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Synthesis of Two-Photon Absorbing Unsymmetrical Branched Chromophores through Direct Tris(bromomethylation) of Fluorene

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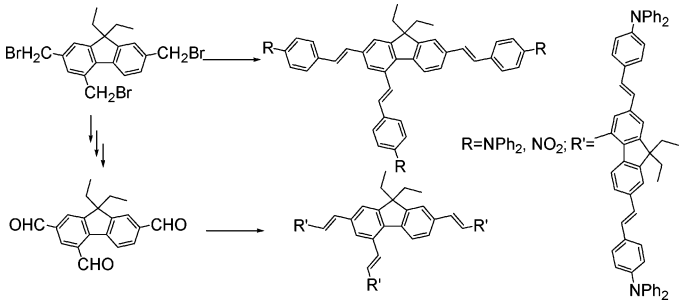

Branched fluorene-based chromophores bearing electron-donating diphenylamino or electron-withdrawing nitro groups were synthesized as well as their linear analogues. An efficient synthetic method was developed via a novel 2,4,7-tris(bromomethyl)-9,9-diethylfluorene intermediate. The bromomethyl groups in this key intermediate were converted to either phosphonate or carboxaldehyde moieties, facilitating preparation of a high functionality branched structure. It was found that the reactivity at position 4 is attenuated in the bromomethyl and phosphorylated derivates, facilitating the selective and systematic functionalization of the fluorenyl system. All compounds were stable up to ca. 350 °C, except for a sterically crowded branched derivative. The linear optical properties of the compounds were investigated by UV−visible, steady-state fluorescence, and excitation anisotropy spectroscopic measurements. Fluorescence quantum yields were greater than or equal to 0.84 for symmetric linear and unsymmetric branched derivatives. Very high two-photon absorption (2PA) cross-sections were achieved (5765 GM at 520 nm and 4194 GM at 570 nm), as determined with use of picosecond and femtosecond laser excitation sources, respectively.

Introduction

Fluorene, a major component of fossil fuels, has unique structural features: two benzene rings are fused into one plane by a five-member ring, providing high electron delocalization through increased overlap of π molecular orbitals between the rings. As a consequence, two α-protons at position 9 are very acidic and can readily react with electrophilic agents, such as aliphatic bromides. These substituents, perpendicularly situated out of the conjugation plane, can efficiently reduce intermolecular interactions. Thus, 9,9-dialkyl-substituted fluorene derivatives often exhibit high fluorescence quantum yields, good solubility in organic solvents, as well as excellent thermo- and photostability. Therefore, fluorenyl-based conjugated derivatives were extensively investigated for electronic and photonic applications, such as light emitting diodes,[1] charge-transfer agents,[2] field effect transistors,[3] sensors,[4] and more recently two-photon absorbing

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(1) Numerous papers have been published in this area, e.g., see: (a) Belfield, K. D.; Bondar, M. V.; Morales, A. R.; Yavuz, O.; Przhonska, O. V. *J. Phys. Org. Chem.* **2003**, *16*, 194−201. (b) Geng, Y.; Chen, A. C. A.; Ou, J. J.; Chen, S. H. *Chem. Mater.* **2003**, *15*, 4352−4360. (c) Geng, Y.; Chen, A. C. A.; Ou, J. J.; Chen, S. H.; Klubek, K.; Vaeth, K. M.; Tang, C. W. *Chem. Mater.* **2003**, *15*, 4352−4360. (d) Son, S. W.; Jung, S. H.; Cho, H. N. *Synth. Metal.* **2003**, *137*, 1065−1066. (e) Zheng, M.; Lin, Z.; Ding, L.; Karasz, F. E. *Macromolecules* **2002**, 35, 9939−9946. (f) Cho, H. N.; Kim, D. Y.; Kim, Y. C.; Lee, J. Y.; Kim, C. Y. *Adv. Mater.* **1997**, *9*, 326−328.

(2) (a) Perepichka, D. F.; Bryce, M. R.; Perepichka, I. F.; Lyubchik, S. B.; Christensen, C. A.; Godbert, N.; Batsanov, A. S.; Levillain, E.; McInnes, E. J. L.; Zhao, J. P. *J. Am. Chem. Soc.* **2002**, *124*, 14227−14238. (b) Omercq, B.; Grasso, C.; Maldonado, J.-L.; Halik, M.; Barlow, S.; Marder, S. R.; Kippelen, B. *J. Phys. Chem. B* **2004**, *108*, 8647−8651. (c) Perepichka, D. F.; Perepichka, I. F.; Bryce, M. R.; Moore, A. J.; Sokolov, N. I. *Synth. Metal.* **2001**, *121* (1−3), 1487−1488.

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materials.[5] In these chromophores, the construction of the π-conjugation system was accomplished by substitution at the chemically reactive para positions 2 and 7 on fluorene core, resulting in relatively linear chromophore systems. Meanwhile, other categories of electrooptical active conjugated compounds, e.g., two-dimensional symmetric[6] and asymmetric[7] dendritic molecules, have recently attracted attention. Fluorenyl-containing dendrimers with branched cores, such as triphenylamino and 1,3,5-triazinyl groups, have also been reported.[8] However, due to its attenuated reactivity at positions other than 2, 7, and 9, no two-dimensional chromophores have been reported with fluorene as a branching center.

We have been developing two-dimensional 2PA chromophores for molecular structure−nonlinear optical property studies. Due to the numerous potential applications, a large number of 2PA chromophores were synthesized over the last several years.[5] Among them, two-dimensional branched chromophores are especially attractive since, in some cases, a positive cooperative effect in 2PA cross-section was reported. For example, Chung et al. reported 2PA cooperative enhancement in dendritic structures using a triphenylamine donor as a branched center and 2-phenyl-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole as acceptor;[8c] however, the results for this type of structure have been contradictory. In our own series of fluorenylphenylamino-based molecules, a linear increase of the 2PA cross-sections was observed.[9] Hence, a more detailed study is needed to understand the mechanism of these phenomena as a guide to aid molecular design. It is generally believed that the $\pi-\pi$ interaction between the branches results in a nonlinear enhancement of the 2PA cross-section. Thus, an ideal candidate for study is an architecture that is fully conjugated,

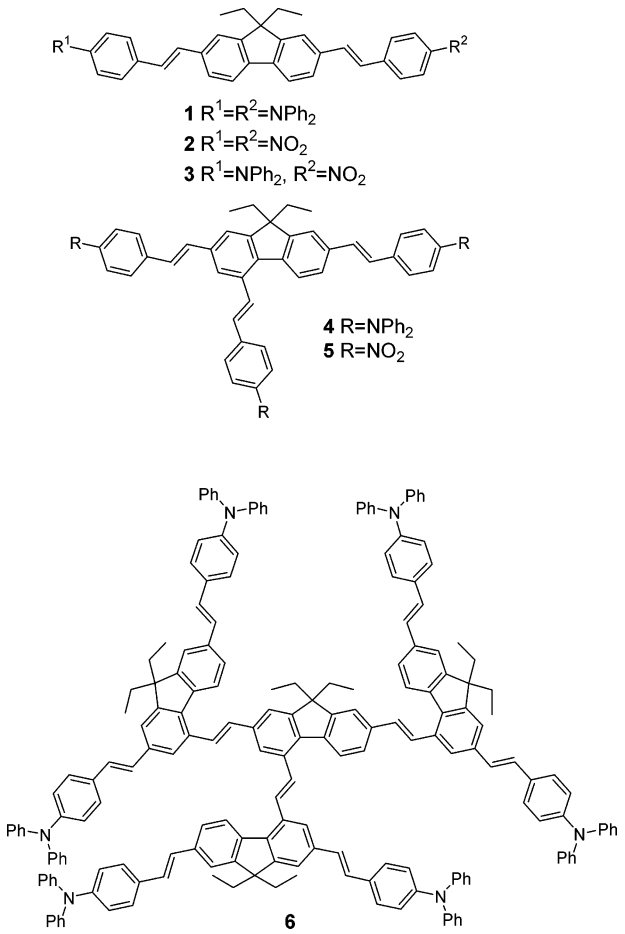

FIGURE 1. Structures of linear compounds **1**−**3** and the branched analogues **4**−**6**.

providing strong electronic interaction, but with two branches oriented in different directions. To begin to address this, we present the synthesis of branched chromophores **4**, **5**, and a higher generation analogue **6** via direct and efficient tris(bromomethylation) of fluorene, and subsequent Horner−Emmons coupling with an aromatic aldehyde (Figure 1). Linear compounds **1**−**3** were also prepared for reference.

Results and Discussion

Synthesis. All fluorene derivatives in this work were synthesized via Horner−Emmons coupling reactions[10] as illustrated in Figures 2 and 4. Thus, the key intermediates fluorenylmethylene phosphonate **10** and **11** were obtained from bromomethylfluorenes **8** and **9**, respectively. To synthesize 2,7-bis(bromomethyl)-9,9-diethylfluroene **8** a literature procedure was employed to perform the bis(bromomethylation) of 9,9-dihexylfluorene,[11] i.e., 9,9-diethylfluorene was treated with 10 equiv of paraformaldehyde and a 33% solution of HBr in HOAc at 60−70 °C. Surprisingly, after a prolonged reaction time, the 2,4,7-tris-substituted product **9** was identified,[12]

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(4) (a) Gaylord, B. S.; Heeger, A. J.; Bazan, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 896−900. (b) Zhang, M.; Lu, P.; Ma, Y.; Shen, J. *J. Phys. Chem. B* **2003**, *107*, 6535−6538. (c) Yang, N. C.; Lee, S. M.; Suh, D. H. *Polym. Bull.* **2003**, *49*, 371−377. (d) Yang, N. C.; Chang, S.; Suh, D. H. *Polymer* **2003**, *44*, 2143-2148.

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(6) For reviews, see: (a) Moore, J. S. *Acc. Chem. Res.* **1997**, *30*, 402−413. (b) Berresheim, A. J.; Muellen, K. *Chem. Rev.* **1999**, *99*, 1747−1785. (c) Grayson, S. M.; Frechet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819−3868.

(7) (a) Peng, Z.; Pan, Y.; Xu, B.; Zhang, J. *J. Am. Chem. Soc.* **2000**, *122*, 6619−6623. (b) Melinger, J. S.; Pan, Y.; Kleiman, V. D.; Peng, Z.; Davis, B. L.; McMorrow, D.; Lu, M. *J. Am. Chem. Soc.* **2002**, *124*, 12002−12012. (c) Wang, J.; Lu, M.; Pan, Y.; Peng, Z. *J. Org. Chem.* **2002**, *67*, 7781−7786. (d) Pan, Y.; Peng, Z.; Melinger, J. S. *Tetrahedron* **2003**, *59*, 5495−5506.

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(9) Belfield, K. D.; Morales, A. R.; Kang, B.-S.; Hales, J. M.; Hagan, D. J.; Van Stryland, E. W.; Chapela, V. M.; Percino, J. *Chem. Mater.* **2004**, *16*, 2267−2273.

(10) An analogue of compound **1** was previously synthesized by the Heck coupling reaction, see: Lee, K.-S.; Lee, J. H.; Choi, H.; Cha, M.; Chung, M.-A.; Kim, Y. J.; Jung, S. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*: *Mole. Cryst. Liq. Cryst.* **2001**, *370*, 155−159. The disadvantage of this method is the use of expensive tributyl(vinyl)tin and Pd catalysts under demanding conditions.

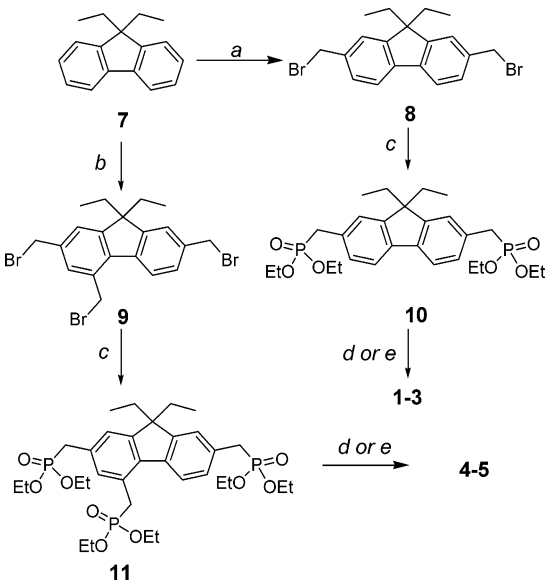

FIGURE 2. Synthesis of dye **1** from **8** and dye **4** from **9**: (a) paraformaldehyde (2.2 equiv), 33% HBr in HOAc, 70 °C, 20 h, 72%, (b) paraformaldehyde (10.0 equiv), 33% HBr in HOAc, 70 °C, 22 h, 75%, (c) triethyl phosphite, reflux, 16−18 h; (d) 4-formyltriphenylamine, NaH, DMF, room temperature under Ar, 24 h, dye **1**, 64% for (c) + (d), dye **4**, 63% for (c) + (d), (e) 4-nitrobenzoaldehyde or 4-formyltriphenylamine, CH_2Cl_2/50% NaOH, Bu_4NBr, room temperature, 20−30 h, dye **2**, 35% for (c) + (e), dye **3**, 24% for (c) + (e), dye **5**, 33% for (c) + (e).

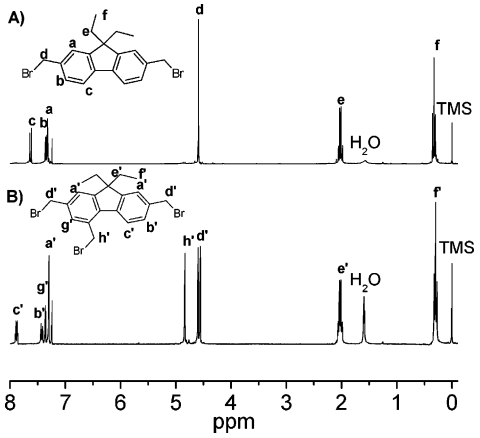

FIGURE 3. ^1H NMR spectra of intermediates **8** and **9** in $CDCl_3$.

a novel compound confirmed by NMR, MS, and elemental analysis. On the other hand, the preparation of **8** was achieved by using 2.2 equiv of paraformaldehyde. In both cases, the product precipitated during the reaction and was simply collected by suction filtration, with no impurity peaks detected by ^1H NMR. The introduction of an additional bromomethyl group can clearly be distinguished in the ^1H NMR spectra, as shown in Figure 3. The 2,7-bis(bromomethyl) protons (d) in symmetric **8** appear as a singlet peak with a chemical shift of 4.59 ppm, while in unsymmetric **9**, the 2,7-bis(bromomethyl) protons (d′) appeared as two singlets due to the influence of the 4-bromomethyl group, whose proton resonance (h′) shifts further downfield to 4.83 ppm. The aromatic proton signals also changed with the additional substituent in **9**. A new singlet resonance at 7.36 ppm (g′) was assigned as the proton at the 3-position of fluorene, which was distinguished from the doublets corresponding to the protons at positions 5 and 6 (b′ and c′) at 7.42 and 7.88 ppm, respectively.

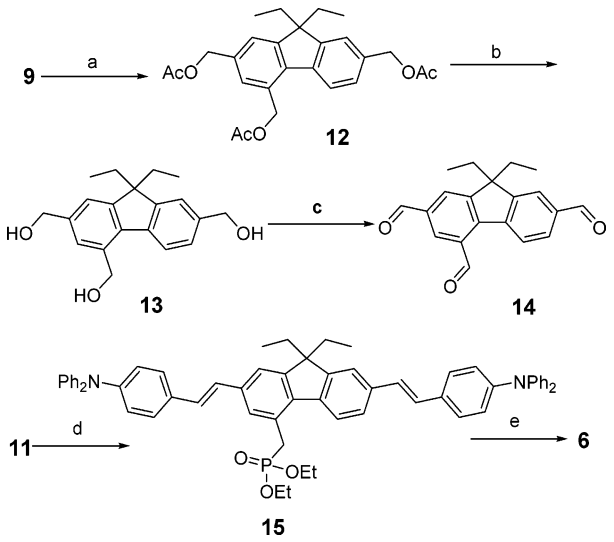

FIGURE 4. Synthesis of **6**. Fluorene **11** (shown in Figure 2) is converted to **15**. Reaction of **14** with **15** leads to **6**. (a) NaOAc, Ac_2O, HOAc, 90 °C, 24 h, 75%; (b) NaOH, EtOH, 40 °C, 21 h, 66%; (c) pyridinium chlorochromate, CH_2Cl_2, room temperature, 6 h, 50%; (d) 4-formyltriphenylamine (2.0 equiv), CH_2Cl_2/50% NaOH, Bu_4NBr, room temperature, 48 h, 9%; (e) *t*-BuOK, HMPA, **14**, room temperature under Ar, 20 h, 32%.

In next step, the phosphonylation of the bromomethyl compounds was straightforward, and the coupling of **10** or **11** with 4-formyltriphenylamine or 4-nitrobenzaldehyde went smoothly in the presence of NaH in DMF, or in CH_2Cl_2/NaOH with tetrabutylammonium bromide as phase transfer agent, with moderate yields. In addition, the bromomethyl groups in **9** can be converted to carboxaldehyde moieties via a three-step reaction sequence shown in Figure 4. Trisaldehyde fluorene **14** was coupled with monomethylene phosphonate fluorene **15**, affording the higher generation derivative **6**. Monophosphonate **15** was obtained from the Horner−Emmons reaction by using a 1:2 mole ratio of **11** and 4-diphenylaminobenzaldehyde.[13] The structures of all six fluorenyl derivatives were confirmed by ^1H NMR, ^{13}C NMR, and elemental analysis.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC). Linear fluor-

(11) (a) Ahn, T.; Song, S.-Y.; Shim, H.-K. *Macromolecules* **2000**, *33*, 6764−6771. (b) Liu, B.; Yu, W.-L.; Pei, J.; Liu, S.-Y.; Lai, Y.-H.; Huang, W. *Macromolecules* **2001**, *34*, 7932−7940.

(12) Under the same conditions, the bromomethylation of 9,9-didecylfluorene is much slower due to phase separation, and the main product is 2,7-bis(bromomethyl)-9,9-didecylfluorene. In most cases, a long alkyl chain is essential for the applications of fluorene based chromophores, and this may be the main reason the tris-(bromomethylation) was not observed. On the other hand, under extreme conditions, i.e., when 9,9-didecylfluorene was refluxed with paraformaldehyde and HBr in HOAc for 4 d, a trace of the tris-product was identified by GC-MS and ^1H NMR.

(13) The products of the reaction have three isomers. While **12** can be identified by ^1H NMR due to the characteristic signal due to methylene protons substituted at the 4-position, the other two with methylene phosphonate at 2- and 7-positions are indistinguishable by ^1H NMR; efforts to further characterize these are on going.

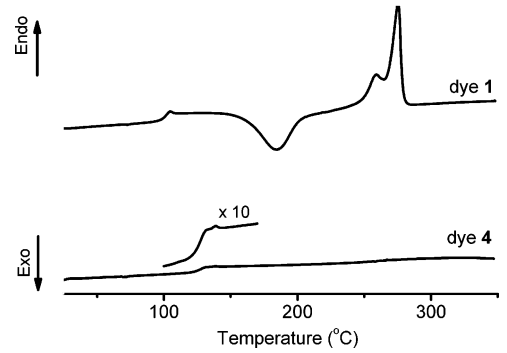

FIGURE 5. DSC analysis of dyes **1** and **4**.

enylvinylene derivatives normally show high thermostability, as demonstrated by the relatively high decomposition temperatures (<3% weight loss) of dyes **1**, **2**, and **3**, >410, >350, and >350 °C, respectively, as determined by TGA. Dyes **4** and **5** exhibited comparable decomposition temperatures of >410 and >350 °C, respectively, in spite of the morphology of **4** in the solid state, i.e., **4** exists as an amorphous glass with T_g = 125 °C, with no discernible melting point up to 350 °C (determined by DSC). In contrast, **1** began crystallizing at 142 °C from its glass form (T_g = 100 °C), exhibiting a crystal phase transition at 259 °C and a melting transition at 278 °C (Figure 5). It is apparent that the steric effects of diethyl groups prevent the dense packing of the molecules, resulting in the observation of the T_g in both dyes, and the asymmetric third branch further disturbs the molecular packing stabilizing the glass form in dye **4**.

The linear dye **2**, bearing the nitro group, was highly crystalline, exhibiting only a sharp melting point at 264 °C, suggesting that these planar molecules are packed tightly by the strong $\pi-\pi$ interactions. DSC analysis of dye **5** was performed up to 360 °C, showing the complete absence of any phase transition and melting process. Such a high melting point (>360 °C) is attributed to very strong electrostatic interactions via a more accessible conjugated surface than that of dye **2**. For dye **6**, a decomposition temperature of 145 °C was observed, possibly due to the crowded peripheral moieties weakening of the vinylene C=C bonds.

Linear Optical Properties. The linear UV−vis absorption and emission spectra in THF for **1**, **4**, and **6** are compared in Figure 6. Introduction of the extra conjugated branch in **4** induced a 5 nm red shift of the λ_{max} to 414 nm compared to that of **1**. The absorption profile of **4** also exhibited a broader band and a new shoulder at the short wavelength side (~370 nm). This shoulder was not present in **6**, implying an absorption transition from the strong diphenylamino donor at the central branch of **4**. The steady-state excitation anisotropy data further confirmed this second transition as shown in the same figure. Through excitation anisotropy, the spectral positions and orientation of the transition dipole moments from the ground state to the first and higher excited states relative to the emission dipole moment orientation can be determined. A change of the anisotropy value is indicative of excitation to a different electronic state.[14] Higher anisotropy values are helpful, and can be obtained by using high-viscosity solvents to increase the rotational correlation time of the molecule in solution.

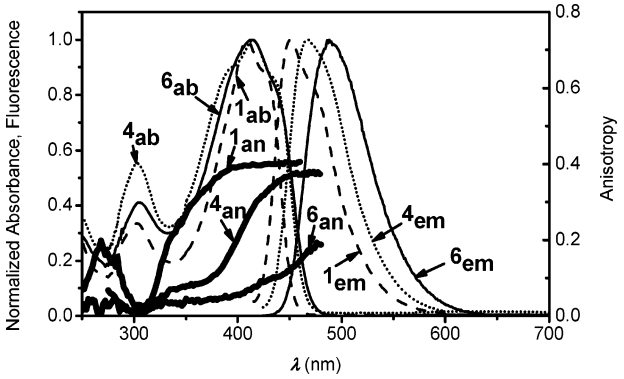

FIGURE 6. Normalized absorption and emission spectra of dye **1** (- - -), **4** (···), and **6** (—) in THF and their fluorescence excitation anisotropy plots (thick lines) in polyTHF.

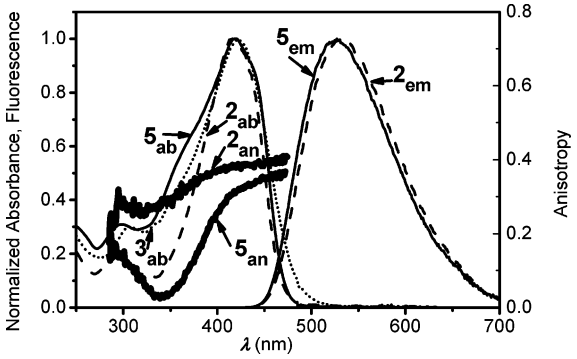

FIGURE 7. Normalized absorption and emission spectra of dye **2** (- - -), **3** (···), and **5** (—) in cyclohexane and fluorescence excitation anisotropic plots (**2** and **5**, thick lines) in polyTHF.

In this study, all anisotropy measurements were performed in polytetrahydrofuran (polyTHF). Two transitions in **1** were identified, i.e., S_0-S_1 at 380−460 nm and S_0-S_2 at about 290−320 nm. In dye **4**, transitions corresponding to S_0-S_1 and S_0-S_3 and a transition at about 340−380 nm (S_0-S_2) were observed, corresponding to the new shoulder observed in the absorption spectrum of **4**. In **6**, due to the close spacing of several excited states, no distinct transitions were identified. The extinction coefficient of **6** (3.0×10^5 L mol^{-1} cm^{-1}) was three times higher than that of **1** and **4** (both at 1.0×10^5 L mol^{-1} cm^{-1}). The three emission spectra exhibited near identical spectral profiles with high quantum yields (0.95, 0.90, and 0.84, respectively). The emission maxima shifted from 450 nm for **1** to 468 nm for **4** to 488 nm for **6**.

The UV−vis absorption and emission spectra for **2**, **3**, and **5** in THF are shown together in Figure 7 since they all possess nitro groups. The absorption maxima of these three dyes are almost identical, from 219 nm for **2** and **5** to 221 nm for **3,** though dye **3**, possessing a diphenylamino donor group, exhibited a slight red shift. The extra branch in **5** again induced a second absorption transition at about 360 nm, consistent with the anisotropy data. The fluorescence was reduced in unsymmetric **3** due to the nitro group, a strong fluorescence quenching moiety.

(14) Belfield, K. D.; Morales, A. R.; Kang, B.-S.; Hales, J. M.; Hagan, D. J.; Van Stryland, E. W.; Chapela, V. M.; Percino, J. *Chem. Mater.* **2004**, *16*, 4634−4641.

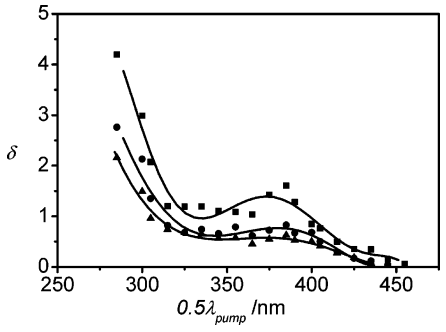

FIGURE 8. Two-photon absorption cross-sections δ (in 10^3 GM, 1 GM = 10^{-50} cm^4 s photon^{-1} molecule^{-1}) of dyes **1** (▲), **4** (●), and **6** (■) in cyclohexane and their fitting curves. The 2PA excitation wavelengths are divided by a factor of 2 for each to allow ready comparison to one-photon UV−vis absorption.

However, in **2** and **5**, very high fluorescence quantum yields (>0.9) were determined, expected for symmetric **2** but unexpected for **5**. It seems that the symmetry broken by the third arm does not influence the fluorescence properties of these dyes.

Nonlinear Optical Properties. Two-photon absorption (2PA) spectra of **1**, **4**, and **6**, determined with femtosecond laser pulse excitation,[15] are shown in Figure 8. The highest 2PA cross-section was obtained for **6** with a value of 4194 GM at 570 nm. The 2PA cross-sections of **6** and **1** at 770 nm were 1603 and 626 GM, respectively, implying that the contribution of three D−π−D subchromophores in dye **6** are additive within experimental error (±15%). It seems that a donor or acceptor group at the focal point[16] or on each branch[17] in a dendrimeric system is essential to achieve a 2PA cooperative effect since the neat fluorene core in **3** exhibited no apparent influence on the 2PA cross-section. By comparison, the additional branch with a donor group in **4** increased the 2PA cross-section by ca. 36% at 760 nm relative to that of **1**, an aspect helpful to future 2PA chromophore design. The 2PA cross-sections of linear chromophores **1** and **2** and branched chromophores **4** and **5** were also determined by using the Z-scan technique with picosecond laser pulses at 520 nm.[18] The dyes with electron-accepting groups, i.e., nitro group, exhibit much larger 2PA cross-section values than the ones with electron-donating diphenylamino groups. Dyes **2** and **5** exhibited 2PA cross-section values of 5215 and 5765 GM, respectively, compared to 2250 GM for **1** and 3115 GM for **4**. Both molecules with an extra central branch exhibited higher 2PA cross-sections than the corresponding linear analogues, with the electron donating group being more effective in enhancing 2PA in the branched compounds.

Conclusion

In summary, a versatile intermediate, 2,4,7-tris(bromomethyl)-9,9′-diethylfluorene, was efficiently prepared and used to synthesize asymmetric branched fluorenylvinylene chromophores. Conversion of the bromomethyl group into the corresponding aldehyde facilitated access to higher generation dendritic-type compounds. The attenuated reactivity of position 4 in the bromomethyl and phosphorylated derivatives facilitated the selective and systematic functionalization of the fluorenyl system. In addition, these reactions also open a door to explore the possibility of further functionalized polyfluorene or other fluorene derivatives. Novel 2D chromophores with diphenylamino groups as donors exhibited stable glass formation due to their asymmetric branching geometries, an advantage for optical applications. All the compounds exhibited relatively high 2PA cross-sections, promising for 2PA applications. Moreover, the broad absorption bands and high fluorescence quantum yields of **4**−**6** indicate that these dyes may have potential in light-harvesting systems and in an OLED emissive layer. In addition, excitation anisotropy measurements have provided valuable information on the excitation energy levels, which is of importance for the understanding of the selection rules for two-photon absorption and the magnitude of the 2PA cross-section.

Experimental Section

General. 9,9-Diethyl-9*H*-fluorene (**3**)[19] and 4-formyltriphenylamine[20] were prepared according to literature methods. DMF was dried according to a standard procedure.[21] All other reagents and solvents were used as received from commercial suppliers. Melting points are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at either 300 or 500 MHz and at 75 MHz, respectively. MS, HRMS, and MALDI-TOF MS were measured on a GC/MS, high-resolution MS and MALDI-TOF MS, respectively. Thermal stability was assessed with a thermogravimetric analyzer (TGA) under N_2 at a heating rate of 20 °C/min. Phase and glass transitions were investigated with a differential scanning calorimeter (DSC) at heating/cooling rates of 10 °C/min under N_2. Absorption spectra were measured with a UV−visible spectrophotometer. Steady-state fluorescence spectra were obtained at room temperature with a spectrofluorimeter, using 10-mm quartz cuvettes.

Preparation of 2,7-Bis(bromomethyl)-9,9-diethylfluorene (8). A mixture of 9,9-diethylfluorene **7** (1.11 g, 5.0 mmol), paraformaldehyde (0.33 g, 11.0 mmol), and 33% HBr solution in acetic acid (10 mL) was heated at 60−70 °C for 20 h. Upon cooling, the precipitates were collected by filtration, carefully washed with water, and dried in vacuo, affording 1.47 g of pale white solid (72%). Recrystallization from toluene/hexane gave an analytically pure sample. Mp 148−150 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 7.5 Hz, 2H, Ph-H), 7.36 (s, 2H, Ph-H), 7.34 (d, J = 7.5 Hz, 2H, Ph-H), 4.59 (s, 4H, $BrCH_2$), 2.02 (q, J = 7.3 Hz, 4H, CH_2), 0.33 (t, J = 7.4 Hz, 6H,

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CH_3); ^{13}C NMR ($CDCl_3$) δ 9.0, 33.0, 34.8, 56.5, 120.3, 123.9, 128.3, 137.2, 141.3, 151.0. Anal. Calcd for $C_{19}H_{20}Br_2$ (408.18): C, 55.91; H, 4.94; N, 0. Found: C, 56.09; H, 5.00; N, 0.

Preparation of 2,4,7-Tris(bromomethyl)-9,9-diethylfluorene (9). A mixture of 9,9- diethylfluorene (**7**) (1.11 g, 5.0 mmol), paraformaldehyde (1.50 g, 50.0 mmol), and 33% HBr solution in acetic acid (10 mL) was heated at 85−90 °C for 22 h. Upon cooling, the precipitate was collected by filtration, carefully washed with water, and dried in vacuo, affording 1.89 g of pale white solid (75%). Recrystallization from toluene/hexane gave an analytically pure sample. Mp 160−161 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 8.1 Hz, 1H, Ph-H), 7.42 (d, J = 7.8 Hz, 1H, Ph-H), 7.36 (s, 1H, Ph-H), 7.29 (s, 2H, Ph-H), 4.83 (s, 2H, $BrCH_2$), 4.59 (s, 2H, $BrCH_2$), 4.55 (s, 2H, $BrCH_2$), 2.02 (q, J = 7.3 Hz, 4H, CH_2), 0.30 (t, J = 7.2 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 8.9, 32.5, 33.2, 33.8, 34.4, 56.2, 123.8, 124.1, 124.3, 128.7, 130.3, 132.5, 137.2, 137.3, 139.5, 140.3, 151.7, 152.7; MS (EI) *m/z* 500 (M^+), 421 (M − Br), 342 (M − 2Br). Anal. Calcd for $C_{20}H_{21}Br_3$ (501.10): C, 47.94; H, 4.22; N, 0. Found: C, 48.27; H, 4.25; N, 0.

Preparation of 4,4′-[[9,9-Bis(ethyl)-9*H*-fluorene-2,7-diyl]di-2,1-ethenediyl]bis(*N*,*N*-diphenyl)benzeneamine (1). A mixture of **8** (0.12 g, 0.29 mmol) and triethyl phosphite (1.0 mL) was refluxed for 16 h under N_2. Excess triethyl phosphite was distilled under reduced pressure. The residue was dried in vacuo and used directly for the Horner−Emmons reaction. ^1H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 8.1 Hz, 2H, Ph-H), 7.24 (d, J = 8.4 Hz, 2H, Ph-H), 7.23 (s, 2H, Ph-H), 3.98 (m, 8H, OCH_2), 3.22 (d, J = 21.6 Hz, 4H, $P(O)CH_2$), 2.00 (m, 4H, CH_2), 1.23 (m, 12H, CH_3), 0.29 (m, 6H, CH_3). The intermediate **10** obtained above was dissolved in dry DMF (3 mL) followed by slow addition of NaH (0.10 g, 4.2 mmol). The mixture was reacted under Ar atmosphere at room temperature for 1 h, followed by addition of 4-formyltriphenylamine (0.16 g, 0.59 mmol). The mixture was then stirred at room temperature for 24 h. Water was added and the precipitate was collected by filtration, carefully washed with water, and dried. The crude product was purified by column chromatography with toluene/hexane 1:1 as eluent. Recrystallization from cyclohexane/hexane afforded 0.15 g of yellow crystals (67%). Mp 276−278 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 7.8 Hz, 2H), 7.46−7.38 (m, 8H), 7.28−7.77 (m, 8H), 7.1−6.99 (m, 20H), 2.07 (q, J = 7.5 Hz, 4H, CH_2), 0.37 (t, J = 7.35 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 9.1, 33.3, 56.4, 120.1, 120.7, 123.3, 123.8, 124.7, 125.9, 127.5, 127.6, 127.9, 129.5, 132.0, 136.7, 141.0, 147.4, 147.8, 150.9. Anal. Calcd for $C_{57}H_{48}N_2$ (761.00): C, 89.96; H, 6.36; N, 3.68. Found: C, 89.96; H, 6.53; N, 3.58.

Preparation of 9,9-Diethyl-2,7-bis[2-(4-nitrophenyl)-vinyl]-9*H*-fluorene (2). A mixture of **8** (1.63 g, 4.0 mmol) and triethyl phosphite (2.4 mL) was refluxed for 16 h under N_2. Excess triethyl phosphite was distilled under reduced pressure and the residue was dried in vacuo. The intermediate **10** obtained above, 4-nitrobenzoaldehyde (1.33 g, 8.8 mmol), and tetrabutylammonium bromide (2.59 g, 8.0 mmol) were dissolved in CH_2Cl_2 (20 mL) followed by addition of a 50% aqueous solution of NaOH (10 mL). After the mixture was reacted at room temperature for 30 h, water was added and the organic layer was separated. The water phase was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic phase was carefully washed with water and dried over $MgSO_4$. Upon solvent removal, the crude product was purified by column chromatography with CH_2Cl_2/cyclohexane 1:3 as eluent. Recrystallization from CH_2Cl_2/hexane afforded 0.73 g of orange crystals (35%). Mp 264−265 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.25 (d, J = 8.0 Hz, 4H, Ph-H), 7.74 (d, J = 8.0 Hz, 2H, fluorene-3,6-H), 7.68 (d, J = 8.0 Hz, 4H, Ph-H), 7.57 (d, J = 8.0 Hz, 2H, fluorene-4,5-H), 7.54 (s, 2H, fluorene-1, 8-H), 7.38 (d, J = 16.5 Hz, 2H, CH=CH), 7.23 (d, J = 16.5 Hz, 2H, CH=CH), 2.12 (q, J = 7.0 Hz, 4H, CH_2), 0.38 (t, J = 7.0 Hz, 6H, CH_3); ^{13}C NMR (DMSO) δ 9.4, 32.7, 56.5, 121.2, 121.9, 124.8, 126.6, 127.7, 127.8, 134.4, 136.3, 141.9, 144.9, 146.6, 151.1; HRMS (EI) calcd 516.2049, found 516.2037. Anal. Calcd for $C_{33}H_{28}N_2O_4$ (516.59): C, 76.73; H, 5.46; N, 5.42. Found: C, 76.76; H, 5.40; N, 5.35.

Preparation of [4-(2-{9,9-Diethyl-7-[2-(4-nitrophenyl)-vinyl]-9*H*-fluoren-2-yl}vinyl)phenyl]diphenylamine (3). A mixture of **8** (0.816 g, 2.0 mmol) and triethyl phosphite (1.2 mL) was refluxed for 16 h under N_2. Excess triethyl phosphite was distilled under reduced pressure and the residue was dried in vacuo. The intermediate **10** obtained above, 4-formyltriphenylamine (0.546 g, 2.0 mmol), and tetrabutylammonium bromide (0.646 g, 2.0 mmol) were dissolved in CH_2Cl_2 (20 mL) followed by addition of a 50% aqueous solution of NaOH (5 mL). After the mixture was reacted at room temperature for 24 h, 4-nitrobenzoaldehyde (0.302 g, 2.0 mmol) and another portion of tetrabutylammonium bromide (0.646 g, 2.0 mmol) were added and the reaction continued for another 24 h. Then water was added and the organic layer was separated. The water phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was carefully washed with water and dried over $MgSO_4$. Upon solvent removal, the crude product was purified by column chromatography with CH_2Cl_2/cyclohexane 1:3 as eluent. Recrystallization from CH_2Cl_2/hexane afforded 0.31 g of product (24% yield). Mp 218−219 °C; ^1H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, J = 9.0 Hz, 2H, Ph-H), 7.63−7.69 (m, 4H), 7.46−7.53 (m, 4H), 7.41 (d, J = 8.5 Hz, 2H, Ph-H), 7.35 (d, J = 17.0 Hz, 1H, CH=CH), 7.24−7.28 (m, 4H), 7.19 (d, J = 17.0 Hz, 1H, CH=CH), 7.02−7.14 (m, 10H), 2.10 (q, J = 7.5 Hz, 4H, CH_2), 0.38 (t, J = 7.5 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 9.3, 33.6, 56.7, 120.4, 120.5, 120.9, 121.6, 123.5, 123.9, 124.6, 124.9, 125.7, 126.1, 127.0, 127.1, 127.7, 128.2, 129.6, 129.7, 131.9, 134.3, 135.3, 137.5, 140.7, 142.8, 144.5, 146.9, 147.6, 147.8, 151.2; HRMS (EI) calcd 638.2933, found 638.2946. Anal. Calcd for $C_{45}H_{38}N_2O_2$ (638.80): C, 84.61; H, 6.00; N, 4.39. Found: C, 84.41; H, 6.01; N, 4.35.

Preparation of 4,4′,4″-{[9,9-bis(ethyl)-9*H*-fluorene-2,4,7-triyl]tri-2,1-ethenediyl}tris(*N*,*N*-diphenyl)benzeneamine (4). A mixture of **9** (0.50 g, 1.0 mmol) and triethyl phosphite (2.5 mL) was refluxed for 18 h under N_2. The extra triethyl phosphite was distilled under reduced pressure. The residue was dried in vacuo and used directly for the Horner−Emmons reaction. ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 1H, Ph-H), 7.25 (s, 2H, Ph-H), 7.17 (d + s, 2H, Ph-H), 3.82 (m, 12H, OCH_2), 3.62 (d, J = 21.6 Hz, 2H, $P(O)CH_2$), 3.24 (d, J = 21.6 Hz, 4H, $P(O)CH_2$), 3.22 (d, J = 21.3 Hz, 4H, $P(O)CH_2$), 2.01 (q, J = 7.3 Hz, 4H, CH_2), 1.24 (m, 12H, CH_3), 1.15 (m, 6H, CH_3), 0.24 (t, J = 7.2 Hz, 6H, CH_3). The intermediate **11** obtained above was dissolved in dry DMF (15 mL) followed by slow addition of NaH (0.51 g, 21 mmol) under Ar. The mixture was reacted at room temperature for 1 h. 4-Formyltriphenylamine (0.90 g, 3.25 mmol) was then added and the resulting pale yellow suspension was stirred at room temperature for 24 h. Water was added, and a precipitate formed and was collected by filtration and carefully washed with water and dried. The crude product was purified by column chromatography by using toluene/hexane from 2:1 to 1:1 as eluent. Recrystallization from cyclohexane/hexane afforded 0.65 g of yellow solid (63% yield). The compound showed no definite melting point. ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 8.7 Hz, 1H), 7.74 (d, J = 15.6 Hz, 1H), 7.57 (s, 1H), 7.50−7.35 (m, 10H), 7.30−7.23 (m, 10H), 7.15−7.00 (m, 30H), 2.08 (q, J = 7.1 Hz, 4H, CH_2), 0.37 (t, J = 7.2 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 9.2, 33.7, 55.8, 119.2, 120.4, 123.2, 123.3, 123.5, 123.8, 124.2, 124.7, 124.8, 125.7, 125.9, 127.5, 127.7, 129.5, 131.0, 131.8, 134.0, 136.2, 136.5, 138.3, 141.5, 147.4, 147.7, 151.3, 151.5. Anal. Calcd for $C_{77}H_{63}N_3$ (1030.34): C, 89.76; H, 6.16; N, 4.08. Found: C, 89.68; H, 6.27; N, 4.07.

Preparation of 9,9-Diethyl-2,4,7-tris[2-(4-nitrophenyl)-vinyl]-9*H*-fluorene (5). A mixture of **9** (0.501 g, 1.0 mmol) and triethyl phosphite (1.5 mL) was refluxed for 18 h. Excess triethyl phosphite was distilled under reduced pressure and

the residue was dried in vacuo. The intermediate **11**, obtained above, 4-nitrobenzoaldehyde (0.499 g, 3.3 mmol), and tetrabutylammonium bromide (1.07 g, 3.3 mmol) were dissolved in CH_2Cl_2 (20 mL) followed by addition of a 50% aqueous solution of NaOH (10 mL). After the mixture was reacted at room temperature for 20 h, water was added and the organic layer was separated. The water phase was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic phase was carefully washed with water and dried over $MgSO_4$. Upon solvent removal, the crude product was purified by column chromatography by using CH_2Cl_2/cyclohexane 1:2 as eluent. Recrystallization from CH_2Cl_2/hexane afforded 0.22 g of orange crystals (33%). Mp >300 °C dec; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 8.5 Hz, 2H, Ph-H), 8.26 (m, 4H, Ph-H), 8.06 (d, J = 16.0 Hz, 1H, CH=CH), 7.84 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 9.0 Hz, 2H), 7.67−7.71 (m, 5H), 7.53−7.59 (m, 4H), 7.41 (d, J = 16.0 Hz, 1H, CH=CH), 7.33 (d, J = 25.0 Hz, 1H, CH=CH), 7.22−7.28 (m, 2H), 2.15 (q, J = 7.3 Hz, 4H, CH_2), 0.38 (t, J = 7.3 Hz, 6H, CH_3); ^{13}C NMR (DMF) δ 8.7, 33.2, 56.2, 121.6, 121.8, 124.4, 124.6, 126.0, 127.1, 127.4, 127.8, 128.4, 130.8, 131.3, 133.6, 133.8, 134.0, 136.5, 136.8, 139.7, 142.1, 144.6, 145.0, 147.0, 147.4, 152.0, 152.4; HRMS (EI) calcd 663.2369, found 663.2359. Anal. Calcd for $C_{41}H_{33}N_3O_6$ (663.72): C, 74.19; H, 5.01; N, 6.33. Found: C, 74.08; H, 4.99; N, 6.28.

Preparation of 2,4,7-Tris(formyl)-9,9-diethylfluorene (14). A mixture of **9** (1.02 g, 2 mmol), anhydrous NaOAc (1.23 g, 15 mmol), acetic anhydride (0.85 mL, 9.0 mmol), and acetic acid (10 mL) was heated at 90 °C for 24 h. Water was added and the mixture was extracted with methylene chloride (3 × 15 mL). The crude product obtained by solvent removal was purified by column chromatography by using hexane/ethyl acetate (2:1) as eluent to give 0.65 g of sticky oil as **12** (75%). ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 7.68 (d, J = 7.8 Hz, 1H, Ph-H), 7.33 (m, 4H, Ph-H), 5.50 (s, 2H, 4-CH_2), 5.18 (s + s, 4H, 2- and 7-CH_2), 2.15 (s, 9H, $COCH_3$), 2.05 (m, 4H, CH_2), 0.32 (t, J = 7.4 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 8.9, 21.4, 21.5, 33.1, 56.1, 64.9, 66.6, 66.8, 123.0, 123.1, 127.6, 128.4, 130.2, 134.9, 135.1, 139.6, 140.7, 151.3, 151.8, 171.0, 171.1. Anal. Calcd for $C_{26}H_{30}O_6$ (438.53): C, 71.21; H, 6.90; N, 0. Found: C, 71.30; H, 7.10; N, 0.

Compound **12** (4.9 g, 11.2 mmol) and NaOH (3.4 g, 85.0 mmol) in EtOH (80 mL) were then heated at 40 °C for 21 h. The mixture was neutralized with 10% HCl and extracted with CH_2Cl_2 (3 × 20 mL). The crude product obtained upon solvent removal was passed through a column with CH_2Cl_2/MeOH (10:1) as eluent to afford 0.28 g of **13** (66% yield). Mp 135−136 °C; ^{1}H NMR (300 MHz, $CDCl_3$-*d*) δ 7.81 (d, J = 8.4 Hz, 1H, Ph-H), 7.33 (m, 4H, Ph-H), 5.10 (s, 2H, 4-CH_2), 4.78 (s + s, 4H, 2- and 7-CH_2), 2.03 (m, 4H, CH_2), 0.27 (t, J = 7.4 Hz, 6H, CH_3); ^{13}C NMR (DMSO) δ 9.3, 33.0, 55.6, 62.4, 63.9, 64.0, 119.8, 121.2, 123.4, 124.8, 125.9, 136.8, 137.3, 140.3, 141.4, 141.5, 150.4, 150.5. Anal. Calcd for $C_{20}H_{24}O_3$ (312.41): C, 76.89; H, 7.74; N, 0. Found: C, 76.70; H, 7.83; N, 0.

To a solution of triol **13** (0.9 g, 2.9 mmol) in CH_2Cl_2 (40 mL) was slowly added pyridinium chlorochromate (3.1 g, 14.4 mmol) with cooling by an ice−water bath. The mixture was reacted at room temperature for 6 h, stirred with ether (50 mL) for 0.5 h, and passed through a short column filled with silica gel. The solvent was removed and the residue was purified with column chromatography by using hexane/ethyl acetate (2:1) as eluent, affording 0.44 g of pure **14** (50%). Mp 146−147 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.63 (s, 1H, CHO), 10.20, (s, 1H, CHO), 10.15 (s, 1H, CHO), 8.88 (d, J = 8.7 Hz, 1H, Ph-H), 8.41 (s, 1H, Ph-H), 8.14 (s, 1H, Ph-H), 7.95 (s + d, 2H, Ph-H), 2.22 (q, J = 7.2 Hz, 4H, CH_2), 0.28 (t, J = 7.4 Hz, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 8.7, 33.1, 56.6, 122.8, 127.2, 127.5, 130.8, 133.5, 135.2, 135.9, 137.1, 144.8, 146.0, 153.3, 154.8, 191.0, 191.1, 192.2. Anal. Calcd for $C_{20}H_{18}O_3$ (501.10): C, 78.41; H, 5.92, N, 0. Found: C, 78.23; H, 5.97, N, 0.

Preparation of 6. 4-Formyltriphenylamine (2.18 g, 8.0 mmol), **9** (2.69 g, 4.0 mmol), and Bu_4NBr (2.58 g, 8.0 mmol) in CH_2Cl_2 (40 mL) were mixed with a 50% aqueous solution of NaOH (6 mL). The mixture was stirred at room temperature for 48 h. The aqueous phase was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phase was washed with water and dried over $MgSO_4$. Solvent was removed in vacuo and the residue was submitted to column chromatograph by using CH_2Cl_2/hex (30/1) as eluent. Fluorene derivative **15** (0.35 g) was isolated as a sticky yellow oil (9%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, J = 7.8 Hz, 1H), 7.34−7.47 (m, 8H), 7.17−7.30 (m, 8H), 6.98−7.15 (m, 20H), 4.00 (m, 4H, $POCH_2$), 3.65 (d, J = 21.3 Hz, 2H, PCH_2), 2.06 (m, 4H, CH_2), 0.87 (m, 6H, CH_3), 0.31 (t, J = 7.1 Hz, 6H). A mixture of **15** (116.7 mg, 0.13 mmol), **14** (13.1 mg, 0.043 mmol), and *t*BuOK (28.0 mg, 0.250 mmol) in HMPA (1 mL) was stirred at room temperature under Ar for 20 h. Water and CH_2Cl_2 were added, the water layer was extracted with CH_2Cl_2 (10 mL) twice, and the combined organic phase was washed with water anddried over $MgSO_4$. Solvent was removed and the crude product was purified with column chromatography by using CH_2Cl_2/hexane (1/6) as eluent. The product **6** (35 mg) was obtained as a bright yellow powder (32%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96−8.12 (m, 9H), 7.84−7.89 (m, 2H), 7.58−7.73 (m, 6H), 7.40−7.49 (m, 23H), 7.19−7.36 (m, 42H), 6.98−7.17 (m, 72H), 2.22 (m, 4H, CH_2), 2.13 (m, 12H, CH_2), 0.53 (t, J = 7.0 Hz, 6H, CH_3), 0.41 (m, 18H, CH_3); MS (MALDI-TOF) $[M + H]^+$ 2574.6. Anal. Calcd for $C_{194}H_{162}N_6$ (2577.49): C, 90.40; H, 6.34, N, 3.26 Found: C, 90.14; H, 6.45, N, 3.41.

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