Chromophore-Labeled Dendrons as Light Harvesting Antennae

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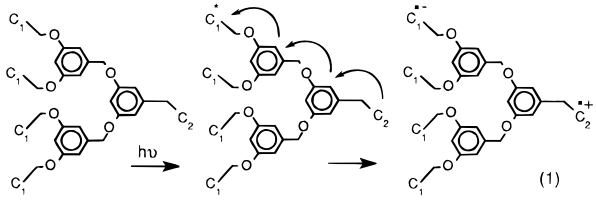
Abstract: A novel series of polyether dendrimer segments (dendrons) end-capped with pyrenyl, naphthyl, or methyl groups has been prepared by a convergent growth method. Steady-state fluorescence measurements indicate the absence of intramolecular naphthalene excimer in the naphthyl-capped dendrons. However, in the pyrenyl-capped dendrons, excimer emission predominates. Fluorescence from both the naphthyl monomer and pyrenyl excimer are quenched when a suitable electron donor (e.g., a 3-[dimethylamino]phenoxy group) is covalently attached at the dendron focal point. No sensitized emission from the dendron backbone is observed in the chromophore-labeled dendrons, although the control methyl-capped dendron fluoresces weakly at 310 nm when excited at 284 nm. Absorption and fluorescence spectra, fluorescence quantum yields, and fluorescence lifetimes for the chromophore-labeled dendrons are reported.

Introduction

In recent years, the study of directional energy transport and electron transfer in chromophore-labeled polymers and supramolecular arrays has been the focus of an ever-increasing number of reports.[1−5] Flexible random-coil polymers bearing electron donor−acceptor pairs exhibit low net efficiency for charge separation because of rapid back-electron transfer through a contact ion pair.[5] In contrast, block copolymers incorporating linear, rigid backbones permit singlet energy migration to the block interface, where exciplex formation takes place, thus functioning as an energy trap.[6] The unusual molecular architecture of dendritic polymers provides a suitable framework for the support of redox-active functionalities since: (1) the spherical shape of these highly branched polymers inhibits the chain entanglement that occurs in many linear polymers;[7,8] (2) the solubilities of dendrimers in organic solvents far exceed those of linear polymers of similar composition and molecular weight;[7] and (3) the synthetic methodology in which the dendron is assembled, one layer or generation at a time,[9] allows for controlled placement of a series of two or more functional groups to produce a thermodynamic driving force gradient for sequential photoinduced electron transfers. A dendrimer architecture also permits variation of the number and ratio of donor and acceptor functionalities and allows for the insertion of a defined number of spacer units between the redox-active chromophores. Although the dendrons reported here are probably too small to adopt the spherical conformation for which dendrimers are known, this study provides valuable information about the suitability of the dendrimer backbone for electronic communication of appended chromophores. The controlled placement of chromophores made possible by the stepwise synthetic scheme is of course advantageous in these early generation dendrons.

A prototypical dendron for our study has aryl chromophores (acting as electron acceptors $\mathbf{C_1}$) at the periphery and an energetically suitable electron donor at the growth focal point. Photoexcitation of the acceptor chromophores should lead to electron transfer from the donor moiety $\mathbf{C_2}$ through the dendrimer backbone to the outer array of acceptors, eq 1. The separation between the benzyl-capped chain ends and an ester-terminated focal point for a Fréchet-type second generation polybenzyl ether dendron as determined by a single-crystal structure is about 14 Å.[10] This measurement gives us an approximation of the $\mathbf{C_1}$-$\mathbf{C_2}$ separation for the chromophore-labeled second generation dendrons reported here. In the current work, we sought to characterize the interactions between the appended aryl chromophores and to determine whether their excited states could be quenched by a covalently bound donor present on the same dendrimer segment. To the best of our knowledge, this work represents the first photophysical study of electron donor−acceptor pairs covalently attached to a dendritic architectural skeleton.



Results and Discussion

Synthesis. First, second, and third generation polyether dendrons bearing aryl functionalities such as substituted naphthalene or pyrene at the periphery have been synthesized. The naphthyl-capped dendrons were produced by condensing 2-bromomethylnaphthalene with 3,5-dihydroxybenzyl alcohol in the presence of potassium carbonate and 18-crown-6 ether in refluxing acetone to give the bis(naphthylether) benzyl alcohol **1a**. This alcohol was then converted to the corresponding

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(1) Fox, M. A. *Acc. Chem. Res.* **1992**, *25*, 569.
(2) Balzani, V. *Tetrahedron* **1992**, *48*, 10443.
(3) Fox, M. A.; Watkins, D. M.; Jones, W. E., Jr. *Chem. Eng. News* **1993**, 38.
(4) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.
(5) Webber, S. E. *Chem. Rev.* **1990**, *90*, 1469.
(6) (a) Watkins, D. M.; Fox, M. A. *J. Am. Chem. Soc.* **1994**, *116*, 6441. (b) Fox, H. H.; Fox, M. A. *Macromolecules* **1995**, *28*, 4570.
(7) Fréchet, J. M. J. *Science* **1994**, *263*, 1710.
(8) Fréchet, J. M. J.; Hawker, C. J.; Wooley, K. L. *Pure Appl. Chem.* **1994**, *A31*, 1627.
(9) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638.
(10) Schlüter, A.-D.; Claussen, W.; Amoulong-Kirstein, E.; Karakaya, B. In *American Chemican Society Division of Polymeric Materials: Science and Engineering*; Chicago, 1995; pp 226−227.

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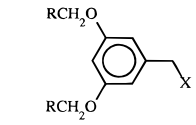
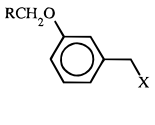
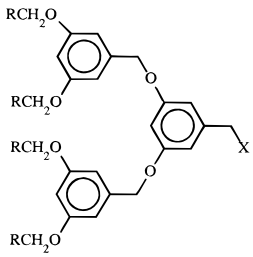
Chart 1

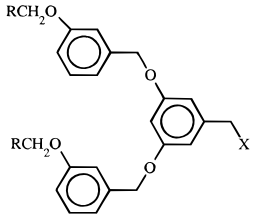




1a R = 2-naphthyl, X = OH
1b R = 2-naphthyl, X = Br
1c R = 2-naphthyl
X = -$OCH_2CH_2N(CH_2CH_3)_2$
1d R = H, X = OH
1e R = H, X = Br

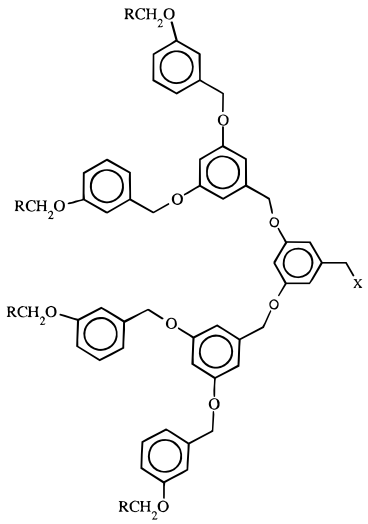
2a R = 2-naphthyl, X = OH
2b R = 2-naphthyl, X = Br
2c R = 1-pyrenyl, X = OH
2d R = 1-pyrenyl, X = Br





3a R = 2-naphthyl, X = OH
3b R = 2-naphthyl, X = Br
3c R = 2-naphthyl
X = -$OCH_2CH_2N(CH_2CH_3)_2$
3d R = 2-naphthyl
X = 3-(dimethylamino)phenoxy
3e R = H, X = OH
3f R = H, X = Br
3g R = H
X = 3-(dimethylamino)phenoxy-

4a R = 2-naphthyl, X = OH
4b R = 1-pyrenyl, X = OH
4c R = 1-pyrenyl, X = Br
4d R = 1-pyrenyl
X = 3-(dimethylamino)phenoxy



5a R = 1-pyrenyl, X = OH
5b R = 1-pyrenyl, X = Br
5c R = 1-pyrenyl, X = 3-(dimethylamino)phenoxy

bromide **1b** by treatment with carbon tetrabromide and triphenylphosphine in tetrahydrofuran (THF). Subsequent generations **3a** and **3b** were built by repetition of this two-step reaction scheme. The methoxy-capped dendrons **3e** and **3f**, lacking absorptive aryl groups at their periphery, serve as controls in the photophysical experiments: they were similarly synthesized from 3,5-dimethoxybenzyl alcohol.

Condensation of 2 equiv of 1-bromomethylpyrene with 3,5-dihydroxybenzyl alcohol proceeded in extremely poor yield, presumably because of steric hindrance. However, a condensation of 1 equiv of 1-bromomethylpyrene with 3-hydroxybenzyl alcohol proceeded cleanly and in high yield to give **2c**. The corresponding series of naphthyl-functionalized dendrons **2a**, **2b**, and **4a** were synthesized for comparison. The subsequent reactions of the dendron-building sequence are unchanged for the pyrenyl- and naphthyl-capped series.

Table 1. Absorption and Emission Data for Naphthyl- and Methoxy-Capped Dendrons Excited at 284 nm[a]

compd	ϵ (cm^{-1} M^{-1})[b]	λ_{em} (nm)[b]	Φ_f[b]	Φ_f[c]
2-naphthalenemethanol	3000	335	0.17	0.069
1a	9800	290, 335	0.014	0.021
2a	7600	292, 335	0.057	0.059
3a	19 000	290, 335	0.020	0.028
3d		290, 335	0.0064	0.025
3e	5500	310	0.0058	0.0099
3g	8200	312, 354	0.0056[d]	0.0067[d]
4a	12 000	290, 335	0.064	0.063

[a] Measured as $\sim 10^{-7}$ M degassed solutions (except extinction coefficient determinations). [b] In acetonitrile. [c] In dichloromethane. [d] Includes fluorescence at 354 nm (attributed to [dimethylamino]phenoxy group).

Table 2. Absorption and Emission Data for Pyrenyl-Functionalized Dendrons Excited at 344 nm[a]

compd	ϵ (cm^{-1} M^{-1})[b]	λ_{em} (nm)[b]	Φ_f[b]	Φ_f[c]	Φ_f[d]
1-pyrenemethanol	38 000	375, 395, 415,[e] 435[e]	0.011	0.17	0.22
2c	44 000	375, 395, 415,[e] 435[e]	0.097	0.24	0.34
4c	53 000	480	0.18	0.34	0.30
4d	62 000	480	0.025	0.15	0.079
5a	70 000[d]	480	0.17[f]	0.38	0.23
5c	92 000[d]	480	0.047[f]	0.31	0.18

[a] Measured as $\sim 10^{-6}$ M degassed solutions (except extinction coeffient determinations). [b] In acetonitrile. [c] In dichloromethane. [d] In tetrahydrofuran. [e] Shoulder. [f] **5a** and **5c** are not very soluble in acetonitrile. Therefore, these quantum yields are approximate.

The (dimethylamino)phenoxy-terminated dendron **3d** was produced as a clear glass by condensation of **3b** with 3-dimethylaminophenol in the presence of K_2CO_3 and 18-crown-6 ether in acetone. The (dimethylamino)phenoxy group was also used to terminate the methoxy- and pyrenyl-capped dendrons to give **3g**, **4d**, and **5c**, which were all obtained as white or pale yellow solids. Computer-generated models using Cache software indicate a through-space separation of the pyrenyl groups from the (dimethylamino)phenoxy groups of approximately 15 Å in **4d** and approximately 22 Å in **5c**. The triethylamino quencher-labeled dendrons **1c** and **3c** were prepared by functionalization at the dendrimer growth focal point by treating diethylaminoethanol with sodium hydride before adding the appropriate dendron **1b** or **3b**. The triethylamino substituted dendrons **1c** and **3c** were obtained as oils and were inseparable from minor residual impurities.

Photophysical Properties. All dendrons were studied either as the alcohols (without a donor) or as the amino-terminated species. Steady-state emission spectra of the naphthyl-capped and methoxy-capped dendrons are summarized in Table 1, as are steady-state emission spectra of the pyrenyl-capped dendrons in Table 2. The methoxy-capped dendrons **3e** and **3g** were used as probes for fluorescence of a polyether dendron lacking aryl chromophores at the chain ends. The second-generation alcohol **3e** fluoresces weakly with a very broad signal at 310 nm when excited at 284 nm (Figure 1). No fluorescence quenching by the covalently attached 3-(dimethylamino)phenoxy group in **3g** was observed. Instead, the 3-(dimethylamino)phenoxy group (which absorbs 284-nm light) competitively absorbs the excitation pulse and fluoresces at 355 nm.

In the naphthyl-capped series consisting of **1a**, **3a**, and **3d**, intermolecular excimer formation was observed only in solutions

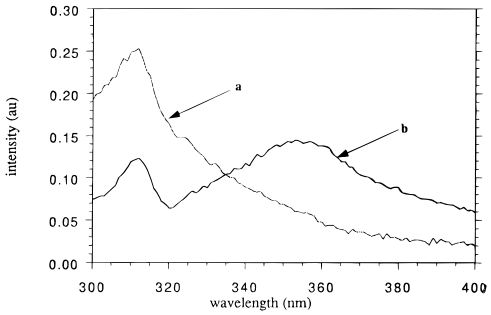


Figure 1. Steady-state fluorescence spectra of **(a) 3e** and **(b) 3g** in degassed acetonitrile ($<10^{-5}$ M); $\lambda_{ex} = 284$ nm.

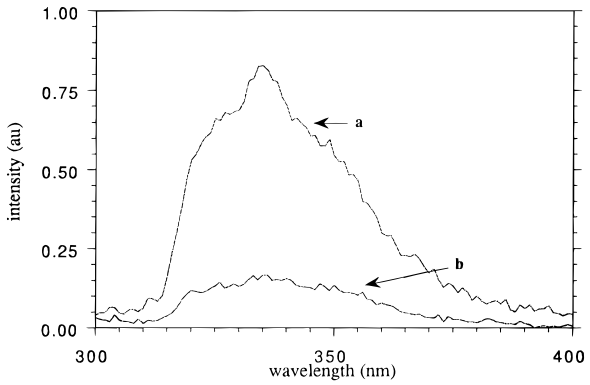


Figure 2. Steady-state fluorescence spectra of **(a) 3a** and **(b) 3c** in degassed acetonitrile ($<10^{-5}$ M); $\lambda_{ex} = 266$ nm.

with concentrations greater than 10^{-6} M; dilution to concentrations below 5×10^{-7} M eliminated the excimer signal. Steady-state fluorescence spectra for naphthyl-capped dendrons **1a**, **2a**, **3a**, and **4a** (both mono- and disubstituted at the chain ends) show strong typical naphthalene fluorescence centered at 335 nm (Figure 2), plus a minor (always <5%) fluorescence at 290 nm. The fluorescence quantum yields (referenced to naphthalene in cyclohexane[11]) for the disubstituted naphthyl-capped dendrons **1a** and **3a** are 1−7% in acetonitrile or dichloromethane. The fluorescence yields for the monosubstituted naphthalene dendrons **2a** and **4a** are several times greater than the fluorescence yields of corresponding disubstituted dendrons **1a** and **3a** in acetonitrile, most likely due to self-quenching by nonradiative pathways. Therefore, in order to maximize dendrimer fluorescence yield it is desirable to use the less-substituted dendrons. This decrease of fluorescence intensity upon polymerization has been observed frequently.[6]

Stern−Volmer bimolecular quenching of **3a** with diethylaminoethanol in acetonitrile gave a quenching constant k_q of 6×10^8 M^{-1} s^{-1}. This k_q is somewhat slower than a typical diffusion-controlled quench ($k_q = 1.9 \times 10^{10}$ in acetonitrile),[12] as has been previously reported for the quenching of naphthalene by aliphatic amines.[13] Intramolecular fluorescence quenching in acetonitrile is observed for **1c** compared to **1a** and for **3c** compared to **3a**. When the donor was changed to a 3-(dimethylamino)phenoxy group in **3d**, 70% intramolecular quenching was observed in acetonitrile (Figure 2). The driving force for photoinduced electron transfer from dimethylaniline to the lowest singlet excited state of naphthalene is 940 mV.[14]

The first generation pyrenyl-capped dendron **2c** exhibits typical pyrene fluorescence (Figure 3) when excited at 344 nm.[15]

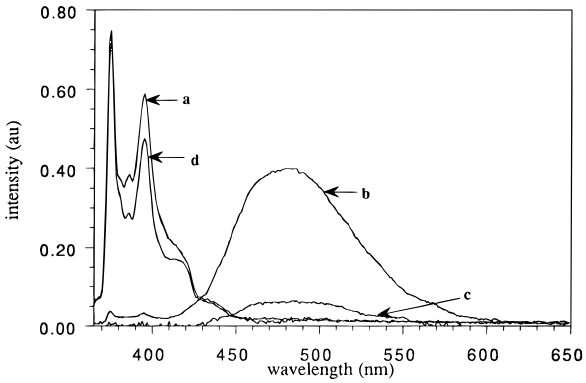


Figure 3. Steady-state fluorescence spectra of **(a) 2c**, **(b) 4b**, **(c) 4d**, and **(d)** 1-pyrenemethanol in degassed acetonitrile ($<10^{-5}$ M); $\lambda_{ex} =$ 344 nm.

Emission from **4b**, a second generation dendron bearing two pyrenyl groups, is dominated by intramolecular excimer fluorescence (∼97%, Figure 3). The emission of **5a** (not shown) also shows predominant excimer fluorescence. Ground state stacking of the pyrenyl groups is probably not responsible, as the absorption spectra of **4b** and **5a** show no observable differences from pyrene itself.

The driving force for intermolecular electron transfer from dimethylaniline to the lowest singlet excited state pyrene is 480 mV,[16] and about 250 mV for electron transfer to pyrene excimer, which is stabilized by 4 kcal/mol (at room temperature) compared to singlet pyrene.[17] Stern−Volmer bimolecular quenching of **4b** by 3-dimethylaminophenol in acetonitrile revealed a k_q of 1×10^{10} M^{-1} s^{-1}, indicating diffusion-controlled quenching with no evident exciplex formation. Stern−Volmer bimolecular quenching of **5a** by 3-(dimethylamino)phenol in THF resulted in a k_q of 4×10^9 M^{-1} s^{-1}. As the integrated intensity of the excimer emission from **4b** (from 420−580 nm) decreased with the addition of each aliquot of the quencher solution, the relative emission intensity from singlet pyrene (in the region 370−400 nm) increased. Thus, the excimer is more efficiently quenched than is the singlet excited state, most likely because a larger solvent reorganization is required in the production of a charge-separated species from a relatively nonpolar precursor (i.e., the singlet excited state) than from a more polar precursor (i.e., the excimer). Pyrene excimer has a dipole moment of 2.5 D.[18] Pyrene excimer emission also was preferentially quenched over pyrene singlet emission for bimolecular quenching of **5a** by 3-(dimethylamino)phenol in THF.

Dilution studies of **4d** and **5c** revealed a linear relationship between fluorescence intensity and concentration (from 10^{-7} to 10^{-6} M), which is consistent with intramolecular fluorescence quenching. Further evidence for intramolecular quenching is found by comparing the intensities of emission steady-state fluorescence spectra of the quencher capped dendrons **4d** and **5c** with the spectra of the corresponding alcohol-terminated dendrons **4b** and **5a**. In the most dramatic case, the strong excimer fluorescence of **4b** in acetonitrile is quenched by almost

(11) Eaton, D. F. *Pure Appl. Chem.* **1988**, *60*, 1107.
(12) Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; VCH Publishers: New York, 1993.
(13) Meeus, F.; Van der Auweraer, M.; De Schryver, F. C. *J. Am. Chem. Soc.* **1980**, *102*, 4017.
(14) The driving force was calculated using $\Delta G = E(D^{\bullet+}/D) - E(A/A^{\bullet+}) - E_{00}(S)$, where $E(D^{\bullet+}/D) = 0.81$ V for *N*,*N*-dimethylaniline (vs SCE in CH_3CN), $E(A/A^{\bullet+}) = -2.29$ V for naphthalene (vs SCE in CH_3CN), and $E_{00}(S) = 92$ kcal/mol, or 3.99 V for naphthalene: Kavarnos, G. J.; Turro, N. J. *Chem. Rev.* **1986**, *86*, 401.
(15) Förster, T.; Kasper, K. *Z. Physik. Chem. N. F.* **1954**, *1*, 275.
(16) Schoburg, M.; Staerk, M.; Weller, A. *Chem. Phys. Lett.* **1973**, *22*, 1.
(17) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.
(18) Gosh, A. S.; Basu, S. *J. Photochem.* **1974**, *3*, 247.

Table 3. Excimer Quenching of Pyrenyl-Capped Dendrons as a Function of Solvent

	Φ_f (Q)/Φ_f (0)[a]		
dendron	in CH_2Cl_2	in THF	in CH_3CN
4d	60	80	90
5c	20	50	70[d]

[a] Ratio of excimer fluorescence yield in the donor-appended dendron to that observed in the analogous dendron lacking the attached donor. [b] **4d** is compared with **4a**. [c] **5c** is compared with **5a**. [d] **5a** and **5c** are not very soluble in acetonitrile. Therefore, this percent quenching is approximate.

Table 4. Fluorescence Lifetimes for Monomer and Excimer in Pyrenyl-Substituted Dendrons[a]

compd	τ (ns) 380 nm	τ (ns) 480 nm growth[b]	τ (ns) 480 nm decay[b]	τ(ns) 480 nm growth[c]	τ (ns) 480 nm decay[c]
1-pyrenemethanol	325				
4a	298	2.8	59	17	62
4d		1.3	23	4.7	41
5a				9.3	60
5c				4.9	48

[a] Dilute solutions ($\sim 10^{-6}$ M) were bubble degassed with argon. λ_{ex} = 355 nm. [b] In acetonitrile. [c] In THF.

90% in **4d** (Figure 3). Quenching was always less efficient in the third generation dendron than in the second generation for each set of conditions studied. The decreased ratio of donor to acceptors (and hence the effective local quencher concentration) and the increased separation of the donor and acceptors on electron transfer are reflected in the diminished quenching in the third generation.

Table 3 shows solvent effects on excimer quenching for **4b** compared to **4d** and for **5a** compared to **5c**. The alcohol-terminated dendrons were used as standards because their fluorescence intensity varies with solvent. For both sets of dendrons, the quenching efficiency increases with increasing solvent polarity (CH_2Cl_2 < THF < CH_3CN), as would be anticipated if a polar, coordinating solvent were to help stabilize the transition state leading to the charge-separated product, thus enhancing the observed steady-state fluorescence quenching efficiency.

Fluorescence lifetimes of monomer (380 nm) and excimer (480 nm) components of 1-pyrenemethanol, **4b**, **4d**, **5a**, and **5c** obtained with single photon counting techniques are listed in Table 4. Singlet emission of both 1-pyrenemethanol and **4b** in acetonitrile can be described by a single exponential decay with lifetimes of approximately 300 ns. In **4b**, **4d**, **5a**, and **5c**, the excimer emission grows in and then decays, and is best described by a biexponential equation[19]

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$[B] = \frac{k_1[A]_0}{k_2 - k_1}(e^{-k_1 t} - e^{-k_2 t})$$

$$\text{when } [B]_0 = 0; \quad k_1 = 1/\tau_1; \quad k_2 = 1/\tau_2$$

$$\text{where } \tau_1 = \text{rise lifetime}; \quad \tau_2 = \text{decay lifetime}$$

where A = singlet pyrene, B = pyrene excimer, and C = ground state pyrene (in the case of **4b**) or the pyrene radical anion attained by intramolecular electron transfer (in the case of **4d**). The excimer signal reaches its maximum intensity 5 ns after the excitation flash, which is comparable to intramolecular pyrene excimer formation in simple model systems such as 1,3-di(1-pyrenyl)propane.[20] Intramolecular quenching of excimer or locally excited pyrene is evident in the shortened decay lifetime of **4d** compared to that of **4b** (in both acetonitrile and THF) and of **5c** compared to that of **5a**. A transient absorption experiment of **4d** in acetonitrile shows evidence for the appearance of a pyrenyl radical anion absorbance at 700 nm,[21] as is consistent with electron transfer as a possible quenching mode. Strong coupling throughout the dendron skeleton, both through-bond and through-space, would be expected by virtue of the small energy gap between the HOMOs of alkoxyaniline and of dialkoxybenzene.

(19) Steinfeld, J. I.; Francisco, J. S.; Hase, W. L. *Chemical Kinetics and Dynamics*; Prentice Hall: Englewood Cliffs, NJ, 1989.

Conclusions

A methoxy-capped model of the dendrimer backbone **3e** fluoresces weakly at 310 nm when excited at 284 nm. No quenching of dendrimer backbone fluorescence in the model compound **3g** by a covalently-attached (dimethylamino)phenoxy electron donor group was observed. Sensitized backbone fluorescence was not detected in the emission spectra of any naphthyl- or pyrenyl-capped dendron in these studies.

Steady-state fluorescence spectra of naphthyl-capped dendrons (both mono- and disubstituted at the chain ends) provide no evidence of intramolecular naphthalene excimer in dilute solution, although intermolecular excimer does form in more concentrated solutions. Naphthyl-capped dendrons with skeletons **1** and **3** had lower fluorescence quantum yields than those with skeletons **2** and **4**, possibly because of competing nonradiative self-quenching. Intramolecular quenching of the fluorescence of the peripheral naphthyl groups by a covalently attached electron donor (such as a triethylamino or [dimethylamino]phenoxy group) has been demonstrated as a highly efficient process.

Pyrene excimer emission dominates the observed fluorescence spectrum for all pyrenyl-capped dendrons of generation two or greater. The pyrene excimer fluorescence is quenched more effectively than the pyrene singlet fluorescence upon bimolecular quenching with 3-(dimethylamino)phenol. Intramolecular quenching in dendrons bearing covalently attached electron donor functionalities has been demonstrated through steady-state and time-resolved fluorescence measurements and is attributed to intramolecular photoinduced electron transfer. The amount of quenching observed is a function of dendrimer generation number and of solvent polarity.

Together, these results suggest substantial electronic coupling between appended chromophores and quenchers across the dendrimer framework, affirming the possibility that these chromophore-labeled dendrons can be used as molecular light harvesters. Experiments to study energy transfer in chromophore-labeled dendrons are under way.

Experimental Section

All chemicals were purchased from Aldrich and were used as received unless otherwise indicated. 1-Pyrenemethanol and 1-bromomethylpyrene were synthesized by literature methods.[22,23] Acetone

(20) For example, see: (a) Zachariasse, K. A.; Kühnle, W.; Leinhos, U.; Reynders, P.; Striker, G. *J. Phys. Chem.* **1991**, *95*, 5476. (b) Goedeweeck, R.; Ruttens, F.; Lopez-Arbeloa, F.; De Schryver, F. C. *Biopolymers* **1987**, *26*, 1833. (c) Collart, P.; Demeyer, K.; Toppet, S.; De Schryver, F. C. *Macromolecular* **1983**, *16*, 1390. (d) Collart, P.; Toppet, S.; Zhou, Q. F.; Boens, N.; De Schryver, F. C. *Macromolecules* **1985**, *18*, 1026.

(21) Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: New York, 1988.

(22) Akiyama, S.; Nakasuji, K.; Nakagawa, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2231.

was distilled from potassium carbonate. Dichloromethane was distilled from calcium chloride. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl. Potassium carbonate was stored in a 130 °C oven. 3-(Dimethylamino)phenol was purified by column chromatography, followed by recrystallization from dichloromethane/hexanes. All column chromatography was performed on silica gel. All solutions were studied at an OD of ∼0.03 to ∼0.10. Single photon counting experiments were conducted at the Center for Fast Kinetics Research in Austin and were analyzed using Kaleidograph software.

Fluorescence quantum yields of all pyrene-labeled dendrons and of 1-pyrenemethanol were determined by reference to 9,10-diphenylanthracene in cyclohexane (Table 2).[11] Dendrons **5a** and **5c** were only sparingly soluble in acetonitrile, so the fluorescence quantum yields for these compounds in acetonitrile should only be taken as approximations.

Preparation of 3,5-Bis-(2-naphthylmethyloxy)benzyl Alcohol [1a]. 2-Bromomethylnaphthalene (2.2 g, 10 mmol), 3,5-dihydroxybenzyl alcohol (640 mg, 4.5 mmol), anhydrous K_2CO_3 (1.6 g, 11 mmol), and 18-crown-6 ether (240 mg, 0.91 mmol) were placed in dry acetone (40 mL) and heated at reflux under Ar for 56 h, before being stirred at room temperature for another 12 h. Acetone was removed *in vacuo*, and the remaining solid was taken up in CH_2Cl_2 (3 × 50 mL) and then washed with distilled water (3 × 50 mL). The aqueous layer was extracted with CH_2Cl_2 (25 mL), and the combined organics were washed with brine (50 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Recrystallization from hot toluene/hexanes gave a white crystalline product in 69% yield, mp 94−95 °C. ^{1}H NMR ($CDCl_3$): δ 7.83−7.97 (m, 8 H), 7.47−7.54 (m, 6 H), 6.68 (d, J = 1.5 Hz, 2 H), 6.64 (d, J = 1.5 Hz, 1 H), 5.22 (s, 4 H), 4.65 (s, 2 H), 2.36 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 160.2, 143.5, 134.3, 133.3, 133.1, 128.4, 128.0, 127.7, 126.3, 126.2, 126.1, 125.3, 105.9, 101.5, 70.3, 65.3. HRMS (*m/z*): calcd. for $C_{29}H_{24}O_3$, 420.1725; found, 420.1716.

Preparation of 3,5-Bis-(2-naphthylmethyloxy)benzyl Bromide [1b]. Carbon tetrabromide (1.6 g, 4.9 mmol) was added to a stirred solution of **1a** (1.6 g, 3.9 mmol) in dry THF (5 mL) under Ar. After 5 min stirring, triphenylphosphine (1.4 g, 5.3 mmol) was added, and the resulting reaction mixture was stirred for 1 h. The reaction mixture was partitioned between water (50 mL) and CH_2Cl_2 (20 mL). The organic layer was washed with water (3 × 100 mL), and the combined aqueous solutions were extracted once with CH_2Cl_2. The combined CH_2Cl_2 solutions were dried over $MgSO_4$, filtered through Celite, and concentrated *in vacuo*. Recrystallized from a mixture of ether, methanol, and hexanes gave a white solid in 23−48% yield, mp 108−109 °C. ^{1}H NMR ($CDCl_3$): δ 7.88−7.83 (m, 8 H), 7.54−7.45 (m, 6 H), 6.70 (d, J = 2.0 Hz, 2 H), 6.64 (d, J = 2.0 Hz, 1 H), 5.20 (s, 4 H), 4.43 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 160.1, 139.8, 134.1, 133.3, 133.1, 128.4, 128.0, 127.7, 126.4, 126.3, 126.1, 125.3, 108.3, 102.3, 70.3, 33.5. HRMS (*m/z*): calcd. for $C_{29}H_{23}O_2Br$, 482.0881; found, 482.0883.

Preparation of 3,5-Bis[3,5-bis-(2-naphthylmethyloxy)benzyloxy]-benzyl Alcohol [3a]. A suspension of **1b** (530 mg, 1.1 mmol), 3,5-dihydroxybenzyl alcohol (70 mg, 0.5 mmol), anhydrous K_2CO_3 (170 mg, 1.3 mmol), and 18-crown-6 ether (26 mg, 0.10 mmol) in dry acetone (10 mL) was heated at reflux under Ar for 45 h. Acetone was removed *in vacuo*, and the remaining solid was taken up in CH_2Cl_2 (2 × 20 mL) and then washed with distilled water (3 × 20 mL). The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The product was purified by flash column chromatography in CH_2Cl_2 to give a fluffy white solid in 62% yield, mp 65−70 °C. ^{1}H NMR in $CDCl_3$: δ 7.93−7.80 (m, 16 H), 7.52−7.46 (m, 12 H), 6.72 (d, J = 2.1 Hz, 4 H), 6.66 (m, 2 H), 6.51 (d, J = 2.1 Hz, 2 H), 6.57 (m, 1 H), 5.20 (s, 8 H), 4.99 (s, 4 H), 4.57 (d, J = 6.1 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 160.2, 160.1, 143.4, 139.4, 134.3, 133.3, 133.1, 128.4, 128.0, 127.7, 126.4, 126.2, 126.1, 125.3, 106.5, 105.8, 101.8, 101.4, 70.28, 69.97, 65.29. HRMS (*m/z*): calcd. for $C_{65}H_{52}O_7$, 944.3713; found, 944.3711.

Preparation of 3,5-Bis[3,5-bis-(2-naphthylmethyloxy)benzyloxy]-benzyl Bromide [3b]. Carbon tetrabromide (130 mg, 0.40 mmol) was added to a stirred solution of **3a** (120 mg, 0.13 mmol) in dry THF (1 mL) under Ar. After 5 min stirring, triphenylphosphine (140 mg, 0.55 mmol) was added, and the resulting reaction mixture was stirred for 3 h. The reaction mixture was partitioned between water (3 mL) and CH_2Cl_2 (10 mL). The organic layer was washed with another 10 mL water, and the combined aqueous solutions were extracted with CH_2Cl_2 (2 × 10 mL). The combined dichloromethane portions were dried over $MgSO_4$, filtered through Celite, and concentrated *in vacuo*. The product was purified by flash column chromatography in 20% ethyl acetate:80% hexanes increasing to 40% ethyl acetate:60% hexanes; the eluent was then dissolved in a minimum amount of CH_2Cl_2 and added dropwise to a mixture of equal parts ether and hexanes. The precipitated white solid was collected on a glass frit to give the desired product in 50−80% yield, mp 120−124 °C. ^{1}H NMR ($CDCl_3$): δ 7.86−7.81 (m, 16 H), 7.52−7.46 (m, 12 H), 6.72 (d, J = 1.6 Hz, 4 H), 6.66 (m, 2 H), 6.59 (d, J = 1.9 Hz, 2 H), 6.51 (m, 1 H), 5.20 (s, 8 H), 4.96 (s, 4 H), 4.36 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 160.2, 159.9, 139.7, 139.2, 134.3, 133.3, 133.1, 128.4, 128.0, 127.7, 126.4, 126.2, 126.1, 125.3, 108.3, 106.5, 102.2, 101.9, 70.30, 70.05, 33.55. HRMS (*m/z*): calcd. for $C_{65}H_{51}O_6Br$, 1007.2947; found, 1007.2938.

Preparation of 3,5-Bis[3,5-bis-(2-naphthylmethyloxy)benzyloxy]-benzyl (3-*N*,*N*-Dimethylaminophenyl) Ether [3d]. A suspension of 3-(dimethylamino)phenol (62 mg, 0.45 mmol), K_2CO_3 (87 mg, 0.63 mmol), and 18-crown-6 ether (24 mg, 0.090 mmol) in dry acetone (25 mL) was heated at reflux for 0.5 h before neat **3b** (500 mg, 1.0 mmol) was added. The mixture was heated at reflux for 2 h and then stirred at room temperature for 16 h. Acetone was removed *in vacuo*, and the product was dissolved in CH_2Cl_2 (3 × 20 mL) before being washed with water (2 × 75 mL) and then brine (100 mL). Solvent was removed *in vacuo*. The product, a clear glass, was isolated in 95% yield upon column chromatography in CH_2Cl_2. ^{1}H NMR ($CDCl_3$): δ 7.86−7.79 (m, 16 H), 7.53−7.45 (m, 12 H), 7.16−7.11 (m, 1 H), 6.74−6.73 (m, 4 H), 6.68−6.65 (m, 4H), 6.55−6.54 (m, 1 H), 6.38−6.33 (m, 3 H), 5.20 (s, 8 H), 4.98 (s, 4 H), 4.96 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 160.2, 160.0, 159.9, 152.0, 139.9, 139.4, 134.3, 133.3, 133.1, 129.7, 128.4, 128.0, 127.7, 126.4, 126.2, 126.0, 125.3, 106.5, 106.5, 106.0, 102.3, 101.8, 101.5, 100.1, 70.28, 70.00, 69.84, 40.55. HRMS (*m/z*): calcd. for $C_{73}H_{61}NO_7$, 1063.4448; found, 1063.4424.

Preparation of 3,5-Dimethoxybenzyl Bromide [1e]. Carbon tetrabromide (12 g, 37 mmol) and triphenylphosphine (9.8 g, 37 mmol) were added to a solution of 3,5-dimethoxybenzyl alcohol (5.0 g, 30 mmol) in dry THF (50 mL) under Ar. After 1 h, the reaction was quenched by the addition of water (100 mL). After having been stirred for 10 min, the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was washed with brine (100 mL) and was concentrated *in vacuo*. Isolation by column chromatography (20% ethyl acetate: 80% hexanes) gave an off-white powder, which was recrystallized from CH_2Cl_2/hexane in 61% yield, mp 69−70 °C. ^{1}H NMR ($CDCl_3$): δ 6.54 (d, J = 2.2 Hz, 2 H), 6.40−6.39 (m, 1 H), 4.42 (s, 2 H), 3.80 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 160.9, 139.7, 107.0, 100.6, 55.38, 33.56. HRMS (*m/z*): calcd. for $C_9H_{12}O_2Br$, 231.0021; found, 231.0022.

Preparation of 3,5-Bis[3,5-(dimethoxy)benzyloxy]benzyl Alcohol [3e]. A suspension of 3,5-dimethoxybenzyl alcohol (1.0 g, 7.3 mmol), K_2CO_3 (2.5 g, 18 mmol), and 18-crown-6 ether (390 mg, 1.5 mmol) in dry acetone (180 mL) was heated at reflux under Ar for 0.5 h before neat **1e** (3.7 g, 16 mmol) was added. The mixture was heated at reflux for 42 h before acetone was removed *in vacuo*. The product was dissolved in CH_2Cl_2 (3 × 75 mL) and washed with water (2 × 200 mL) and then with brine (250 mL). Removal of solvent *in vacuo* gave a white solid, isolated in 88% yield upon column chromatography in CH_2Cl_2, mp 83−86 °C. ^{1}H NMR ($CDCl_3$): δ 6.62 (d, J = 1.9 Hz, 2 H), 6.57 (d, J = 1.9 Hz, 4 H), 6.54 (t, J = 1.8 Hz, 1 H), 6.41 (t, J = 1.9 Hz, 2 H), 4.98 (s, 4 H), 4.63 (d, J = 6.1 Hz, 2 H), 3.80 (s, 12 H), 1.61 (t, J = 5.9 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 161.0, 160.1, 143.4, 139.2, 105.8, 105.2, 101.4, 99.93, 70.03, 65.28, 55.35. HRMS (*m/z*): calcd. for $C_{25}H_{28}O_7$, 440.1835; found, 440.1819.

Preparation of 3,5-Bis[3,5-(dimethoxy)benzyloxy]benzyl Bromide [3f]. Carbon tetrabromide (2.38 g, 7.18 mmol) and triphenylphosphine (1.88 g, 7.18 mmol) were added to a solution of **3e** (2.53 g, 5.74 mmol) in dry THF (50 mL) under Ar. After 2 h, the reaction was quenched

(23) Okamoto, H.; Arai, T.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 2881.
(24) Reimann, E. *Liebigs Ann. Chem.* **1971**, *750*, 109.
(25) Pitt, C. G.; Seltzman, H. H.; Sayed, Y.; Twine, C. E., Jr.; Williams, D. L. *J. Org. Chem.* **1979**, *44*, 677.
(26) Sargent, M. V.; Stanojevic, E. *J. Chem. Soc., Perkin Trans. I* **1984**, 1919.

by the addition of water (100 mL). After having been stirred for 30 min, the mixture was extracted with CH_2Cl_2 (2 × 100 mL). The organic layer was washed with brine (200 mL) and was concentrated *in vacuo*. The product was isolated by column chromatography (50% CH_2Cl_2: 50% hexanes) as a white powder in 83% yield, mp 127−129 °C. ^{1}H NMR ($CDCl_3$): δ 6.63 (d, J = 2.2 Hz, 2 H), 6.57 (d, J = 2.2 Hz, 4 H), 6.54 (t, J = 2.2 Hz, 1 H), 6.42 (t, J = 2.2 Hz, 2 H), 4.97 (s, 2 H), 4.41 (s, 2 H), 3.80 (s, 12 H). ^{13}C NMR ($CDCl_3$): δ 160.0, 160.0, 139.8, 139.0, 108.2, 105.6, 102.3, 100.0, 70.14, 55.36, 33.52. HRMS (*m/z*): calcd. for $C_{25}H_{27}O_6Br$, 502.0991; found, 502.0985.

Preparation of 3,5-Bis[3,5-(dimethoxy)benzyloxy]benzyl (3-*N*,*N*-Dimethylaminophenyl) Ether [3g]. A suspension of 3-(dimethylamino)phenol (110 mg, 0.80 mmol), K_2CO_3 (170 mg, 1.3 mmol), and 18-crown-6 ether (42 mg, 0.16 mmol) in dry acetone (25 mL) was heated at reflux under Ar for 1 h before neat **3f** (500 mg, 1.0 mmol) was added. The mixture was heated at reflux for 2 h and then stirred at room temperature for 16 h before acetone was removed *in vacuo*. The product was dissolved in CH_2Cl_2 (100 mL) and then washed with water (150 mL) and then brine (150 mL). Removal of solvent *in vacuo* a clear glass, isolated in 69% yield by column chromatography in 50% CH_2Cl_2:50% hexanes increasing to 100% CH_2Cl_2. ^{1}H NMR ($CDCl_3$): δ 7.14 (t, J = 7.8 Hz, 1 H), 6.70 (s, 2 H), 6.58−6.56 (m, 4 H), 6.42−6.33 (m, 6 H), 4.98 (s, 6 H), 3.80 (s, 12 H), 2.93 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 161.0, 160.1, 159.9, 152.0, 139.9, 139.2, 127.9, 106.5, 106.0, 105.3, 102.3, 101.6, 100.1, 100.0, 70.09, 69.86, 55.36, 40.57. HRMS (*m/z*): calcd. for $C_{33}H_{37}NO_7$, 559.2570; found, 559.2571.

Preparation of 3-(2-Naphthylmethyloxy)benzyl Alcohol [2a]. A solution of 3-hydroxybenzyl alcohol (1.6 g, 13 mmol), anhydrous K_2CO_3 (2.1 g, 15 mmol), and 18-crown-6 ether (68 mg, 2.6 mmol) in dry acetone (25 mL) was heated at reflux under Ar for 30 min, and then neat 2-bromomethylnaphthalene (3.1 g, 14 mmol) was added. The mixture was heated at reflux for 16 h before acetone was removed *in vacuo*. The product was dissolved in CH_2Cl_2 (300 mL) and washed with water (2 × 200 mL) and then with brine (300 mL). Removal of solvent *in vacuo* followed by flash column chromatography in CH_2Cl_2 gave a white solid in 78% yield, mp 106−108 °C. ^{1}H NMR ($CDCl_3$): δ 7.89−7.83 (m, 4 H), 7.55−7.46 (m, 3 H), 7.31−7.25 (m, 1 H), 7.07, (s, 1 H), 6.97−6.94 (m, 2 H), 5.25 (s, 2 H), 4.68 (d, J = 6.0 Hz, 2 H), 1.63 (t, J = 6.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 159.1, 142.6, 134.5, 133.3, 133.1, 129.7, 128.4, 127.9, 127.7, 126.3, 126.2, 126.1, 125.2, 119.4, 114.2, 113.4, 70.14, 65.28. HRMS (*m/z*): calcd. for $C_{18}H_{16}O_2$, 264.1150; found, 264.1137.

Preparation of 3-(2-Naphthyloxy)benzyl Bromide [2b]. Carbon tetrabromide (4.2 g, 13 mmol) and triphenylphosphine (3.3 g, 13 mmol) were added to a solution of **2a** (2.6 g, 10 mmol) in dry THF (20 mL) under Ar. After 0.5 h, the reaction was quenched by the addition of water (40 mL). After having been stirred for 10 min, the mixture was extracted with CH_2Cl_2 (3 × 25 mL). The organic layer was washed with brine (100 mL), concentrated *in vacuo*, and purified by column chromatography (30% CH_2Cl_2:70% hexanes to 50% CH_2Cl_2:50% hexanes) to give a white powder in 86% yield, mp 105−106 °C. ^{1}H NMR ($CDCl_3$): δ 7.89−7.84 (m, 4 H), 7.56−7.48 (m, 3H), 7.29−7.24 (m, 1 H), 7.07 (s, 1 H), 7.02−6.94 (m, 2 H), 5.24 (s, 2 H), 4.47 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 159.0, 139.2, 134.2, 133.3, 133.1, 129.9, 128.4, 128.0, 127.7, 126.4, 126.3, 126.1, 125.2, 121.6, 115.6, 115.0, 70.23, 33.41. HRMS (*m/z*): calcd. for $C_{18}H_{15}OBr$, 326.0306; found, 326.0303.

Preparation of 3,5-Bis[3-(1-naphthyloxy)benzyloxy]benzyl Alcohol [4a]. A suspension of 3,5-dimethyoxybenzyl alcohol (486 mg, 3.47 mmol), K_2CO_3 (1.20 g, 8.68 mmol), and 18-crown-6 ether (180 mg, 0.69 mmol) in dry acetone (150 mL) was heated at reflux under Ar for 1 h, and then neat **2b** (2.50 g, 7.64 mmol) was added. The mixture was heated at reflux for 41 h. Acetone was removed *in vacuo*. The product was taken up in CH_2Cl_2 (2 × 100 mL) and then washed with water (2 × 150 mL) and brine (250 mL). Removal of solvent *in vacuo* and column chromatography in CH_2Cl_2 gave a colorless glass in 75% yield. ^{1}H NMR ($CDCl_3$): δ 7.89−7.84 (m, 8 H), 7.56−7.48 (m, 6 H), 7.32 (t, J = 8.1 Hz, 2 H), 7.13 (s, 2 H), 7.04−6.97 (m, 4 H), 6.62 (d, J = 1.9 Hz, 2 H), 6.56 (d, J = 2.1 Hz, 1 H), 5.23 (s, 4 H), 5.02 (s, 4 H), 4.60 (s, 2 H), 2.38 (s, 1 H). ^{13}C NMR ($CDCl_3$): δ 160.1, 159.1, 143.4, 138.5, 134.4, 133.3, 133.0, 129.7, 128.4, 127.9, 127.7, 126.3, 126.2, 126.0, 125.2, 119.9, 114.4, 113.9, 105.7, 101.3, 69.87, 65.21. HRMS (*m/z*): calcd. for $C_{43}H_{36}O_5$, 633.2641; found, 633.2619.

Preparation of 3-(1-Pyrenylmethyloxy)benzyl Alcohol [2c]. A suspension of 3-hydroxybenzyl alcohol (120 mg, 1.0 mmol), anhydrous K_2CO_3 (260 mg, 1.2 mmol), 18-crown-6 ether (28 mg, 0.20 mmol), and 1-bromomethylpyrene[22,23] (350 mg, 1.2 mmol) in dry acetone (25 mL) was heated at reflux under Ar for 22 h before acetone was removed *in vacuo*. The remaining solid was dissolved in CH_2Cl_2 (2 × 20 mL), and the resulting solution was extracted with distilled water (3 × 20 mL). The organic layer was washed with brine and concentrated *in vacuo*. Upon column chromatography in CH_2Cl_2 a pale yellow solid was obtained in 96% yield, mp 117−119 °C. ^{1}H NMR ($CDCl_3$): δ 8.31−8.00 (m, 9.5 H), 7.35 (t, J = 7.8 Hz, 1 H), 7.30 (s, 1 H), 7.16−6.99 (m, 2 H), 5.75 (s, 2 H), 4.70 (d, J = 5.8 Hz, 2 H), 1.73 (t, J = 6.0 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ 159.2, 142.7, 131.6, 131.2, 130.7, 129.7, 129.3, 128.0, 127.6, 127.4, 126.8, 126.0, 125.4, 125.4, 124.9, 124.7, 124.6, 123.0, 119.5, 114.3, 114.3, 113.4, 68.76, 65.26. HRMS (*m/z*): calcd. for $C_{24}H_{18}O_2$, 338.1307; found, 338.1304.

Preparation of 3-(1-Pyrenylmethyloxy)benzyl Bromide [2d]. Carbon tetrabromide (1.9 g, 5.7 mmol) and triphenylphosphine (1.5 g, 5.7 mmol) were added to a solution of **2c** (1.5 g, 4.5 mmol) in dry THF (10 mL) under Ar. After 1 h, the reaction was quenched by the addition of water (20 mL). After 30 min stirring, the mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was washed with brine (50 mL) and concentrated *in vacuo*. Column chromatography (20% CH_2Cl_2:80% hexanes to 50% CH_2Cl_2:50% hexanes) yielded a pale yellow solid in 96% yield, mp 110−112 °C. ^{1}H NMR ($CDCl_3$): δ 8.30−8.00 (m, 9 H), 7.31 (t, J = 8.0 Hz, 1 H), 7.16 (s, 1 H), 7.15 (d, J = 7.9 Hz, 2 H), 5.73 (s, 2 H), 4.50 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 159.1, 139.3, 131.6, 131.2, 130.7, 129.9, 129.5, 129.3, 128.1, 127.7, 127.4, 126.9, 126.0, 125.4, 125.4, 124.9, 124.6, 124.6, 123.0, 121.7, 115.6, 115.1, 68.83, 33.42. HRMS (*m/z*): calcd. for $C_{24}H_{17}OBr$, 400.0463; found, 400.0472.

Preparation of 3,5-Bis[3-(1-pyrenylmethyloxy)benzyloxy]benzyl Alcohol [4b]. A suspension of 3,5-dimethoxybenzyl alcohol (640 mg, 4.6 mmol), K_2CO_3 (1.6 g, 11 mmol), and 18-crown-6 ether (240 mg, 0.91 mmol) in acetone (180 mL) was heated at reflux under Ar for 30 min before neat **2d** (4.0 g, 10 mmol) was added. The mixture was heated at reflux for 96 h. Acetone was removed *in vacuo*. The product was dissolved in CH_2Cl_2 (2 × 75 mL), and the resulting solution was extracted with distilled water (3 × 150 mL). The organic layer was washed with brine (50 mL) and concentrated under reduced pressure to give a pale yellow solid. Column chromatography in CH_2Cl_2 gave a pale beige powder (55%), mp 77−79 °C, and 1.45 g of recovered **2d**. ^{1}H NMR ($CDCl_3$): δ 8.31−7.98 (m, 18 H), 7.36 (t, J = 7.8 Hz, 2 H), 7.19 (s, 2 H), 7.07−7.03 (m, 4 H), 6.60 (d, J = 1.8 Hz, 2 H), 6.54 (d, J = 2.0 Hz, 1 H), 5.75 (s, 4 H), 5.04 (s, 4 H), 4.59 (d, J = 6.2 Hz, 2 H) (benzyl alcohol proton signal was obscured by water). ^{13}C NMR ($CDCl_3$): δ 160.1, 159.2, 143.4, 138.6, 131.6, 131.2, 130.7, 129.8, 129.7, 129.3, 128.0, 127.6, 127.4, 126.9, 126.0, 125.4, 125.4, 124.9, 124.7, 124.6, 123.0, 120.0, 114.6, 113.9, 105.8, 101.4, 69.93, 68.81, 65.29. HRMS (*m/z*): calcd. for $C_{55}H_{40}O_5$, 780.2876; found, 780.2817.

Preparation of 3,5-Bis[3-(1-pyrenylmethyloxy)benzyloxy]benzyl Bromide [4c]. Carbon tetrabromide (988 mg, 2.98 mmol) and triphenylphosphine (782 mg, 2.98 mmol) were added to a solution of **4b** (1.86 g, 2.38 mmol) in dry THF (20 mL) under Ar. After 1.5 h, the reaction was quenched by the addition of water (40 mL). After being stirred for 30 min, the mixture was extracted with CH_2Cl_2 (2 × 30 mL). The organic layer was washed with brine (30 mL) and was concentrated *in vacuo* to give a yellow foam. Column chromatography (50% CH_2Cl_2:50% hexanes to 70% CH_2Cl_2:30% hexanes) gave a pale yellow solid in 90% yield, mp 128−129 °C. ^{1}H NMR ($CDCl_3$): δ 8.31−7.98 (m, 18 H), 7.35−7.31 (t, J = 8.1 Hz, 2 H), 7.19 (s, 2 H), 7.08−7.05 (m, 4 H), 6.62 (d, J = 2.1 Hz, 2 H), 6.54 (d, J = 2.0 Hz, 1 H), 5.75 (s, 4 H), 5.02 (s, 4 H), 4.37 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 160.0, 159.2, 139.8, 138.4, 131.6, 131.2, 130.8, 129.8, 129.7, 129.3, 128.1, 127.6, 127.4, 126.9, 126.0, 125.4, 125.4, 124.9, 124.7, 124.7, 123.0, 120.1, 114.7, 114.0, 108.3, 102.2, 70.01, 68.84, 33.52. HRMS (*m/z*): calcd. for $C_{55}H_{39}O_4Br$, 842.2032; found, 842.2037.

Preparation of 3,5-Bis[3-(1-pyrenylmethyloxy)benzyloxy]benzyl (3-*N*,*N*-Dimethylaminophenyl) Ether [4d]. A suspension of 3-(dimethylamino)phenol (66 mg, 0.048 mmol), K_2CO_3 (80 mg, 0.58 mmol),

and 18-crown-6 ether (25 mg, 0.096 mmol) in acetone (30 mL) was heated at reflux for 0.5 h before neat **4c** (410 mg, 0.48 mmol) was added. The mixture was heated at reflux for 17 h before acetone was removed *in vacuo*. The product was dissolved in CH_2Cl_2 (25 mL), and the resulting solution was washed with distilled water (2 × 25 mL). The organic layer then was washed with brine (25 mL) and concentrated under reduced pressure. The product, a very faint yellow solid, was isolated in 45% yield by column chromatography (50% CH_2Cl_2:50% hexanes increasing to 100% CH_2Cl_2), mp 78 °C. ^{1}H NMR ($CDCl_3$): δ 8.29−7.97 (m, 18 H), 7.33 (t, J = 7.9 Hz, 2 H), 7.21 (s, 2 H), 7.20−7.03 (m, 1 H), 7.06−7.03 (m, 4 H), 6.71 (d, J = 2.0 Hz, 2 H), 6.58 (m, 1 H), 6.36 (m, 2 H), 5.72 (s, 4 H), 5.04 (s, 4 H), 4.97 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 160.1, 159.9, 159.2, 152.0, 139.9, 138.6, 131.5, 131.2, 130.7, 129.7, 129.7, 129.7, 129.2, 128.0, 127.6, 127.4, 126.9, 126.0, 125.4, 125.4, 124.9, 124.7, 124.6, 123.0, 120.1, 114.6, 113.9, 106.5, 106.0, 102.2, 101.5, 100.1, 69.96, 69.82, 68.79, 40.53. HRMS (*m/z*): calcd. for $C_{63}H_{49}NO_5$, 899.3611; found, 899.3615.

Preparation of 3,5-Bis{3,5-bis-[3-(1-pyrenylmethyloxy)benzyloxy]-benzyloxy}benzyl Alcohol [5a]. A suspension of 3,5-dimethoxybenzyl alcohol (140 mg, 1.0 mmol), K_2CO_3 (360 mg, 2.6 mmol), and 18-crown-6 ether (50 mg, 0.2 mmol) in acetone (60 mL) was heated at reflux under Ar for 1 h before neat **4c** (1.8 g, 2.2 mmol) was added. The mixture was heated at reflux for 48 h. Dry benzene (15 mL) was added in an attempt to solubilize a yellow film coating the flask. After a total reflux time of 72 h, solvent was removed *in vacuo*. The product was dissolved in CH_2Cl_2 (3 × 100 mL), and the resulting solution was extracted with distilled water (2 × 200 mL). The organic layer was washed with brine (250 mL) and concentrated under reduced pressure to give a pale yellow solid. Column chromatography (50% CH_2Cl_2: 50% hexanes increasing polarity to 100% CH_2Cl_2 to 95% CH_2Cl_2:5% methanol) gave a pale yellow solid in 95% yield, mp 113−115 °C. ^{1}H NMR ($CDCl_3$): δ 8.21−7.93 (m, 36 H), 7.34−7.24 (m, 4 H), 7.14−7.13 (m, 4 H), 7.03−6.97 (m, 12 H), 6.61 (d, J = 2.2 Hz, 2 H), 6.52−6.51 (m, 2 H), 6.46 (t, J = 2.2 Hz, 1 H), 5.64 (s, 8 H), 4.97 (s, 8 H), 4.88 (s, 4 H), 4.51 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 160.0, 159.9, 159.1, 143.6, 139.3, 138.5, 131.4, 131.1, 130.6, 129.7, 129.5, 129.1, 127.9, 127.8, 127.5, 127.4, 127.2, 126.7, 125.9, 125.2, 124.7, 124.5, 122.8, 120.0, 114.5, 113.9, 106.4, 105.6, 101.5, 101.2, 69.85, 69.78, 68.58, 64.98. HRMS (*m/z*): calcd. for $C_{117}H_{84}O_{11}$, 1664.6014; found, 1664.3024.

Preparation of 3,5-Bis{3,5-bis-[3-(1-pyrenylmethyloxy)benzyloxy]-benzyloxy}benzyl Bromide [5b]. Carbon tetrabromide (300 mg, 0.91 mmol) and triphenylphosphine (240 mg, 0.91 mmol) were added to a solution of **5a** (1.21 g, 0.727 mmol) in dry THF (30 mL) under Ar. After 1 h, carbon tetrabromide (300 mg) and triphenylphosphine (240 mg) were added. After an additional hour, the reaction was quenched by the addition of water (50 mL). After having been stirred for 15 min, the mixture was transferred to a separatory funnel, and water (50 mL) and dichloromethane (100 mL) were added. Layers were separated, and the aqueous portion was extracted with CH_2Cl_2 (2 × 50 mL). The organic layer was washed with brine (100 mL) and was concentrated *in vacuo*. Column chromatography (75% CH_2Cl_2:25% hexanes) yielded a pale beige solid (97%), mp 105−109 °C. ^{1}H NMR ($CDCl_3$): δ 8.18−7.91 (m, 36 H), 7.26 (t, J = 7.9 Hz, 4 H), 7.13 (s, 4 H), 6.99−6.97 (m, 8 H), 6.59 (d, J = 2.1 Hz, 4 H), 6.55 (d, J = 2.2 Hz, 2 H), 6.53 (t, J = 2.2 Hz, 2 H), 6.46 (t, J = 2.1 Hz, 1 H), 5.61 (s, 8 H), 4.96 (s, 8 H), 4.84 (s, 4 H), 4.31 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 160.1, 159.2, 139.0, 138.5, 131.5, 131.2, 130.7, 129.7, 129.6, 129.2, 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 126.8, 125.9, 125.3, 124.9, 124.6, 124.5, 122.9, 120.0, 114.6, 113.9, 108.2, 106.4, 101.7, 69.9, 69.9, 68.7, 33.6. HRMS (*m/z*): calcd. for $C_{117}H_{84}O_{10}Br$, 1727.5287; found, 1727.5269.

Preparation of 3,5-Bis{3,5-bis-[3-(1-pyrenylmethyloxy)benzyloxy]-benzyloxy}benzyl (3-*N*,*N*-Dimethylaminophenyl) Ether [5c]. A suspension of 3-(dimethylamino)phenol (32 mg, 0.23 mmol), K_2CO_3 (32 mg, 0.23 mmol), and 18-crown-6 ether (3.0 mg, 0.010 mmol) in acetone (15 mL) was heated at reflux for 0.5 h before neat **5b** (40 mg, 0.023 mmol) was added. The mixture was heated at reflux overnight before acetone was removed. The burgundy-colored residue was dissolved in CH_2Cl_2 (25 mL), and the resulting solution was washed with distilled water (2 × 25 mL). The organic layer then was washed with brine (25 mL) and concentrated *in vacuo*. The product, a very faint yellow film, was isolated in 83% yield by column chromatography (50% CH_2Cl_2:50% hexanes increasing to 75% CH_2Cl_2:25% hexanes). ^{1}H NMR ($CDCl_3$): δ 8.20−7.80 (m, 36 H), 7.26 (t, J = 8.0 Hz, 4 H), 7.14 (t, J = 1.7 Hz, 4 H), 7.08−7.06 (m, 1 H), 6.99 (d, J = 7.9 Hz, 4 H), 6.98 (d, J = 7.9 Hz, 4 H), 6.64 (d, J = 2.2 Hz, 2 H),6.61 (d, J = 2.3 Hz, 4 H), 6.52 (t, J = 2.2 Hz, 2 H), 6.49 (t, J = 2.2 Hz, 1 H),6.30−6.29 (m, 3 H), 5.64 (s, 8 H), 4.97 (s, 8 H), 4.90 (s, 2 H), 4.89 (s, 4 H), 2.82 (s, 6 H). ^{13}C NMR ($CDCl_3$): δ 160.1, 160.0, 159.2, 139.9, 139.3, 138.6, 131.5, 131.2, 130.7, 129.8, 129.7, 129.7, 129.2, 128.0, 127.7, 127.6, 127.3, 126.8, 126.0, 125.3, 124.9, 124.6, 123.0, 120.0, 114.7, 113.9, 110.1, 106.5, 106.4, 106.4, 106.0, 102.2, 102.2, 101.6, 101.5, 100.1, 69.9, 69.9, 69.8, 68.7, 40.5. HRMS (*m/z*): calcd. for $C_{125}H_{94}NO_{11}$, 1784.6827; found, 1784.6883.

Preparation of 3,5-Dihydroxybenzyl Alcohol [29654-55-5] by a Modified Procedure.[24−26] Excess 1 M solution of borane in tetrahydrofuran (260 mL) was added dropwise over an 80-min period to a 0 °C solution of 3,5-dihydroxybenzoic acid (Pfaltz and Bauer, 12.5 g) in anhydrous THF (40 mL) under Ar. A white precipitate formed after ∼50 mL of borane solution was added. The resulting mixture was allowed to warm to room temperature over a 2 h period, stirred overnight at room temperature, and then heated at reflux for an additional 2 h. Distilled water (80 mL) was added dropwise to the cooled reaction mixture. The resulting clear solution was allowed to stir for 45 min before being transferred to a separatory funnel. Brine (∼50 mL) was added, and the layers were separated. Excess NaCl was added to the aqueous layer, which was subsequently extracted with diethyl ether (2 × 75 mL). The combined organics were washed with brine (100 mL), dried over $MgSO_4$, filtered, and concentrated *in vacuo* to give a pale yellow solid. The solid was recrystallized from acetone/hexanes to give the product in 76−81% yield.

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