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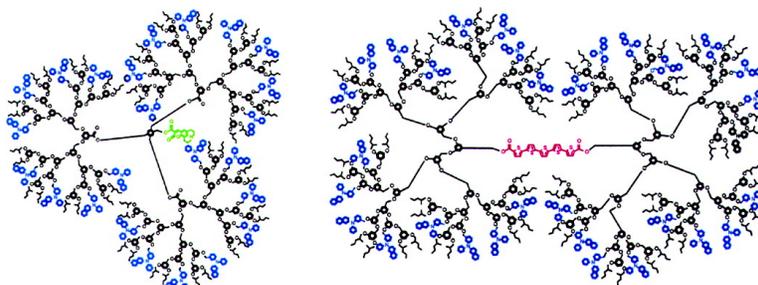# Controlling Solubility and Modulating Peripheral Function in Dendrimer Encapsulated Dyes

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Controlling Solubility and Modulating Peripheral Function in Dendrimer Encapsulated Dyes

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Abstract: The synthesis of large dendrons and dendrimers with site-isolated dyes at their core has been explored. The dyes selected for this work were coumarin 343 and pentathiophene, as energy transfer processes prevail when the two dyes are intimately mixed but each should behave independently of the other if site-isolation is achieved. Because the two dyes have very different functional characteristics, a protocol involving orthogonal protecting groups and allowing the use of a single family of electroactive dendrons for their encapsulation had to be developed. The synthetic protocol must balance the need to incorporate electroactive groups at the periphery of the dendrons with the requirement for high solubility and a size sufficient to fully encapsulate the central dye. Because of their poor solubility and tendency to crystallize, dendrons with uniform triarylamine substitution proved unsatisfactory leading to the development of new unsymmetrical dendrons with alternating branched alkyl groups and triarylamine moieties at their periphery. These dendrons, which show excellent solubility and no tendency to crystallize, were assembled into large dendrimers using a modular protocol with the light emitting dye at their core. It is expected that the large size of the dendritic shell will provide effective site-isolation for the encapsulated central dyes enabling them to exhibit their intrinsic emission properties with minimal energy transfer between neighboring core fluorophores when processed in bulk thin films.

Introduction

The concept of site isolation is widespread in nature with systems in which proteins or other naturally occurring macromolecular assemblies encapsulate an active center to endow it with unique properties that would not prevail in the absence of encapsulation. Dendrimers can be thought of as ideal synthetic structures that can be prepared in an attempt to mimic nature's encapsulation of functional molecules such as hemes in cytochromes or hemoglobin. The structures of dendrimers[1] can be tailored to spatially arrange different functionalities at the periphery, while placing a single functionality at the core, or focal point. Both divergent[2] and convergent[3] synthetic strategies have been used successfully to create macromolecules possessing "isolated" microenvironments within the dendrimer.[4] Their flexible synthetic methodology allows for the design of well-defined structures, where both the number of peripheral groups as well as their distance from the core can be precisely controlled.

An attractive target in dendrimer chemistry is one that makes use of the size and isolated internal environment of dendrimers to make catalysts with enhanced reactivity.[5] Examples include the manganese porphyrin dendrimer of Bhyrappa et al.,[5a,b] in which epoxidation of olefins is more selective to less hindered subtrates,[5c] and the amphiphilic dendrimer of Piotti et al.[6] The latter behaves as a reverse unimolecular micelle where the polar interior acts as a transition state catalyst for E1 elimination reactions, while also performing as a thermodynamic pump, bringing in the polar reactants and expelling the less polar products.

Besides providing reactive environments, dendrimers have also been used to enhance the photophysical behavior of chromophores they encapsulate.[7] Kawa and Fréchet have shown that self-assembled luminescent dendrimers holding a light emitting rare earth cation at their core[8] were free of the self-quenching behavior characteristic of the unshielded cations and had a luminescence efficiency that increased with the size of the dendrons surrounding the cation. Such site-isolation is an important feature for application in optical amplifiers. In earlier work,[9] the concept of dendritic antennae was demonstrated with systems in which an energy transfer (ET) interaction or similar

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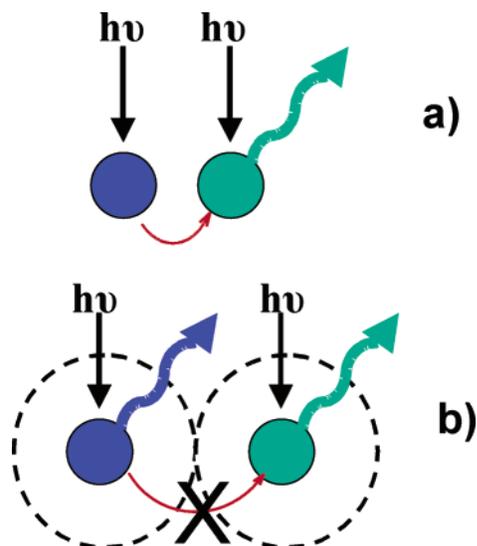
Figure 1. Schematic representation of energy transfer between dyes (a) and steric encapsulation preventing energy transfer between dyes (b)

electronic link was introduced between the periphery and the core. In a dendritic antenna, an array of terminal donor chromophores collects many photons and transfers their energy through space (Förster energy transfer) to the core or focal point acceptor unit, which can also be excited independently of the periphery. Because emission is observed from the core only, the system serves as a spatial and spectral energy concentrator, in other words it acts as a "molecular lens".

In contrast, it is normally difficult to prepare a light-emitting layer in which two or more dyes emit simultaneously as energy transfer between the dyes leads to light emission by the dye with the lowest band gap[10] as shown schematically in Figure 1a. Best results for simultaneous emission are generally obtained by using highly diluted systems in which the dye molecules are kept at mutual distances that exceed their Förster radius, thereby reducing these nonluminescent interactions. The challenge posed by the creation of a single layer light emitting diode capable of emitting two or more colors simultaneously—ultimately perhaps the three primary colors of the visible spectrum to afford white light—is an excellent vehicle to test a dual function dendrimer design affording not only site-isolation at its core but also contributing key electronic transport through its periphery. The dendritic encapsulation shown schematically in Figure 1b would enable multicolor emission from a single layer containing a mixture of encapsulated dyes.

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In a preliminary report,[11] we have demonstrated that some degree of encapsulation of light emitting dyes within dendritic shells might enable two dyes to coexist as a mixture while still preserving some of their ability to emit individually as a result of partial site-isolation. Following early work by Devadoss et al.,[9c] with a single color emitter that was subject to self-quenching caused by solid-state aggregation, Freeman et al.[11] successfully utilized triarylamine (TAA) HT-labeled poly(benzyl ether) dendrimers possessing Coumarin 343 (C343) and pentathiophene (T5) core to give blue and green OLEDs, respectively. Initial attempts to achieve synergistic emission from the two types of dendrimers by blending them in a single layer were only slightly successful due to detrimental energy transfer from the C343 laser dye to the smaller band-gap T5. Due to the large Förster radius of these dyes, energy transfer was an unfortuitous consequence of the small size and flexibility of the surrounding dendrons that were attached at a single point of the lumophores. Attempts to synthesize larger, more highly shielding dendrimers were unsuccessful due to the poor solubility and increased crystallinity of the triarylamine dendrons beyond the second generation. In general, such crystallinity is also highly detrimental to device performance due to the inhomogeneity of the resulting solid films.

We now describe the use of a new synthetic protocol and the design of novel building blocks that enable the preparation of dual function—site isolating *and* electroactive—dendrimers with vastly improved solubilities and molecular dimensions that may be adjusted readily to test more fully the fundamental concept of site-isolation through simultaneous emission from two vicinal dyes in a dendritic light emitting diode configuration. Several recent reports have also described the use of dendrimers as components of monochromatic light emitting diodes.[12]

In an accompanying manuscript the photoluminescence and electroluminescence properties of the dendrimer-encapsulated dyes and their mixtures are described.

Results and Discussion

A. Design of the Light Emitting Dendrimers. To maximize site-isolation, our dendrimer design features the light emitting chromophore at the center of the dendrimer with a multifunctional periphery held by large Fréchet-type poly(aryl ether) dendrons.[3] With a two chromophore system involving for example coumarin 343 (C343) and pentathiophene (T5) as the central dyes, this arrangement keeps the core moieties separated from each other to limit both self-quenching and the transfer of energy from the dye with the higher band gap (C343) to the lower band gap emitter (T5). The periphery of the dendrimers is fitted with triarylamine (TAA) moieties that serve a charge transport function—hole transport (HT)—for the device and also act as energy donors for the core acceptor chromophores. The dendrimer generation can then be used to control the average distance between the TAA units and the acceptor chromophores. The hole transport moieties are expected to work in conjunction with an oxadiazole (PBD) electron transporter added to the

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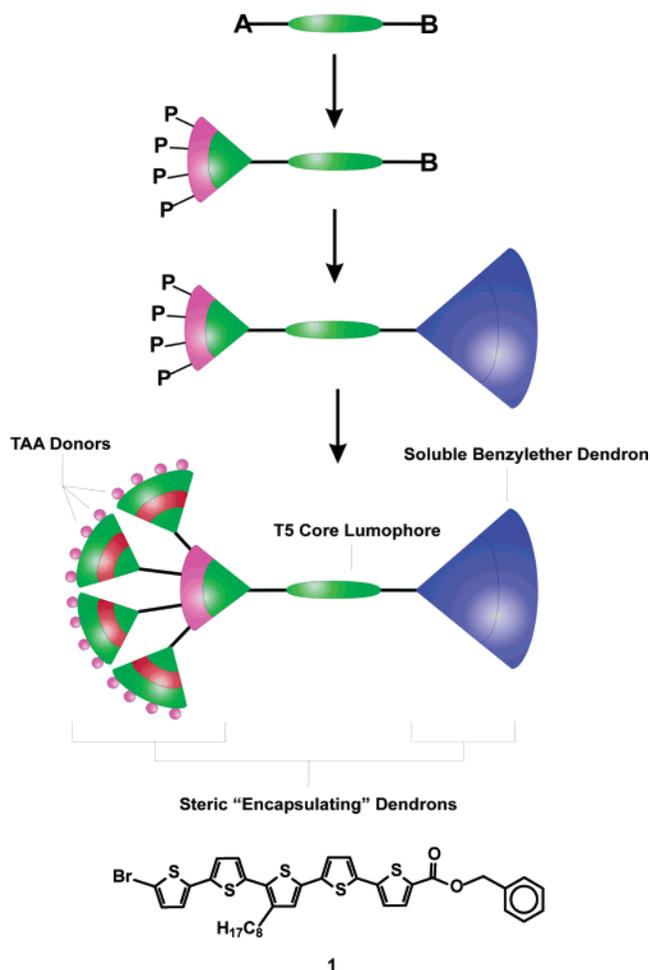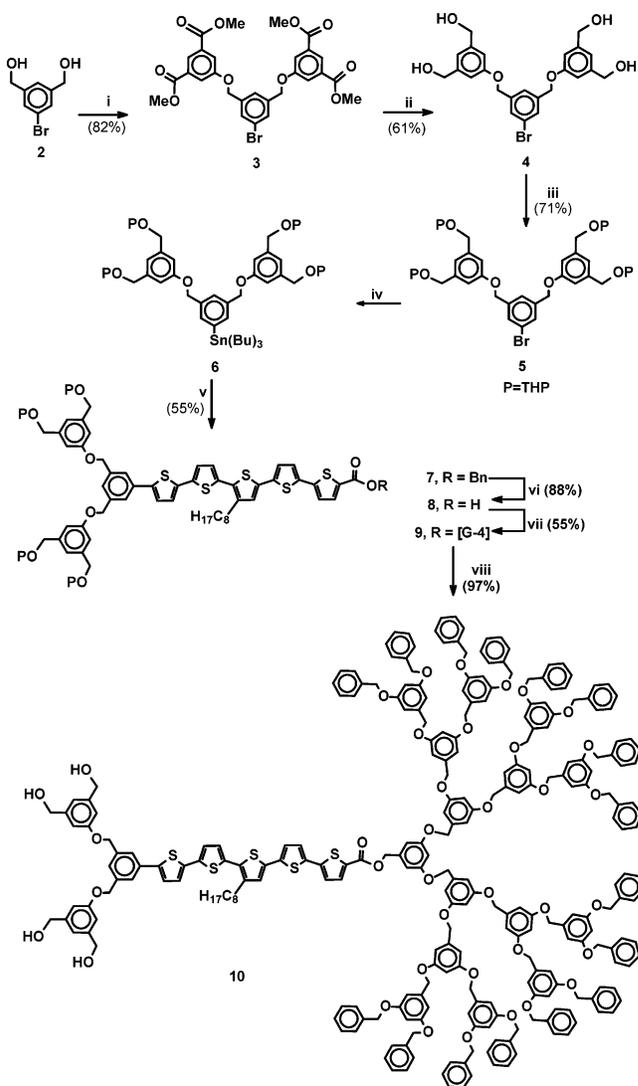
Figure 2. Schematic representation of asymmetric encapsulation of pentathiophene (T5) **1**.

Scheme 1

Conditions: (i) Ph$_3$P, DEAD, CH$_2$Cl$_2$, 2 eq dimethyl-5-hydroxyisoph-thalate; (ii) LAH, THF, 55 °C; (iii) DHP, p-TSA, DMF; (iv) n-BuLi, THF, −78 °C, (Bu)$_3$SnCl; (v) **1**, Pd(II), DMF, 90 °C; (vi) KOH, pH5 buffer; (vii) [G-4]-CH$_2$OH, DCC, DPTS; (viii) p-TSA, MeOH, THF.

dendrimer layer of the device. The photoemission band of the TAAs overlaps well with both the C343 and the T5 core absorption bands ensuring efficient energy transfer. Due to both the favorable band overlap and the limited distance between the donor TAAs and acceptor cores, the probability of photon emission via energy transfer is favored over nonemissive or core−core energy transfer, provided that the overall dendrimer framework is large enough. Energy transfer in these dendrimers may occur via photoinduced excitation as observed in other light harvesting dendrimer systems,[7−9] but it also occurs when a voltage potential is applied to a bulk film of the dendrimer, as in a device where electrons recombine with hole transporting TAAs in their excited state.

B. Dendronizing both Extremities of an Unsymmetrical T5 for Site-Isolation. Given the poor solubility of TAA dendrons above the second generation, larger TAA dendrons are difficult to purify and cannot be used to help solubilize T5. In addition, the sheer length of the T5 chromophore used in our previous work makes it impossible to achieve a high degree of encapsulation through dendronization of one of its extremities only. Therefore, a new strategy involving a bifunctional T5 moiety of the type shown in Figure 2 was explored. In this strategy, one terminus of an unsymmetrically substituted T5 chromophore, **1**,[13] is capped with a small end-protected dendron followed by attachment of a solubilizing poly(benzyl ether) dendron at the other extremity. Following deprotection of the

first extemity, final assembly is achieved by attachment of small, second generation TAA dendrons affording the desired encapsulated, yet still soluble structure with a fourth generation electroactive [G-4] TAA terminus.

1. Preparing the Pentathiophene for Dendron Attachment. Given the intrinsic low solubility of the pentathiophene core, our synthetic blueprint requires that the poorly soluble TAA functionalities be added last. We have shown earlier that attaching appropriately chosen dendrons to oligo- and even poly-thiophenes can greatly increase their solubility.[13a,13b] Therefore the unsymmetrical pentathiophene **7**, with one end protected by a benzyl ester group and the other by a small dendron containing four latent tetrahydropyranyl-protected alcohol coupling sites, was prepared (Scheme 1). The benzyl ester of **7** will later

(13) (a) Malenfant, P. R. L.; Groenendaal, L.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1998**, *120*, 10 990. (b) Malenfant, P. R. L.; Jayaraman, M.; Fréchet, J. M. J. *Chem. Mater.* **1999**, *11*, 3420. (c) Malenfant, P. R. L.; Fréchet, J. M. J. *Macromolecules* **2000**, *33*, 3634. (d) Briehn, C. A.; Schiedel, M.; Bonsen, E. M.; Schuhmann, W.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 4680. (e) Caras-Quintero, D.; Bäuerle, P. *Chem. Commun.* **2002**, 2690.

Scheme 2
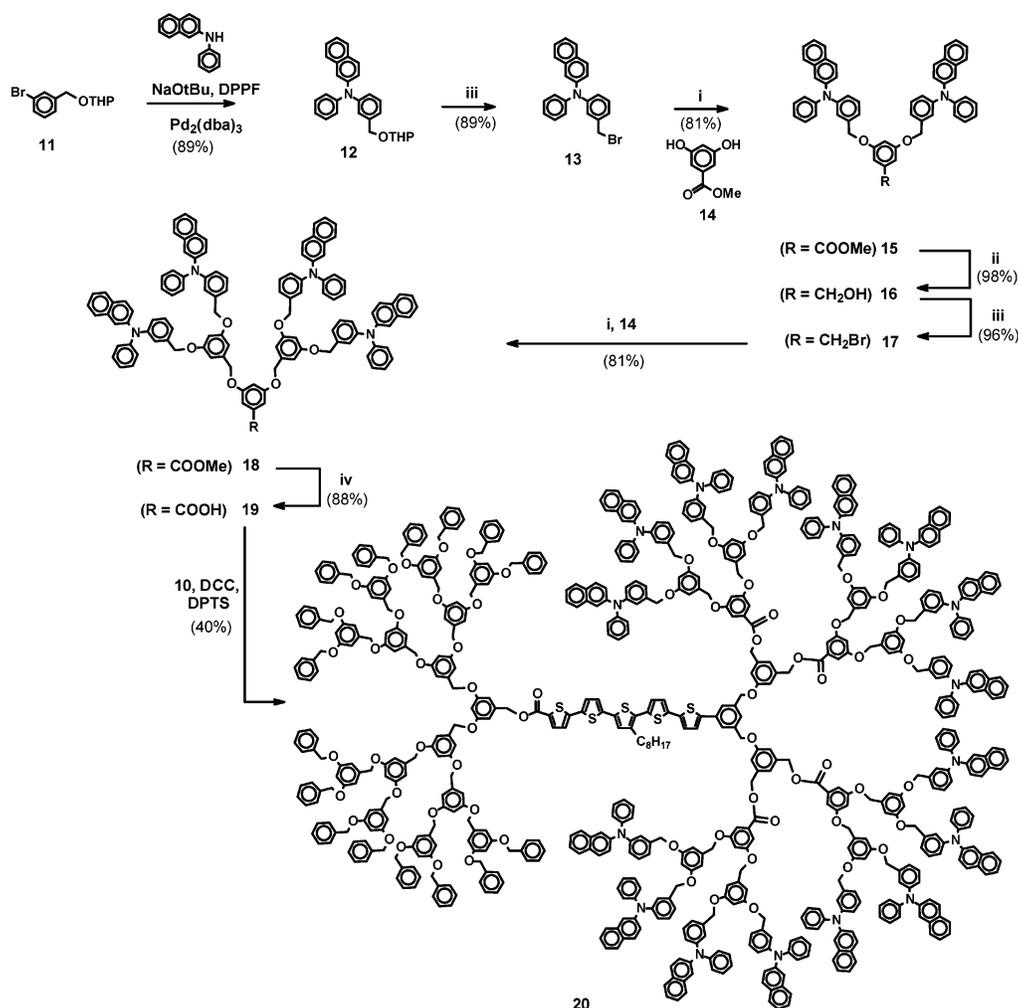
Conditions: (i) K$_2$CO$_3$, 18-Crown-6, Acetone, 60 °C; (ii) LAH, THF, 0 °C; (iii) CBr$_4$, Ph$_3$P, DIPEA, THF; (iv) KOH, MeOH, H$^+$.

be replaced by a solubilizing fourth generation Fréchet-type poly(benzyl ether) dendron, while the four coupling sites at the other extremity will be used to introduce low generation electroactive dendrons containing TAA termini.

Pentathiophene **1** was selected as the starting material as it has orthogonal bromide and carboxylic ester functionalities to facilitate the construction of the type of asymmetric "barbell"[13a] structure shown in Figure 2. The protected tetrafunctional [G-2] dendron **5** was chosen to provide the desired latent tetraol functionality of **7**. Compound **5** was obtained using the "reversed" convergent benzyl ether approach of Tyler and Hanson.[14] Starting with diol **2**,[15] treatment with two equivalents of dimethyl-5-hydroxyisophthalate under Mitsunobu etherification conditions[16] afforded the [G-2] tetraester dendron **3** in 82% yield after purification. Reduction of **3** into **4** had to be carried out at 55 °C using LiAlH$_4$ in THF due to the poor solubility of the starting tetraester. After recrystallization of **4**, THP protection of its four hydroxyl groups led to hypermonomer **5**, which is freely soluble in many aprotic solvents, including hexane. The focal point of **5** was subsequently activated by

lithiation followed by stannylation to afford the corresponding tributyltin derivative **6**, which could be used directly without further purification. Finally, attachment of **6** to the pentathiophene core **1** to form **7**, was achieved in 55% yield using Stille coupling conditions.[17]

2. Attachment of the Solubilizing Dendron: Preparation of Unsymmetrical Dendrimer 10. Although the solubility of pentathiophene carboxylic acids is generally too low to enable their efficient use in the elaboration of dendronized structures, the excellent solubilizing properties of the THP-protected dendron located at one extremity of **7** allow removal of the benzyl ester protecting group from the other extremity. Because solubility is preserved, the subsequent coupling of a large dendron can be achieved without the adverse effects that would arise from undue dilution or the use of solvents inappropriate for the coupling step. Therefore, highly soluble pentathiophene benzyl ester **7** was saponified and washed with pH 5 buffer to liberate the free acid **8**, without affecting the acid-labile THP acetals. A fourth generation Fréchet-type poly(benzyl ether) dendron[3] [G-4]-OH was then coupled to **8** using DCC and DPTS[18] in CH$_2$Cl$_2$ to afford **9** in 54% yield. The terminal poly-

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(16) Mitsunobu, O. *Synthesis* **1981**, *1*, 1.

(17) (a) Milstein, D.; Stille, J. K.. *J. Am. Chem. Soc.* **1979**, *101*, 4992. (b) Stille, J. K.; *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
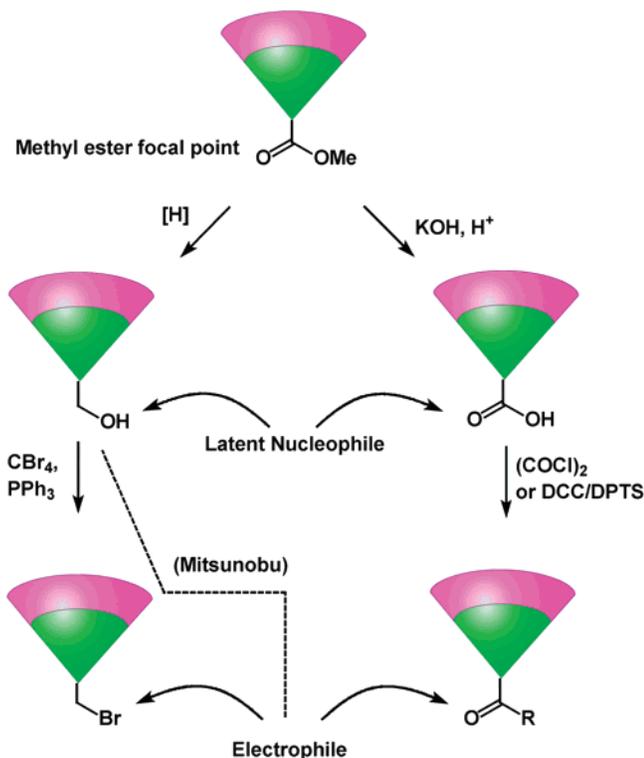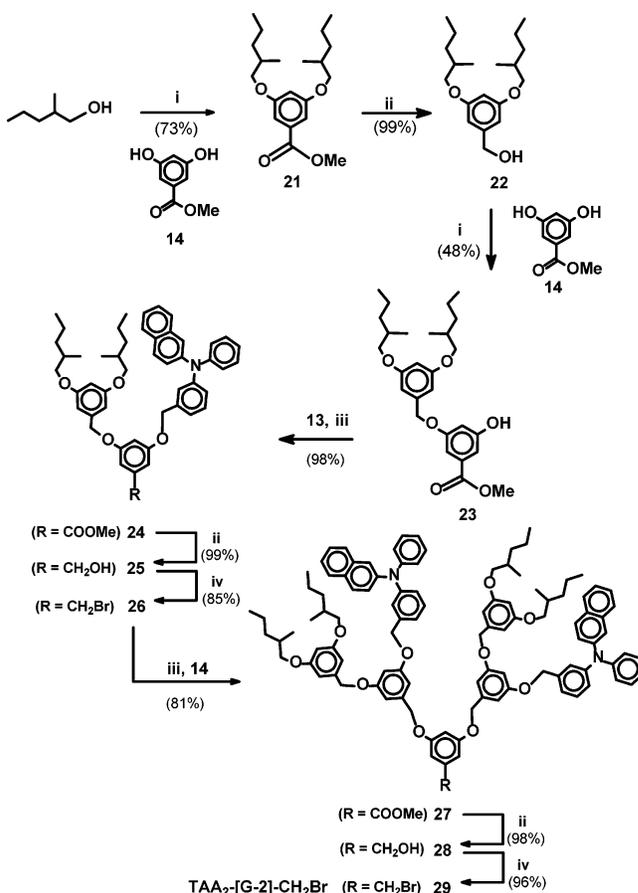(18) Moore, J. S.; Stupp, S. I. *Macromolecules* **1990**, *23*, 65.

Figure 3. Schematic representation of the utility of methyl ester focal point transformations.

(benzyl ether) dendron now contributes to the solubility of the whole and allows removal of the THP acetals to give soluble tetraol **10**.

3. Preparation of the TAA Dendrons and their Attachment to Unsymmetrical Dendrimer 10. The strategy chosen (Figure 2) requires the preparation of small, soluble [G-2] TAA dendrons, and their single-step attachment to the four coupling sites of dendrimer **10** to form the desired pentathiophene **20** in which the chromophore is flanked by two encapsulating generation four dendrons (Scheme 2). The hole transporting TAA dendrons, which serve as emissive donors while also providing steric bulk for encapsulation of the core T5 lumophore, were synthesized using a convergent approach. THP acetal **11**,[19] obtained from commercially available 3-bromobenzyl alcohol was used in a palladium cross coupling reaction[20] with *N*-phenyl-2-naphthylamine to afford **12**. After bromination using Ph$_3$P and Br$_2$ in CH$_2$Cl$_2$ at 0 °C, the first generation hole transporting dendron **15** (TAA$_2$-[G-1]-COOCH$_3$) was prepared from **13** by Williamson etherification[17] of methyl 3,5-dihydroxybenzoate **14**. The methyl ester focal point was then reduced quantitatively to the corresponding alcohol **16** using LAH in THF at 0 °C followed by Baeckström's[21] workup. Although the use of methyl-3,5-dihydroxybenzoate instead of the commonly employed 3,5-dihydroxybenzyl alcohol for the preparation of benzyl ether dendrons requires an additional reduction step, the electron withdrawing ester group of methyl-3,5-dihydroxybenzoate suppresses C-alkylation side reactions and increases the overall yield as the additional reduction step is

(19) Delorme, D.; Ducharme, Y.; Brideau, C.; Chan, C.; Chaulet, N. *J. Med. Chem.* **1996**, *39*, 3951.
(20) Driver, M. S.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217.
(21) Baeckström, P.; Li, L.; Mahinda, W.; Norin, T. *Synth. Commun.* **1990**, *20*, 423. This procedure greatly simplifies the workup and purification of the product via a single filtration.

Scheme 3

Conditions: (i) DEAD, Ph$_3$P, THF; (ii) LAH, THF, 0 °C; (iii) K$_2$CO$_3$, 18-Crown-6, Acetone, 60 °C; (iv) CBr$_4$, Ph$_3$P, DIPEA, THF.

quantitative. The methyl ester focal point is also a useful precursor for a variety of coupling reactions used in the synthesis of our dendrimers (Figure 3). It can be reduced and transformed to the corresponding electrophilic bromide for reaction with a nucleophilic reactant or core. It can also be saponified, to produce the corresponding nucleophilic carboxylates useful in subsequent assembly with appropriate electrophiles under mildly basic conditions, or to form an activated ester capable of coupling with suitable nucleophiles. The routes ultimately chosen for construction of the dendrimers must take into account solubility issues, the compatibility of functional groups, and the type of bond desired. This functional versatility is also useful for our purposes because one of the fluorescent dyes we plan to use as a core is nucleophilic while the other is electrophilic.

Alcohol **16** was transformed into bromide **17** using *N,N*-diisopropylethylamine (DIPEA), CBr$_4$, and Ph$_3$P in THF at 0 °C. DIPEA was used to neutralize any trace of potentially harmful acid that may be formed in the reaction. The [G-2] dendron **18** was constructed from **17** and diol **14** under the same alkylation conditions used previously for **15**. The ester focal point was saponified and subsequently acidified to give TAA$_4$-[G-2]-COOH **19,** which was coupled to tetraol **10** using DCC as a coupling agent to give the target encapsulated lumophore **20** in 40% yield.
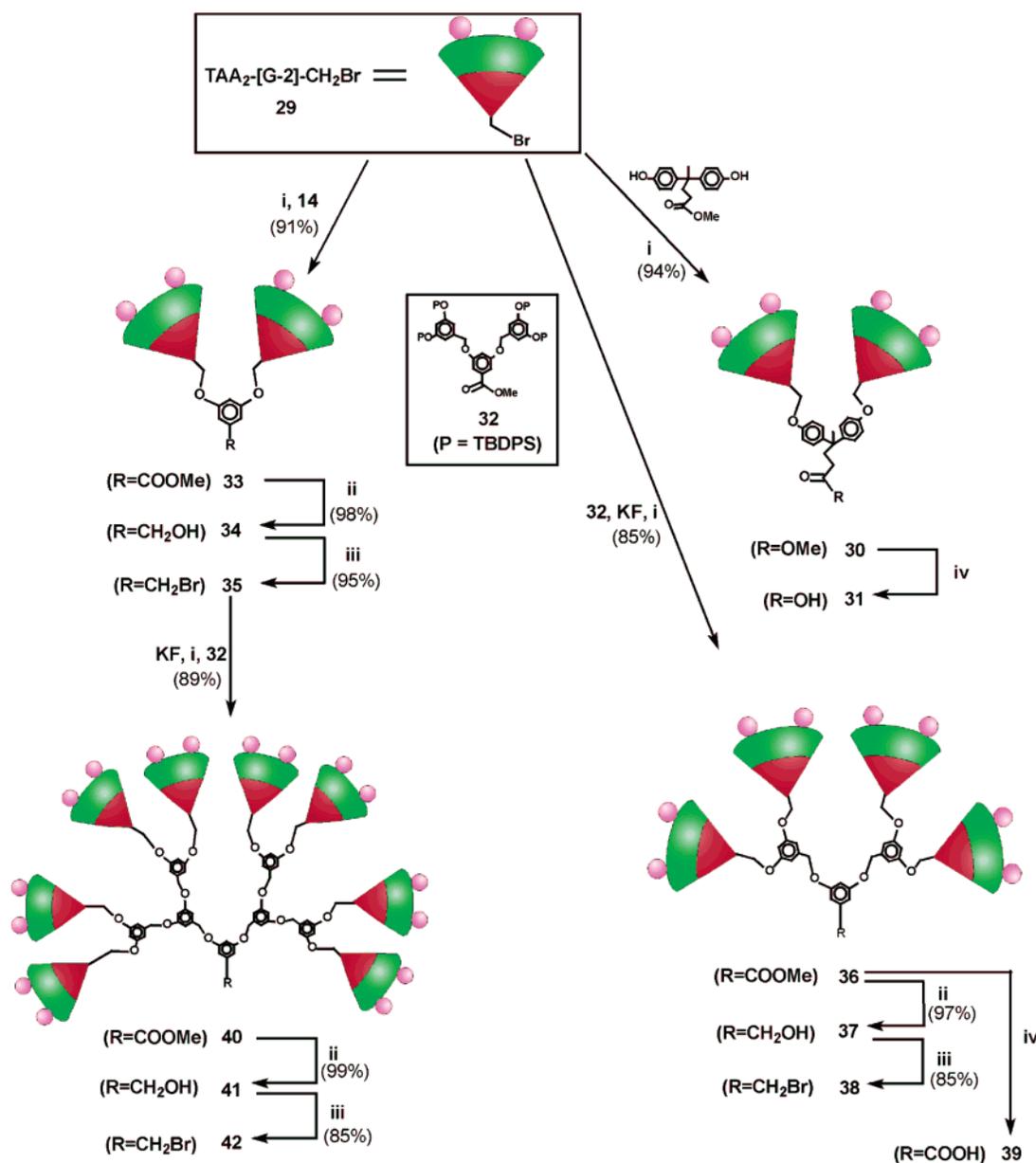
With dendrimer **20**, the solubility issue appeared to have been solved as **20** was soluble in common organic solvents (acetone, chloroform, THF, etc.), and preliminary studies of mixtures of

Scheme 4

Conditions: (i) K_2CO_3, 18-Crown-6, Acetone, 60 °C; (ii) LAH, THF, 0 °C; (iii) CBr_4, Ph_3P, THF, DIPEA; (iv) KOH, MeOH, H^+.

20 with coumarin dyes suggested that the encapsulating dendrons were large enough to show some improved isolation. However, the large [G-4] TAA terminated dendrons show a strong tendency to crystallize causing the rapid appearance of haziness in solution cast films of **20**, thus negating their use in organic light emitting diodes. Although other examples of triarylamine dendrimers[22] with *meta* substituents on their aromatic rings have been shown to form amorphous films from vacuum deposition, the poor quality of solution cast films of **20** could not be changed by the use of other solvents. As a result, the functional testing of the light emission and encapsulation characteristics of **20** required the solution casting of films containing 50 wt % of poly(vinyl carbazole). Therefore, while **20** achieved the initial goals of solubility and increased size,

the presence of the large dendron with TAA end groups confers undesirable properties that interfere with the measurement of site isolation.

C. Designing a New, More Soluble and Less Crystalline Dendrimer Periphery. The problem of crystallinity uncovered with dendrimer **20** is likely to re-occur with any other encapsulated chromophoric system based on a dense TAA periphery since both the TAA dendrons and the chromophores selected for encapsulation, coumarin 343 and T5 have limited intrinsic solubilities.

A new strategy was therefore developed both to solve the problems of solubility and crystallinity, and to allow the construction of larger dendrimers thereby enabling a more thorough exploration of the concept of dye encapsulation. To reduce the stacking of the TAA groups, which is likely to be the major contributor to any issue of crystallinity, a new dendron in which electroactive peripheral TAA groups alternate with

(22) (a) Shirota, Y.; Kuwabara, Y.; Inada, H.; Wakimoto, T.; Nakada, H.; Yonemoto, Y.; Kawami, S.; Imai, K. *Appl. Phys. Lett.* **1994**, *65*, 807–809. (b) Okumoto, K.; Shirota, Y. *Chem. Lett.* **2000**, *29*, 1034–1035.

Scheme 5
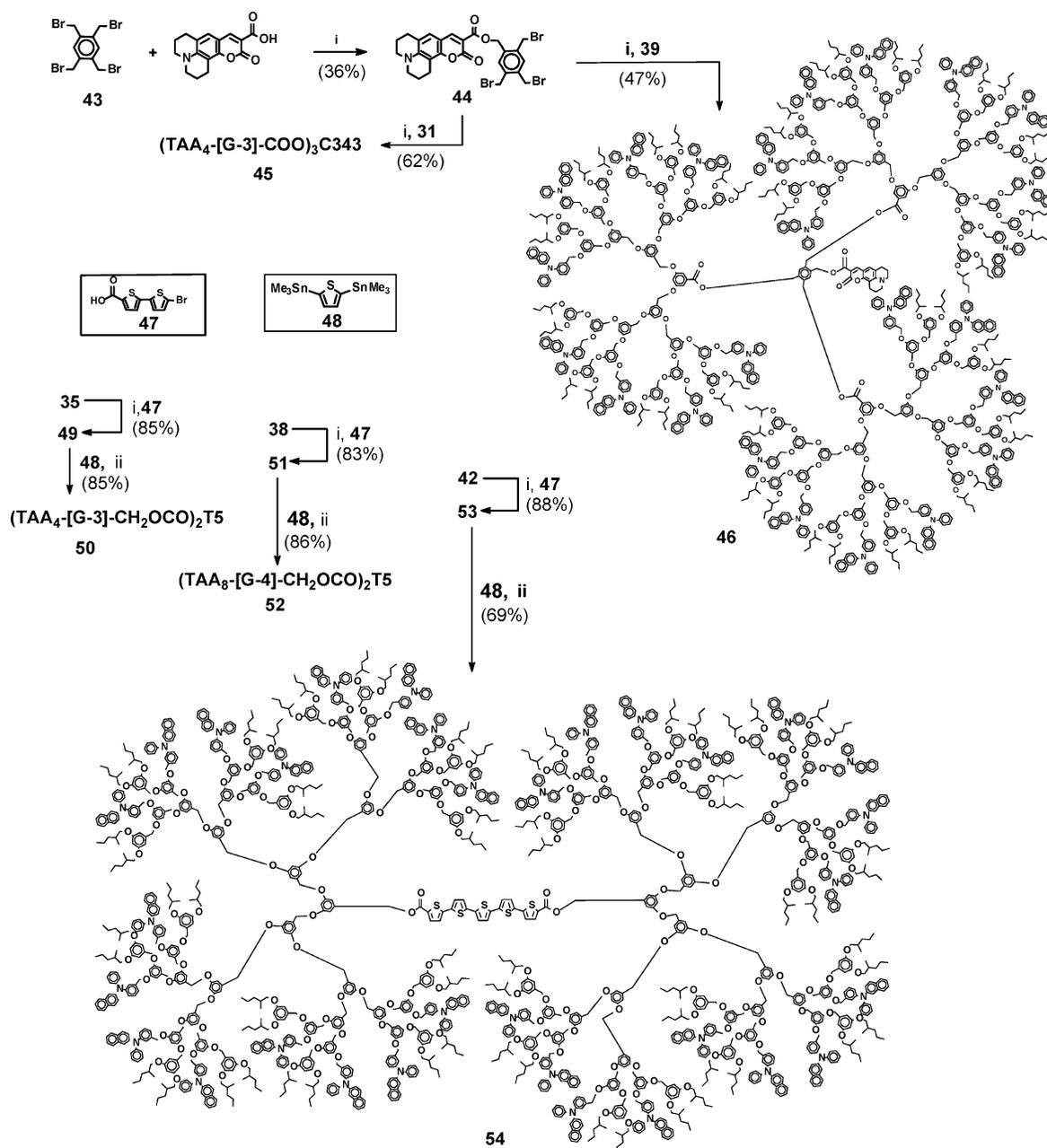
Conditions: (i) K$_2$CO$_3$, 18-Crown-6, Acetone, 56 °C; (ii) Pd(II), DMF, 90 °C.

solubilizing[23] branched alkyl ether groups was designed (Scheme 3). The synthesis of the unsymmetrical TAA-alkyl ether [G-1]-COOMe dendron **24** was only slightly more complicated than that of symmetrical dendron **15**, requiring an additional step to monofunctionalize the basic building block **14**. Once the terminal moieties have been introduced, the subsequent growth steps used to construct higher generation dendrons involve a conventional convergent protocol with both growth and workup facilitated by the high solubility of the new structures.

D. Synthesis of the Unsymmetrical Dendrons. A combination of divergent and convergent steps, also known as the double-stage convergent approach,[24] enabled the construction of dendrons that remained soluble and amorphous through the

largest fifth generation molecules we studied. The solubilizing terminal moiety with its twin alkyl ether groups was obtained by coupling 2-methyl-1-pentanol with **14** under Mitsunobu conditions, generating methyl ester **21** (Scheme 3). Following reduction of the ester, the resulting alcohol **22** was attached to only one of the two hydroxyls of **14**, affording phenol ester **23**. Williamson etherification of TAA **13** with **23** produced the first generation dendron **24**, having both TAA and alkyl ether terminal functionalities. LAH reduction of **24** generated alcohol **25**, which was subsequently brominated to obtain benzylic bromide **26**. The standard dendron growth procedure involving stepwise alkylation of **14** followed by reduction and activation of **28** to the bromide **29** was then applied. Both [G-3] and [G-4] dendrons with methyl ester focal points are available in one

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step from **29** (Scheme 4), depending on whether **14**, methyl 4,4-di(4-hydroxyphenyl)pentanoate, or the tetrafunctional hypermonomer[25] **32** is used. Standard etherification methodologies were used for all of these coupling reactions leading to third generation (**30** and **33**), and fourth generation (**36**) methyl ester dendrons. A similar synthetic strategy was used to build the fifth generation methyl ester **40**.

E. Synthesis of the Encapsulated Chromophores. The electrophilic C343 core moiety[11] **44** was prepared by reaction of coumarin 343 with a large excess of tetra-bromide[26] **43** under standard phase transfer conditions to maximize monosubstitution. The resulting core moiety still possesses three electrophilic benzylic bromide groups that can each be used to attach encapsulating electroactive dendrons. In contrast to our preliminary work,[11] in which only small coumarin dendrimers could be used due to their poor solubility, much larger third and fourth generation dendrons such as **31** and **39** with enhanced potential for encapsulation can be used as a result of the introduction of the terminal solubilizing groups. An initial attempt at encapsulation of the somewhat congested functionalized core dye **44** was made using the soluble electroactive dendron **31** as it was expected that its extended focal point would facilitate the coupling step via nucleophilic substitution with its carboxylate anion. This reaction was effected using 3.15 mol of carboxylic acid dendrons **31** per mole of **44** under standard phase transfer conditions affording dendrimer **45** with its coumarin core encapsulated in generation three dendrons. Although the use of the extended focal point in dendron **31** was successful, subsequent studies with a shorter focal point were also carried out in an attempt to provide added rigidity to the final product. Therefore, the coupling of **44** with the large fourth generation dendron **39** with its shorter and less flexible focal point led to a 47% isolated yield of encapsulated C343 dye **46**.

Given the success achieved in the preparation of larger encapsulating moieties for the coumarin chromophores, similar building blocks were used in the preparation of the encapsulated T5 dyes. In this case however, the great solubility of the dendritic arms enabled the use of a vastly simplified synthetic blueprint. Scheme 5 details the construction of generation 3, 4, and 5 dendrons with a bromo-bithiophene focal point by coupling the respective benzylic bromide dendrons with bromobithiophene carboxylic acid **47**.[27] In all three cases these dendrons **49**, **51**, and **53** were obtained in excellent yields of 85, 83, and 88%, respectively.

Assembly of the final dendrimers with two generation 3, 4, or 5 dendrons surrounding a pentatiophene core was achieved using the double Stille coupling[17] of the electroactive bithiophene dendrons (**49**, **51**, and **53**) onto bis(trimethylstannyl)thiophene **48**. Surprisingly high yields are obtained in this coupling reaction despite the rather large size of the dendrons. For example, the large bis-G-3 (**50**), bis-G-4 (**52**), and bis-G-5 (**54**) encapsulated pentathiophenes are obtained in yields of 85%, 86%, and 69%, respectively by reaction of only a very slight excess (less than 3%) of **49**, **51**, or **53** with the small bifunctional thiophene **48**. It is worth noting that the largest encapsulated dye obtained by this process has a molecular weight of more than 27 000 Daltons.
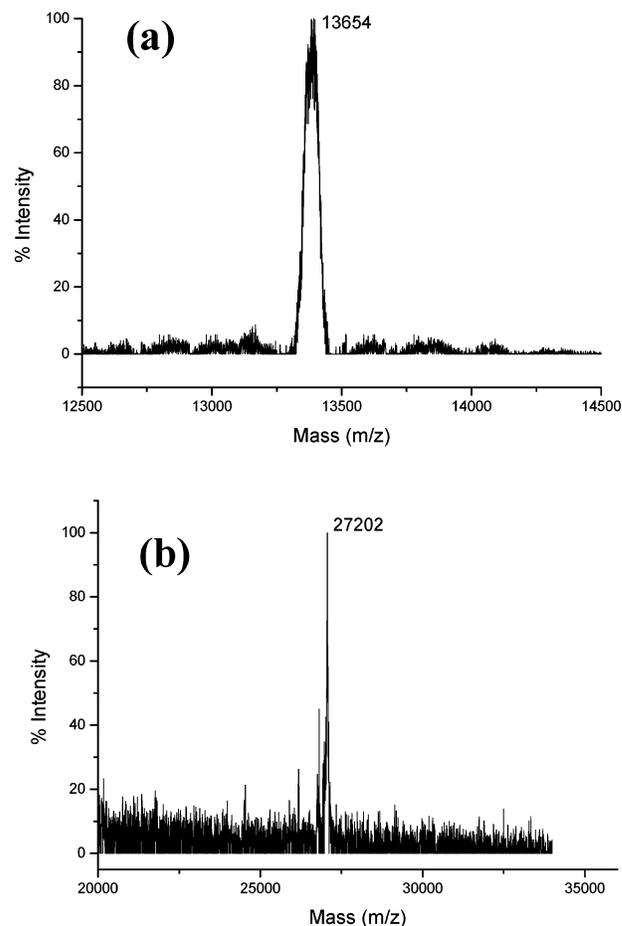
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Figure 4. MALDI-TOF of (a) bithiophene [G-5] dendron **53** and (b) pentathiophene bis [G-5] dendrimer **54**.

F. Characterization of the Dendrons and Dendrimers. The dendrons and dendrimers were characterized by a combination of IR, NMR, and MALDI mass spectroscopy. The main utility of IR was the monitoring of transformations involving ester focal points. As the ester focal point is transformed into a carboxylic acid, the C=O stretch shifts from 1745 to 1692 cm^{-1}. Similarly, the ^{1}H NMR chemical shifts of methyl ester protons, as well as the benzyl protons of the alcohol and bromide focal points are easily followed confirming focal point transformations.

MALDI-TOF mass spectroscopy is most valuable for higher molecular weight compounds (MW > 1500) where other methods become less applicable because diagnostic NMR signals become more difficult to discern due to the growing intensities of the signals corresponding to the dendrimer interior and periphery. For example, few differences are observable in the NMR signals for **54** and its precursor **53** as the peak corresponding to the additional thiophene ring is hidden within the large aromatic resonances of the dendrons, whereas the masses of the two compounds differ widely (27 203 vs 13 640 Daltons) (Figure 4a,b).

Conclusion

Since chromophores such as C343 and T5 are capable of energy transfer over a range of several nanometers, site isolation requires that fairly large structures be built, and the measurement

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of the relative degree of encapsulation they afford mandates experiments involving light emission that require the fabrication of thin film devices. As a result, the dendrimers must not only possess the required radial arrangement of a central chromophore surrounded by peripheral electroactive groups, but also appropriate physical properties allowing the preparation of good amorphous films. Although early dendrimers based on TAA dendrons were capable of providing a sterically demanding environment, their tendency to crystallize led to synthetic difficulties with lowered yields and film-forming properties too poor to allow the measurement of ultimate properties derived from site isolation. The synthetic versatility of the convergent growth approach has now enabled the introduction of groups that contribute both physical (solubility) and electronic properties, while also allowing the high yield preparation of structures sufficiently large to provide a significant level of steric shielding and site isolation. Not surprisingly, site isolation required the development of very large structures with a size comparable to

that of many enzymes. The demonstration of site-isolation and the functional properties of these light-emitting dendrimers are described in the accompanying paper.

Supporting Information Available: Detailed experimental procedures and characterization data for compounds **2**−**13**, **15**−**31**, **33**−**42**, **44**−**46**, and **48**−**54** are available in the complete Experimental Section included in Supporting Information (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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