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Synthesis of Nonconjugated Dendrons with a Redox Gradient

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Macromolecules with built-in redox gradients are of much interest due to their potential in a variety of optoelectronic and energy-harvesting applications. In this paper, the design and synthesis of nonconjugated dendrons with redox gradients to guide the charge flow from the core to the periphery is described. The dendrons reported here are based on benzyl ether connectivities. The repeat units of the dendrons are based on triarylamines, and the periphery units of the dendrons are based on *N*,*N*,*N*′,*N*′-tetraarylbenzidine units. The presence of a redox gradient after incorporation of these charge-transporting units into the dendrons is supported by cyclic voltammetric studies.

Introduction

Interest in triarylamines has grown over the past several years due to their high propensity to act as hole-transporting materials for applications such as xerography, nonlinear optics, photorefractives, and organic light-emitting diodes.[1] Since they form stable radical cations, triarylamines have also attracted significant interest as potential organic ferromagnets and as molecules for intervalence charge-transfer studies.[2] We have been interested in triarylamine-based dendrimers for intramolecular charge migrations.[3] Vectorial, intramolecular charge migrations have potential in applications such as artificial photosynthesis, thin-film transistors, and optical data storage.[4] Dendrimers[5] provide new opportunities for precisely placing charge-transporting units with respect to each other in a three-dimensional architecture. Triarylamine-based dendrimers have been previously synthesized and used in studies of potential materials for molecular magnetism and information storage,[6] energy transfer,[7] light-emitting diodes,[8] and metal-organic frameworks.[9] In all these cases, the dendrimers are based on a conjugated backbone. Fréchet and Thompson have reported a dendrimer for organic light-emitting diodes where the triarylamines are incorporated in the periphery of a nonconjugated benzyl ether dendrimer.[8b] We have been particularly interested in synthesizing nonconjugated dendrimers where the triarylamine moiety constitutes the repeat unit in the entire dendrimer.[3] Due to the difference in the number of units in each layer of the

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dendrimer, it could be an ideal scaffold for funneling energy or electrons through the backbone. Gradients have been built within these layers in order to facilitate unidirectional transport of energy.[10] Similarly, redox gradients can be built within dendrimers to direct the vectorial migration of charges. Conjugated triarylamine dendrimers with redox gradients have been synthesized, in which the most easily oxidizable triarylamine unit is near the focal point of the dendrimer.[6b] This arrangement dictates that the charges are funneled toward the core of the dendrimer. To have the flexibility in transporting the charges intramolecularly from periphery to the core or vice versa, nonconjugated dendrimers provide the advantage since the redox potentials of the triarylamine units can be independently tuned.

In this paper, we describe the synthesis of dendrons with a redox gradient in which the triarylamine-based repeat units are connected with benzyl ether linkages. It has been previously shown that the redox potentials of triarylamine-based compounds can be tuned by incorporating electron-withdrawing or electron-donating groups in one of the aryl rings.[11,12] However, the linear optical spectra of the radical cations of triarylamines with different functionalities in them are essentially indistinguishable. Therefore, we have been interested in dendrons in which the peripheral triarylamine-based units would have different radical cation spectra compared to the repeating units in the interior. Since benzidines exhibit lower oxidation potential compared to the triarylamines and since their radical cation spectra are distinct from those of triarylamines, *N*,*N*,*N*′,*N*′-tetraarylbenzidine units were chosen as the peripheral units. Note that this design should facilitate the migration of charges from the core of the dendron to the periphery since the periphery contains the most easily oxidizable benzidine units. In addition to the built-in redox gradients, dendrimers provide an inherent architectural advantage to transport charges from the core to the periphery. As the charge moves from the core to the periphery, the number of possible charge transporting units that can hold the charge doubles with each layer. This feature provides an entropic advantage for the intramolecular charge transport from the core to the periphery.

Results and Discussion

Synthesis. Benzyl ether dendrimers synthesized from AB_2 repeat units require building blocks that contain one hydroxymethyl and two phenolic functionalities. Triarylamine repeat units with two different redox potentials are shown in Figure 1 as structures **1a** and **1b**. The fluoro moiety in one of the aryl rings of **1b** is expected to increase the oxidation potential of the triarylamines compared to that of **1a**, which contains a methyl group.

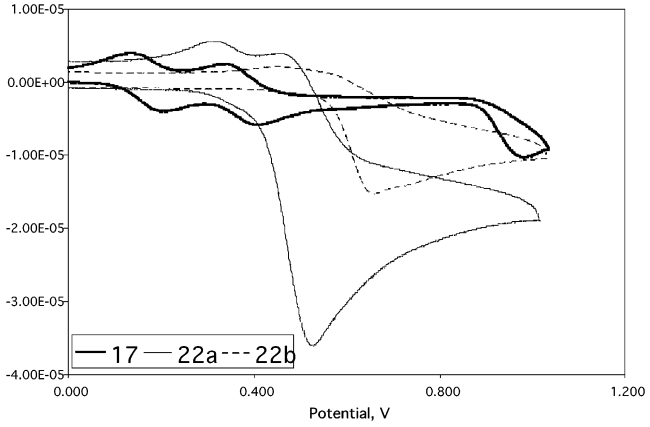
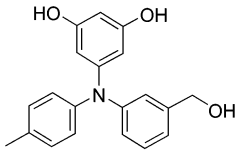
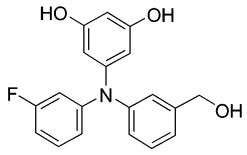


FIGURE 1. Cyclic voltammograms of compounds **17**, **22a**, and **22b**.

Note that the hydroxymethyl group is placed meta to the amino moiety in both repeat units. If this functionality were placed in the ortho or para position, the ensuing bromomethyl moiety in the synthesis could be destabilized by the electron-donating amino group.



1a



1b

We have previously described the synthesis of **1a**.[3] The repeat unit **1b** was synthesized using a similar route with one exception (Scheme 1). The triarylamine skeleton of compound **1a** was synthesized using the one-pot palladium-catalyzed C−N bond formation methodology.[3,12] However, when this strategy was attempted for the synthesis of **1b**, the isolated yield of the triarylamine was very low. This was mainly due to an inseparable byproduct obtained during the one-pot reaction. This problem was circumvented by first synthesizing the diarylamine **4** in 93% yield from dimethoxyaniline (**2**) and *m*-bromofluorobenzene (**3**). The isolated compound **4** was then subjected to the palladium-catalyzed reaction with 1,3-dibromobenzene (**5**) to afford the desired triarylamine **6** in 18% yield. Compound **6** was converted to the diphenol **7** using BBr_3 in 90% yield. The diphenol was protected with TBS groups in 68% yield to form compound **8** in order to render the substrate compatible to the following bromine−lithium exchange reaction condition. The bromo functionality was converted to the aldehyde **9** in 61% yield by bromine−lithium exchange and treating the lithioarene intermediate with DMF. The aldehyde **9** was reduced using sodium borohydride to the corresponding benzyl alcohol **10** in 97% yield. Finally, the TBS− groups of **10** were deprotected using TBAF to afford the corresponding diphenolic compound **1b** in 99% yield.

As mentioned above, the peripheral units of these redox gradient dendrons contains *N*,*N*,*N*′,*N*′-tetraarylbenzidine units. An electrophilic bromomethyl group is a necessary functionality in the peripheral building block unit for the construction of benzyl ether dendrons.

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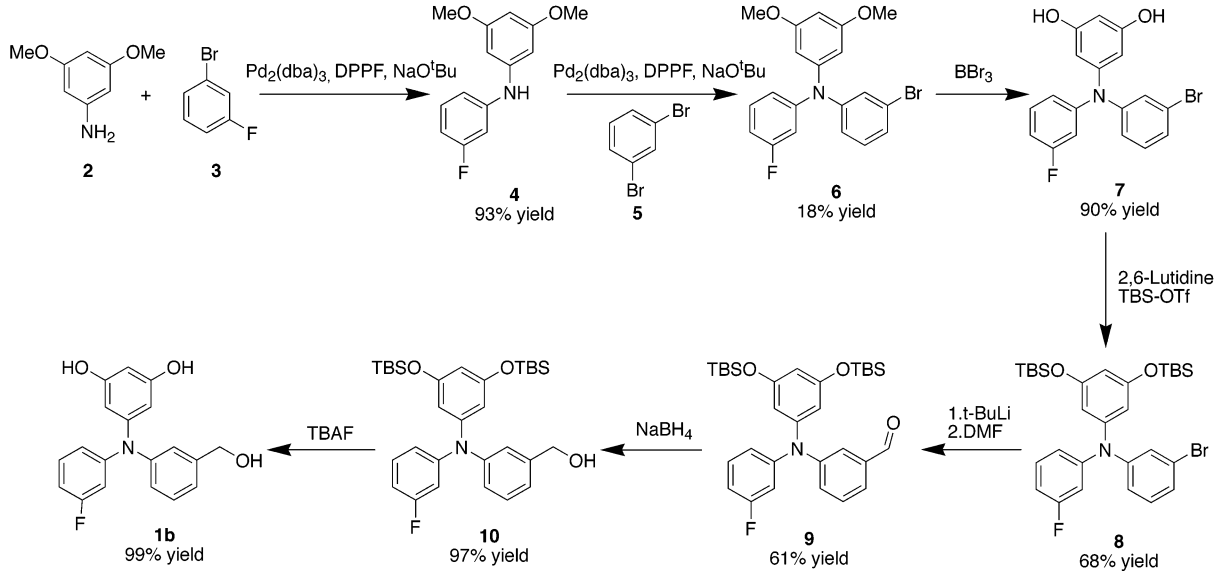
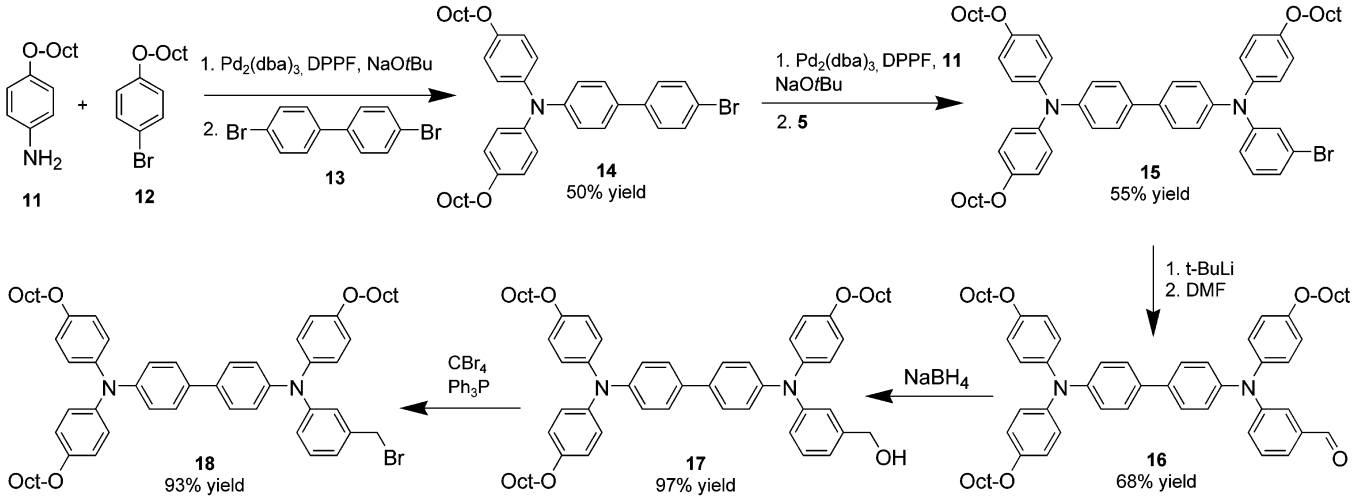
SCHEME 1



SCHEME 2



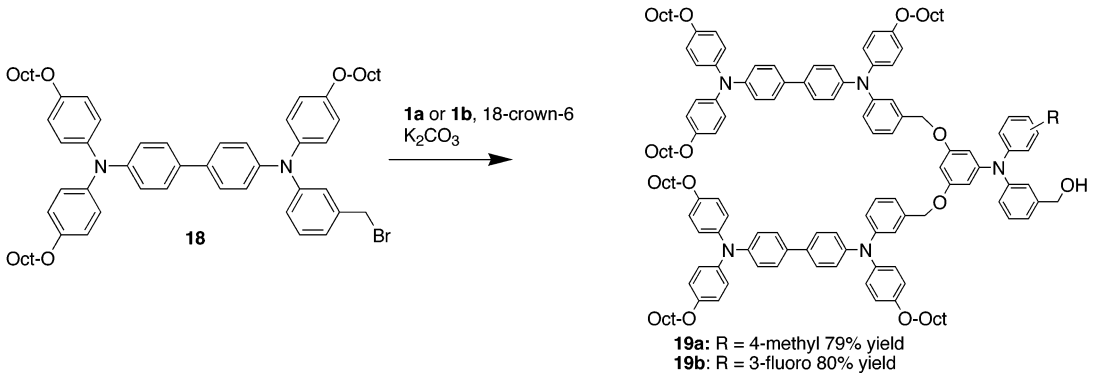
Therefore, the tetraarylbenzidine **18** was assembled as shown in Scheme 2. The *p*-octyloxybromobenzene (**12**), which was synthesized from *p*-bromophenol, was treated with *p*-octyloxyaniline (**11**) followed by the addition of 4,4′-dibromobiphenyl (**13**) under palladium-catalyzed conditions. The one-pot strategy above afforded the product **14** in 50% overall yield. Compound **14** was again subjected to an one-pot palladium-catalyzed reaction with aniline **11** followed by 1,3-dibromobenzene (**5**) to afford the tetraarylbenzidine **15** in 55% overall yield. The bromo functionality in **15** was converted to a carboxaldehyde group by treatment with *t*-BuLi followed by DMF. The aldehyde **16** was converted to the corresponding hydroxymethyl compound **17** in 97% yield using sodiumborohydride. Treatment of compound **17** with triphenylphosphine and carbontetrabromide afforded the targeted bromomethyl tetraarylbenzidine compound **18** in 93% yield.

To prepare the 3-mer dendrons **19** from the building blocks, 2 equiv of the peripheral unit **18** was treated with 1 equiv of the repeating unit **1a** or **1b** in the presence of potassium carbonate and 18-crown-6 in refluxing THF. The product **19a** was obtained in 79% yield and **19b** in 80% yield, as depicted in Scheme 3.

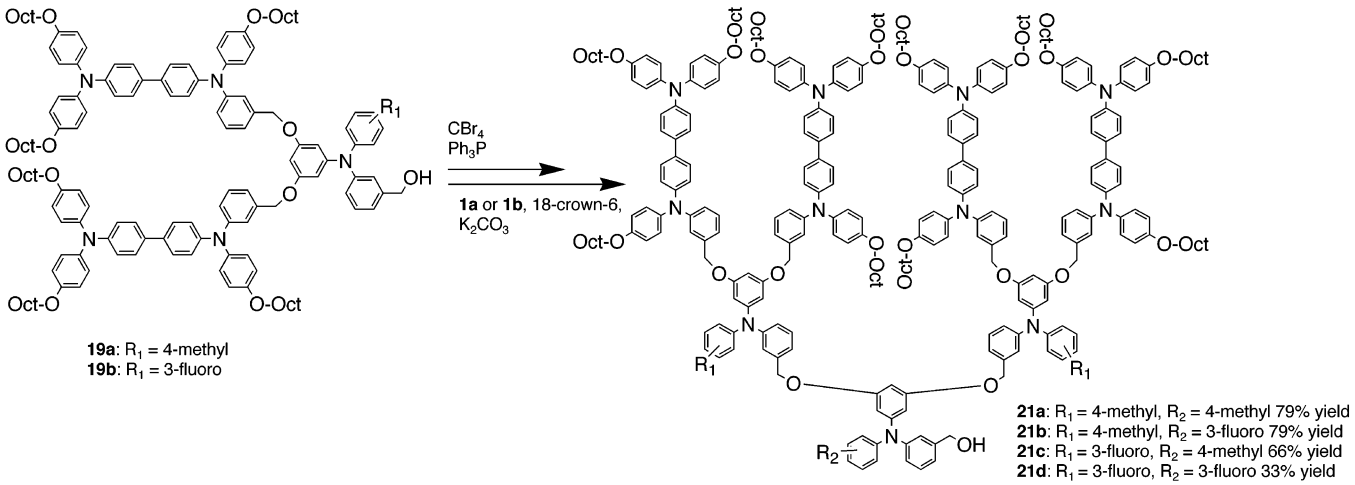
To synthesize a dendron with three layers of redox gradient CT units, 7-mer dendrons (**21**) were synthesized as shown in Scheme 4. The 3-mer hydroxymethyl compounds **19a** and **19b** were converted to the corresponding bromomethyl compounds **20a** and **20b** in 87% and 84% yields, respectively. The bromomethyl compound **20a** was treated with 0.5 equiv of **1a** in the presence of potassium carbonate and 18-crown-6 in THF under reflux to afford the 7-mer dendron **21a** in 79% yield, as outlined in Scheme 4. Similarly, **21b** was obtained from **20a** and **1b** in 79% yield; compound **21c** was obtained from **20b** and **1a** in 66% yield; and the dendron **21d** was obtained from **20b** and **1b** in 33% yield. The lower yield for the synthesis of **21d** is not clear at this time.

Using the modular nature of the synthesis of these dendrons, we were able to achieve three different kinds of redox gradients in structure **21**. In compounds **21a** and **21c**, there is a difference in redox potential between the peripheral units and the triarylamines in the interior layers. But, there is no difference in the redox potentials

SCHEME 3



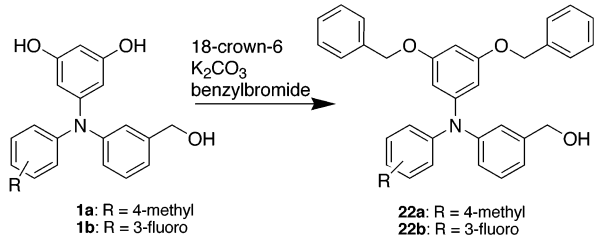
SCHEME 4



of the triarylamines within the interior layers. In dendrons **21b** and **21d**, in addition to the difference between the peripheral and the interior units, there is also difference in redox potential between the triarylamine unit at the focal point of the dendron and the triarylamine units at the intermediate layer. Also, since the fluoro- group is expected to increase the oxidation potential of the triarylamine, compound **21b** has a redox gradient that will direct the flow of positive charge from the focal point of the dendron toward the periphery of the dendron. However, in **21d**, the methyl- and fluoro-substituted triarylamines are switched. Compound **21d** could serve as a control to investigate whether the redox gradients do provide the expected advantages in charge migrations.

Electrochemistry. To investigate whether the redox potential of the individual units is maintained in the benzyl ether dendrons, we studied the individual building block units and the dendrons by cyclic voltammetry. The oxidation potentials of **17**, **22a**, and **b** were used as the standard for tetraarylbenzidine, methyl-substituted triarylamine, and fluoro-substituted triarylamine building block units, respectively. Compounds **22a** and **22b** were synthesized from **1a** and **1b**, respectively, as shown in Scheme 5. The electrochemical studies were performed in 0.1 M solution of $(Bu_4N)PF_6$ in 1:1 toluene/acetonitrile mixture with a platinum working electrode. The oxidation potentials are reported here with respect to ferrocene/ferrocenium couple, which was used as the internal standard. The compound **17** exhibited two reversible

SCHEME 5



oxidation peaks. The $E_{1/2}$ values for these oxidations centered at 0.18 and 0.38 V. The compounds **22a** and **22b** exhibited irreversible oxidations and the E_0 values for these compounds are 0.54 and 0.68 V, respectively. The cyclic voltammograms of **17**, **22a**, and **22b** are shown in Figure 1.

Similarly, the redox potentials of the triarylamine and benzidine units in dendrons **19a** and **19b** were investigated (Figure 2). The dendron **19a** exhibited $E_{1/2}$ values at 0.19 and 0.41 V corresponding to the benzidine moiety and an irreversible peak at 0.57 V from the triarylamine unit. Similarly, the compound **19b** exhibited the oxidation potentials corresponding to the benzidine unit at 0.19 and 0.39 V and the fluorotriarylamine unit at 0.72 V.

In the 7-mer dendrons **21a**−**d**, the benzidine oxidations are clear in all four voltammograms (Figure 3). In all four dendrons, the first oxidation for the benzidine unit was 0.20 V and the second oxidation was 0.41 V. In compounds **21a** and **21d**, the irreversible peak corresponding to the interior triarylamine units is clear. In dendron **21a**,

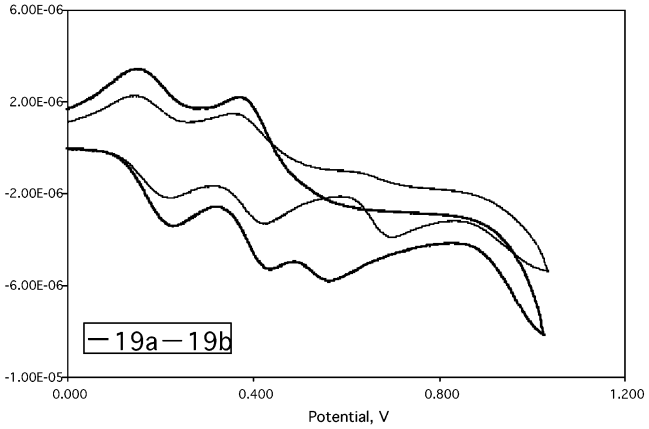


FIGURE 2. Cyclic voltammograms of compounds **19a**,**b**.

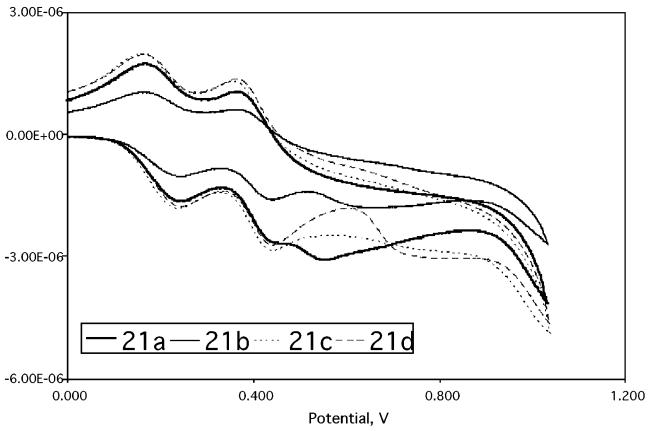


FIGURE 3. Cyclic voltammograms of compounds **21a**−**d**.

the methyl triarylamine oxidation was 0.56 V and in dendron **21d**, the fluorotriarylamine oxidation was 0.74 V. However, in dendrons **21b** and **21c**, the identification of the oxidation potentials for the irreversible peaks posed difficulties due to rather broad peaks. From the voltammogram, it is obvious that oxidation is taking place, but the identification of exact oxidation potential is nontrivial.

The observation of unclear oxidation peaks in dendrons **21b** and **21c** could be attributed to the effect of the ratio of the benzidine units compared to the triarylamines in the intermediate layer and the triarylamine at the core (4:2:1, respectively). Also, note that the internal triarylamines seem more difficult to oxidize by 0.07 V in **19** and **21**. The shift in oxidation potential could be attributed to the literature-documented dendritic encapsulation of redox units.[13] However, note that these potentials are extracted from rather irreversible and broad peaks. Therefore, while the cyclic voltammograms clearly indicate that there is a built-in redox gradient within the dendrons, quantitative estimate of the oxidation potentials of the triarylamines in the dendritic interiors remains challenging. Nevertheless, to further support our claim that these dendrons do have built-in redox gradients, we synthesized the 3-mer dendron **25**. This dendron does not contain benzidine units and therefore the redox waves corresponding to the triarylamine units are much clearer. Synthesis of the dendron **25** is shown in Scheme 6. The observed oxidation potentials of 0.54 and 0.75 V correspond to the methyl- and fluoro-substituted triarylamines, respectively. This result suggests that the charge transport units in these nonconjugated dendrons can be independently tuned.

One possible concern about the design reported here is the usefulness of these dendrons, considering the irreversible nature of the redox waves for the triarylamine building block units. We expect that the time scale of intramolecular charge transfer to afford a stable benzidine cation would be much faster than the decomposition of the radical cation of the triarylamine. Note that triarylamines have been used as hole transport materials in organic light emitting diodes applications.[14] Also, note that it has been previously shown that the decomposition of triarylamine radical cation is much faster on surfaces such as ITO.[15] Therefore, it is likely that the unstable nature of radical cations in triarylamines is exaggerated in electrochemical studies. Moreover, we have previously developed mechanism-based design strategies to stabilize radical cations of triarylamines.[11] This design will be incorporated in our dendrimers, if the stability issues do arise in our future studies.

Conclusion

A series of dendrons that have oxidizable triarylamine based repeat units and benzidine based peripheral units have been designed and synthesized. The connectivities among these units are based on nonconjugated benzyl ether functionalities, to allow the independent tuning of oxidation potentials in each layer of the dendrimer. The dendrimers reported here have the easily oxidizable tetraarylbenzidine units in the periphery and the triarylamines, which are relatively more difficult to oxidize, constitute the interior. Electrochemical studies suggest that the redox potentials of the individual building block units are only slightly altered upon incorporating into a dendritic architecture. These types of molecules could be of interest in a variety of applications that rely on vectorial charge migrations.

Experimental Section

^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer using the residual proton resonance of the solvent as the internal standard. Chemical shifts are reported in parts per million (ppm). When peak multiplicities are given,

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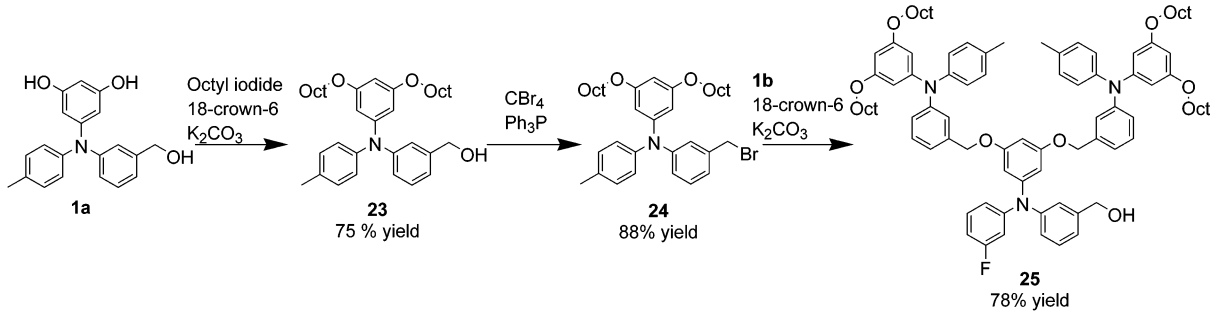
(15) Anderson, J. D. Ph.D. Thesis, University of Arizona, 1999.

SCHEME 6



the following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet; quin., quintet; d of d, doublet of a doublet; m, multiplet; b, broad. ^{13}C NMR spectra were proton decoupled and recorded on a 400 MHz NMR spectrometer using the carbon signal of the deuterated solvent as the internal standard. Due to the highly viscous nature of some of the compounds, the solvent was not completely removed. These solvent peaks are labeled in the proton spectrum reported in the Supporting Information. MALDI-ToF and EI mass spectra were obtained at the Coordinated Instrumentation Facility of Tulane University. Flash chromatography was performed with 37−75 μm silica gel. Analytical thin-layer chromatography was performed on silica plates with F-254 indicator and the visualization was accomplished by UV lamp or using the phosphomolybdic acid stain mixture. THF and toluene were distilled over Na/Ph_2CO ketyl. All other chemicals obtained from commercial sources were used without further purification, unless otherwise mentioned.

Cyclic voltammetry experiments were carried out at room temperature using a conventional three electrodes configuration: a platinum working electrode, platinum auxiliary electrode, and a Ag/Ag^+ reference electrode. The solvent for all the experiments was a 1:1 mixture of acetonitrile and toluene supporting 0.1 M of tetrabutylammonium hexafluorophosphate as the electrolyte. Acetonitrile was distilled over calcium hydride prior to use. The $E_{1/2}$ for the benzidine units was determined as $(E_{ox} + E_{red})/2$. The E_0 for the triarylamines was determined as E_{ox}, since the oxidation was not reversible. All potentials are reported as referenced to Fc/Fc^+ as an internal standard.

General Procedure for the Synthesis of Dendritic Hydroxymethyl Compounds. A mixture of repeat unit (1 equiv), appropriate bromomethyl compound (2 equiv), potassium carbonate (6−8 equiv), 18-crown-6 (catalytic amount), and THF were refluxed under nitrogen for 36−72 h. Water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2).

General Procedure for the Synthesis of Bromomethyl Compounds. To a stirring solution of benzyl alcohol (1 equiv), CBr_4 (1 equiv), and Ph_3P (1 equiv) were added under N_2. The reaction was monitored until completion by TLC. If the reaction was not complete after 10 min, an additional 1 equiv of CBr_4 and Ph_3P were added. Upon completion of the reaction, water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2).

Synthesis of 3,5-Dimethoxy-3′-fluorodiphenylamine (4). To a flame dried three neck round-bottom flask were added $Pd_2(dba)_3$ (897 mg, 0.98 mmol) and DPPF (814 mg, 1.47 mmol) under N_2. Dry toluene (400 mL) was added followed by *m*-bromofluorobenzene (11.4 g, 65.3 mmol) to the stirring reaction mixture. Then, NaO^{t}Bu (6.27 g, 65.3 mmol) and 3,5-dimethoxyaniline (10.0 g, 65.3 mmol) were added to the reaction mixture. The system was then purged with N_2 for 5 min. The mixture was heated at 95 °C for 24 h. The mixture was then cooled, and water was added. The aqueous layer was extracted with toluene and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 20% ethyl acetate in hexanes) to afford 14.96 g (93% yield) of product **4**. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.31−7.25 (m, 1 H), 6.95−6.91 (m, 2 H), 6.74−6.69 (m, 1 H), 6.41 (d, J = 2.1 Hz, 2 H), 6.29−6.28 (t, J = 2.2 Hz, 1 H), 6.16 (s, 1 H), 3.83 (s, 6 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 165.3, 162.8, 162.0, 145.4, 145.3, 144.6, 130.9, 130.8, 113.7, 133.6, 107.5, 107.3, 104.7, 104.5, 97.0, 94.1, 55.4. MS (*m*/*z*, r.i.): 248 (M^+, 19), 247 (100), 246 (21), 218 (41).

Synthesis of 3-Bromo-3′,5′-dimethoxy-3″-fluorotriphenylamine (6). To a flame-dried three-neck round-bottom flask were added $Pd_2(dba)_3$ (790 mg, 0.86 mmol) and DPPF (716 mg, 1.29 mmol) under N_2. Dry toluene (400 mL) was added followed by *m*-dibromobenzene (20.3 g, 8.62 mmol) to the stirring reaction mixture. Then, NaO^{t}Bu (5.52 g, 5.74 mmol) and **4** (14.2 g, 5.74 mmol) were added to the reaction mixture. The system was then purged with N_2 for 5 min. The mixture was heated at 95 °C for 48 h, at which time the reaction was complete as assessed by TLC. The mixture was then cooled, and water was added. The aqueous layer was extracted with toluene and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 10% ethyl acetate in hexanes) to afford 4.23 g (18% yield) of product **6**. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.25−7.22 (m, 1 H), 7.21−7.18 (m, 1 H), 7.17−7.12 (m, 2 H), 7.05−7.02 (m, 1 H), 6.87−6.84 (m, 1 H), 6.79−6.71 (m, 2 H), 6.26−6.25 (m, 1 H), 6.24−6.23 (m, 2 H), 3.71 (s, 6 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.8, 162.4, 161.8, 148.0, 148.8, 148.6, 130.7, 130.6, 130.5, 127.0, 126.2, 122.9, 122.9, 119.5, 119.4, 110.9, 110.7, 109.9, 109.7, 103.9, 96.5, 55.6. MS (*m*/*z*, r.i.): 403 (M^+, 100), 401 (84), 321 (19).

Synthesis of 3-Bromo-3′,5′-dihydroxy-3″-fluorotriphenylamine (7). To a flame-dried flask, **6** (4.01 g, 9.97 mmol) was dissolved in dry CH_2Cl_2 (200 mL). The flask was cooled to −78 °C. To the solution was added BBr_3 (2.72 mL, 29.9 mmol) under N_2. The solution was stirred for 60 h. The solution was quenched with a saturated sodium bicarbonate solution and separated with CH_2Cl_2. The CH_2Cl_2 was evaporated under reduced pressure to afford the crude product, which was purified by column chromatography (SiO_2, 5% ethyl acetate in CH_2Cl_2) afforded 3.36 g (90% yield) of product **7**. ^1H NMR (400 MHz, CD_2Cl_2): δ 7.18−7.01 (m, 4 H), 6.97−6.91 (m, 1 H), 6.77−6.62 (m, 3 H), 6.07−5.97 (m, 3 H), 5.48 (bs, 2 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.8, 162.4, 157.8, 149.1, 148.9, 148.8, 148.6, 130.9, 130.7, 130.6, 127.5, 126.6, 123.4, 122.9, 120.0, 119.9, 111.4, 111.2, 110.3, 110.1, 104.4, 98.8. MALDI-ToF (*m*/*z*): 374.25 (M^+ calcd for $C_{18}H_{13}FNO_2$ 374.2).

Synthesis of 3-Bromo-3′,5′-bis(*tert*-butyldimethylsilyloxy)-3″-fluorotriphenylamine (8). In a round-bottom flask was added **7** (3.2 g, 8.55 mmol) in CH_2Cl_2 (125 mL). To the reaction mixture was added 2,6-lutidine (3.66 g, 34.2 mmol) and TBS-OTf (7.94 g, 34.2 mmol). The reaction mixture was stirred under N_2 for 8 h. Water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure

to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 100% hexanes) to afford 3.51 g (68% yield) of product **8**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.09−6.94 (m, 4 H), 6.88−6.86 (m, 1 H), 6.71−6.69 (m, 1 H), 6.64−6.55 (m, 2 H), 6.06 (s, 2 H), 6.01 (s, 1 H), 0.80 (s, 18 H), 0.01 (s, 12 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 169.3, 166.8, 162.0, 153.4, 153.2, 152.7, 135.1, 135.0, 134.9, 131.4, 130.6, 127.3, 127.2, 124.1, 124.0, 115.5, 115.2, 114.5, 114.3, 113.3, 30.1, 22.8, 0.00. EI-MS (*m*/*z*, r.i.): 603 (M^+, 5), 601 (5), 73 (100), 59 (17), 57 (53), 56 (17).

Synthesis of 3′,5′-Bis(*tert*-butyldimethylsilyloxy)-3″-fluorotriphenylamine-3-carboxaldehyde (9). To a flame-dried round-bottom flask were added **8** (3.42 g, 5.68 mmol) and dry THF (175 mL) under N_2. The mixture was then cooled to −78 °C. To the stirring reaction mixture, 1.7 M solution of ^{t}BuLi (8.3 mL, 14.2 mmol) was added and allowed to stir for 15 min. This was followed by the addition of dry DMF (1.46 mL, 19.9 mmol) and allowed to stir for 30 min. The reaction mixture was then removed from the bath and allowed to stir at room temperature for 24 h. Water was added to the reaction mixture. The aqueous layer was extracted with ether and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 25% CH_2Cl_2 in hexanes) to afford 1.92 g (61% yield) of product **9**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.73 (s, 1 H), 7.45 (s, 1 H), 7.37−7.35 (d, J = 7.2 Hz, 1 H), 7.28−7.20 (m, 2 H), 7.08−7.03 (q, J = 7.6 Hz, 1 H), 6.73−6.71 (d, J = 8.2 Hz, 1 H), 6.66−6.63 (d, J = 10.9 Hz, 1 H), 6.59−6.55 (t, J = 8.1 Hz, 1 H), 6.09 (s, 2 H), 6.04 (s, 1 H), 0.79 (s, 18 H), 0.00 (s, 12 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 196.1, 169.3, 166.9, 162.1, 153.5, 153.4, 152.8, 152.7, 142.4, 135.1, 135.0, 134.6, 134.2, 128.9, 128.8, 124.0, 123.9, 115.4, 115.2, 115.1, 114.6, 114.3, 113.4, 30.2, 22.8, 0.00. EI-MS (*m*/*z*, r.i.): 552 (M^+, 4), 551 (9), 494 (6), 73 (100), 57 (26).

Synthesis of 3-Hydroxymethyl-3′,5′-bis(*tert*-butyldimethylsilyloxy)-3″-fluorotriphenylamine (10). In a round-bottom flask was dissolved **9** (1.82 g, 3.30 mmol) in ethanol (100 mL). To this solution was added $NaBH_4$ (0.15 g, 3.96 mmol), and the mixture was allowed to stir under N_2 for 2 h. Water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 15% ethyl acetate in hexanes) to afford 1.77 g (97% yield) of **10**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.11−7.08 (t, J = 7.8 Hz, 1 H), 7.03−6.95 (m, 2 H), 6.90−6.86 (t, J = 7.9 Hz, 2 H), 6.69−6.67 (d, J = 8.2 Hz, 1 H), 6.62−6.60 (d, J = 11.3 Hz, 1 H), 6.53−6.49 (t, J = 8.1 Hz, 1 H), 6.07 (s, 2 H), 5.99 (s, 1 H), 4.38 (s, 2 H), 2.56 (bs, 1 H), 0.79 (s, 18 H), 0.00 (s, 12 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 169.3, 166.8, 161.9, 154.1, 154.0, 153.3, 151.8, 147.3, 134.8, 134.7, 134.1, 128.5, 127.8, 126.7, 123.4, 123.3, 114.9, 114.8, 114.6, 113.6, 113.4, 112.6, 69.2, 65.1, 30.2, 22.8, 0.0. EI-MS (*m*/*z*, r.i.): 554 (M^+, 6), 553 (14), 364 (6), 133 (8), 75 (43), 73, (100), 57 (37).

Synthesis of 3-Hydroxymethyl-3′,5′-dihydroxy-3″-fluorotriphenylamine (1b). In a round-bottom flask was added **10** (1.58 g, 2.85 mmol). Added to the flask was a 1.0 M solution of TBAF (17 mL, 17.1 mmol). The reaction mixture was allowed to stir under N_2 for 18 h. Water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 50% ethyl acetate in hexanes) to afford 920 mg (99% yield) of **1b**. ^{1}H NMR (400 MHz, CD_3O CD_3): δ 7.30−7.17 (m, 3 H), 7.11−7.09 (d, J = 7.6 Hz, 1 H), 7.01−6.98 (m, 1 H), 6.82−6.80 (m, 1 H), 6.73−6.66 (m, 2 H), 6.16−6.15 (t, J = 2.1 Hz, 1 H), 6.09 (d, J = 2.1 Hz, 2 H), 4.59 (s, 2 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 206.8, 164.7, 162.3, 159.4, 150.1, 150.0, 149.2, 147.3, 144.1, 130.6, 129.6, 129.4, 124.2, 123.8, 123.7, 122.6, 122.5, 118.6, 109.6, 109.4, 109.3, 109.2, 108.6, 108.4, 108.2, 103.7, 103.5, 99.0, 98.8, 63.9, 63.8, 63.6. MALDI-ToF (*m*/*z*): 325.68 (M^+ calcd for $C_{19}H_{16}FNO_3$ 325.3).

Synthesis of 4-Octyloxybromobenzene (12). To a round-bottom flask, *p*-bromophenol (16.7 g, 97.0 mmol) and *n*-octyliodide (27.96 g, 116.4 mmol) were dissolved in dry THF (200 mL). Added to this solution were 18-crown-6 (15.37 g, 58.2 mmol) and K_2CO_3 (40.22 g, 291 mmol). The mixture was refluxed for 48 h. Water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 100% hexanes) to afford 17.11 g (62% yield) of **12**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.42−7.38 (m, 2 H), 6.83−6.79 (m, 2 H), 3.95−3.92 (t, J = 6.6 Hz, 2 H), 1.83−1.76 (quin., J = 7.1 Hz, 2 H), 1.52−1.45 (m, 2 H), 1.40−1.34 (m, 8 H), 0.96−0.93 (m, 3 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 158.6, 132.4, 116.5, 112.5, 68.5, 32.1, 29.6, 29.5, 29.4, 26.3, 23.0, 14.2. MS (*m*/*z*, r.i.): 286 (M^+, 33), 284 (29), 174 (100), 172 (91).

Synthesis of 14. To a flame-dried three-neck round-bottom flask were added $Pd_2(dba)_3$ (0.48 g, 0.53 mmol) and DPPF (0.43 g, 0.79 mmol) under N_2. Dry toluene (400 mL) was added followed by **12** (10.0 g, 35.1 mmol) to the stirring reaction mixture. Then NaO^{t}Bu (3.37 g, 35.1 mmol) and *p*-octyloxyaniline (7.76 g, 35.1 mmol) were added to the reaction mixture. The system was then purged with N_2 for 5 min. The mixture was heated at 90 °C for 5 h, at which time the reaction was complete as assessed by TLC. To the reaction mixture was added NaO^{t}Bu (3.37 g, 35.1 mmol) and 4,4′-dibromobiphenyl (10.94 g, 35.1 mmol), and the mixture was stirred at 90 °C for 15 h. The mixture was then cooled, and water was added. The aqueous layer was extracted with toluene, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 10% CH_2Cl_2 in hexanes) to afford 11.50 g (50% yield) of product **14**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.57−7.52 (m, 2 H), 7.48−7.39 (m, 4 H), 7.14−7.06 (m, 4 H), 6.97−6.89 (m, 2 H), 6.87−6.85 (d, J = 9.0 Hz, 4 H), 3.97−3.94 (t, J = 6.4 Hz, 4 H), 1.83−1.76 (quin, J = 7.0 Hz, 4 H), 1.52−1.45 (m, 4 H), 1.37−1.33 (m, 16 H), 0.95−0.91 (m, 6 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 140.0, 132.0, 131.9, 128.3, 128.1, 127.7, 127.4, 127.1, 123.1, 120.9, 120.5, 115.5, 68.5, 32.1, 29.7, 29.6, 29.5, 26.3, 22.9, 14.2. MALDI-ToF (*m*/*z*): 656.91 (M^+ calcd for $C_{40}H_{50}$ $BrNO_2$ 655.3).

Synthesis of 15. To a flame-dried three-neck round-bottom flask were added $Pd_2(dba)_3$ (0.24 g, 0.26 mmol) and DPPF (0.21 g, 0.38 mmol) under N_2. Dry toluene (300 mL) was added followed by **14** (11.21 g, 17.1 mmol) to the stirring reaction mixture. Then NaO^{t}Bu (1.64 g, 17.1 mmol) and *p*-octyloxyaniline (3.78 g, 17.1 mmol) were added to the reaction mixture. The system was then purged with N_2 for 5 min. The mixture was heated at 90 °C for 5 h, at which time the reaction was complete as assessed by TLC. To the reaction mixture were added NaO^{t}Bu (1.64 g, 17.1 mmol) and 1,3-dibromobenzene (4.83 g, 20.5 mmol); and the mixture was stirred at 90 °C for 38 h, at which time the reaction was complete as assessed by TLC. The mixture was then cooled and water was added. The aqueous layer was extracted with toluene, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 20% CH_2Cl_2 in hexanes) to afford 8.89 g (55% yield) of product **15**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.48−7.41 (m, 2 H), 7.40−7.38 (d, J = 8.6 Hz, 2 H), 7.15−7.14 (t, J = 2.0 Hz, 2 H), 7.09−7.01 (m, 9 H), 6.95−6.92 (m, 3 H), 6.90−6.83 (m, 6 H), 3.97−3.93 (m, 6 H), 1.82−1.74 (m, 6 H), 1.49−1.43 (m, 6 H), 1.39−1.31 (m, 24 H), 0.93−0.89 (m, 9 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 156.7, 146.1, 139.7, 130.5, 128.0, 127.3, 124.2, 124.0, 122.8, 120.2, 115.7, 115.4, 68.5, 32.1, 29.6, 29.6, 29.5, 29.4, 26.3, 22.9, 14.1. MALDI-ToF (*m*/*z*): 951.89 (M^+ calcd for $C_{60}H_{75}$ BrN_2O_3 950.5).

Synthesis of 16. To a flame-dried round-bottom flask, **15** (8.49 g, 8.92 mmol) was added. The solid was dissolved in dry THF (250 mL) under N_2. Once completely dissolved, the

reaction mixture was cooled to −78 °C. To the stirring reaction mixture was added a 1.7 M solution of ^{t}BuLi (11.5 mL, 19.6 mmol) and the mixture was allowed to stir for 15 min. This was followed by the addition of dry DMF (2.42 mL, 31.2 mmol) and allowed to stir for 30 min. The reaction mixture was then removed from the bath and allowed to stir at room temperature for 18 h. Water was added to the reaction mixture. The aqueous layer was extracted with ether, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 35% CH_2Cl_2 in hexanes) to afford 5.43 g (68% yield) of product **16**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 9.87 (s, 1 H), 7.48−7.45 (m, 3 H), 7.41−7.35 (m, 4 H), 7.31−7.28 (m, 1 H), 7.12−7.05 (m, 7 H), 6.95−6.87 (m, 5 H), 6.85−6.83 (d, J = 9.0 Hz, 4 H), 3.98−3.92 (m, 6 H), 1.83−1.74 (m, 6 H), 1.48−1.43 (m, 6 H), 1.39−1.31 (m, 24 H), 0.92−0.89 (m, 9 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 192.4, 156.8, 149.3, 146.2, 156.8, 139.7, 137.8, 135.6, 129.9, 128.0, 127.3, 124.1, 122.5, 121.7, 115.7, 115.4, 68.5, 32.1, 29.6, 29.6, 29.5, 29.4, 26.3, 22.9, 14.1. MALDI-ToF (m/z): 901.25 (M^+ calcd for $C_{61}H_{75}N_2O_4$ 900.6).

Synthesis of 17. In a round-bottom flask, **16** (5.30 g, 5.89 mmol) was dissolved in ethanol (300 mL). To this solution was added $NaBH_4$ (0.27 g, 7.06 mmol), and the mixture was allowed to stir under N_2 for 13 h. Water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 70% CH_2Cl_2 in hexanes) to afford 5.31 g (97% yield) of **17**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.43−7.38 (m, 4 H), 7.24−7.20 (t, J = 7.8 Hz, 1 H), 7.09−7.04 (m, 9 H), 6.99−6.94 (m, 4 H), 6.88−6.83 (m, 6 H), 4.56−4.55 (d, J = 5.7 Hz, 2 H), 3.97−3.93 (m, 6 H), 1.91−1.88 (t, J = 5.9 Hz, 1 H), 1.84−1.76 (m, 6 H), 1.65−1.45 (m, 6 H), 1.41−1.31 (m, 24 H), 0.95−0.91 (m, 9 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 156.3, 155.8, 148.6, 148.0, 147.0, 142.6, 140.9, 140.5, 134.4, 132.6, 129.4, 128.9, 127.7, 127.0, 126.8, 123.3, 121.9, 121.1, 120.9, 120.4, 115.5, 115.4, 68.5, 65.1, 32.1, 29.6, 29.6, 29.5, 26.3, 22.9, 14.2. MALDI-ToF (m/z): 906.07 (M^+ calcd for $C_{61}H_{79}N_2O_4$ 902.6).

Synthesis of 18. Compound **17** (2.00 g, 2.22 mmol), Ph_3P (0.58 g, 2.22 mmol), CBr_4 (0.73 g, 2.22 mmol), and THF (100 mL) were used. The crude product was purified using 20% CH_2Cl_2 in hexanes as the eluent. Yield: 2.00 g (93%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.45−7.38 (m, 4 H), 7.21−7.17 (t, J = 7.9 Hz, 1 H), 7.10−7.06 (m, 9 H), 6.98−6.95 (m, 3 H), 6.90−6.83 (m, 7 H), 4.41 (s, 2 H), 3.98−3.93 (m, 6 H), 1.83−1.75 (m, 6 H), 1.49−1.44 (m, 6 H), 1.39−1.32 (m, 24 H), 0.93−0.89 (m, 9 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 156.5, 146.6, 139.1, 129.6, 127.8, 127.2, 123.7, 122.5, 122.2, 115.6, 68.5, 34.0, 32.1, 29.6, 29.5, 29.4, 26.3, 22.9, 14.1. MALDI-ToF (m/z): 966.55 (M^+ calcd for $C_{61}H_{77}BrN_2O_3$ 964.5).

Synthesis of 3-Mer Alcohol (19a). Compounds **1a** (180 mg, 0.56 mmol) and **18** (1.08 g, 1.12 mmol), 18-crown-6 (148 mg, 0.56 mmol), K_2CO_3 (464 mg, 3.36 mmol), and THF (60 mL) were used. The reaction was refluxed for 60 h. The crude product was purified using 45% CH_2Cl_2 in hexanes as the eluent. Yield: 920 mg (79%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.42−7.38 (t, J = 9.2 Hz, 8 H), 7.24−7.19 (d of t, J_{ab} = 7.8 Hz, J_{ac} = 1.9 Hz, 2 H), 7.10−7.04 (m, 22 H), 7.01−6.95 (m, 12 H), 6.88−6.85 (m, 12 H), 6.25 (d, J = 2.0 Hz, 2 H), 6.19−6.18 (t, J = 2.0 Hz, 1 H), 4.82 (s, 4 H), 4.54 (s, 2 H), 3.98−3.95 (t, J = 6.5 Hz, 12 H), 2.34 (s, 3 H), 1.88−1.79 (m, 12 H), 1.53−1.48 (m, 12 H), 1.39−1.37 (m, 48 H), 0.98−0.95 (m, 18 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.5, 156.3, 155.8, 150.0, 148.5, 148.1, 148.0, 146.8, 145.1, 142.7, 141.0, 140.4, 138.3, 134.6, 133.5, 132.6, 130.2, 129.5, 127.7, 127.1, 126.8, 125.6, 123.4, 122.7, 122.1, 121.6, 121.3, 121.0, 120.9, 115.6, 115.5, 102.9, 96.3, 70.1, 68.5, 65.0, 32.1, 29.7, 29.6, 29.5, 26.4, 23.0, 14.2. MALDI-ToF (m/z): 2087.56 (M^+ calcd for $C_{142}H_{171}N_5O_9$ 2090.3).

Synthesis of 3-Mer Alcohol (19b). Compounds **1b** (51 mg, 0.16 mmol) and **18** (300 mg, 0.31 mmol), 18-crown-6 (41 mg, 0.16 mmol), K_2CO_3 (85 mg, 0.62 mmol), and THF (25 mL) were used. The reaction was refluxed for 72 h. The crude product was purified using 50% CH_2Cl_2 in hexanes as the eluent. Yield: 260 mg (80%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.42−7.34 (m, 8 H), 7.26−7.11 (m, 4 H), 7.09−6.91 (m, 29 H), 6.89−6.82 (m, 12 H), 6.74−6.64 (m, 3 H), 6.26−6.25 (d, J = 2.0 Hz, 2 H), 6.24−6.23 (m, 1 H), 4.82 (s, 4 H), 4.55 (s, 2 H), 3.96−3.91 (m, 12 H), 1.81−1.74 (p, J = 7.0 Hz, 12 H), 1.48−1.44 (m, 12 H), 1.36−1.32 (m, 48 H), 0.93−0.86 (m, 18 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 164.9, 162.5, 160.7, 156.5, 155.9, 149.7, 149.6, 149.2, 148.7, 148.2, 147.5, 146.9, 143.2, 141.0, 140.4, 138.2, 134.7, 132.7, 130.4, 129.8, 129.6, 127.9, 127.2, 126.9, 124.6, 123.8, 122.6, 122.2, 121.7, 121.1, 121.0, 119.2, 115.7, 115.6, 109.3, 104.5, 97.7, 70.3, 68.2, 65.0, 32.2, 29.8, 29.7, 29.6, 26.4, 23.1, 14.3. MALDI-ToF (m/z): 2104.47 (M^+ + Na calcd for $C_{140}H_{166}FN_5O_9$ 2104.8).

Synthesis of 3-Mer Bromide (20a). The 3-mer alcohol **19a** (1.09 g, 0.52 mmol), CBr_4 (173 mg, 0.52 mmol), Ph_3P (137 mg, 0.52 mmol), and THF (60 mL) were used. The crude product was purified using 35% CH_2Cl_2 in hexanes as the eluent. Yield: 970 mg (87%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.30−7.22 (m, 7 H), 7.08−7.03 (m, 6 H), 6.98−6.72 (m, 43 H), 6.10−6.09 (d, J = 2.1 Hz, 2 H), 6.06−6.05 (t, J = 2.3 Hz, 1 H), 4.71 (s, 4 H), 4.26 (s, 2 H), 3.84−3.81 (t, J = 6.5 Hz, 12 H), 2.21 (s, 3 H), 1.71−1.64 (m, 12 H), 1.38−1.33 (m, 12 H), 1.25−1.21 (m, 48 H), 0.81−0.79 (m, 18 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.4, 149.6, 148.2, 146.8, 144.6, 139.1, 133.9, 130.2, 129.7, 127.1, 125.8, 124.1, 123.6, 123.3, 123.0, 115.5, 103.1, 96.7, 70.1, 68.5, 33.9, 32.1, 29.6, 29.5, 29.4, 26.3, 22.9, 20.8, 14.1. MALDI-ToF (m/z): 2152.03 (M^+ calcd for $C_{142}H_{170}BrN_5O_8$ 2152.2).

Synthesis of 3-Mer Bromide (20b). The 3-mer alcohol **19b** (220 mg, 0.11 mmol), CBr_4 (35 mg, 0.11 mmol), Ph_3P (28 mg, 0.11 mmol), and THF (10 mL) were used. The crude product was purified using 40% CH_2Cl_2 in hexanes as the eluent. Yield: 190 mg (84%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.82−7.36 (m, 8 H), 7.23−6.68 (m, 48 H), 6.27−6.25 (m, 3 H), 4.82 (s, 4 H), 4.38 (s, 2 H), 3.95−3.92 (t, J = 6.3 Hz, 12 H), 1.81−1.74 (quin, J = 7.0 Hz, 12 H), 1.49−1.44 (m, 12 H), 1.37−1.32 (m, 48 H), 0.93−0.90 (m, 18 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.5, 160.8, 149.4, 149.3, 149.0, 147.6, 139.6, 130.7, 130.6, 130.1, 125.4, 124.9, 124.4, 123.5, 119.6, 115.7, 111.0, 109.8, 109.6, 104.6, 98.0, 70.4, 68.6, 32.2, 29.8, 29.7, 29.6, 23.1, 14.3. MALDI-ToF (m/z) 2080.58 (M^+ − Br calcd for $C_{141}H_{167}BrFN_5O_8$ 2078.8).

Synthesis of 7-Mer Alcohol (21a). Compound **1a** (41 mg, 0.13 mmol), the 3-mer bromide **20a** (550 mg, 0.26 mmol), 18-crown-6 (34 mg, 0.13 mmol), K_2CO_3 (141 mg, 1.02 mmol), and THF (40 mL) were used. The reaction was refluxed for 72 h. The crude product was purified using 10% ethyl acetate in hexanes as the eluent. Yield: 450 mg (79%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.33−7.31 (d, J = 7.6 Hz, 15 H), 7.16−7.11 (m, 9 H), 7.03−6.78 (m, 96 H), 6.16 (d, J = 2.1 Hz, 4 H), 6.15 (d, J = 2.0 Hz, 2 H), 6.11−6.08 (m, 3 H), 4.75 (s, 8 H), 4.67 (s, 4 H), 4.48−4.47 (d, J = 5.5 Hz, 2 H), 3.91−3.88 (m, 24 H), 2.36 (m, 9 H), 1.79−1.71 (m, 24 H), 1.45−1.43 (m, 24 H), 1.40−1.30 (m, 96 H), 0.91−0.87 (m, 36 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.4, 130.1, 129.4, 127.1, 125.6, 123.3, 115.5, 102.9, 68.5, 32.1, 29.6, 29.5, 29.4, 26.3, 22.9, 14.1. MALDI-ToF (m/z): 4483.96 (M^+ + Na calcd for $C_{304}H_{357}N_{11}O_{19}$ 4488.7).

Synthesis of 7-Mer Alcohol (21b). Compound **1b** (23 mg, 0.070 mmol), the 3-mer bromide **20a** (300 mg, 0.14 mmol), 18-crown-6 (17 mg, 0.070 mmol), K_2CO_3 (58 mg, 0.42 mmol), and THF (25 mL) were used. The reaction was refluxed for 36 h. The crude product was purified using 10% ethyl acetate in hexanes as the eluent. Yield: 247 mg (79%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.35−7.32 (t, J = 8.4 Hz, 16 H), 7.24−7.09 (m, 10 H), 7.04−6.94 (m, 46 H), 6.93−6.88 (m, 22 H), 6.83−6.62 (m, 26 H), 6.28−6.13 (m, 9 H), 4.76 (s, 8 H), 4.72 (s, 4 H), 4.53 (s, 2 H), 3.94−3.89 (m, 24 H), 2.28 (s, 6 H), 1.81−1.74 (m, 24 H), 1.47−1.45 (m, 24 H), 1.36−1.32 (m, 96 H), 0.94−0.90 (m, 36 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.8, 160.5, 156.4, 155.9, 149.9, 148.2, 148.1, 146.9, 145.0, 141.0, 140.4, 138.3, 138.2, 134.2, 133.7, 132.7, 130.3, 129.6, 127.8, 127.2, 126.9,

125.8, 123.7, 123.5, 122.5, 122.2, 121.7, 121.0, 115.7, 115.5, 70.2, 68.6, 32.2, 29.8, 29.7, 29.6, 26.4, 23.1, 14.3. MALDI-ToF (*m*/*z*): 4478.17 (M^+ calcd for $C_{303}H_{354}FN_{11}O_{19}$ 4473.1).

Synthesis of 7-Mer Alcohol (21c). Compound **1a** (48 mg, 0.15 mmol), the 3-mer bromide **20b** (640 mg, 0.30 mmol), 18-crown-6 (37 mg, 0.15 mmol), K_2CO_3 (123 mg, 0.89 mmol), and THF (70 mL) were used. The reaction was refluxed for 48 h. The crude product was purified using 15% ethyl acetate in hexanes as the eluent. Yield: 440 mg (66%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.39−7.35 (m, 16 H), 7.26−7.12 (m, 12 H), 7.07−7.01 (m, 50 H), 6.97−6.94 (m, 20 H), 6.85−6.83 (m, 16 H), 6.72−6.65 (m, 6 H), 6.47−6.23 (m, 8 H), 6.17 (s, 1 H), 4.84−4.81 (m, 8 H), 4.76 (s, 4 H), 4.52 (s, 2 H), 3.96−3.93 (m, 24 H), 2.31 (s, 3 H), 1.80−1.79 (m, 24 H), 1.50 (m, 24 H), 1.38−1.28 (m, 96 H), 0.95−0.93 (m, 36 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 162.5, 160.8, 160.6, 156.5, 155.9, 149.6, 149.1, 148.2, 147.5, 146.9, 145.2, 142.9, 141.5, 138.8, 138.2, 134.7, 132.7, 130.4, 149.7, 127.9, 127.2, 126.9, 123.6, 122.2, 121.7, 121.0, 115.6, 68.6, 32.3, 29.8, 29.7, 29.6, 26.5, 23.2, 14.4. MALDI-ToF (*m*/*z*) 4501.12 (M^+ calcd for $C_{302}H_{351}F_2N_{11}O_{19}$ 4500.1).

Synthesis of 7-Mer Alcohol (21d). Compound **1b** (28 mg, 0.086 mmol), the 3-mer bromide **20b** (372 mg, 0.17 mmol), 18-crown-6 (21 mg, 0.086 mmol), K_2CO_3 (95 mg, 0.69 mmol), and THF (30 mL) were used. The reaction was refluxed for 48 h. The crude product was purified using 50% CH_2Cl_2 in hexanes as the eluent. Yield: 127 mg (33%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.39−7.34 (m, 16 H), 7.26−7.11 (m, 10 H), 7.05−6.99 (m, 38 H), 6.96−6.92 (m, 17 H), 6.84−6.76 (m, 25 H), 6.72−6.61 (m, 14 H), 6.26−6.25 (m, 9 H), 6.24−6.23 (m, 3 H), 4.82 (s, 8 H), 4.55 (s, 6 H), 3.95−3.91 (m, 24 H), 1.81−1.74 (m, 24 H), 1.45 (m, 24 H), 1.34−1.32 (m, 96 H), 0.93−0.90 (m, 36 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.7, 156.5, 155.9, 149.2, 148.6, 148.2, 147.4, 146.9, 143.2, 141.0, 140.3, 138.2, 134.7, 132.7, 129.6, 127.2, 126.2, 123.5, 122.2, 121.7, 121.0, 115.6, 70.3, 68.6, 65.0, 32.2, 29.8, 29.7, 29.6, 26.4, 23.1, 14.3. MALDI-ToF (*m*/*z*): 4506.40 (M^+ + Na calcd for $C_{301}H_{348}F_3N_{11}O_{19}$ 4504.7).

Synthesis of 22a. In a round-bottom flask were dissolved **1a** (100 mg, 0.31 mmol) and benzyl bromide (106 mg, 0.62 mmol) in dry THF (30 mL). Added to this solution were 18-crown-6 (41 mg, 0.16 mmol) and K_2CO_3 (430 mg, 3.1 mmol). The mixture was refluxed for 20 h. Water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 100% CH_2Cl_2) to afford 139 mg (89% yield) of **22a**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.40−7.32 (m, 10 H), 7.25−7.22 (t, J = 7.8 Hz, 1 H), 7.13−7.10 (m, 2 H), 7.07 (s, 1 H), 7.02−6.98 (m, 4 H), 6.30−6.28 (m, 3 H), 4.93 (s, 4 H), 4.54 (s, 2 H), 2.35 (s, 3 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 160.7, 150.2, 148.2, 145.1, 142.8, 137.3, 133.7, 130.3, 129.6, 128.8, 128.2, 127.9, 125.8, 123.6, 122.9, 121.5, 102.7, 96.1, 70.2, 65.1, 20.9. MALDI-ToF (*m*/*z*): 501.72 (M^+ calcd for $C_{34}H_{31}NO_3$ 501.6).

Synthesis of 22b. In a round-bottom flask were dissolved **1b** (100 mg, 0.31 mmol) and benzyl bromide (105 mg, 0.62 mmol) in dry THF (30 mL). Added to this solution were 18-crown-6 (41 mg, 0.15 mmol) and K_2CO_3 (425 mg, 3.1 mmol). The mixture was refluxed for 20 h. Water was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2, and the organic layer was concentrated under reduced pressure to afford the crude reaction mixture, which was purified by column chromatography (SiO_2, 100% CH_2Cl_2) to afford 89 mg (57% yield) of **22b**. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.40−7.22 (m, 11 H), 7.20−7.17 (m, 1 H), 7.13 (s, 1 H), 7.11−7.09 (m, 1 H), 7.06−7.04 (m, 1 H), 6.86−6.84 (m, 1 H), 6.80−6.76 (m, 1 H), 6.74−6.70 (m, 1 H), 6.40−6.39 (m, 1 H), 6.37−6.36 (m, 2 H), 4.96 (s, 4 H), 4.58 (s, 2 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 165.0, 162.5, 160.9, 149.7, 149.6, 149.4, 147.4, 143.2, 137.2, 130.5, 130.4, 129.8, 128.8, 128.3, 128.0, 124.6, 123.8, 122.6, 119.2, 110.6, 110.4, 109.4, 109.1, 104.3, 97.6, 70.3, 64.9. MALDI-ToF (*m*/*z*): 506.82 (M^+ calcd for $C_{33}H_{28}FNO_3$ 505.6).

Synthesis of 3,5-Dioctyloxy-4′-methyl-3″-hydroxymethyltriphenylamine (23). Compound **1a** (500 mg, 1.6 mmol), *n*-octyliodide (747 mg, 3.1 mmol), 18-crown-6 (247 mg, 0.93 mmol), K_2CO_3 (1.29 g, 9.3 mmol), and THF (25 mL) were used. The reaction was refluxed for 48 h. The crude product was purified using 20% ethyl acetate in hexanes as the eluent. Yield: 650 mg (75%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.26−7.22 (t, J = 7.8 Hz, 1 H), 7.14−7.11 (m, 3 H), 7.06−6.99 (m, 4 H), 6.22 (d, J = 2.0 Hz, 2 H), 6.17 (t, J = 1.9 Hz, 1 H), 4.54 (s, 2 H), 3.88−3.85 (t, J = 6.5 Hz, 4 H), 2.72 (bs, 1 H), 2.36 (s, 3 H), 1.78−1.72 (m, 4 H), 1.46−1.28 (m, 20 H), 0.98−0.94 (t, J = 6.7 Hz, 6 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 161.3, 150.2, 148.5, 145.5, 142.3, 133.4, 130.3, 129.6, 125.7, 123.4, 122.7, 121.4, 102.9, 95.8, 68.4, 65.1, 60.8, 32.3, 29.9, 29.8, 29.7, 26.5, 23.2, 14.5. MALDI-ToF (*m*/*z*): 548.14 (M^+ calcd for $C_{36}H_{51}NO_3$ 545.4).

Synthesis of 3,5-Dioctyloxy-4′-methyl-3″-bromomethyltriphenylamine (24). The alcohol **23** (480 mg, 0.88 mmol), CBr_4 (292 mg, 0.88 mmol), Ph_3P (231 mg, 0.88 mmol), and THF (25 mL) were used. The crude product was purified using 10% CH_2Cl_2 in hexanes as the eluent. Yield: 444 mg (88%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.21−7.17 (t, J = 7.9 Hz, 1 H), 7.13−7.06 (m, 3 H), 7.05−6.93 (m, 4 H), 6.20−6.19 (d, J = 2.1 Hz, 2 H), 6.17−6.16 (t, J = 2.1 Hz, 1 H), 4.40 (s, 2 H), 3.86−3.76 (t, J = 6.5 Hz, 4 H), 2.34 (s, 3 H), 1.75−1.68 (m, 4 H), 1.42−1.24 (m, 20 H), 0.96−0.90 (m, 6 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 161.2, 149.6, 148.5, 145.0, 139.1, 133.7, 130.3, 129.6, 125.8, 123.8, 123.4, 122.8, 102.9, 96.2, 68.2, 33.9, 32.1, 29.7, 29.6, 29.5, 26.3, 23.0, 20.9, 14.2. MALDI-ToF (*m*/*z*): 609.57 (M^+ calcd for $C_{36}H_{51}BrNO_2$ 607.3).

Synthesis of 3-Mer Alcohol (25). Compound **1b** (130 mg, 0.40 mmol), compound **23** (448 mg, 0.80 mmol), 18-crown-6 (53 mg, 0.20 mmol), K_2CO_3 (443 mg, 3.2 mmol), and THF (25 mL) were used. The reaction was refluxed for 48 h. The crude product was purified using 60% CH_2Cl_2 in hexanes as the eluent. Yield: 430 mg (78%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.32−7.17 (m, 4 H), 7.14−7.07 (m, 8 H), 7.04−7.00 (m, 9 H), 6.87−6.85 (d of d, J_{ab} = 8.2 Hz, J_{ac} = 1.4 Hz, 1 H), 6.80−6.77 (t of d, J_{ab} = 11.1 Hz, J_{ac} = 2.2 Hz, 1 H), 6.74−6.70 (d of t, J_{ab} = 7.8 Hz, J_{ac} = 2.1 Hz, 1 H), 6.34−6.32 (m, 3 H), 6.25−6.22 (m, 4 H), 6.19−6.18 (m, 2 H), 4.86 (s, 4 H), 4.60−4.59 (d, J = 3.3 Hz, 4 H), 3.87−3.84 (t, J = 6.5 Hz, 2 H), 2.35 (s, 3 H), 1.78−1.71 (quin, J = 6.9 Hz, 8 H), 1.47−1.41 (m, 8 H), 1.35 (bs, 32 H), 0.97−0.93 (m, 12 H). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 165.0, 162.6, 161.2, 160.9, 149.9, 149.8, 149.7, 149.3, 148.5, 147.5, 145.3, 143.3, 138.2, 133.6, 130.5, 130.3, 129.9, 129.6, 125.7, 124.6, 123.8, 123.5, 123.1, 122.6, 121.8, 119.2, 104.5, 103.0, 102.9, 97.6, 96.0, 70.3, 68.3, 65.0, 32.3, 29.8, 29.7, 26.5, 23.1, 21.1, 21.0, 14.4. MALDI-ToF (*m*/*z*): 1383.84 (M^+ calcd for $C_{91}H_{114}FN_3O_7$ 1380.9).

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Supporting Information Available: ^{1}H NMR spectral data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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