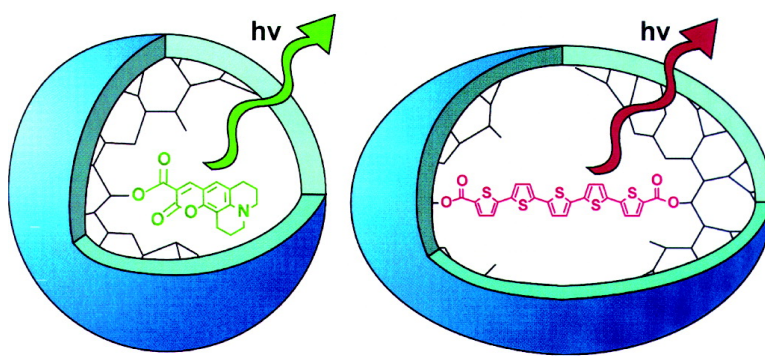


Simultaneous Light Emission from a Mixture of Dendrimer Encapsulated Chromophores: A Model for Single-Layer Multichromophoric Organic Light-Emitting Diodes

Paul Furuta, Jason Brooks, Mark E. Thompson, and Jean M. J. Frchet

J. Am. Chem. Soc., **2003**, 125 (43), 13165-13172 • DOI: 10.1021/ja0371348 • Publication Date (Web): 07 October 2003

Downloaded from <http://pubs.acs.org> on March 30, 2009



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 29 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

[View the Full Text HTML](#)



ACS Publications
 High quality. High impact.

Simultaneous Light Emission from a Mixture of Dendrimer Encapsulated Chromophores: A Model for Single-Layer Multichromophoric Organic Light-Emitting Diodes

Paul Furuta,[†] Jason Brooks,[‡] Mark E. Thompson,^{*,‡} and Jean M. J. Fréchet^{*,†}

Contribution from the Department of Chemistry, University of California, Berkeley, California 94720-1460 and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, and Department of Chemistry, University of Southern California, Los Angeles, California 90089-0744

Received July 8, 2003; E-mail: frechet@cchem.berkeley.edu; mthomps@chem1.usc.edu

Abstract: The site isolation of two dyes capable of electronic interaction via Forster energy transfer has been studied with the two dyes coumarin 343 and pentathiophene encapsulated by dendrons containing both solubilizing and electroactive moieties. Photoluminescence studies of mixtures of the dendritic dyes show that at high dendron generation, significant site isolation is achieved with relative emission characteristics influenced by both the degree of site isolation and the emission quantum yield of the dyes. Electroluminescence studies carried out in organic light emitting diode devices confirm that color tuning may be achieved by mixing the two encapsulated dyes in a single layer. However, selective carrier trapping by one of the core component dyes can dramatically influence the effectiveness of other components in the device.

Introduction

It is well-known that the environment of a chromophore is able to affect its photophysical behavior including its absorption and emission characteristics. Nature has been able to perfect a variety of microenvironments to enhance performance by spatially arranging multiple chromophores with respect to one another in a highly ordered fashion thereby also maximizing synergism between various species.¹ Although proteins are nature's main building blocks for the precise assembly of most functional moieties, including chromophores, synthetic systems do not benefit from the structural precision achievable with proteins. Recently, dendrimers have been used in an attempt to build multichromophoric systems that mimic some of the primary events of photosynthesis. Therefore, using a dendritic framework, multiple peripheral chromophores can be assembled around a single core unit with which they can "communicate" via an energy transfer interaction to form a light-harvesting antenna.² In such an antenna, the energy harvested at the periphery of the dendrimer is funneled to the core where it is reprocessed, for example through amplified core emission. In this instance, the dendritic framework facilitates the communication between the chromophores by keeping them at an appropriate average distance—within the Forster radius—of the core. In other instances, nature uses proteins to accomplish site isolation of a reactive site, thereby preventing destructive interaction. This is the case with a variety of catalytic enzymes such as the Cytochromes for which isolation of the catalytic

hemes is essential to derive function. Once again, dendrimers have been used to perform analogous site isolation, for example, bulky dendrons assembled around a central moiety have been used to prevent the self-aggregation of dye molecules in the solid state.²⁰ Encapsulating individual chromophores greatly enhances their optical properties due to reduced self-quenching.³ As described below, a challenging test of the ability of dendrimers to afford site isolation is afforded by light emitting diodes containing multiple emitters in a single layer.

In an OLED application,⁴ it is difficult to tune the color of emission by mixing several light emitting dyes in a single layer

- (2) (a) Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354. (b) Devadoss, C.; Bharati, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635. (c) Wang, P.-W.; Liu, Y.-J.; Devadoss, C.; Bharathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *3*, 237. (d) Shortreed, M. R.; Swallen, S. F.; Shi, Z.-Y.; Tan, W.; Xu, Z.; Devadoss, C.; Moore, J. S.; Kopelman, R. *J. Phys. Chem. B.* **1997**, *101*, 6318. (e) Jiang, D.-L.; Aida, T. *Nature* **1997**, *388*, 454. (f) Aida, T.; Jiang, D.-L. *J. Am. Chem. Soc.* **1998**, *120*, 10 895. (g) Sato, T.; Jiang, D.-L.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 10 658. (h) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26. (i) Maruo, N.; Uchiyama, M.; Kato, T.; Arai, T.; Akisada, H.; Nishino, N. *Chem. Commun.* **1999**, 2057. (j) Plevoets, M.; Vögtle, F.; Cola, L. D.; Balzani, V. *New J. Chem.* **1999**, *23*, 63. (k) Adronov, A.; Fréchet, J. M. J. *Chem. Commun.* **2000**, *18*, 1701. (l) Peng, Z.; Pan, Y.; Xu, B.; Zhang, J. *J. Am. Chem. Soc.* **2000**, *122*, 6619. (m) Weil, T.; Wiesler, U. M.; Herrmann, A.; Bauer, R.; Hofkens, J.; De Schryver, F. C.; Mullen, K. *J. Am. Chem. Soc.* **2001**, *123*, 8101. (n) Balzani, V.; Ceroni, P.; Juris, A.; Venturi, M.; Campagna, S.; Puntoriero, F.; Serroni, S. *Coord. Chem. Rev.* **2001**, *219*, 545. (o) Herrmann, A.; Weil, T.; Sinigersky, V.; Wiesler, U.-M.; Vosch, T.; Hofkens, J.; De Schryver, F. C.; Müllen, K. *Chem. Eur. J.* **2001**, *7*, 4844–4853. (p) Campagna, S.; Di Pietro, C.; Loiseau, F.; Maubert, B.; McClenaghan, N.; Passalacqua, R.; Puntoriero, F.; Ricevuto, V.; Serroni, S. *Coord. Chem. Rev.* **2002**, *229*, 67. (q) Hahn, U.; Gorka, M.; Vögtle, F.; Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V. *Angew. Chem., Int. Ed.* **2002**, *41*, 3595. (r) Weil, T.; Reuther, E.; Müllen, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 1900–1904.
- (3) Kawa, M.; Fréchet, J. M. J. *Chem. Mater.* **1998**, *10*, 286. Zhu, L.; Tong, X.; Li, M.; Wang, E. *J. Phys. Chem. B.* **2001**, *105*, 2461. Chou, C.-H.; Shu, C.-F. *Macromolecules* **2002**, *35*, 9673.
- (4) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913.

[†] Department of Chemistry, University of California and Materials Science Division, Lawrence Berkeley National Laboratory.

[‡] Department of Chemistry, University of Southern California.

(1) Glazer, A. N. *Annu. Rev. Biophys. Chem.* **1995**, *14*, 47.

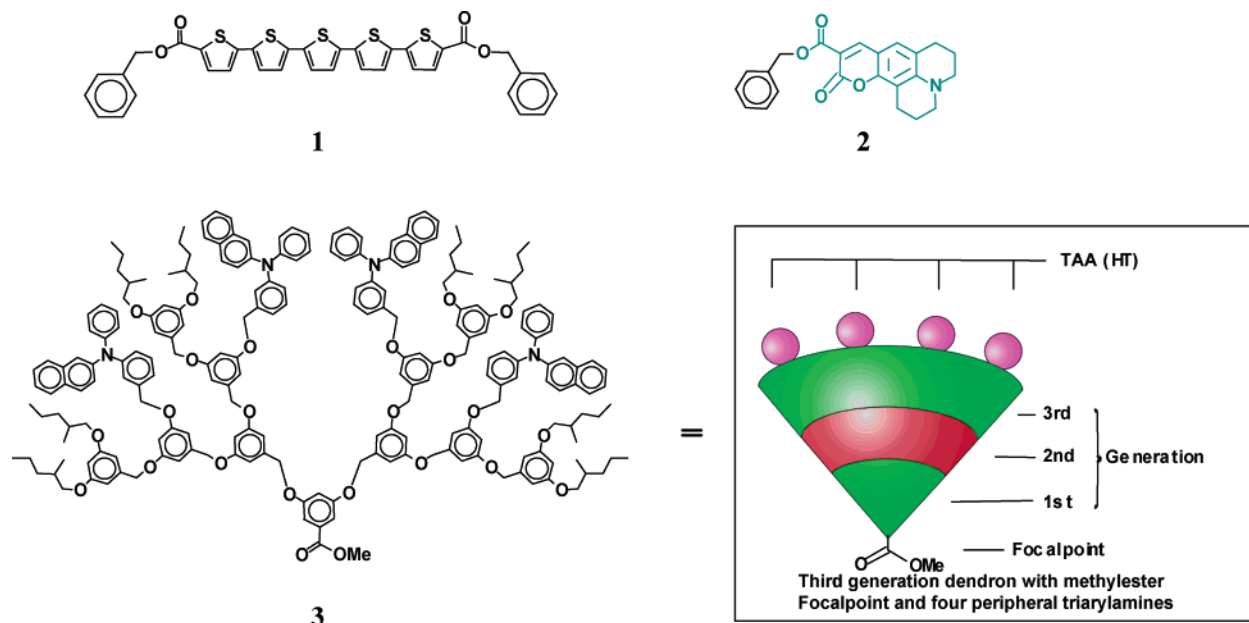


Figure 1. Fluorescent dyes, Coumarin 343 (C343) **1** and pentathiophene dicarboxylic ester (T5) **2**, used as cores for the dendrimers of this study. The surrounding dendrons architecture and periphery are shown with a third generation dendron **3** that features hole transporting (TAA) and solubilizing (alkyl ether) end-groups.

because energy transfer between the dyes lead to emission solely from the dye with the lowest HOMO–LUMO band gap.⁵ In addition, the emitting fluorophores can self-quench via excimer formation when doped at high concentrations. These problems can, at least in principle, be overcome by the use of dendrimers. For example, a fluorophore surrounded by a dendritic shell of sufficient size can isolate the emitting moieties from one another, thereby enabling simultaneous emission from several dyes, as site-isolation should inhibit both energy transfer between dyes and self-quenching.³ Color tuning in a single layer device would be achieved by the proper selection and mixing of dendrimers with different site-isolated fluorescent dyes as their cores. Moreover, the solubility and processing behavior will be greatly affected by the dendritic shell, allowing for a wide range of dyes to be encapsulated within the dendrimer while peripheral structural changes can be used to optimize and control process parameters.⁶

Recently, a variety of OLEDs⁷ in which dendrimers or dendronized polymers used as both hole transporting (HT)⁸ and electron transporting (ET)⁹ components, as well as unimolecular emitters¹⁰ have been reported. Building upon an early design of Devadoss et al.,^{2b} Freeman et al.¹¹ successfully utilized triarylamine (TAA) HT-labeled poly(benzyl ether) dendrimers possessing Coumarin 343 (C343) and pentathiophene (T5) core dyes 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 moderately successful due to detrimental energy transfer from C343 to the smaller band-gap T5. Due to the large Förster radius of these dyes, energy transfer is an unfortunate consequence of the small size and flexibility (i.e., poor shielding effect) of the surrounding dendrons that were attached at a single point to the lumophores. Attempts to synthesize larger dendrimers were unsuccessful due to the poor solubility and increased crystallinity of the triarylamine dendrons beyond generation 2, which resulted in very poor device performance. In the accompanying report (this issue), we describe the design and synthesis of novel dendrimers

containing not only triarylamine groups, but also solubilizing alkyl ether groups at the periphery of the dendrimers to solve both the solubility and crystallinity problems, enabling the synthesis of larger dendrimers for a fundamental investigation of the concept of color tuning via site isolation.

Results and Discussion

Dendrimer Encapsulated Chromophores. Both coumarin 343 (C343) and pentathiophene (T5) labeled dendrimers were utilized to effect the site isolation of light emitting lumophores in an OLED configuration. The two core dyes were chosen as models primarily on the basis of the overlap of their absorbances with the emission of the peripheral TAA hole transporting moieties at 425 nm. The dendritic structure we tested in a preliminary study¹¹ has now been completely redesigned with a periphery containing a combination of alkyl ether groups¹² and TAA donors (Figure 1). This combination has enabled the construction of much larger dendrimers for a more realistic testing of dye encapsulation while removing the issues of solubility and crystallization that earlier plagued film coating

- (5) Shoustikov, A.; You, Y.; Thompson, M. E. *IEEE J. Sel. Top. Quant.* **1998**, *4*, 3.
- (6) Halim, M.; Samuel, I. D. W.; Pillow, J. N. G.; Monkam, A. P.; Burn, P. L. *Synth. Met.* **1999**, *102*, 1571–1574.
- (7) (a) Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. *Synth. Met.* **1999**, *102*, 922–923. (b) Halim, M.; Samuel, I. D. W.; Pillow, Burn, P. L. *Synth. Met.* **1999**, *102*, 1113–1114. (c) Lo, S.-C. L.; Male, N. A. H.; Markham, J. P. J.; Magennis, S. W.; Burn, P. L.; Salata, O. V.; Samuel, D. W. *Adv. Mater.* **2002**, *14*, 975–979.
- (8) Kuwabara, Y.; Ogawa, H.; Inada, H.; Noma, N.; Shirota, Y. *Adv. Mater.* **1994**, *6*, 677. (b) Satoh, N.; Cho, J.; Higuchi, M.; Yamamoto, K. *J. Am. Chem. Soc.* **2003**, *125*, 8104.
- (9) Bettenhausen, J.; Greczmiel, M.; Jandke, M.; Strohiel, P. *Synth. Met.* **1997**, *91*, 223.
- (10) Shirshendu, K. D.; Maddux, T. M.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 9079. (b) Pogantsch, A.; Wenzl, F. P.; List, E. J. W.; Leising, G.; Grimsdale, A. C.; Müllen, K. *Adv. Mater.* **2002**, *14*, 1061. (c) Anthopoulos, T. D.; Markham, J. P. J.; Namdas, E. B.; Samuel, I. D. W.; Lo, S.; Burn, P. L. *Appl. Phys. Lett.* **2003**, *82*, 4824.
- (11) (a) Freeman, A. W.; Fréchet, J. M. J.; Koene, S. C.; Thompson, M. E. *Polym. Prepr.* **1999**, *40*, 1246. (b) Freeman, A. W.; Koene, S. C.; Malenfant, P. R. L.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2000**, *122*, 12 385.
- (12) Robinson, M. R.; O'Regan, M. B.; Bazan, G. C. *Chem. Com.* **2000**, 1645.

Scheme 2

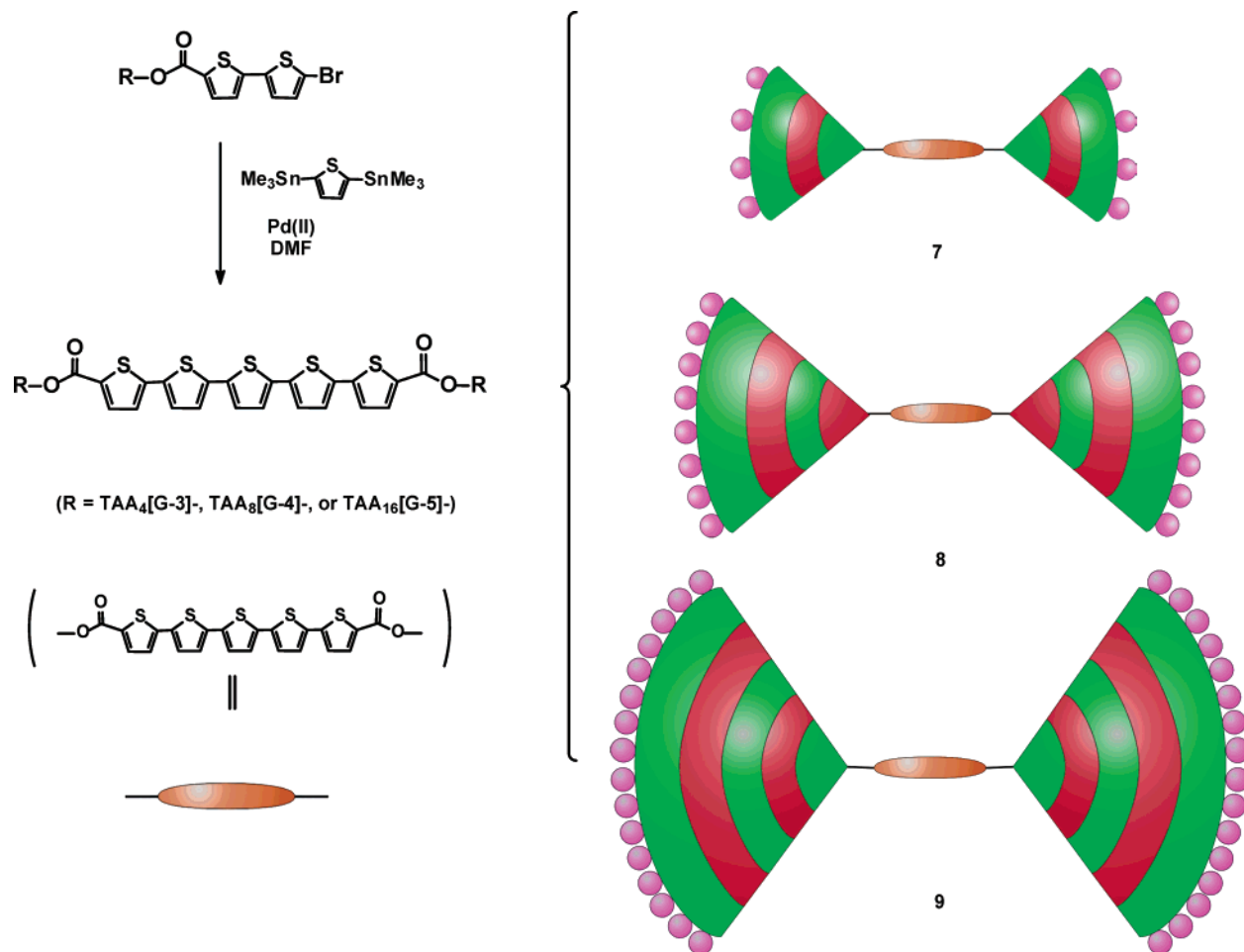


Table 1. Mixtures of C343 and T5 Dendrimers

mixture	composition		
	C343	T5	C343:T5
1	5 ([G-3])	7 ([G-3])	1:1
2	5	7	5:1
3	5	8 ([G-4])	5:1
4	5	9 ([G-4])	5:1
5	6 ([G-5])	7	5:1
6	6	8	5:1
7	6	9	1:1
8	6	9	3:1
9	6	9	5:1

increases. The PL spectra of dendrimer mixtures 1 and 2 (Figure 3) display emission at ~ 525 nm corresponding primarily to the T5 with a very small contribution from C343 at ~ 470 nm, which increases slightly as the molar ratio of **5** to **7** increases. As expected, the smaller generation 3 (G-3) dendrons provide only modest isolation and significant energy transfer occurs from C343 to T5. Therefore, a second series of films were prepared using mixtures of the larger dendrimers **6** and **9** in the same 1:1 and 5:1 molar ratios (mixtures 7 and 9, Table 1). With the higher generation dendrimers, the increase in the degree of site isolation can be seen from the noticeable increase of C343 emission compared to that observed for the corresponding third generation dendrimers. In a 1:1 molar ratio of **6** and **9**, the observed emission for the higher energy C343 chromophore far exceeded that of a 5:1 molar ratio of **5** and **7** giving a strong

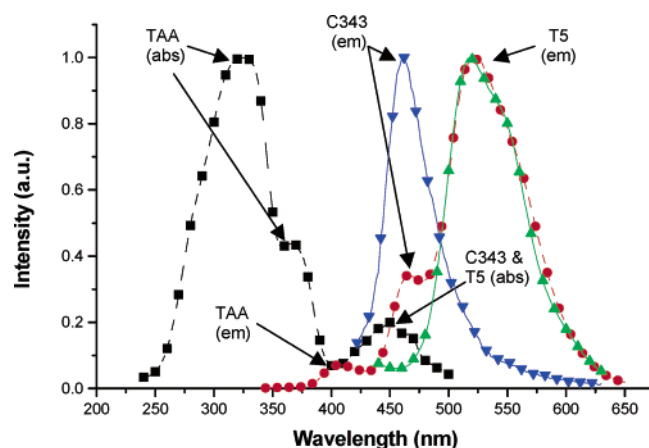


Figure 2. Normalized PL emission of **6** (blue downward-pointing triangle) and **9** (green upward-pointing triangle). Dendrimer mixture: PL absorbance (black square) and emission (red circle) spectra of a single layer mixture of **6** and **9** in a 1:1 molar ratio of C343: T5 dye cores.

indication that there is increased average spatial separation between the two dendronized dyes.

A further set of experiments was done in order to investigate the effect of changing dendrimer size at a constant 5:1 molar ratio of C343 to T5. Figure 4 shows the PL spectra of the third and fourth generation C343 dendrimers (**5**, **6**) with third, fourth, and fifth generation T5 dendrimers (**7**, **8**, and **9**). These results clearly demonstrate the effect of increasing isolation via an increase in dendrimer size. In the cases where the C343 is

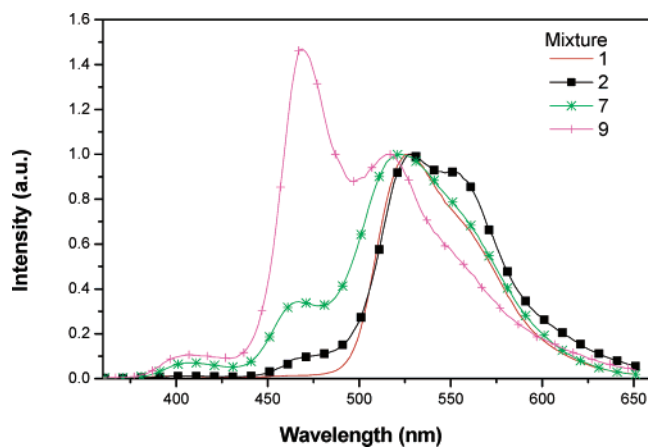


Figure 3. PL emission of mixtures of “small” dendrimers **5** and **7** (mixtures 1 and 2, Table 1), and “large” dendrimers **6** and **9** (mixtures 7 and 9, Table 1), in both 1:1 and 5:1 molar ratios of C343: T5 dye cores.

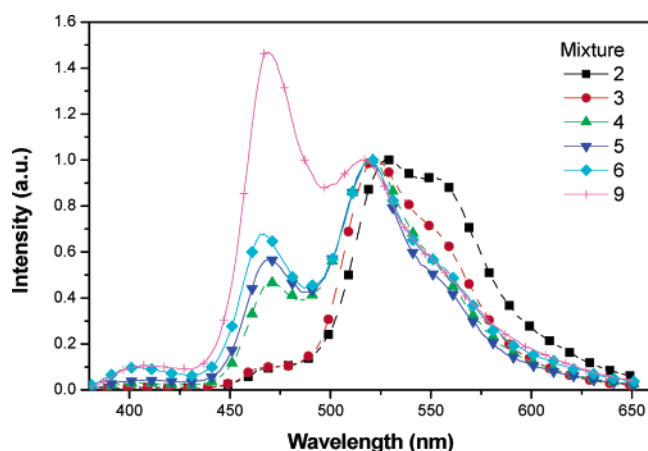


Figure 4. PL emission of different size mixtures of C343 and T5 dendrimers at 5:1 molar ratios of C343: T5 dye cores, normalized to T5 emission. (See Table 1 for the compositions of the various dendrimer mixtures).

changed from third to fourth generation with each size thiophene (mixtures 2 and 5, 3 and 6, 4 and 9), a large increase in the C343 emission is observed, an indication of increased site-isolation for the fourth generation C343 (resulting in a decrease in the C343 to T5 energy transfer). A similar trend is also seen for increased generations of thiophene dendrimers, but in this case only a very small increase in C343 emission is seen between the third and fourth generation T5's (mixtures 2 and 3, 5 and 6), whereas a much larger increase in C343 emission is measured between the fourth and fifth generations (mixtures 3 and 4, 6 and 9).

It follows that T5 dendrimers only begin to have adequate site-isolation after the fifth generation while an appreciable amount of isolation is already observed for fourth generation C343. This finding is not unexpected as the elongated shape of the T5 moiety makes encapsulation difficult, even when both ends of the T5 are capped in a “dumbbell” arrangement. Therefore, with G-3 or G-4 dendrons the T5 core remains exposed, whereas the more compact C343 core is relatively well shielded by three G-4 dendrons.

To measure the spectrum of a dendrimer mixture in the absence of interdendrimer energy transfer, we have also examined the PL spectra of dendrimer mixtures diluted into a glassy polystyrene matrix. All of the polystyrene samples studied

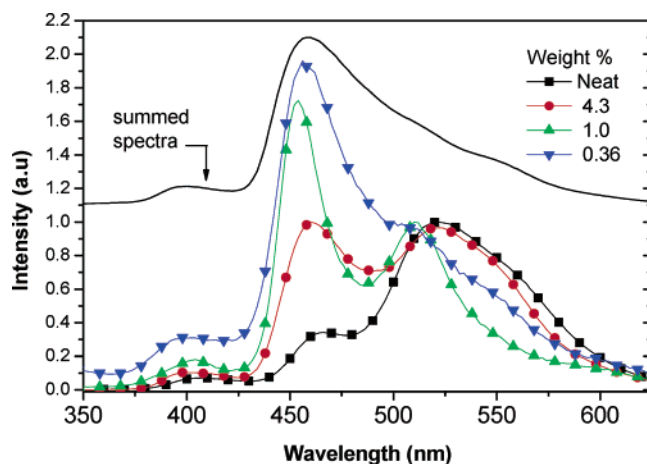


Figure 5. PL emission of **6** and **9** at 1:1 molar ratios neat and diluted with polystyrene (showing the % dendrimer by weight), normalized to T5 emission. The offset (upper) spectrum was generated by summing the spectra of pure samples of **6** and **9**, weighted by their PL quantum efficiencies (i.e., $0.63 \times 6 + 0.15 \times 9$).

contained a 1:1 molar mixture of **6** and **9**. Figure 5 shows the PL spectra of samples ranging in concentration from 0.35 to 4.2%, as well as a neat film of a mixture of dendrimers **6** and **9**. As the polystyrene solution is made more dilute, thereby reducing interdendrimer interactions, the T5 contribution to the spectrum decreases. At the highest dilution (0.36% dendrimer by weight in PS), the intensity of the C343 emission is about twice that of the T5 emission, whereas it is roughly a third of the T5 emission in the neat dendrimer film. The ratio of **6** to **9** emission is not thought to involve different absorption characteristics for the two, since the principal absorber for the dendrimers are the TAA groups, which are present in relatively similar numbers in the two dendrimers (24 TAA groups for **6** compared to 32 for **9**). The imbalance in C343 and T5 in the most dilute sample can be attributed to differences in the quantum yields of emission for the coumarin and thiophene. The ϕ_{em} of C343 is 0.63,¹⁴ whereas that for T5, estimated from related pentathiophenes, is approximately $\phi_{em} = 0.15$.¹⁵ To provide a perspective for the PL measurements made with the 0.36% mixed dendrimer film, a simulated PL spectrum was created by summing the emission spectra of pure **6** and **9**, weighted by their relative quantum yields. Although photoinduced electron transfer between TAAs and the C343¹⁶ could be a possible reason for the reduced C343 emission in the mixtures, the absence of noticeable quenching^{16a} of the C343 in the most dilute samples compared to the weighted relative quantum yields suggests that electron transfer is not a significant factor for the dendrimers of this study. As shown in Figure 5, the weighted simulated spectra very closely match that of the highly diluted PS film, showing that a spectrum rich in C343 emission is expected for a sample with complete site isolation. Hence, although not completely isolating the dyes from energy transfer in neat films, these higher generation dendrimers do provide a considerable degree of site-isolation when compared

(14) Adronov, A.; Gilat, S. L.; Fréchet, J. M. J.; Ohta, K.; Neuwahl, F. V. R.; Fleming, G. R. *J. Am. Chem. Soc.* **2000**, *122*, 1175–1185.

(15) Donat-Bouillud, A.; Mazerolle, L.; Gagnon, P.; Goldenberg, L.; Petty, M. C.; Leclerc, M. *Chem. Mater.* **1997**, *9*, 2815–2821.

(16) (a) Nad, S.; Pal, H. *J. Photochem. Photobiol. A: Chem.* **2000**, *134*, 9–15. (b) Lor, M.; Thielemans, J.; Viaene, L.; Cotlet, M.; Hofkens, J.; Weil, T.; Hampel, C.; Müllen, K.; Verhoeven, J. W.; Van der Auweraer, M.; De Schryver, F. C. *J. Am. Chem. Soc.* **2002**, *124*, 9918–9925.

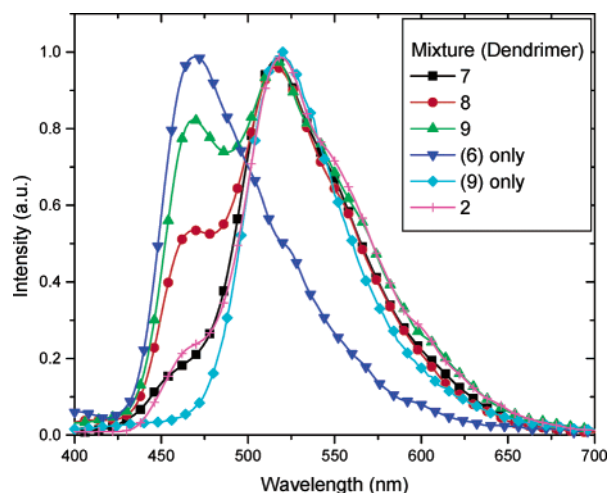


Figure 6. Device EL emission of **6** and **9** alone and in 1:1, 3:1, and 5:1 molar ratio mixtures. EL emission of 5:1 molar ratio mixture of **5** and **7** shown for comparison. (See Table 1 for the compositions of the various dendrimer mixtures).

to the free dye¹¹ or to the lower generation dendrimers (mixtures of dendrimers **5** and **7** give mostly T5 emission).

OLED devices were fabricated using the same molar ratios and spin casting parameters used for the previously described thin film PL spectra. ITO substrates were pretreated with a layer of poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS) which is known to facilitate hole injection and provides for planarization of the substrate.¹⁷ Additionally, an electron transporter, 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD), was incorporated in the dendrimer solutions using 1:1 molar ratio of PBD to peripheral TAA moiety. The purpose of the PBD is to transport electrons, which should help to balance electron–hole transport within the device.^{11,18} The holes are expected to be transported by the easily oxidized TAA groups, and exciton recombination is expected to occur on the dye cores. Furthermore, a thin 100 Å thick film of 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) was subsequently vapor deposited as a hole blocker to confine exciton recombination, and prevent the loss of the faster moving holes to the cathode.^{6,19} This was followed by a 150 Å electron injecting layer of aluminum-tris(8-hydroxyquinolate) (AlQ₃) and a LiF/Al cathode. It was found that devices with BCP/AlQ₃ layers were an order of magnitude more efficient than those without these blocking and injecting layers, demonstrating their importance in the device.

Figure 6 shows the electroluminescent (EL) emission spectra of devices with only dendrimers **6** and **9** (as well as varying mixtures of the two), compared to a 5:1 mixture of the smaller sized dendrimers **5** and **7**. These measurements are in qualitative agreement with those for PL spectra as site isolation is also significantly enhanced in the EL spectra for dendrimers in which the dyes are shielded by the larger dendrons. Interestingly, a greater amount of T5 emission relative to C343 emission is observed in the EL compared to the PL. Because the films used

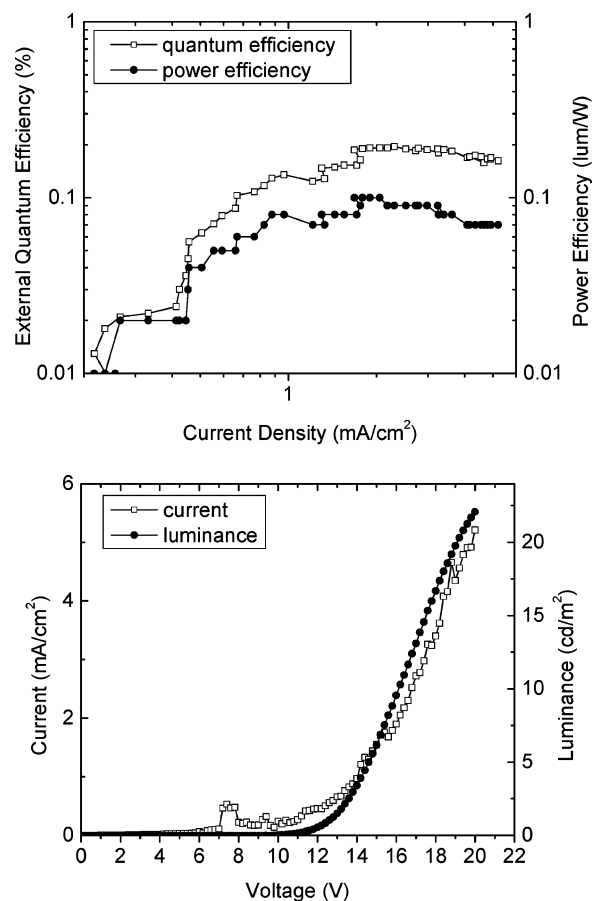


Figure 7. Efficiency (top) and IV/luminescence characteristics (bottom) for ITO/PEDOT/G4C:G5T(5:1)-PBD/BCP/AlQ₃/LiF/Al device.

for PL and EL were spin cast from the same stock solutions, the observed differences in intensities are unlikely to be related to differences in composition. It is believed that the difference between EL and PL characteristics may be due to direct hole or electron (carrier) trapping on the T5 core. Hence, if carrier recombination were to occur more efficiently at the T5 than at C343, it could result in preferential exciton formation at T5. This carrier trapping process gives T5 an added pathway for exciton formation that may not be present for C343, thereby shifting the spectra further toward the lower energy T5 emitter. This effect results in nearly equal emission intensities of both T5 and C343 at a 5:1 molar ratio (mixture 9) whereas in the PL, the same mixture gives a much higher relative intensity for the C343.

The device performance data for a film obtained from mixture 9 with its 5:1 ratio of C343 to T5, which affords balanced EL intensities for the two chromophores, are shown in Figure 7. The maximum external quantum efficiency of the mixed [G4]₃C-343: [G-5]₂T5 device was 0.2% with a power efficiency of 0.1 lum/W. The device had a turn-on voltage of approximately 12 V and a maximum luminescence of only 22 cd/m² at 20V. Device performance data for an OLED prepared from the [G-5]₂T5 (**9**) alone is shown in Figure 8. Interestingly, while the turn-on voltages are comparable, the T5-only device had much better performance characteristics. A maximum luminance of 420 cd/m² was recorded at 20V. The device had a maximum efficiency of 0.59 lm/W (0.76% photon/electron) at a brightness of 100 cd/m².

(17) Lamansky, S.; Djurovich, P. I.; Abdel-Razzaq, F.; Garon, S.; Murphy, D. L.; Thompson, M. E. *J. Appl. Phys.* **2002**, *92*, 1570–1575.

(18) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*(16), 2281–2283.

(19) (a) Baldo, M. A.; Lamansky, S.; Burrows, P. E.; Forrest, S. R.; Thompson, M. E. *Appl. Phys. Lett.* **1999**, *75*, 4. (b) Tsutsui, T.; Yang, M. J.; Masayuki, M.; Nakamura, Y.; Wanabe, T.; Tsuji, T.; Fukuda, Y.; Wakimoto, T.; Miyaguchi, S. *Jpn. J. Appl. Phys.* **1999**, *38*, L1502.

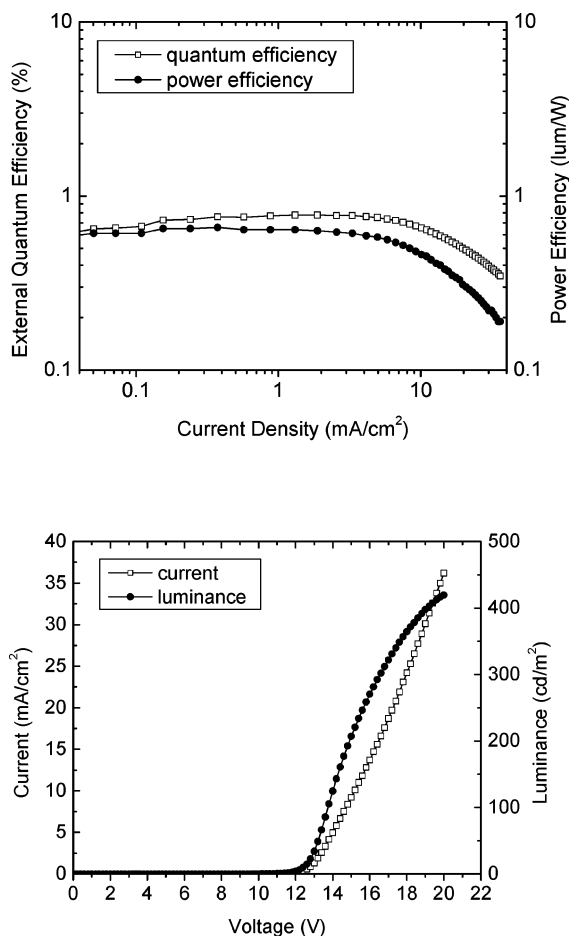


Figure 8. Caption: Efficiency (top) and IV/luminescence characteristics (bottom) for ITO/PEDOT/G5T-PBD/BCP/AlQ₃/LiF/Al device.

When the PL and EL spectra of a material are significantly different, as is seen for the 5:1 mixture of **6:9**, the cause can generally be attributed to carrier trapping affects. If one or both of the carriers were preferentially trapped at the T5 core of **9**, then a higher than statistical amount of hole-electron recombination will occur at **9**, leading to an EL spectrum which is richer in T5 emission than expected, as is in fact observed. To determine if a trapping assignment makes sense, a series of solution electrochemical measurements were made to estimate the hole and electron levels of the individual components. For this study, model T5 **1** and C343 **2** (Figure 1) compounds were capped with benzyl esters to simulate the cores, and a G3 TAA methyl ester dendron **3** was used to simulate the characteristics of the hole transporting periphery. Electrochemical measurements were recorded in dimethylformamide (DMF) solution and potentials are given relative to an internal ferrocene reference (Fc/Fc⁺). In addition, all literature values were adjusted to Fc/Fc⁺ for clarity. The T5 core had two reversible oxidations at 0.62 V and 0.76 V and a reversible reduction at -1.79 V. These oxidation values are consistent with two similar T5 containing polymers that were previously measured to have single reversible oxidations in the solid state at 0.61 and 0.51 V.¹⁵ The reduction potential of the PBD electron transport material is reported to be -2.34.²⁰ Thus, it is expected that the T5 core will trap electrons, from the electron transporting PBD

molecules. Unfortunately, the oxidation and reduction potentials of both the C343 core and TAA dendron were irreversible, so we cannot estimate their HOMO and LUMO energies reliably. The irreversible oxidation of the TAA dendron was observed at 0.49 V, which is greater than the 0.3 V oxidation potential reported for the corresponding benzidine derivative (*N,N'*-diphenyl-*N,N'*-bis-1-naphthyl-4,4'-biphenyl, NPD), a commonly used hole transport material.²¹ This sort of difference is expected when comparing a monoamine to a conjugated diamine. The irreversible oxidation for C343 is between 0.49 and 0.59 V, thus we do not expect either C343 or T5 to effectively trap holes from the TAA groups. Hence, the likely explanation for the enhanced performance of T5 involves the trapping of electrons at the T5 core, followed by hole-electron recombination at that emitter. This gives an additional pathway for exciton localization at T5, other than energy transfer from C343 or TAA, leading to enhanced T5 emission in EL, relative to the PL measurements.

Conclusion

The use of dendrons to site isolate chromophores capable of electronic “communication” has been explored through their use in organic light emitting diodes. The novel design of the peripheral moieties of the dendrons allowed tuning of properties for the casting of films that did not show a tendency to crystallize thereby enabling both photoluminescence and electroluminescence studies to be carried out. These studies confirm that the size of the dendritic shell is critical to site isolation. Although energy transfer between dendrimers still occurs to some extent, even with the largest dendrimers we have prepared, several important findings have emerged. First, it is clear that the film forming properties of the dendrimers are critical and the addition of peripheral alkyl groups to the electroactive but low solubility TAA moieties helps with the formation of clear films and solves the issues associated with the inherent crystallinity of the TAA dendrons at higher generations. Furthermore, moderately efficient devices can be fabricated using these dendrimers along with BCP/AlQ₃ hole blocking/electron injecting films. Best results based on these unoptimized dendrimer systems were an external quantum efficiency of 0.2% for mixed films containing two chromophores in the same layer, and 0.76% for a fifth generation thiophene-only device.

These results also demonstrate a potential problem that may occur in many dendrimer based OLEDs. Carrier trapping at the dendrimer core can lead to significant changes in the properties of the devices. This is evidenced by the different device performances observed for the mixed dendrimer devices and the T5-only device, as well as differences in PL and EL emission intensity for mixed films. Therefore, care must be taken when choosing dye cores for such dendrimer-based devices. Selective carrier trapping by one of the core components can dramatically influence the effectiveness of other components in the device. We believe that the high voltages required to run these dendrimer based OLEDs was due, at least in part, to carrier trapping at the T5 dye cores. When choosing dye cores for dendrimers of this type it is important to select dyes whose HOMO levels are below the hole transporting material, and whose LUMO levels are above the electron transporting

(20) Wu, C.-C.; Sturm, J. C.; Register, R. A.; Tian, J.; Dana, E. P.; Thompson, M. E. *IEEE Trans. Elec. Dev.* **1997**, *44*, 1269–1281.

(21) Koene, B.; Loy, D.; Thompson, M. E. *Chem. Mater.* **1998**, *10*, 2235–2250.

materials, to prevent charge trapping within the dendrimer. In addition, even at large generations, complete site-isolation remains a difficult problem for chromophores with large Förster radii. It is believed that once these issues are understood, dendritic systems such as these could provide access to color tunable solution processed large area displays.

Acknowledgment. Financial support of this research by the Air Force Office of Scientific Research and by the U.S.

Department of Energy under Contract No. DE-AC03-76SF00098 is acknowledged with thanks.

Supporting Information Available: OLED fabrication procedures and equipment: a full Experimental Section (PDF) is provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA0371348