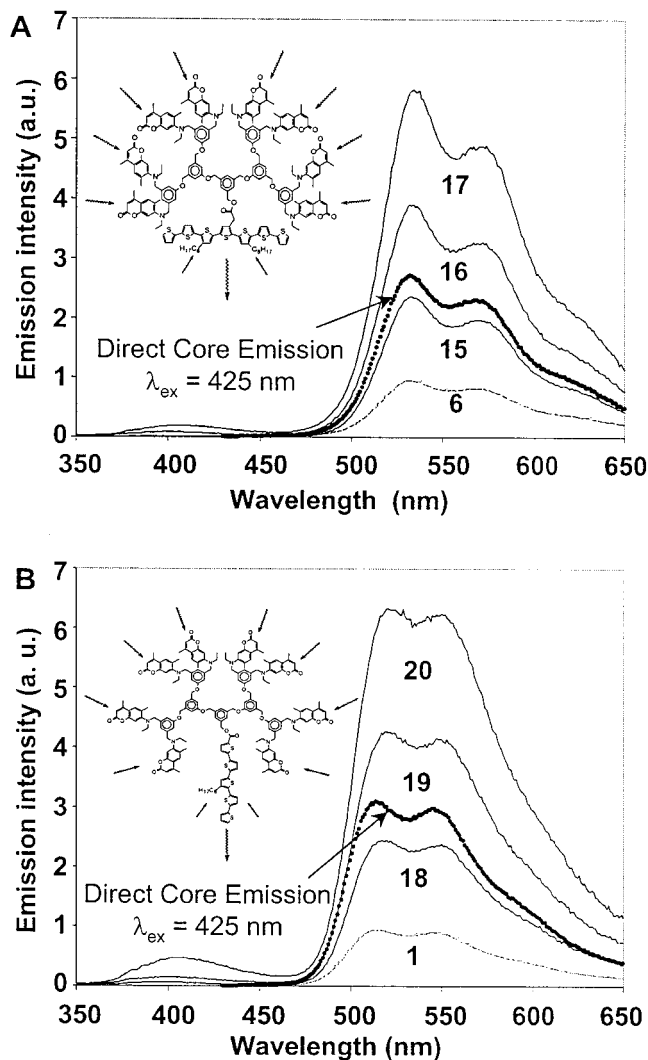
given by the enhancement of oligothiophene emission intensity when compared to the emission of the acceptor model compound, again irradiated at 343 nm. Furthermore, the oligothiophene emission spectra resulting from direct excitation at 425 nm ( $\lambda_{\max}$  for the core) is indicated by the dotted lines in Figure 4. A comparison of the core emission intensity as a result of sensitized vs direct excitation indicates that it is possible to gain a more intense emission from the core when it is excited via sensitization from a large light-harvesting antenna ( $\geq$ G-2). The increase in emission intensity is proportional to the increase in extinction coefficients of the donor dendron at 343 nm over that of the core acceptor at 425 nm. This again indicates that the energy-transfer interaction is extremely efficient in these molecules, allowing the energy of a large collection of photons to be funneled to the core as a result of absorption by the peripheral chromophores. This is an important attribute of the light-harvesting antenna, since such a system is capable of enhancing the emission intensity of chromophores with inherently low fluorescence quantum yields. Such an amplification phenomenon could be exploited to enhance the sensitivity and/or output capacity of photonic devices or be used in the labeling of bioactive moieties.

Energy-transfer efficiencies for these molecules were determined by comparing the emission of the donor model compounds at each generation to the fully labeled dendrimers. These calculations indicate that for all six compounds, the donor emission quenching, and hence energy-transfer efficiency, is in excess of 99%. It should be noted that although it is possible to detect emission from coumarin-2 in the fully labeled dendrimers, this emission is extremely small (<1%) when compared to the unquenched emission from the donor model compounds.

**Comparison between Coumarin and Oligothiophene Cores.** It is interesting to compare the present oligothiophene-core dendrimers to the previously studied light-harvesting dendrimers having coumarin-343

(12) (a) Becker, R. S.; Sexas de Melo, J.; Maçanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, *100*, 18683–18695. (b) Chosrovian, H.; Rentsch, S.; Grebner, D.; Dahm, D. U.; Birckner, E.; Naarmann, H. *Synth. Met.* **1993**, *60*, 23–26. (c) van Hutten, P. F.; Gill, R. E.; Herrema, J. K.; Hadziioannou, G. *J. Phys. Chem.* **1995**, *99*, 3218–3224.





**Figure 4.** Fluorescence emission spectra for the two dendrimer series along with the model acceptor compounds in toluene, with excitation at 343 nm. Emission from the model compounds as a result of excitation at 425 nm is also shown. The spectra are corrected for differences in lamp output at the two different wavelengths: (A) T-7 core dendrimers at  $5.06 \times 10^{-6}$  M and (B) T-5 core dendrimers at  $3.93 \times 10^{-6}$  M.

at the core.<sup>7</sup> Since the energy-transfer efficiency is dependent on (a) donor–acceptor distances, (b) spectral overlap between donor emission and acceptor absorption, and (c) the transition dipole moments of the donor and the acceptor, the two systems should be compared on the basis of these criteria. It is reasonable to assume that the donor–acceptor distances in both cases will be similar, since the dendrimer structure is essentially identical. Although the spectral overlap in both cases is very large, it is somewhat larger in the case of the oligothiophene-core dendrimers compared to the coumarin core analogues. Finally, the transition dipole moments of the penta- and heptathiophene chromophores were calculated to be 9.98 and 10.61 D,

(13) Structural features observed in the emission spectra are the result of different conformational rotamers that can form in the excited state as well as vibronic coupling. (a) Herrema, J. K.; van Hutten, P. F.; Gill, R. E.; Wildeman, J.; Wieringa, R. H.; Hadziioannou, G. *Macromolecules* **1995**, *28*, 8102–8116. (b) Yassar, A.; Horowitz, G.; Wintgens, V.; Hmyene, M.; Deloffre, F.; Srivastava, P.; Lang, P.; Garnier, F. *J. Phys. Chem.* **1995**, *99*, 9155–9159.

respectively,<sup>14</sup> which are both higher than the corresponding value for coumarin-343 (7.21 D). Hence, it is not surprising that the energy-transfer efficiency is nearly quantitative for the oligothiophene-core dendrimers, since all of the requirements for efficient Förster energy transfer have been met.

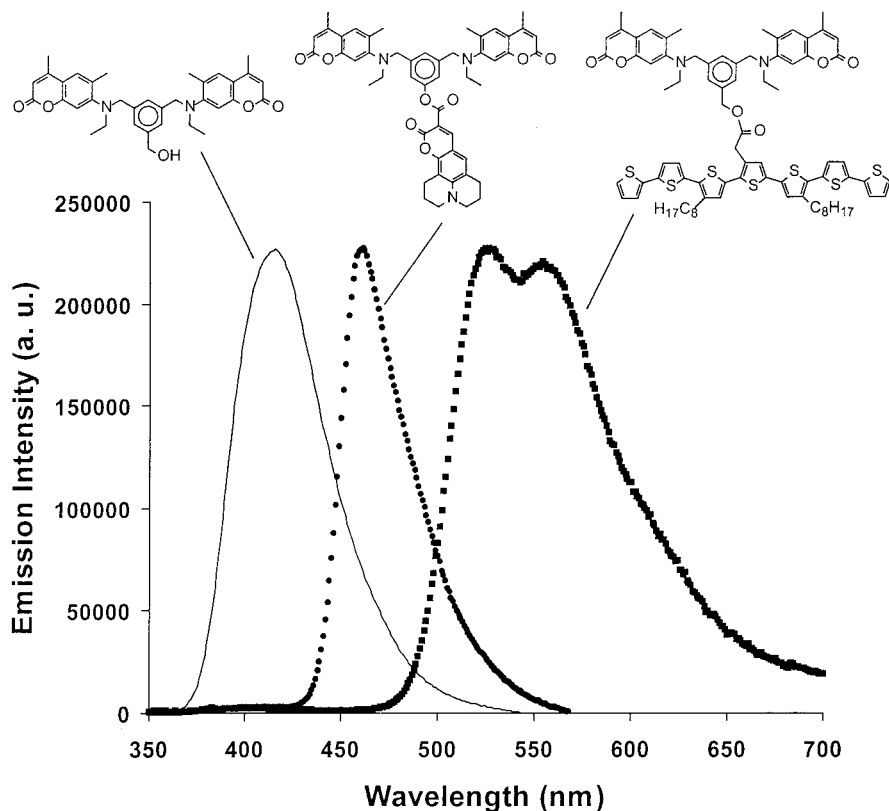
It is also important to note that the emission spectra of the two cores differ significantly. The oligothiophene emission is red-shifted by more than 70 nm from that of coumarin-343. Since both the coumarin-343 and the oligothiophene cores can be used in conjunction with the same peripheral antenna, emission wavelength tunability is easily possible within this homologous set of structures. Figure 5 shows the emission spectra for dendrimers having no core chromophore, a coumarin-343 core, and an oligothiophene core, all excited at 343 nm. Clearly, the emission spectra in these three cases are significantly shifted from one another, allowing coverage of almost the entire visible spectrum as a result of excitation at a single wavelength. Such simple access to a wide range of “output” colors resulting from a single “input” wavelength could prove useful in the design of white light emitting devices based on organic materials. Additionally, in the field of fluorescent conjugates for biological molecules, the need for highly luminescent materials with easily tunable emission spectra has been identified.<sup>15</sup> In fact, the ideal probes for experiments requiring simultaneous excitation of different targets must have a narrow emission spectrum, should emit at distinctly different wavelengths, and excitation of the entire set of probes should occur at a single wavelength.<sup>15</sup> In this report, we have demonstrated that the dendritic antennas are excellent candidates for such applications.

## Conclusion

Using the versatility of the convergent approach to dendrimer synthesis in combination with appropriate matching of photophysical properties of a variety of chromophores, it is possible to prepare novel light-emitting dendrimers with easily tunable properties. Additionally, by coupling a large light-harvesting antenna with a core chromophore to which energy is efficiently transferred, it is possible to enhance the intensity of emission emanating from the core by a factor that is proportional to the difference in extinction coefficients between the donor dendron and the core acceptor. We have prepared a series of oligothiophene-core dendrons which exhibit extremely high energy-transfer efficiencies and distinct emission spectra from the previously prepared coumarin-343 core dendrimers. These molecules may find applications in photonic devices such as light-emitting diodes, fluorescent sensors, frequency converters, and fluorescent labels for biological molecules.

(14) Calculation of transition dipole moments from absorption spectra was based on the method described in: (a) Birks, J. B. *Photophysics of Aromatic Molecules* Wiley-Interscience: New York, 1970; pp 50–51. (b) Langeveld-Voss, B. M. W.; Beljonne, D.; Shuai, Z.; Janssen, R. A. J.; Meskers, S. C. J.; Meijer, E. W.; Brédas, J.-L. *Adv. Mater.* **1998**, *10*, 1343–1348.

(15) (a) Ju, J.; Ruan, C.; Fuller, C. W.; Glazer, A. N.; Mathies, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1995**, *92*, 4347–4351. (b) Bruchez, M., Jr.; Moronne, M.; Gin, P.; Weiss, S.; Alivisatos, A. P. *Science* **1998**, *281*, 2013–2016.



**Figure 5.** Overlaid fluorescence emission spectra for G-1 dendrimers having no core chromophore, coumarin-343 at the core, and heptathiophene at the core.

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**Supporting Information Available:** Full experimental details for the synthesis of all described compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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