Articles

Synthesis of New Two-Photon Absorbing Fluorene Derivatives via Cu-Mediated Ullmann Condensations

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The Ullmann amination reaction was utilized to provide access to a number of fluorene analogues from common intermediates, via facile functionalization at positions 2, 7, and 9 of the fluorene ring. Through variation of amine or iodofluorene derivative, analogues bearing substitutents with varying electron-donating and electron-withdrawing ability, e.g., diphenylamino, bis-(4-methoxyphenyl)amine, nitro, and benzothiazole, were synthesized in good yield. The novel fluorene derivatives were fully characterized, including absorption and emission spectra. Didecylation at the 9-position afforded remarkably soluble derivatives. Target compounds 4, 5, and 9 are potentially useful as fluorophores in two-photon fluorescence microscopy. Their UV−vis spectra display desirable absorption in the range of interest suitable for two-photon excitation by near-IR femtosecond lasers. Preliminary measurements of two-photon absorption indicate the derivatives exhibit high two-photon absorptivity, affirming their potential as two-photon fluorophores. For example, using a 1210 nm femtosecond pump beam, diphenylaminobenzothiazolylfluorene 4 exhibited nondegenerate two-photon absorption, with two-photon absorptivity (δ) of ca. 820×10^{-50} cm^4 s photon^{-1} molecule^{-1} at the femtosecond white light continuum probe wavelength of 615 nm.

Introduction

Organic materials exhibiting significant nonlinear optical effects have been a subject of intense investigation recently.[2] In particular, compounds that undergo strong nonlinear, multiphoton absorption are being investigated as materials for a wide variety of potential applications in areas ranging from optical sciences, biophotonics, materials sciences, and photochemistry, to name a few.

Multiphoton absorption can be defined as simultaneous absorption of two or more photons through virtual states in a medium.[3] More specifically, the nonlinear process of two-photon absorption (TPA) has been gaining greater interest among these multidisciplinary areas, particularly in the rapidly developing field of multiphoton fluorescence imaging.[4] Since the probability of a TPA process is proportional to the square of the intensity, photoexcitation and upconverted fluorescence is confined to the focal volume. Many other applications of TPA have been suggested, ranging from their use as three-dimen-

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sional optical data storage devices, optical switching devices for optical computing and telecommunications applications, as dyes in laser technology, optical storage devices, and photodynamic cancer therapy.[5–9] Recently, we reported two-photon induced polymerization as a means of three-dimensional microfabrication.[10]

The theory of the simultaneous absorption of two photons was developed by Goeppert-Mayer in 1931,[3] but remained mainly a conceptual curiosity until the advent of the pulsed laser providing very high-intensity light. For simplicity, two-photon absorption can be conceptualized from a semiclassical perspective.[11] In the TPA process, molecules exposed to high intensity light can undergo near simultaneous absorption of two photons mediated by a so-called "virtual state", a state with no classical analogue. The combined energy of the two photons accesses a stable excited state of the molecule. As light passes through a molecule, the virtual state may form, persisting for a very short duration (on the order of a few femtoseconds). TPA can result if a second photon arrives before decay of this virtual state, with the probability of TPA scaling with the square of the light intensity. This process is generally termed simultaneous two-photon absorption. Two-photon absorption, thus, involves the *concerted* interaction of both photons that combine their energies to produce an electronic excitation analogous to that conventionally caused by a single photon of a correspondingly shorter wavelength. Unlike single photon absorption, whose probability is linearly proportional to the incident intensity, the TPA process depends on both a spatial and temporal overlap of the incident photons and takes on a quadratic (nonlinear) dependency on the incident intensity.

For nonpolar molecules with a low-lying, strongly absorbing state near the virtual level, only excited states that are forbidden by single-photon selection rules can be populated via two-photon absorption.[11] The probability that this low-lying state can contribute to the virtual state is predicted by Heisenberg's uncertainty principle, with a virtual state lifetime approximated as $h/(4\pi\Delta E)$, where h is Planck's constant and ΔE is the energy difference between the virtual and actual states. In contrast, strong TPA can occur in polar molecules by a different mechanism in which a large change in dipole moment ($\Delta\mu > 10$ D) occurs upon excitation of the ground to an excited state. Single-photon allowed states can then be accessed via TPA, and the virtual state lifetime is proportional to $\Delta\mu^2$. In this case, both the ground and excited states can participate in formation of the virtual state, enhancing TPA. Two-photon absorptivity, δ, is expressed in Goppert-Mayers units (GM), with 1 GM = 1×10^{-50} cm^4 s molecule^{-1} photon^{-1}. In polar molecules

with large $\Delta\mu$ between the ground and excited states, δ values in excess of 10 GM have been observed.[11]

Particular molecules can undergo upconverted fluorescence through nonresonant two-photon absorption using near-IR radiation, resulting in an energy emission greater than that of the individual photons involved (upconversion). The use of a longer wavelength excitation source for fluorescence emission affords advantages not feasible using conventional UV or visible fluorescence techniques, e.g., deeper penetration of the excitation beam and reduction of photobleaching.[4] Ar ion (488 nm) and frequency-doubled Nd:YAG (532 nm) lasers are the commonly used light sources for conventional (single-photon) laser scanning confocal microscopy (due to their ready availability and low cost). Such light sources require fluorophores with strong absorbance near these wavelengths. Two-photon laser scanning fluorescence microscopy systems, on the other hand, are generally configured with a Ti:sapphire laser with 80–120 fs pulse output in the near-IR region (700–900 nm). Consequently, many typical single-photon fluorophores undergo only weak TPA in this region, since a fluorophore with λ_{max} of 490 nm would be expected to undergo two-photon absorption at ca. 980 nm (a wavelength where the output power of commercial Ti:sapphire lasers is practically too low to be useful). Thus, commercial fluorophores are far from being optimized for use in two-photon fluorescence microscopy. A more reasonable absorption maximum for such chromophores is 380–420 nm (facilitating use of near-IR femtosecond sources in the range of 760–840 nm), since the TPA λ_{max} will be approximately twice the wavelength of the single-photon λ_{max}.

Although numerous fluorophores for conventional fluorescence microscopy are commercially available, few efforts have addressed the need for multiphoton absorbing fluorophores. As part of a program to establish an empirical body of nonlinear absorptivity as a function of molecular structure, and prepare efficient two-photon absorbing fluorophores, we are preparing and characterizing a series of compounds with systematic variation in molecular structure. Polar organic compounds such as 4-nitroaniline and 4-amino-4′nitrobiphenyl undergo increases in dipole moments on excitation from 6 to 14 D and from 6 to 20 D, respectively.[12] Thus, such compounds are expected to possess high two-photon absorptivity, as discussed above. We chose the fluorenyl ring system to serve as a thermally and photochemically stable π-conjugated analogue of the 4,4′-disubstituted biphenyl derivatives. Locking the biphenyl unit into the fluorenyl ring provides greater electron delocatization through increased π molecular orbital overlap between the rings, enhancing molecular polarizability. Importantly, fluorene can be readily functionalized in the 2, 7, and/or 9-positions. We recently reported the synthesis, linear optical, and nonlinear optical characterization of two fluorene derivatives, prepared by Pd-catalyzed Heck coupling, with high two-photon absorptivities.[13]

To prepare a series of derivatives for nonlinear absorption studies, we sought efficient preparation of key, common intermediates using synthetic methodology that would be readily adaptable for rapid functionalization.

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Scheme 1
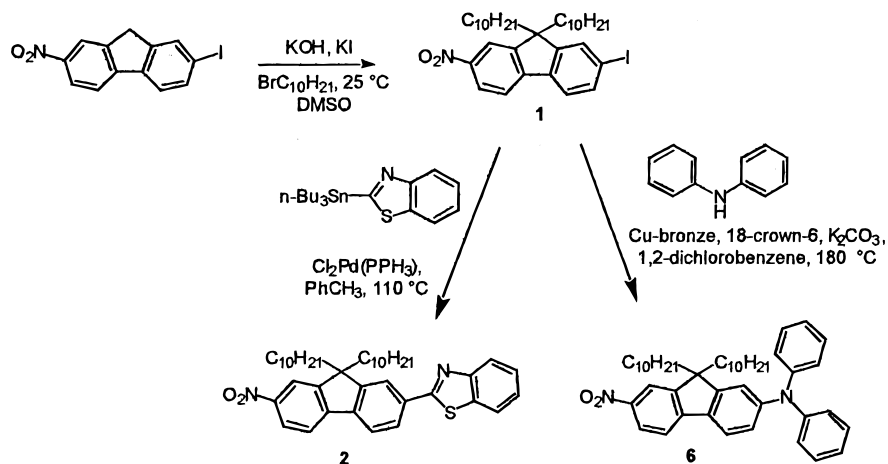
We wish to report utilization of the Ullmann condensation reaction of arylamines with aryl iodides[14–16] to prepare a series of fluorene derivatives of varying electronic characteristics. Like 4-amino-4′nitrobiphenyl, such molecules should possess large transition dipoles and strong two-photon absorptivity. Structural confirmation data for these new derivatives are presented. Importantly, linear absorption and emission spectra and preliminary TPA data indicate that this class of compounds may be useful as two-photon fluorophores, providing new materials for imaging and other two-photon related applications.

Results and Discussion

The synthetic strategy employed involved the efficient preparation of key intermediates from fluorene. The fluorenyl ring system was chosen to suffice as a thermally and photochemically stable π-conjugated system, that can be readily functionalized on the 2, 7, and/or 9-positions. The electronic character of the π-conjugated central fluorene ring system was altered by varying the substitutents at the 2 and/or 7 positions. In addition, long alkyl groups at the 9-position were incorporated to enhance solubility. Details of the synthetic methodology and characterization data for the series of fluorene derivatives shown in Schemes 1–3 are discussed below.

2-Nitrofluorene was prepared in 80% yield by regiospecific nitration of fluorene with nitric acid in AcOH at 85 °C, following a literature preparation.[17] Regiospecific iodonation of 2-nitrofluorene with I_2, $NaNO_2$, AcOH, and H_2SO_4 at 115 °C afforded 7-iodo-2-nitrofluorene in 79% yield after recrystallization from AcOH (mp = 245–246 °C, lit.[18] mp 244–245 °C). CHN analysis was in good agreement with calculated values. Dialkylation of 7-iodo-2-nitrofluorene (Scheme 1) was accomplished by generation of the fluorenyl anion with KOH in DMSO and subsequent didecylation with 1-bromodecane in the presence of KI at room temperature.[19] 7-Iodo-9,9-didecyl-2-nitrofluorene (**1**) was obtained as a yellow solid in 77%

isolated yield after column chromatography. MS, ^{1}H, and ^{13}C NMR spectroscopic analysis confirmed formation of the desired product, with CHNI analysis in good agreement with calculated values. Evident in the ^{1}H NMR spectrum were characteristic resonances of the decyl groups, with the six terminal methyl protons appearing as a triplet centered at 0.83 ppm, broad multiplets at 0.56, 1.05, and 1.18 corresponding to 32 of the 36 methylene protons, and the four methylene protons α to the fluorenyl benzylic carbon (C9) at 1.99 ppm, a signature that will be common for the fluorene derivatives described hereafter. (2-Tri-*n*-butylstannyl)benzothiazole was prepared in 90% yield by treating benzothiazole with *n*-BuLi in THF at −75 °C, followed by addition of tri-*n*-butyltin chloride, as previously reported.[19] Pd-catalyzed Stille coupling was subsequently performed between **1** and (2-tri-*n*-butylstannyl)benzothiazole (Scheme 2) in refluxing toluene with either tetrakis(triphenylphosphine)palladium(0) or dichlorobis(triphenylphosphine)-palladium(II).[20] 2-(9,9-Didecyl-7-nitrofluoren-2-yl)benzothiazole (**2**) was obtained as yellow crystals in 61% isolated yield after column chromatography. Clearly evident in the FT-IR spectrum were absorptions attributable to the asymmetric and symmetric NO_2 stretching vibrations at 1519 and 1337 cm^{-1}, respectively. Also present was the benzothiazole C=N stretching vibration at 1589 cm^{-1}. Nitro derivative **2** exhibited UV−visible absorption ranging from 220 to 420 nm with λ_{max} at 365 nm. CHNS analysis results were in excellent agreement with calculated values. ^{1}H and ^{13}C NMR spectra were consistent, with the hallmark imine carbon of the benzothiazole ring (C2′) appearing downfield as expected at 168 ppm.[21]

Fast, quantitative reduction of **2** was achieved using hydrazine hydrate and 10% Pd/C in a 1:1 mixture of EtOH and THF at 70 °C (Scheme 2),[22] providing 7-benzothiazole-2-yl-9,9-didecylfluoren-2-ylamine (**3**) as a bright yellow viscous oil. Amine **3** was used directly in subsequent steps due to its oxidative lability. The UV−visible spectrum of **3** ranged from 210 to 450 nm, with the $\lambda_{max} = 380$ nm, exhibiting an expected 15 nm bathochromic shift in its spectrum relative to **2**. The amine also

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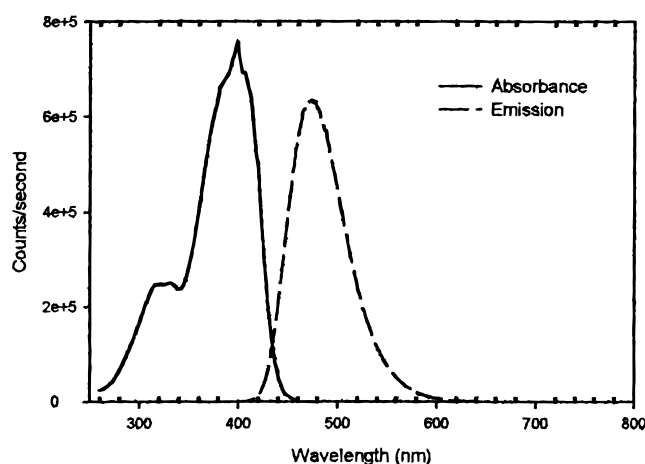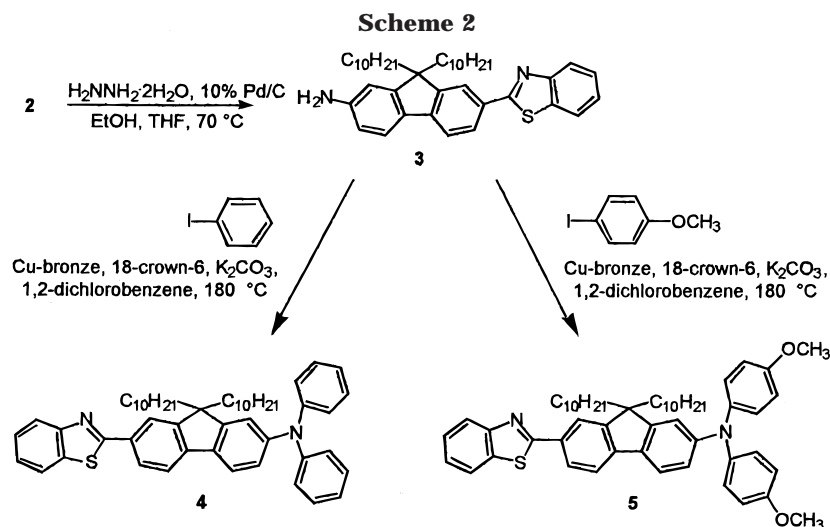**Scheme 2**

Figure 1. Absorption and emission spectra of (7-benzothiazol-2-yl-9,9-didecylfluoren-2-yl)diphenylamine (**4**) in THF.
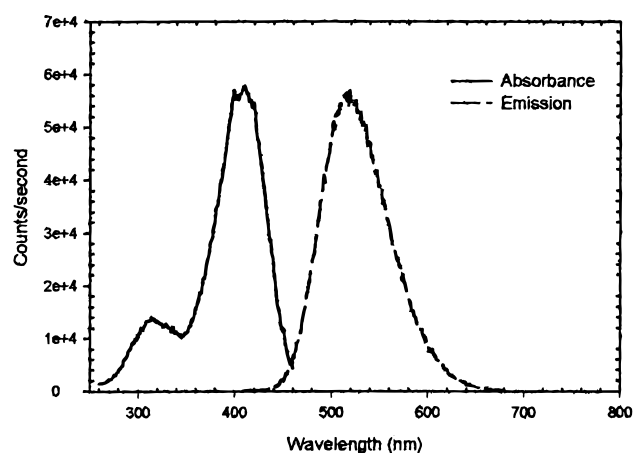
Figure 2. Absorption and emission spectra of (7-benzothiazol-2-yl-9,9-didecyl-fluoren-2-yl)bis(4-methoxyphenyl)amine (**5**) in THF.

displayed a brilliant blue fluorescence in solution upon irradiation with long wavelength UV radiation. The FT-IR spectrum of **3** revealed characteristic stretching absorptions for NH_2 (3741 and 3383 cm^{-1}) and benzothiazole C=N (1603 cm^{-1}). MS, ^{1}H, and ^{13}C NMR spectroscopic data provided additional structural confirmation of **3**, with the NH_2 resonances observed as a broad singlet at 3.82 ppm in the ^{1}H NMR spectrum and a concomitant upfield shift of the protons on C1 and C3 of the fluorene ring upon reduction of NO_2 to NH_2. Amine **3** was a key intermediate from which funcitonalization of the structure was performed using Ullmann amination reaction conditions. A new TPA dye was attained via a Cu-meditated Ullmann condensation of **3** with iodobenzene in *o*-dichlorobenzene using K_2CO_3 as base and 18-crown-6 at 180 °C (Scheme 2).[23] (7-Benzothiazol-2-yl-9,9-didecyl-fluoren-2-yl)diphenylamine **4** was obtained in 80% yield as a yellow viscous oil after column chromatographic purification. The FT-IR spectrum revealed the complete disappearance of the NH_2 stretching vibrations observed in **3**, likewise the NH_2 resonances were no longer observed in the ^{1}H NMR spectrum of **4**. The absorption and emission spectra of **4** are illustrated in Figure 1. The UV−vis absorption of **4** ranges from 239 to 450 nm with a λ_{max} of 392 nm. Fluorenylbenzothiazole **4** emitted

brilliant yellow-green fluorescence in solution upon exposure to long wavelength UV radiation. As can be seen, the fluorescence emission spectrum of **4** ranges from 400 to 630 nm with an emission λ_{max} of 475 nm upon excitation at 380 nm. Fluorene derivative **4** possesses highly desirable characteristics for use in two-photon fluorescence microscopy, i.e., since it has a λ_{max} of 392 nm.

Amine **3** was used to prepare another TPA dye with the aim to increase the electron density of the donor relative to that of **4**, producing a slight bathochromic shift in the absorption spectrum. Hence, **3** was subjected to similar Ullmann amination conditions with 4-iodoanisole, providing (7-benzothiazol-2-yl-9,9-didecylfluoren-2-yl)-bis-(4-methoxyphenyl)amine (**5**) as a bright yellow viscous oil in 82% yield after column chromatography (Scheme 2). CHN analysis was in good agreement with calculated values, and FT-IR spectroscopic analysis revealed the asymmetric and symmetric C−O−C stretches at 1241 and 1038 cm^{-1}, respectively. The ^{1}H NMR spectrum of **5** was similar to that of **4** with a major distinction of a singlet at 3.78 ppm, characteristic of the methoxy protons. A new signal was evident in the ^{13}C NMR spectrum at 55.3 ppm, ascribable to the methoxy carbons. Absorption and emission spectra for methoxy derivative **5** are presented in Figure 2. The UV−visible absorption of **5** ranged from 239 to 480 nm with a λ_{max} at 408 nm. The

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Scheme 3
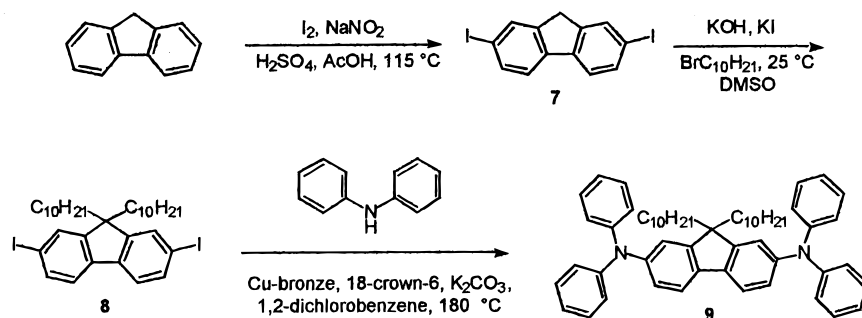
fluorescence emission spectrum of **5** ranged from 410 to 675 nm with an emission λ_{max} of 516 nm upon excitation at 400 nm. Fluorene derivative **5** also possesses highly desirable characteristics for use in two-photon fluorescence microscopy, i.e., it has a λ_{max} of 408 nm.

7-Iodo-9,9-didecyl-2-nitrofluorene (**1**) was also employed as a key intermediate, whereby both the nitro and iodo groups in the 2 and 7 positions allowed for relatively easy derivitization of the fluorene ring system. The Ullmann amination conditions discussed above were applied to **1** with diphenylamine, affording (9,9-didecyl-7-nitro-fluoren-2-yl)diphenylamine **6** (Scheme 1) as an orange oil in ca. 80% yield. Fluorene **6** exhibited absorption from 220 to 520 nm with a λ_{max} of 300 nm in THF, and, as anticipated, no fluorescence detectable upon exposure to long wavelength UV light. CHN analysis was found to be in good agreement with calculated values, and the FT-IR spectrum displayed asymmetric and symmetric NO_2 stretches at 1519 and 1334 cm^{-1}, respectively.

The versatility of the Ullmann condensation reaction for the preparation of another dye of varying electronic character was demonstrated in the formation of 9,9-didecyl-2,7-bis-(*N,N*-diphenylamino)fluorene (**9**). The symmetrically situated bis-diphenylamino donor groups were incorporated at the fluorenyl 2 and 7 positions, affording a pale yellow crystalline solid in ca. 20% yield from fluorene. CHN analysis was found to be in excellent agreement with calculated values. Additional structural confirmation was secured by ^{1}H and ^{13}C NMR spectroscopic analysis, with broad resonances observed for aromatic protons from 6.7 to 7.30 ppm in the ^{1}H NMR spectrum. Also evident in the ^{1}H NMR spectrum were characteristic resonances of the decyl groups, with the six terminal methyl protons appearing as a triplet centered at 0.85 ppm, broad multiplets at 0.65, 1.05, and 1.20, corresponding to 32 of the 36 methylene protons, and the four methylene protons α to the fluorenyl benzylic carbon (C9) at 1.85 ppm. Evident in the absorption and emission spectra (Figure 3) was absorption from 240 to 410 nm with a λ_{max} of 378 nm, suitable for two-photon excitation at ca. 760 nm. Fluorene **9** exhibited fluorescence emission from 375 to 525 nm with an emission λ_{max} of 400 nm upon excitation at 370 nm. Two-photon absorption measurements are currently underway using a nondegenerate femtosecond pump/probe technique.[24] Preliminary data indicate that the fluorene derivatives prepared in this study have high two-photon absorptivity. For example, diphenylaminobenzothiazolyl-
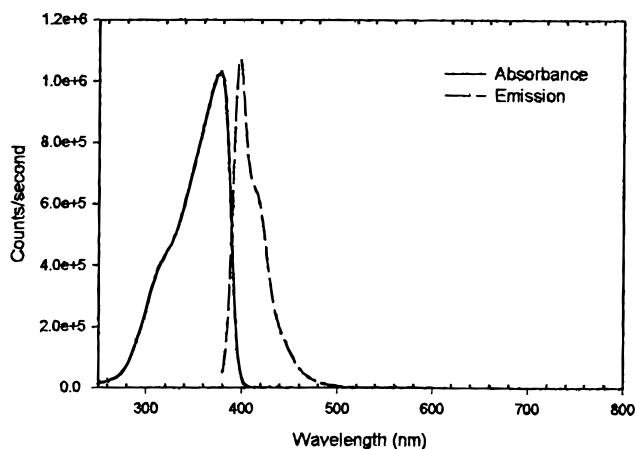

Figure 3. Absorption and emission spectra of 9,9-didecyl-2,7-bis(*N,N*-diphenylamino)fluorene (**9**) in THF.

fluorene **4** exhibited nondegenerate TPA in a pump probe experiment in which TPA was induced by spatial and temporal overlap of a 1210 nm femtosecond pump beam and a femtosecond white light continuum (wlc) probe beam. The wavelength of the pump beam was selected as 1210 nm (the photon energy at this wavelength is not energetic enough to cause degenerate TPA). At a probe wavelength of 615 nm from the wlc, the TPA cross section (δ) was ca. 820 × 10^{-50} cm^4 s photon^{-1} molecule^{-1}. This is consistent with δ values expected for molecules that undergo large dipole moment changes upon photoexcitation and compares quite favorably with δ's for recently reported chromophores with high two-photon absorptivity.[19,25] Details of nonlinear absorption spectroscopic analysis and quantum mechanical calculations of the derivatives reported herein will be reported elsewhere.

Conclusions

A strategy was developed in which the Ullmann amination reaction provided access to a number of fluorene analogues from common intermediates. The synthetic methodology facilitated facile functionalization at positions 2, 7, and 9 of the fluorene ring. Thus, efficient synthesis of key intermediates (**1** and **3**) afforded new TPA chromophores from fluorene. Systematic variation of molecular structure was accomplished, providing derivatives of varying electronic character. Through conversion of amine or iodofluorene derivatives, analogues bearing substitutents with varying electron-donat-

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ing and electron-withdrawing ability, e.g., diphenylamino, bis-(4-methoxyphenyl)amine, nitro, and benzothiazole, were prepared. The versatility of the Ullmann condensation reaction provided target compounds **4**, **5**, **6**, and **9** in reasonable yields. All target compounds were fully characterized, including mp, UV−vis, IR, elemental analysis, and ^{1}H and ^{13}C NMR, resulting in a series of well characterized, highly functionalized fluorene derivatives.

A remarkable feature of these materials is their solubility in common organic solvents (e.g., hexane, THF, CH_2Cl_2), due, in large part, to the decyl groups at the 9 position of the fluorene ring system. Unlike the unalkylated parent, most of the decylated derivatives were readily soluble in hexane. Target compounds **4**, **5**, and **9** are potentially useful as fluorophores in two-photon fluorescence microscopy. Their UV−vis spectra display desirable absorption in the range of interest suitable for two-photon excitation by near-IR femtosecond lasers used in two-photon fluorescence imaging. Preliminary measurements of nonlinear absorption indicate select derivatives exhibit high two-photon absorptivity, affirming their potential as two-photon fluorophores. Current efforts are directed at correlation of the fluorene derivatives' molecular structure with nonlinear absorption, determination of their photophysical properties (e.g., fluorescence quantum yields), and their use in two-photon fluorescence imaging.

Experimental Section

General Methods. Reactions were conducted under N_2 or Ar atmospheres. THF was distilled over sodium before use. All other reagents and solvents were used as received from commercial suppliers. 2-Nitrofluorene,[17] 7-iodo-2-nitrofluorene,[18] and 2-(tri-*n*-butylstannyl)benzothiazole[19] were synthesized according to the respective literature preparations.

Synthesis of 7-Iodo-9,9-didecyl-2-nitrofluorene (1). A mixture of 7-iodo-2-nitrofluorene (9.6 g, 28 mmol), 1-bromodecane (12.58 g, 57 mmol), KI (0.49 g, 3 mmol), and DMSO (65 mL) was stirred at room temperature, to which powdered KOH (6.65 g, 119 mmol) was slowly added under N_2. The color of the reaction mixture changed from bright yellow to dark green immediately after KOH addition, and, after 1h, the reaction mixture was poured into water and extracted with hexanes. The organic extract was washed with water, dried over MgSO$_4$, and concentrated, affording 16.5 g of a viscous dark orange oil that crystallized upon standing. Purification was accomplished by column chromatography using silica gel (40:1 hexanes/ EtOAc), providing 13.6 g of yellow solid (77% yd, mp = 58.5−60 °C). MS (EI, 70 eV) *m/z*: 617 (M$^+$); 477 (M − C$_{10}$H$_{21}$); 476 (M − C$_{10}$ H$_{21}$); 350 (M − C$_{19}$H$_{40}$); 336 (M − C$_{40}$H$_{41}$); 85 (C$_6$H$_{13}$$^+$); 71 (C$_4H_{11}$$^+$); 57 (C$_4H_9$$^+$); 43 (C$_3H_7$$^+$). Anal. Calcd for C$_{33}H_{48}INO_2$: C, 64.17; H, 7.83; I, 20.55; N, 2.27. Found: C, 64.47; H, 8.16; I, 20.40; N, 2.15. ^{1}H NMR (300 MHz, CDCl$_3$) δ: 8.25 (d, 1H), 8.18 (d, 1H), 7.79 (s, 1H), 7.72 (m, 2H), 7.53 (d, 1H), 1.99 (m, 4H), 1.18 (bm, 14H), 1.05 (bm, 14H), 0.83 (t, 6H), 0.56 (m, 4H). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 154.4, 151.3, 147.5, 146.5, 138.3, 136.5, 132.5, 123.3, 122.6, 120.0, 118.2, 95.5, 55.9, 39.9, 31.8, 29.7, 29.4, 29.2, 29.1, 23.6, 22.6, 14.1.

Synthesis of 2-(9,9-Didecyl-7-nitrofluoren-2-yl)benzothiazole (2). Fluorene derivative **1** (10.1 g, 16 mmol) and 2-(tri-*n*-butylstannyl)benzothiazole (8.5 g, 20 mmol) were dissolved in 200 mL of toluene and degassed under vacuum and Ar. Pd(PPh$_3$)$_4$ (0.47 g, 0.4 mmol) was added and the mixture was degassed. The reaction mixture was heated to 110 °C under Ar. and found to be complete after about 4.5 h during which the mixture turned black in coloration. Toluene was removed in vacuo, and the resulting dark orange oil was passed through a Si-gel column (30:1 hexanes/EtOAc) and

recrystallized from hexanes affording 6.24 g of bright yellow crystals (61% yd, mp = 94−95 °C). MS (EI, 70 eV) *m/z*: 624 (M$^+$); 497 (M − C$_9$H$_{19}$); 483 (M − C$_{10}$H$_{21}$); 357 (M − C$_{19}$H$_{39}$); 343 (M − C$_{20}$H$_{41}$); 311 (M − C$_{20}$H$_{43}$ − NO); 297 (M − C$_{20}$H$_{42}$ − NO$_2$); 71 (C$_5$H$_{11}$$^+$); 57 (C$_4H_9$$^+$); 43 (C$_3H_7$$^+$). UV−vis (THF): λ_{max} = 365 nm (220−420 nm). Anal. Calcd for C$_{40}$H$_{48}$N$_2$O$_2$S: C, 76.88; H, 7.83; N, 4.48; S, 5.13. Found: C, 76.90; H, 8.41; N, 4.32; S, 5.14. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 8.32, 8.37 (dd, 1H), 8.24, 8.18 (dd, 1H), 8.14 (m, 1H), 8.10 (m, 1H), 7.96, 7.92 (dm, 1H), 7.91, 7.88 (dd, 1H), 7.87, 7.84 (dd, 1H), 7.57, 7.38 (dd, 1H), 7.53, 7.42 (dm, 1H), 7.49, 7.46 (dd, 1H), 2.14 (m, 4H), 1.14 (bm, 14H), 1.04 (bm, 14H), 0.81 (t, 6H), 0.62 (m, 4H). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 168.0, 154.4, 153.4, 152.9, 147.9, 146.7, 141.6, 135.3, 134.6, 127.8, 127.6, 126.7, 125.6, 123.6, 123.5, 122.0, 121.8, 120.6, 118.6, 56.4, 40.2, 32.0, 30.4, 30.0, 29.7, 29.4, 24.0, 22.8, 14.3. FT-IR (KBr, cm^{-1}): 3066 (ArCH), 2924, 2852 (alCH), 1589 (C=N), 1519 (NO$_2$ as), 1337 (NO$_2$ sy).

Synthesis of 7-Benzothiazol-2-yl-9,9-didecylfluoren-2-ylamine (3). Nitro compound **2** (4.0 g, 6.4 mmol) was dissolved in a mixture of 15 mL of EtOH and 15 mL of THF at room temperature. To this was added 0.2 g of 10% Pd/C, and the mixture was heated to 70 °C under Ar. Hydrazine hydrate (2 mL, 38 mmol) was added dropwise via syringe over 20 min. The reaction mixture was stirred for 12 h at 70 °C, cooled to room temperature, and concentrated, affording a yellow oil. Purification was accomplished by passing a hexane solution of the amine through a silica gel plug, eluting with hexanes, providing 3.6 g of viscous, sticky yellow oil (95% yd). MS (EI, 70 eV) *m/z*: 594 (M$^+$); 453 (M − C$_{10}$H$_{21}$); 327 (M − C$_{19}$H$_{39}$); 313 (m-C$_{20}$H$_{41}$); 163 (C$_{13}$H$_7$$^+$); 57 (C$_4H_9$$^+$); 43 (C$_3H_7$$^+$). UV−vis (THF): λ_{max} = 380 nm (210−450 nm). ^{1}H NMR (200 MHz, CDCl$_3$) δ: 8.09, 8.05 (dm, 1H), 8.04 (d, 1H), 7.99, 7.95 (dd, 1H), 7.90, 7.86 (dd, 1H), 7.63, 7.59, 7.56, 7.51 (dd, 1H), 7.51, 7.44, 7.39, 7.32, (dq, 1H), 7.48, 7.35 (dm, 1H), 7.19 (m, 1H), 6.67 (M, 2H), 3.82 (bs, 2H), 1.98 (m, 4H), 1.15 (bm, 14H), 1.04 (bm, 14H), 0.82 (t, 6H), 0.66 (m, 4H). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 169.3, 154.5, 153.8, 150.8, 147.1, 145.1, 131.6, 130.8, 129.2, 128.4, 127.3, 126.4, 125.0, 123.0, 121.5, 118.8, 114.3, 109.8, 55.4, 40.8, 32.1, 30.4, 30.3, 29.8, 29.7, 29.5, 24.0, 22.8, 14.3. FT-IR (KBr, cm^{-1}): 3741, 3383 (NH$_2$), 2926, 2855 (alCH), 1460 (ArC=C), 1603 (C=N).

General Procedure for the Ullmann Condensation Used for the Preparation of 4, 5, 6, and 9. Synthesis of (7-Benzothiazol-2-yl-9,9-didecylfluorene-2-yl)diphenylamine (4). The amine **3** (0.53 g, 0.891 mmol) was dissolved in 3 mL of 1,2-dichlorobenzene at room temperature under N_2. To this were added K$_2$CO$_3$ (0.99 g, 7.16 mmol), 18-crown-6 (0.07 g, 0.265 mmol), and copper bronze (0.28 g, 4.41 mmol) at room temperature, resulting in an orange solution. Iodobenzene (0.25 mL, 3.56 mmol) was added, and the reaction mixture was heated to 180 °C for 43 h. Upon completion, the dark brown mixture was filtered hot through a short silica gel plug and the yellow solution was concentrated resulting in an yellow-orange oil. The high boiling solvent 1,2-dichlorobenzene, and excess iodobenzene were removed under reduced pressure. The orange oil was further purified by column chromatography on silica gel using first 10:1:3 hexanes/EtOAc/THF, followed by 15:1 hexanes/EtOAc resulting in 0.53 g of a bright yellow-orange oil (80% yd). UV−vis (THF): λ_{max} = 392 nm (239−450 nm). Anal. Calcd for C$_{52}$H$_{62}$N$_2$S: C, 83.59; H, 8.36; N, 3.75. Found: C, 83.53; H, 8.47; N, 3.83. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 8.13 (dm, 1H), 8.07 (dm, 1H), 7.04, 8.00 (dd, 1H), 7.93, 7.89 (dd, 1H), 7.51 (d, 1H), 7.63 (d, 1H), 7.54, 7.50, 7.49, 7.46 (dd, 1H), 7.42, 7.38, 7.37, 7.34 (1H), 7.31, 7.27 (dd, 4H), 7.16 (d, 1H), 7.13 (t, 2H), 7.07 (dm, 1H), 7.04 (dm, 4H), 1.90 (m, 4H), 1.20 (bm, 14H), 1.05 (bm, 14H), 0.85 (t, 6H), 0.70 (m, 4H). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 168.7, 154.2, 152.9, 151.4, 147.9, 147.7, 144.0, 135.0, 134.8, 131.4, 129.1, 127.1, 126.1, 124.8, 124.0, 123.1, 122.8, 122.7, 121.4, 121.3, 120.9, 119.3, 118.7, 55.3, 40.1, 31.8, 29.9, 29.5, 29.2, 23.8, 22.6, 14.0. FT-IR (KBr, cm^{-1}): 3060 (ArCH), 2925, 2853 (alCH), 1595 (C=N), 1461 (ArC=C).

(7-Benzothiazol-2-yl-9,9-didecylfluoren-2-yl)-bis-(4-methoxyphenyl)amine (5). A bright yellow oil was obtained after column chromatographic purification (0.58 g, 82% yd).

UV−vis (THF): λ_{max} = 408 nm (239−480 nm). Anal. Calcd for $C_{54}H_{66}N_2O_2S$: C, 80.35; H, 8.224; N, 3.47. Found: C, 80.08; H, 8.20; N, 3.35.; ^{1}H NMR (200 MHz, CDCl$_3$) δ: 8.09 (dm, 1H), 8.04 (dm, 1H), 8.02, 7.97 (dd, 1H), 7.92, 7.88 (dd, 1H), 7.66 (d, 1H), 7.35 (d, 1H), 7.32, 7.49, 7.48, 7.45 (dd, 1H), 7.40, 7.37, 7.36, 7.33 (dd, 1H), 7.10, 7.06 (dd, 1H), 6.98 (d, 1H), 6.92, 6.85 (dd, 4H), 8.88, 6.82 (dd, 4H), 3.78 (s, 6H), 1.90 (m, 4H), 1.20 (bm, 14H), 1.05 (bm, 14H), 0.85 (t, 6H), 0.75 (m, 4H). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 169.0, 155.7, 154.2, 152.8, 151.2, 150.0, 144.3, 141.2, 134.9, 133.1, 130.9, 127.1, 126.1, 124.8, 122.8, 121.4, 121.3, 120.7, 118.9, 115.8, 114.6, 55.3, 55.2, 40.1, 31.8, 29.8, 29.5, 29.3, 23.8, 22.6, 14.1. FT-IR (KBr, cm^{-1}): 3060 (ArCH), 2925, 2853 (alCH, methyl), 1603 (ArC=C), 1241 (C−O−C as), 1038 (C−O−C sy).

Synthesis of (9,9-Didecyl-7-nitrofluoren-2-yl)diphenyl-amine (6). An orange oil was obtained (4 g, 93% yd). UV−vis (THF): λ_{max} = 300 nm (220−520 nm). Anal. Calcd for $C_{45}H_{58}N_2O_2$: C, 82.02; H, 8.87; N, 4.25.; Found: C, 82.15; H, 8.95; N, 4.05. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 8.25, 8.22 (dd, 1H), 8.14 (d, 1H), 7.67 (d, 1H), 7.62 (d, 1H), 7.32, 7.29 (dd, 4H), 7.16 (d, 1H), 7.10 (m, 2H), 7.06 (dm, 1H), 7.03 (dm, 4H), 1.85 (m, 4H), 1.20 (bm, 14H), 1.05 (bm, 14H), 0.85 (t, 6H), 0.65 (m, 4H). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 153.9, 151.6, 149.3, 147.6, 147.5, 146.2, 132.8, 129.3, 124.6, 123.5, 123.4, 122.6, 121.9, 118.7, 118.0, 117.8, 55.8, 39.9, 31.9, 29.8, 29.5, 29.3, 23.8, 22.6, 14.1. FT-IR (KBr, cm^{-1}): 3060, 3038 (ArCH), 2923, 2852 (alCH), 1519 (NO$_2$ as), 1334 (NO$_2$ sy).

Synthesis of 9,9-Didecyl-2.7-bis(*N,N*-diphenylamino)-fluorene (or 2,7-Dibenzhydryl-9,9-didecyl-fluorene) (9). Fluorene was diiodinated using similar iodination conditions employed previously to yield crystalline 2,7-diiodofluorene (**7**, mp = 206−210 °C). ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.89 (s, 2H), 7.70 (d, 2H), 7.50 (d, 2H), 3.85 (s, 2H). Compound **7** was didecylated using the previous alkylation conditions to generate 9,9-didecyl-2,7-diiodofluorene (**8**) as a yellow oil. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 7.65 (d, s, 3H), 7.40 (d, 2H), 1.85 (m, 4H), 1.20 (bm, 14H), 1.05 (bm, 14H), 0.85 (t, 6H), 0.55 (m, 4H). The alkylated diiodofluorene **8** was subjected to similar Ullmann condensation reaction with diphenylamine to yield the desired product **9** as off-white crystals (20% yd from fluorene, mp = 81.5−83.5 °C). Anal. Calcd for $C_{57}H_{68}N_2$: C, 87.64; H, 8.77; N, 3.58. Found: C, 87.27; H, 8.77; N, 3.58. ^{1}H NMR (200 MHz, CDCl$_3$) δ: 6.70−7.30 (bm, 26H), 1.85 (m, 4H), 1.20 (bm, 14H), 1.05 (bm, 14H), 0.85 (t, 6H), 0.65 (m, 4H). ^{13}C NMR (50 MHz, CDCl$_3$) δ: 151, 145, 128, 123, 121.9, 119, 39, 39.9, 31.9, 29.8, 29.5, 29.3, 23.8, 22.6, 14.1.

Supporting Information Available: ^{1}H and ^{13}C NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.