

Synthesis of Novel Cross-Conjugated Dendritic Fluorophores Containing Both Phenylenevinylene and Phenyleneethynylene Moieties

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New dendrons and dendrimers with dendritic arms composed of alternate phenyleneethynylene and phenylenevinylene moieties have been efficiently synthesized using orthogonal and convergent syntheses that combine Sonogashira and Horner–Wadsworth–Emmons reactions. Two different iterative routes have been developed that allow specific control over the placement of double and triple bonds within the interior of the dendrimers. A preliminary study of the UV and photoluminescence (PL) properties of the resulting compounds is also described. All of the examples prepared are blue-luminescent.

Introduction

In recent years organic molecules with high photoluminescence efficiencies have been the focus of intensive research effort. Such compounds have been considered as advanced materials for electronic and photonic applications.¹ For this reason, it is important to devise efficient methods for the synthesis of novel fluorophores that are amenable to further chemical functionalization or modification, which in turn can be elaborated to obtain materials with tunable optoelectronic properties. In the context of light-emitting polymers, the search for blue-luminescent compounds is an ongoing challenge.² Three main strategies for the synthesis of blue-emitting polymers have been reported: (i) a random interruption of the conjugation along the chain, (ii) the presence of backbone twists caused by steric interactions,³ and (iii) the use of cross conjugation. The first approach affords polymers that suffer from the drawback that emission usually occurs from the more conjugated segments only. The second set of materials, on the other hand, have very little potential for fine-tuning. Only cross-conjugation gives rise to an efficient and predictable method to interrupt the conjugation in the system.⁴

Monodisperse dendritic materials have emerged as attractive candidates for photonic applications. There has been a substantial body of work published over the past decade regarding the synthesis of new dendrimeric structures and the study of such systems in the develop-

ment of new applications.⁵ Dendrimers with polyconjugated branches represent an important group within this class of material. These compounds are interesting because of their electrical, optical, nonlinear optical, electroluminescent, and photophysical properties. For example, such compounds have been used successfully as both charge transporting⁶ and light-emitting materials.⁷ On the other hand, several authors have also demonstrated that both phenyleneethynylene⁸ and phenylenevinylene dendritic^{7c} arms can function as light-harvesting antennae. Thus, conjugated dendrimers also represent a promising new class of material for organic LEDs.

Several studies have been published to date concerning the synthesis and properties of conjugated light-emitting

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dendrimers based on either the phenylenevinylene or phenyleneethynylene structure. However, to the best of our knowledge there is no precedent for the synthesis of dendrimers whose branches incorporate both of these moieties at the same time—although it has recently been demonstrated that the presence of both double and triple bonds in a conjugated structure has a strong influence on the resulting optoelectronic properties. For example, poly(*p*-phenylenevinylene)s (PPVs) with tolane-bis-benzyl moieties,⁹ conjugated oligomers and polymers with double and triple bonds,¹⁰ and dithiafulvene–acetylene hybrid chromophores¹¹ have been studied as PLEDs, fluorophores, and materials with electronic properties of interest, respectively. In this context, and as a part of our research program aimed at the construction of extended and cross-conjugated π -electronic systems,¹² we planned to develop an efficient orthogonal and convergent synthesis¹³ of new dendrimer architectures containing both phenyleneethynylene and phenylenevinylene in an alternating manner within the dendritic arms. These materials were synthesized using two routes that allow specific control over the placement of double and triple bonds on the interior of the dendrimers. Our plan is based on the combination of two coupling methods: the Sonogashira and Horner–Wadsworth–Emmons (HWE) reactions. These reactions were used in an alternating order to build up each successive layer. The methodology reported here may be used as an accelerated access to a wide range of conjugated dendrimers. We also present a preliminary study of the UV and photoluminescence (PL) properties of the resulting dendrons and dendrimers.

Results and Discussion

Synthesis of Dendrons and Dendrimers. In the convergent, orthogonal approach to the synthesis of dendrimers bearing both phenylenevinylene and phenyleneethynylene linkages, two reactions—the HWE and Sonogashira reactions—were employed alternately to construct the successive layers of dendrons. Three different AB₂-type building blocks (**A**, **B**, and **E**, Scheme 1) were required as starting materials, as well as commercially available 4-dodecyloxybenzaldehyde and (4-pentylphenyl)acetylene, which both bear long-chain substituents aimed at improving the solubility of these systems. The key to the overall strategy is that building blocks **A**, **B**, and **E** possess mutually complementary functional groups at the terminal positions while avoiding

the need for the introduction of additional functional group protection/deprotection steps.

Scheme 1 shows our two approaches to obtain homogeneous single functionality dendrons, which contained either an iodo or formyl group at the focal point.

The first reaction sequence involved the HWE reaction of two molecules of *p*-dodecyloxybenzaldehyde with diphosphonate **A** to form the first generation aryl iodide (OC₁₂H₂₅)₂G**1-I**. This step was followed by a Sonogashira coupling with 3,5-bisethynylbenzaldehyde (**B**) to give the corresponding second generation aldehyde (OC₁₂H₂₅)₄G**2-CHO**. A second HWE reaction between two molecules of the second generation aldehyde and **A** afforded (OC₁₂H₂₅)₈G**3-I**.

The second method started with the Sonogashira coupling of two molecules of (4-pentylphenyl)acetylene with **E** to give the aldehyde dendron (C₅H₁₁)₂G'**1-CHO**. The higher generations were obtained by orthogonal use of the Sonogashira and HWE coupling reactions between the preceding generation and the appropriate building blocks, **A** and **B**, respectively. In this manner the systems up to and including the fourth generation dendron (C₅H₁₁)₁₆G'**4-I** were prepared.

Each generation of the dendrons is functionalized at the central core and so further chemical manipulation was possible. For example, (C₅H₁₁)₈G'**3-CHO** could be used to couple with triphosphonate **D** to give (C₅H₁₁)₂₄G'**4**. Dendrimers (OC₁₂H₂₅)₆G**2**, (OC₁₂H₂₅)₁₂G**3**, (C₅H₁₁)₆G'**2**, and (C₅H₁₁)₁₂G'**3** were also prepared in a similar way by either Sonogashira or HWE reactions from the corresponding dendrons and cores **C** or **D** (Scheme 1). The G'-type dendrimers have their double bonds situated in the odd layers and their triple bonds in the even layers, whereas the G-type dendrimers have these bonds in the opposite sense, i.e., double bonds in even layers and triple bonds in odd layers.

In principle, both reaction sequences could be further progressed through multiple cycles, although in practice one would expect that higher molecules would be difficult to prepare because of the well-documented progressive reduction in the reactivity of the focal point in successive generations. This phenomenon also accounts for the decrease in yield with increasing generation of dendrimer. Thus, unfortunately, the fourth generation dendrimer (OC₁₂H₂₅)₂₄G**4** could not be obtained by reaction of (OC₁₂H₂₅)₈G**3-I** with 1,3,5-trisubstituted benzene, **C**. The MALDI-TOF analysis of the crude product of this reaction did not show any peak in the region of 9067 amu (the value expected for a structure of this size). It is also worth noting that HWE reactions generally gave better yields than Sonogashira couplings.

The peripheral groups selected in this work provided good control of the solubility. All new compounds prepared are highly soluble in THF as well as in chlorinated solvents such as dichloromethane and chloroform, thus allowing purification by conventional silica gel chromatography. A suitable choice of starting materials could provide a wide variety of dendritic architectures with different peripheral moieties, although peripheral pendant groups other than alkyl would be expected to afford molecules with decreased solubility. An example of this potential is shown by the synthesis of the second generation dendrimer **3** starting from the nucleus **1** and the dendron **2** (Scheme 2).

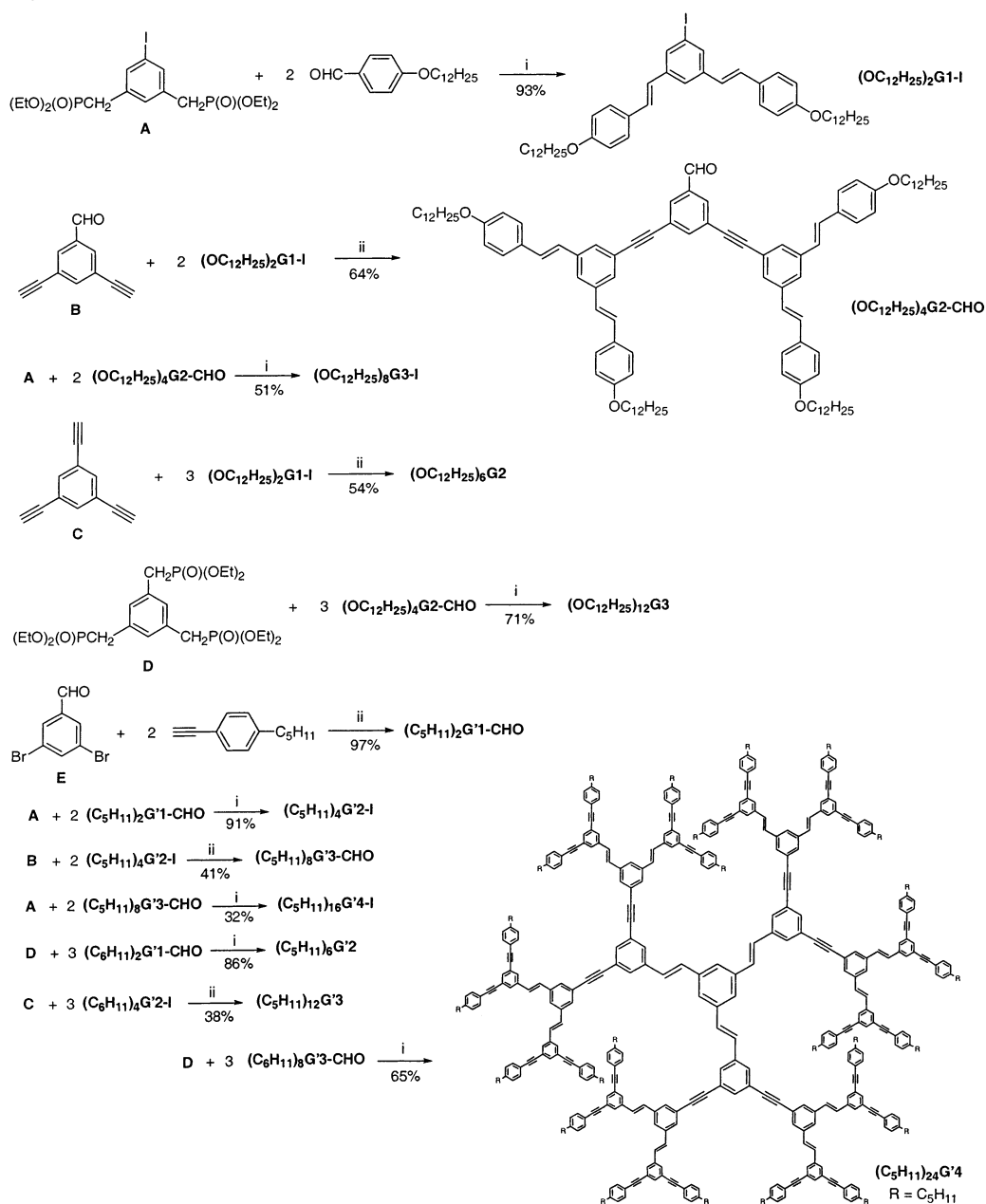
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SCHEME 1. Synthesis of Dendrons and Dendrimers^a

^a Reagents and conditions: (i) KBu^tO , THF; (ii) $\text{PdCl}_2(\text{PPh}_3)_2$, CuI, PPh_3 , $\text{Et}_3\text{N}/\text{DMF}$, 60 °C.

Characterization. All new compounds were characterized by various analytical techniques. MS and NMR experiments proved very useful to confirm the structures of the new compounds (see Experimental Section and Supporting Information). The selectivity of the HWE reaction is sufficiently high to generate all-trans isomers within the limits of NMR detection. This stereochemistry for the double bonds was established on the basis of the coupling constant of the vinylic protons in the ^1H NMR spectra ($J = 16\text{--}17$ Hz).

One drawback in the synthesis of these systems concerns the determination of the purity, which can prove difficult. The ^1H NMR spectra of low-generation compounds are well-resolved and did not show any evidence of impurities. However, the broad lines observed in the

^1H NMR spectra of higher generations preclude the use of this technique for the assessment of purity.

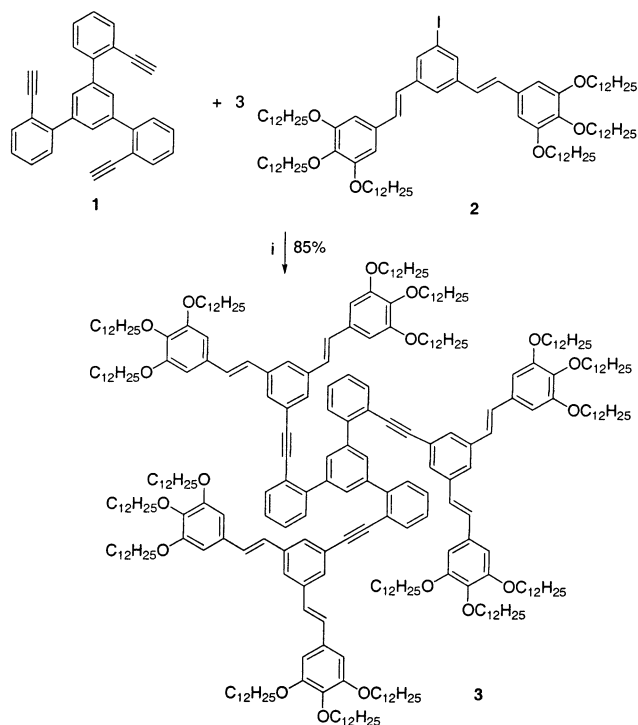
HRMS analyses of first-generation dendrons gave the expected molecular ions. The MALDI-TOF technique proved to be very useful for the identification of the higher structures. All the spectra registered for the higher generations showed peaks matching the calculated molecular weights.

Optical Spectroscopic Studies. The UV-vis absorption and photoluminescence (PL) spectra of the dendrimers and dendrons synthesized were recorded in CH_2Cl_2 at room temperature. The data obtained are summarized in Table 1. As one would expect, the *meta* arrangement through which the dendrons are linked causes the absorption spectra to consist essentially of a simple

TABLE 1. UV/Vis and Photoluminescence (PL) Data

compd	UV/Vis ^a (CH ₂ Cl ₂)	PL ^b (CH ₂ Cl ₂)	Stokes shifts, cm ⁻¹	Φ _f ^c
	λ _{max} , nm (ε, M ⁻¹ cm ⁻¹)	λ _{max} , nm		
(OC ₁₂ H ₂₅) ₄ G ₂ -CHO	322.0 (142 100)	412	6784	<0.01
(OC ₁₂ H ₂₅) ₈ G ₃ -I	321.0 (381 300)	409	6752	0.14
(OC ₁₂ H ₂₅) ₆ G ₂	320.5 (250 800)	412	7027	0.23
(OC ₁₂ H ₂₅) ₁₂ G ₃	321.5 (546 400)	407	6583	0.10
(C ₅ H ₁₁) ₄ G ₂ -I	311.0 (171 100)	377, 393	5630, 6709	0.01
(C ₅ H ₁₁) ₈ G ₃ -CHO	311.5 (424 500)	389, 403	6396, 7289	<0.01
(C ₅ H ₁₁) ₁₆ G ₄ -I	311.5 (958 900)	388	6330	0.06
(C ₅ H ₁₁) ₆ G ₂	311.5 (245 500)	397, 414	6965, 8000	0.12
(C ₅ H ₁₁) ₁₂ G ₃	311.5 (562 500)	388, 403	6330, 7289	0.13
(C ₅ H ₁₁) ₂₄ G ₄	311.0 (1 079 800)	400	7103	0.07

^a All spectra were recorded at room temperature at $c \approx 3 \times 10^{-6}$ M. ^b All spectra were recorded at room temperature at $c \approx 3 \times 10^{-7}$ M. ^c Fluorescence quantum yield in dichloromethane determined relative to quinine sulfate dissolved in 1 N H₂SO₄.

SCHEME 2. Preparation of Compound 3^a

^a Reagents and conditions: (i) PdCl₂(PPh₃)₂, CuI, PPh₃, Et₃N/DMF, 60 °C.

superposition of the absorptions due to the different chromophores, stilbene, and tolane moieties. These molecules are almost colorless and are absolutely transparent above 400 nm (see Figure 1). Only small changes were observed in the onset of the absorption in the UV/Vis spectra of the different generations. The absorptions become much stronger, higher ε, as the dendritic generation increases, a consequence of the increase in the number of light absorbing stilbene and tolane units. The absorption maxima, on the other hand, are very similar since the *meta* linkages between the units cause little change in conjugation as the dendrimer grows. When spectra were registered at lower concentrations (10⁻⁷ range), changes were often observed in the chromicity of the bands, with a higher value of ε usually observed. Very small changes in the shift were also detected. A satisfactory explanation for these effects is not clear at the moment, although, as it has been reported for the UV–

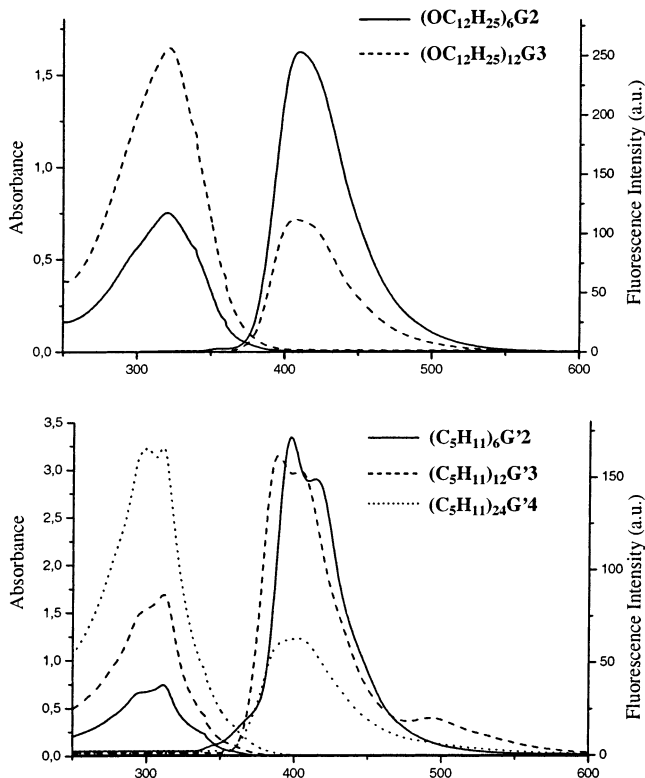


FIGURE 1. (a) Absorption and fluorescence emission spectra of dendrimers (OC₁₂H₂₅)₆G₂ (continuous line) and (OC₁₂H₂₅)₁₂G₃ (dashed line) in CH₂Cl₂. (b) Absorption and fluorescence emission spectra of dendrimers (C₅H₁₁)₆G₂ (continuous line), (C₅H₁₁)₁₂G₃ (dashed line), and (C₅H₁₁)₂₄G₄ (dotted line) in CH₂Cl₂. The fluorescence spectra were measured by exciting at the absorption maxima and are normalized to a constant absorbance.

visible and fluorescence spectra of stilbenoid units,^{14,15} a concentration-dependent aggregation is one possibility that must be considered.

All of the molecules prepared in this work are fluorescent and emit blue light when irradiated at the absorption maxima. The fluorescence quantum yields, Φ_f, were determined by using a solution of quinine sulfate in 1 N

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H₂SO₄ as the reference standard ($\Phi_s = 0.546$). The intensity of the fluorescence from the higher generation dendrimers is substantially lower than that from the lower generations at the same molar concentration. A comparable behavior was noted by Moore et al. in a phenylacetylene dendrimer series,^{8b} as well as in monodendrons based on 9-phenylcarbazole.¹⁶ This phenomenon has been explained because the through-space interaction between the fluorescent units becomes more significant with increasing molecular size, providing additional fluorescence quenching pathways. On the other hand, (C₅H₁₁)₄G'2-I shows a low fluorescence quantum yield that can be attributed to effective quenching by the iodine atom. The heavy atom effect should be lower for (OC₁₂H₂₅)₈G3-I and (C₅H₁₁)₁₆G'4-I because the iodine atoms are far away from the peripheral fluorescent units. The fluorescence of dendrons bearing formyl groups at the focal point is also strongly quenched. The higher quantum yield observed for (OC₁₂H₂₅)₆G2 when compared with (C₅H₁₁)₆G'2 might be a consequence of the different peripheral functionalization, although the bigger dendrimers, (OC₁₂H₂₅)₁₂G3 and (C₅H₁₁)₁₂G'3, showed similar values. A complete explanation of these results is beyond the scope of this work and will need further investigations. The magnitudes of the Stokes shifts decrease as the generation number increases, a situation that has also been observed in a phenylenevinylene series.¹²

Conclusions

New dendrons and dendrimers with alternating phenyleneethynylene and phenylenevinylene units in the dendritic arms have been effectively synthesized up to the fourth generation using orthogonal and convergent synthetic routes that combine Sonogashira and Horner–Wadsworth–Emmons reactions. The choice of the appropriate iterative route afforded specific control over the placement of double and triple bonds within the interior of the dendrimers. The *meta*-substitution pattern causes all chromophores to be independent and all of the molecules showed good transparency in the visible region. In addition, cross-conjugation led to blue-luminescent molecules.

Experimental Section

General experimental conditions have been reported previously.¹² NMR spectra were recorded in CDCl₃ solutions. Chemical shifts are given in ppm relative to TMS (¹H, 0.0 ppm) or CDCl₃ (¹³C, 76.9 ppm). All commercially available compounds were used without further purification. The following chemicals were prepared according to literature procedures: 1,3,5-trisethynylbenzene (**C**),¹⁷ 1,3,5-tris(diethoxyphosphorylmethyl)benzene (**D**),¹⁸ 3,5-dibromobenzaldehyde (**E**),¹⁸ 1,3,5-(*o*-ethynylphenyl)benzene (**1**),¹⁹ and 3,4,5-tridodecyloxybenzaldehyde.²⁰ Diphosphonate **A** was prepared by Arbuzov reaction of 1,3-bis(bromomethyl)-5-iodobenzene²¹ with triethyl phosphite following a standard methodology. 3,5-Bisethynyl-

benzaldehyde, **B**, was prepared by Sonogashira coupling of **E** and trimethylsilylacetylene followed by desilylation with NaOH/THF/H₂O. See the Supporting Information for full experimental procedures and spectroscopic data.

General Procedures for Horner–Wadsworth–Emmons Reactions. Method A. All glassware was oven-dried and cooled under Ar. To a stirred solution of the corresponding phosphonate and aromatic aldehyde in anhydrous THF (30 mL per mmol of aldehyde), under argon, was added potassium *tert*-butoxide in small portions (3 equiv per phosphonate group). The deeply colored mixture was stirred at room temperature for the period of time indicated. After hydrolysis with water, the mixture was concentrated under vacuum and the precipitated solid was filtered off. **Method B.** All operations were identical with those described for method A except that, after hydrolysis with water, the mixture was extracted with CH₂Cl₂ (×3). The combined organic layers were successively washed with water and brine, and then dried (MgSO₄). The solution was filtered and the solvent evaporated under reduced pressure. The crude products were purified by column chromatography (silica gel) and/or crystallization as indicated.

General Procedure for Sonogashira Reactions. All glassware was oven-dried and cooled under Ar. To a stirred solution of the corresponding alkyne and aromatic iodide in anhydrous DMF/Et₃N (1:1, 30 mL per mmol of iodide) and molecular sieves (4 Å) heated at 60 °C under argon was added a catalyst mixture of 5% PdCl₂(PPh₃)₂, 5% CuI, and 10% PPh₃. The mixture was stirred for the indicated period of time at 60 °C. After evaporation of the solvent under reduced pressure, chloroform was added and the molecular sieves were filtered off. The solution was washed with saturated ammonium chloride and brine and then dried (MgSO₄). The solution was filtered and the chloroform evaporated under vacuum. The crude products were purified by column chromatography (silica gel) and/or crystallization as indicated. In many cases, a second chromatographic purification was performed.

(OC₁₂H₂₅)₂G1-I: method A; reaction time 2 h; purified by crystallization from CHCl₃/EtOH; white solid; yield 93%. ¹H NMR (CDCl₃) δ 0.88 (t, 6H, *J* = 6.6 Hz), 1.2–1.6 (m, 36H), 1.79 (m, 4H), 3.98 (t, 4H, *J* = 6.6 Hz), 6.86 (A of ABq, 2H, *J* = 16.5 Hz), 6.90 (A of ABq, 4H, *J* = 8.7 Hz), 7.07 (B of ABq, 2H, *J* = 16.5 Hz), 7.44 (B of ABq, 4H, *J* = 8.7 Hz), 7.49 (br s, 1H), 7.69 (d, 2H, *J* = 1.5 Hz). ¹³C NMR and DEPT (CDCl₃): δ 159.2 (C), 140.0 (C), 133.4 (CH), 129.7 (CH), 129.4 (C), 127.9 (CH), 124.6 (CH), 123.7 (CH), 114.7 (CH), 95.2 (C), 68.1 (CH₂), 31.9 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 26.0 (CH₂), 22.7 (CH₂), 14.1 (CH₃). MS (EI) *m/e* 776.7 (88), 440.2 (15), 269.2 (19), 253.2 (36), 251.2 (12), 228.2 (15), 213.2 (100), 207.1 (13), 165.1 (9), 119.1 (36). HRMS, *m/e* calcd for C₄₆H₆₅IO₂ 776.4029, found 776.4077.

(OC₁₂H₂₅)₄G2-CHO: reaction time 20 h; purified by column chromatography (hexanes/CH₂Cl₂, 8:2) followed by washing with hot EtOH, further purification was achieved by crystallization from hexanes; white solid; yield 64%. ¹H NMR (CDCl₃) δ 0.89 (t, 12H, *J* = 6.9 Hz), 1.2–1.6 (m, 72H), 1.79 (m, 8H), 3.98 (t, 8H, *J* = 6.6 Hz), 6.90 (A of ABq, 8H, *J* = 8.7 Hz), 6.95 (A of ABq, 4H, *J* = 16.2 Hz), 7.13 (B of ABq, 4H, *J* = 16.2 Hz), 7.45 (B of ABq, 8H, *J* = 8.4 Hz), 7.54 (s, 6H), 7.95 (t, 1H, *J* = 1.5 Hz), 7.98 (d, 2H, *J* = 1.5 Hz), 10.02 (s, 1H). ¹³C NMR and DEPT (CDCl₃) δ 190.8 (CHO), 159.2 (C), 139.6 (CH), 138.4 (C), 136.7 (C), 132.0 (CH), 129.5 (CH), 127.8 (CH), 125.2 (CH), 124.9 (CH), 123.0 (C), 114.8 (CH), 91.7 (C), 87.1 (C), 68.1 (CH₂), 31.9 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.6 (CH₂), 29.4 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 26.1 (CH₂), 22.7 (CH₂), 14.1 (CH₃). MALDI-TOF (C₁₀₃H₁₃₄O₅), *m/e* 1452.0.

(OC₁₂H₂₅)₈G3-I: method B; reaction time 2 h; purified by column chromatography (hexanes/CH₂Cl₂, 8:2) followed by crystallization from CHCl₃/EtOH; pale yellow solid; yield 51%.

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^1H NMR (CDCl_3) δ 0.88 (t, 24H, $J = 6.6$ Hz), 1.2–1.5 (m, 144H), 1.75 (m, 16H), 3.90 (t, 16H, $J = 6.6$ Hz), 6.84 (A of ABq, 16H, $J = 8.7$ Hz), 6.8–7.1 (m, 20H), 7.40 (B of ABq, 16H, $J = 8.7$ Hz), 7.4–7.7 (m, 21H). ^{13}C NMR and DEPT (CDCl_3) δ 159.0 (C), 139.2 (C), 138.2 (C), 137.2 (C), 134.7 (CH), 133.9 (CH), 129.5 (CH), 129.2 (CH), 128.4 (CH), 128.2 (CH), 127.8 (CH), 127.4 (C), 125.3 (CH), 124.6 (CH), 124.3 (C), 124.1 (C), 123.4 (C), 114.7 (CH), 92.5 (C), 90.5 (C), 88.4 (C), 68.0 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3). MALDI-TOF ($\text{C}_{214}\text{H}_{273}\text{IO}_8$), m/e 3099.7.

(OC₁₂H₂₅)₆G₂: reaction time 24 h; purified by column chromatography (hexanes/ CH_2Cl_2 , 9:1) followed by washing with hot hexanes; pale yellow solid; yield 54%. ^1H NMR (CDCl_3) δ 0.88 (t, 18H, $J = 6.9$ Hz), 1.2–1.6 (m, 108H), 1.79 (m, 12H), 3.97 (t, 12H, $J = 6.6$ Hz), 6.90 (A of ABq, 12H, $J = 8.7$ Hz), 6.94 (A of ABq, 6H, $J = 16.2$ Hz), 7.13 (B of ABq, 6H, $J = 16.2$ Hz), 7.46 (B of ABq, 12H, $J = 9.0$ Hz), 7.54 (br s, 9H), 7.72 (s, 3H). ^{13}C NMR (CDCl_3) δ 159.1, 138.3, 134.2, 129.6, 129.4, 127.9, 127.9, 125.4, 124.7, 124.1, 123.4, 114.7, 90.7, 87.8, 68.1, 31.9, 29.7, 29.6, 29.6, 29.6, 29.4, 29.4, 29.3, 26.1, 22.7, 14.1. MALDI-TOF ($\text{C}_{150}\text{H}_{198}\text{O}_6$), m/e 2096.6.

(OC₁₂H₂₅)₁₂G₃: method B; reaction time 1 h; purified by column chromatography (CH_2Cl_2) followed by washing with hot EtOH; white solid; yield 71%. ^1H NMR (CDCl_3) δ 0.88 (t, 36H, $J = 6.6$ Hz), 1.2–1.6 (m, 216H), 1.73 (m, 24H), 3.89 (t, 24H, $J = 6.6$ Hz), 6.7–7.7 (m, 90H). ^{13}C NMR and DEPT (CDCl_3) δ 158.9 (C), 138.0 (C), 137.5 (C), 137.5 (C), 129.6 (C), 129.4 (CH), 129.0 (CH), 127.8 (CH), 125.3 (CH), 124.5 (CH), 124.1 (C), 123.5 (CH), 114.6 (CH), 90.5 (C), 88.7 (C), 68.0 (CH_2), 31.9 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3). MALDI-TOF ($\text{C}_{318}\text{H}_{408}\text{O}_{12}$), m/e 4422.6.

(C₅H₁₁)₂G₁-CHO: reaction time 7 h; purified by column chromatography (hexanes/ CH_2Cl_2 , 8:2); colorless oil; yield 97%. ^1H NMR (CDCl_3) δ 0.90 (t, 6H, $J = 6.9$ Hz), 1.2–1.4 (m, 8H), 1.55–1.70 (m, 4H), 2.62 (t, 4H, $J = 7.5$ Hz), 7.19 (A of ABq, 4H, $J = 8.3$ Hz), 7.46 (B of ABq, 4H, $J = 8.3$ Hz), 7.89 (t, 1H, $J = 1.5$ Hz), 7.94 (d, 2H, $J = 1.5$ Hz), 10.00 (s, 1H). ^{13}C NMR and DEPT (CDCl_3) δ 190.9 (CHO), 144.1 (C), 139.4 (CH), 136.6 (C), 131.6 (CH), 128.6 (CH), 125.1 (C), 119.6 (C), 91.7 (C), 86.6 (C), 35.9 (CH_2), 31.4 (CH_2), 30.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3). MS (EI) m/e 446.3 (100), 389.2 (60), 343.1 (11), 332.1 (25), 166.2 (14). HRMS, m/e calcd for $\text{C}_{33}\text{H}_{34}\text{O}$ 446.2610, found 446.2590.

(C₅H₁₁)₄G₂-I: method B; reaction time 2 h; purified by crystallization from $\text{CHCl}_3/\text{EtOH}$; white solid; yield 91%. ^1H NMR (CDCl_3) δ 0.90 (t, 12H, $J = 6.6$ Hz), 1.20–1.45 (m, 16H), 1.63 (m, 8H, $J = 7.8$ Hz), 2.62 (t, 8H, $J = 7.8$ Hz), 7.06 (s, 4H), 7.18 (A of ABq, 8H, $J = 8.4$ Hz), 7.47 (B of ABq, 8H, $J = 8.4$ Hz), 7.56 (br s, 1H), 7.60–7.62 (m, 6H), 7.77 (d, 2H, $J = 1.5$ Hz). ^{13}C NMR and DEPT (CDCl_3) δ 143.7 (C), 139.3 (C), 137.1 (C), 134.6 (CH), 133.7 (CH), 131.6 (CH), 129.2 (CH), 128.8 (CH), 128.5 (CH), 128.2 (CH), 124.4 (CH), 124.3 (C), 120.0 (C), 95.2 (C), 90.4 (C), 87.8 (C), 35.9 (CH_2), 31.5 (CH_2), 30.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3). MS (FAB+), m/e 1089.5 (100), 963.6 (11), 686.3 (25). HRMS, m/e calcd for $\text{C}_{74}\text{H}_{73}\text{I}$ 1088.4757, found 1088.4749.

(C₅H₁₁)₈G₃-CHO: reaction time 24 h; purified by column chromatography (CCl_4) followed by washing with hot EtOH; further purification was achieved by crystallization from hexanes; pale yellow solid; yield 41%. ^1H NMR (CDCl_3) δ 0.89 (t, 24H, $J = 6.6$ Hz), 1.20–1.40 (m, 32H), 1.61 (m, 16H, $J = 7.5$ Hz), 2.60 (t, 16H, $J = 7.8$ Hz), 7.1–7.2 (m, including A of ABq, 24H, $J = 8.4$ Hz), 7.46 (B of ABq, 16H, $J = 8.4$ Hz), 7.56–7.62 (m, 18H), 8.00 (t, 1H, $J = 1.5$ Hz), 8.02 (d, 2H, $J = 1.5$ Hz), 10.02 (s, 1H). ^{13}C NMR and DEPT (CDCl_3) δ 190.7 (CHO), 143.7 (C), 139.5 (CH), 137.7 (C), 137.3 (C), 136.7 (C), 133.6 (CH), 132.1 (CH), 131.6 (CH), 130.9 (CH), 129.2 (CH), 129.0 (CH), 128.7 (CH), 128.5 (CH), 125.5 (CH), 124.7 (C), 124.3 (C), 123.4 (C), 120.1 (C), 91.2 (C), 90.4 (C), 87.8 (C), 87.6 (C), 35.9 (CH_2), 31.5 (CH_2), 30.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3). MALDI-TOF ($\text{C}_{159}\text{H}_{150}\text{O}$), m/e 2077.0.

(C₅H₁₁)₁₆G₄-I: method B; reaction time 12 h; purified by column chromatography (CCl_4) followed by crystallization from $\text{CHCl}_3/\text{EtOH}$; pale yellow solid; yield 32%. ^1H NMR (CDCl_3) δ 0.87 (t, 48H, $J = 6.6$ Hz), 1.2–1.4 (m, 64H), 1.5–1.7 (m, 32H), 2.53 (t, 32H, $J = 7.8$ Hz), 6.8–7.2 (m, including A of ABq, 52H, $J = 8.1$ Hz), 7.3–7.7 (m, including B of ABq, 77H, $J = 8.1$ Hz). ^{13}C NMR (CDCl_3) δ 143.5, 143.4, 138.9, 137.3, 137.1, 137.0, 134.7, 133.5, 132.0, 131.6, 129.6, 129.0, 128.4, 127.8, 125.1, 124.1, 123.9, 123.6, 120.2, 95.3, 90.2, 89.9, 88.1, 35.9, 31.5, 30.9, 22.5, 14.1. MALDI-TOF ($\text{C}_{326}\text{H}_{305}\text{I}$), m/e 4349.9.

(C₅H₁₁)₆G₂: method B; reaction time 1 h; purified by column chromatography (hexanes/ CH_2Cl_2 , 8:2) followed by crystallization from $\text{CHCl}_3/\text{EtOH}$; white solid; yield 86%. ^1H NMR (CDCl_3) δ 0.90 (t, 18H, $J = 6.9$ Hz), 1.2–1.4 (m, 24H), 1.63 (m, 12H, $J = 7.2$ Hz), 2.62 (t, 12H, $J = 7.5$ Hz), 7.1–7.2 (m, including A of ABq, 18H, $J = 8.1$ Hz), 7.47 (B of ABq, 12H, $J = 8.1$ Hz), 7.59 (m, 6H), 7.66 (br s, 6H). ^{13}C NMR and DEPT (CDCl_3) δ 143.7 (C), 137.7 (C), 137.5 (C), 133.5 (CH), 131.6 (CH), 129.6 (CH), 129.2 (CH), 128.5 (CH), 127.9 (CH), 124.5 (CH), 124.2 (C), 120.1 (C), 90.3 (C), 87.9 (C), 35.9 (CH_2), 31.5 (CH_2), 30.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3). MS (FAB+), m/e 1406.0 (100), 1004.8 (23), 776.5 (25). HRMS, m/e calcd for $\text{C}_{108}\text{H}_{109}$ 1405.8529, found 1405.8475.

(C₅H₁₁)₁₂G₃: reaction time 12 h; purified by column chromatography (CCl_4) followed by crystallization from EtAcO/EtOH; pale yellow solid; yield 38%. ^1H NMR (CDCl_3) δ 0.88 (t, 36H, $J = 6.6$ Hz), 1.2–1.4 (m, 48H), 1.5–1.7 (m, 24H), 2.56 (t, 24H, $J = 7.2$ Hz), 7.0–7.2 (m, including A of ABq, 36H, $J = 6.8$ Hz), 7.42 (B of ABq, 24H, $J = 6.9$ Hz), 7.50–7.72 (m, 30H). ^{13}C NMR and DEPT (CDCl_3) δ 143.5 (C), 137.5 (C), 137.2 (C), 134.3 (CH), 133.6 (CH), 131.6 (CH), 129.1 (CH), 128.7 (CH), 128.4 (CH), 128.2 (CH), 125.2 (CH), 124.2 (C), 123.9 (C), 123.7 (C), 120.1 (C), 90.3 (C), 88.3 (C), 88.0 (C), 35.9 (CH_2), 31.5 (CH_2), 30.9 (CH_2), 22.5 (CH_2), 14.0 (CH_3). MALDI-TOF ($\text{C}_{234}\text{H}_{222}$), m/e 3033.6.

(C₅H₁₁)₂₄G₄: method B; reaction time 12 h; purified by column chromatography (hexanes/ CH_2Cl_2 , 8:2) followed by crystallization from $\text{CHCl}_3/\text{EtOH}$; pale yellow solid; yield 65%. ^1H NMR (CDCl_3) δ 0.85 (t, 72H, $J = 6.6$ Hz), 1.15–1.40 (m, 96H), 1.40–1.50 (m, 48H), 2.49 (br s, 48H), 6.7–7.7 (m, 192H). ^{13}C NMR (CDCl_3) δ 143.2, 137.1, 133.5, 131.6, 128.9, 128.3, 123.9, 120.3, 120.2, 90.1, 89.1, 88.2, 88.1, 35.9, 31.6, 30.8, 22.5, 14.0. MALDI-TOF ($\text{C}_{486}\text{H}_{456}$), m/e 6296.6.

Compound 2: reaction time 1 h 30 min; purified by crystallization from EtAcO/EtOH; white solid; yield 97%. ^1H NMR (CDCl_3) δ 0.88 (t, 18H, $J = 6.6$ Hz), 1.2–1.6 (m, 108H), 1.7–1.9 (m, 12H), 3.95–4.04 (m, 12H), 6.71 (s, 4H), 6.86 (A of ABq, 2H, $J = 16.2$ Hz), 7.02 (B of ABq, 2H, $J = 16.2$ Hz), 7.51 (br s, 1H), 7.72 (d, 2H, $J = 1.2$ Hz). ^{13}C NMR and DEPT (CDCl_3) δ 153.3 (C), 139.7 (C), 138.7 (C), 133.8 (CH), 131.9 (C), 130.4 (CH), 125.8 (CH), 123.8 (CH), 105.3 (CH), 95.2 (C), 73.6 (CH_2), 69.2 (CH_2), 31.9 (CH_2), 31.9 (CH_2), 30.3 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.6 (CH_2), 29.4 (CH_2), 29.4 (CH_2), 26.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3). HRMS, m/e calcd for $\text{C}_{94}\text{H}_{162}\text{IO}_6$ 1514.1416, found 1514.1380.

Compound 3: reaction time 7 h; purified by column chromatography (hexanes/ CH_2Cl_2 , 7:3); yellow oil; yield 85%. ^1H NMR (CDCl_3) δ 0.84–0.88 (m, 54H), 1.2–1.6 (m, 324H), 1.78 (m, 36H), 3.90–4.00 (m, 36H), 6.65 (s, 12H), 6.79 (A of ABq, 6H, $J = 16.2$ Hz), 6.86 (B of ABq, 6H, $J = 16.2$ Hz), 7.24 (br s, 6H), 7.39 (br s, 3H), 7.55–7.59 (m, 6H), 7.62–7.66 (m, 6H), 8.08 (s, 3H). ^{13}C NMR and DEPT (CDCl_3) δ 153.2 (C), 143.8 (C), 140.1 (C), 138.5 (C), 137.8 (C), 132.8 (CH), 132.2 (C), 129.7 (CH), 129.6 (CH), 129.4 (CH), 128.8 (CH), 128.2 (CH), 127.3 (CH), 126.5 (CH), 124.2 (CH), 123.8 (C), 121.5 (C), 105.2 (CH), 92.8 (C), 89.6 (C), 73.5 (CH_2), 69.2 (CH_2), 31.9 (CH_2), 30.4 (CH_2), 29.8 (CH_2), 29.7 (CH_2), 29.7 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 26.2 (CH_2), 22.7 (CH_2), 14.1 (CH_3). MALDI-TOF ($\text{C}_{312}\text{H}_{498}\text{O}_{18}$), m/e 4536.8.

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Supporting Information Available: Additional experimental procedures, compound characterization data, and

copies of ^1H NMR and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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