

Synthesis of Two-Photon Absorbing Unsymmetrical Fluorenyl-Based Chromophores

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Unsymmetrical fluorenyl-based chromophores, flanked on either side by electron-acceptor (A) and/or electron-donating (D) groups, separated by conjugated (π) moieties, were synthesized. Heck coupling and Wittig reactions were utilized to prepare target fluorene derivatives that possess very high solubility in organic solvents, high thermal stability (up to 395 °C), and generally high fluorescence quantum yields (0.6–0.9). The systematic alteration of the structural design allowed for investigation of numerous factors that affect the optical nonlinearity, as well as probing effects of molecular symmetry, solvent polarity, strengths of electron donating and/or withdrawing end groups, and π -conjugation length. A detailed spectroscopic study of these molecules, including absorption, fluorescence emission, excitation, and excitation anisotropy, was conducted. Two-photon absorption (2PA) cross sections (δ) were determined by a nonlinear transmission method employing a femtosecond white-light continuum (WLC) pump–probe method, with all compounds exhibiting high two-photon absorption under femtosecond excitation. Compound **3** had a peak 2PA cross section, δ , of $1093 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ at 828 nm. In addition, excitation anisotropy studies permitted the determination of the spectral position of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transitions.

Introduction

Organic compounds are considered key elements for nonlinear optics given that their chemical structures can be modified through molecular engineering. Conjugated organic molecules generally provide large electron delocalization of the π electrons over the molecule, enhancing nonlinear optical properties. Among the various classes of nonlinear optical materials, multiphoton absorbing materials continue to be a subject of growing interest. Two-photon absorption (2PA) is the nonlinear process that involves the unusual capability of some molecules to absorb two photons simultaneously to populate an energy level within the molecule with energy equal to the sum of the energies of the two photons absorbed.¹ In particular 2PA fluorene derivatives have attracted interest in the last decades because of their utility or potential in multiple applications such as nondestructive fluorescence imaging,^{2–9} two-photon power-limiting

devices,^{10–12} and two-photon photodynamic therapy.^{13–15} In the 1990s, synthetic efforts focused on the preparation and characterization of new nonlinear absorbing organic dyes and the measurement of their 2PA cross sections. Several reports from various research groups revealed design strategies for efficient 2PA molecules by a systematic variation of chromophores with various electron-donor (D) and electron-acceptor (A) moieties, which are attached symmetrically or unsymmetrically to a conjugated electron bridge (π).^{9,16–23} The effects of varying the electron-donating or electron-

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accepting strength of end groups, introduction of additional groups in the center of the molecule to vary the charge redistribution, and altering the effective conjugation length have been studied to understand design criteria for producing structures with enhanced two-photon absorptivity.

Extending the conjugation length of a molecule can maximize the distance over which charge density can be distributed, with the polarizability of the molecule increasing the 2PA cross section, δ . This effect has been observed in a symmetrical series of chromophores of the A- π -A and A- π - π -A types, resulting in large enhancements of the 2PA cross section, δ .^{24–27} Thus, one can expect a similar effect in dipolar chromophores of the D- π - π - π -A and D- π - π - π - π -A type. The systematic modification of these molecules gives rise to numerous factors which affect the nonlinearity, and effects of structural symmetry, solvent polarity, strengths of electron-withdrawing end groups, and π -conjugation extensions were analyzed under one- and two-photon excitation.^{24,26–28}

We have been involved in the design and development of fluorenyl-based organic dyes, for example, symmetric chromophores of the A- π -A and D- π -D type,^{26,27} unsymmetrical D- π -A type chromophores,^{24–25,27} unsymmetrical branched chromophores,²⁹ and polymers³⁰ with high 2PA cross sections for molecular structure–nonlinear properties studies and multiphoton biological imaging.³¹ The fluorene ring, a π -conjugated system, exhibits several advantages as an aromatic core; that is, it has several sites (2, 4, 5, 7, and 9 positions) for functionalization to generate molecules with tailored photophysical properties, solubility, and high photostability. To expand the utility of two-photon absorbing materials in a number of new areas such as multiphoton

fluorescent probes and biomarkers for biomedical applications, it is necessary to develop new chromophores with 2PA cross sections orders of magnitude larger than endogenous chromophores in the red–near-infrared range (700–1200 nm), while maintaining high fluorescence quantum yields. For this reason, there is significant motivation to carefully study the effects of molecular structure variation on two-photon processes for the design of even more efficient two-photon absorbing materials.

Herein, we describe the synthesis, structural characterization, and the one- and two-photon photophysical properties of novel fluorene derivatives with unsymmetrical molecular structures of the D- π - π -A and D- π - π - π -A type, where D is an electron-donating group (diphenylamine), A is an electron-accepting group (nitro or benzothiazole), and π represents a conjugating construct. The conjugation length was extended via styryl and fluorenyl–vinylene moieties. These compounds possess both high two-photon absorptivity and high fluorescence quantum yield. Fluorene derivatives **1**, **2**, and **3** were synthesized via Heck coupling reactions as illustrated in Figures 2–4. Linear and nonlinear photophysical results are compared and analyzed with those obtained for the model compound **4**.

Experimental Section

Materials and Methods. (7-Bromo-9,9-didecylfluorene-2-yl)-diphenylamine (**A**),³² 9,9-didecyl-2-nitro-7-vinylfluorene (**B**),³³ and 9,9-didecylfluorene-2,7-dicarbaldehyde (**C**) were prepared as described previously,³⁰ and 2-(4-iodophenyl)benzothiazole (**H**) was prepared according to a literature procedure.³⁴ Reactions were carried out under a N₂ or Ar atmosphere. Tetrahydrofuran (THF) was distilled over sodium before use. All other reagents and solvents were used as received from commercial suppliers.

¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Varian 300 NMR spectrometer (300 MHz for ¹H, referenced to tetramethylsilane at $\delta = 0.0$ ppm and 75 MHz for ¹³C, referenced to CDCl₃ at $\delta = 77.0$ ppm). Fourier transform infrared (FT-IR) spectra were recorded on a Perkin-Elmer spectrophotometer model PE-1300 F0241. Elemental analyses were performed at Atlantic Microlab. Thermal stability was assessed with a TA Instruments model 2050 thermogravimetric analyzer under N₂ at a heating rate of 20 °C/min from room temperature to 550 °C.

Techniques. Steady-state absorption and fluorescence emission spectra of fluorene derivatives **1–3** were investigated in cyclohexanone, CH₂Cl₂, THF, and hexane, with concentrations $\leq 2 \times 10^{-6}$ M at room temperature in 1 cm quartz cuvettes using a Cary-3 UV–visible spectrophotometer and PTI Quantamaster spectrofluorimeter, respectively. All solvents and solutions used in these experiments were checked for spurious emission in the region of interest and purged with N₂ gas for 20 min prior to spectroscopic measurements. The concentrations did not exceed 2×10^{-6} M, and processes of reabsorption were negligible. Excitation anisotropy spectra were measured using three polarizers in the L-format method, with the correction for background signals,³⁵ in high viscosity solvents (silicon oil at 200 cP and polytetrahydrofuran,

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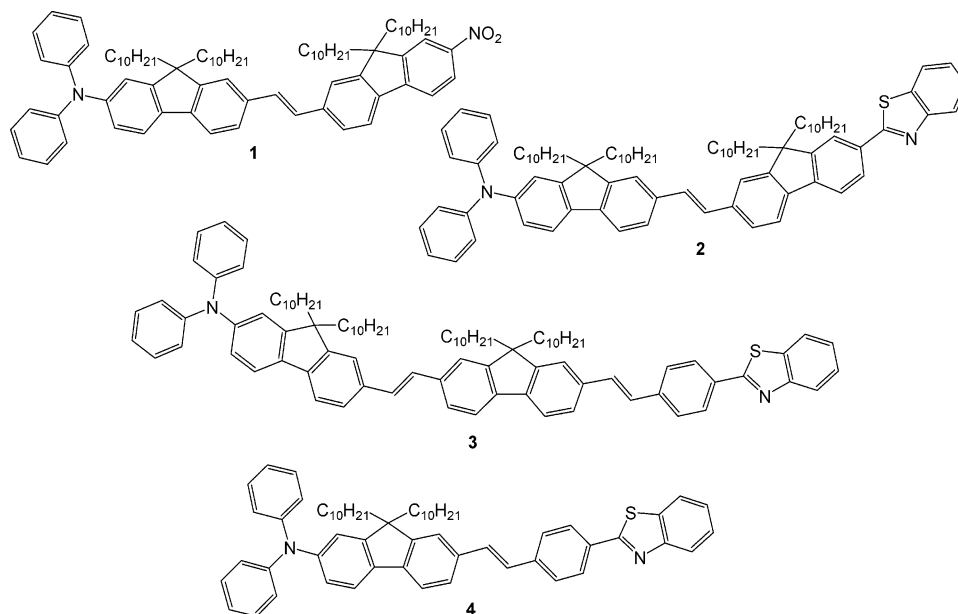


Figure 1. Molecular structures of fluorene derivatives 1, 2, 3, and 4.

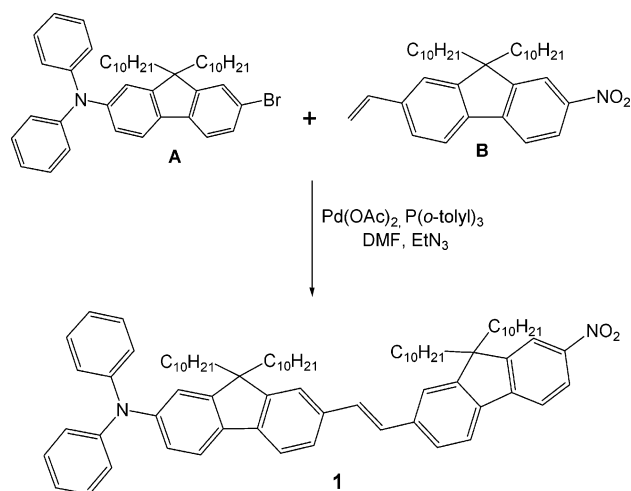


Figure 2. Synthesis of fluorene 1.

pTHF) at room temperature. Experimental details of anisotropy measurements were previously reported.^{35–38} Fluorescence quantum yields, Q , were measured for all compounds by a standard method,³⁹ relative to Rhodamine 6G in ethanol ($Q = 0.94$).³⁵

2PA cross sections (δ) were measured using the femtosecond white-light continuum (WLC) pump–probe method. Details of the 2PA measurements have been described elsewhere.^{28,40} Briefly, a Ti:sapphire based laser system (CPA-2001, CLARK-MXR) was used as a source for the nondegenerate WLC pump–probe method, providing laser pulses at 775 nm of 150 fs duration at a 1 kHz repetition rate. This laser, in turn, pumps an optical parametric amplifier (OPA) system (TOPAS, Light Conversion) which can be tuned from 570–2100 nm (0.6–2.2 eV) and provides up to 60

μJ of energy. The OPA provided the strong pump beam whose irradiance can be varied from 30 to 90 GW/cm^2 . Another identical OPA is used to generate a weak, broadband WLC probe beam by focusing 1–2 mJ of 1300 nm light into a 2.5 mm thick piece of calcium fluoride. The nondegenerate 2PA process requires simultaneous absorption of one photon from both the pump and the probe beams. Because the WLC possesses a broad bandwidth (400–700 nm or 0.7–3.1 eV), the full 2PA spectrum of the compound can be sampled provided the proper pump wavelength is chosen. In fact, the broadband nature of the WLC probe should, in principle, allow for a method which is single-shot in nature. However, in practice, the creation of the WLC imposes chirp on the probe beam which requires us to vary the temporal delay of the pump with respect to the probe to obtain the entire 2PA spectrum. By correcting for this temporal chirp and accounting for linear propagation effects, a sample's 2PA spectrum can be effectively characterized.

Synthesis of {7-[2-(9,9-Didodecyl-7-nitrofluoren-2-yl)vinyl]-9,9-didodecylfluorene-2-yl}diphenylamine (1). (7-Bromo-9,9-didodecylfluorene-2-yl)diphenylamine (A; 0.5 g, 0.72 mmol), 9,9-didodecyl-2-nitro-7-vinylfluorene (B; 0.44 g, 0.86 mmol), $\text{Pd}(\text{OAc})_2$ (37 mg, 0.16 mmol), tri-*o*-tolylphosphine (0.08 g, 0.26 mmol), and Et_3N (4 mL) were combined in a screw cap vial and heated at 90 °C for 96 h. The mixture was cooled to room temperature and filtered. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 . The organic layer was washed with distilled water, dried over MgSO_4 , filtered, and concentrated. The crude product was purified by column chromatography on silica gel eluting first, with hexane/toluene (85:15), followed by hexane/ EtOAc (95:5), affording 0.585 g of an orange oil (72% yield). Anal. Calcd for $\text{C}_{80}\text{H}_{108}\text{N}_2\text{O}_2$: C, 85.05%; H, 9.64%; N, 2.47%. Found: C, 84.99%; H, 9.67%; N, 2.40%. ^1H NMR (300 MHz, CDCl_3) δ : 8.25, 8.22 (dd, 1H), 8.17 (s, 1H), 7.76 (d, 2H), 7.60–7.46 (complex multiplets, aromatic protons 4H and olefinic protons 2H), 7.33–6.97 (complex multiplets, aromatic protons, 14H), 2.05 (bt, 4H, CH_2), 1.90 (bd, 4H, CH_2), 1.25–0.67 (m, 76H, CH_2 , CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ : 153.0, 152.4, 152.1, 151.3, 148, 147.5, 147.3, 146.9, 141.2, 138.9, 138.2, 135.9, 135.3, 130.4, 129.3, 127.6, 126.1, 124, 123.6, 123.5, 122.7, 121.6 (sp^2 carbon of $\text{RCH}=\text{CHR}$), 120.9, 120.7, 120.6, 119.7, 119.5, 119.4, 118.4, 56, 55.4, 40.8, 40.6, 32.3, 32.2, 30.5, 30.3, 30.1, 30, 29.9, 29.9, 29.8, 29.7, 29.6, 24.3, 24.2, 23.1, 23.0, 14.6.

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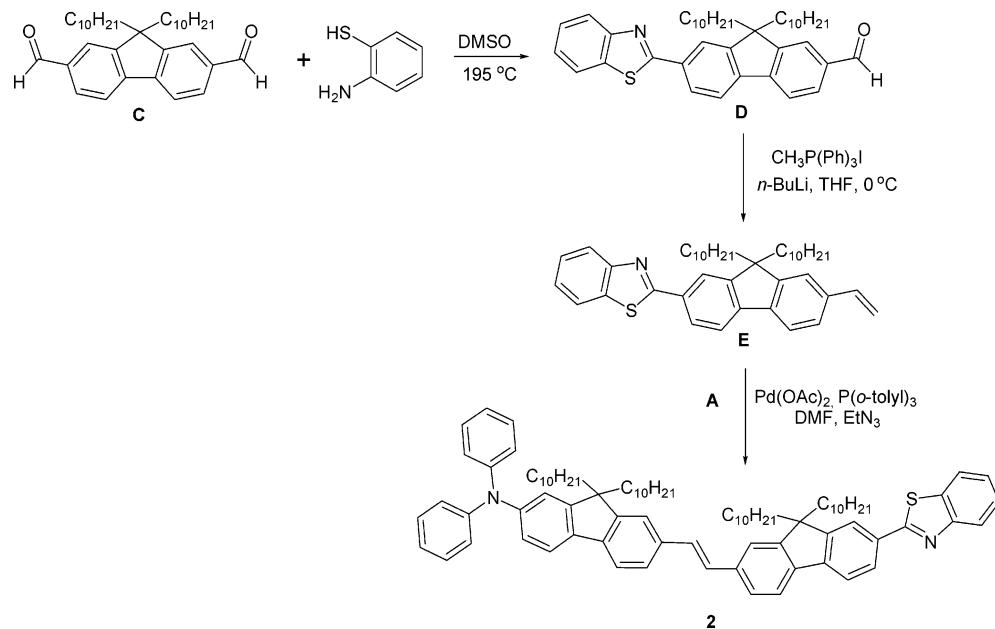


Figure 3. Synthesis of fluorene 2.

Synthesis of 2-(7-(9,9-Didecylfluorene-2-yl)benzothiazol-2-yl)benzothiazole (D). A mixture of 9,9-didecylfluorene-2,7-dicarbaldehyde (**C**; 0.57 g, 1.27 mmol), 2-aminothiophenol (0.07 g, 0.56 mmol), and dimethylsulfoxide (3 mL) was heated in an oil bath to 195 °C, held at that temperature for 1.5 h, and then poured into 300 mL of distilled water. The product was extracted with CH_2Cl_2 , and the organic phase was washed with AcOH/ H_2O (1:4), water and then with a dilute sodium bicarbonate solution. The extract was dried over MgSO_4 , filtered, and concentrated to afford a yellow oil. The crude product was chromatographed over silica gel; the column was eluted with (80:20) hexane/ CH_2Cl_2 to give 0.22 g of yellow oil that solidified (mp = 79–80 °C, 68% yield). Anal. Calcd for $\text{C}_{41}\text{H}_{53}\text{NOS}$: C, 81.00%; H, 8.79%; N, 2.30%; S, 5.27%. Found: C, 80.91%; H, 8.74%; N, 2.26%; S, 5.54%. ^1H NMR (300 MHz, CDCl_3) δ : 10.03 (s, 1H; CHO proton), 8.14 (s, 1H), 8.08 (t, 2H), 7.88 (bt, 5H), 7.50 (t, 1H), 7.39 (t, 1H), 2.11 (bs, 4H; CH_2), 1.12 (bm, 28H; CH_2), 0.83 (bt, 6H; CH_3), 0.61 (bs, 4H; CH_2). ^{13}C NMR (75 MHz, CDCl_3) δ : 192.3 (sp^2 carbon of CHO), 168.1, 154.2, 153.1, 152.3, 146.4, 142.4, 135.9, 135.1, 133.9, 130.6, 127.4, 126.6, 125.5, 123.4, 123.3, 121.8, 121.7, 121.6, 120.8, 56.1, 40.5, 32.2, 30.3, 29.9, 29.9, 29.6, 24.2, 23.1, 14.5.

Synthesis of 2-(9,9-Didecyl-7-vinyl-fluorene-2-yl)benzothiazole (E). In a two-necked flask was dissolved methyltriphenylphosphonium iodide (0.42 g, 1.05 mmol) in 4 mL of dry THF at 0 °C under Ar. *n*-BuLi (0.77 mL, 1.6 M solution in hexane) was then added over 15 min. The reaction mixture turned from colorless to orange. A solution of 2-(7-(9,9-didecylfluorene-2-yl)benzothiazole (**D**) in 3 mL of dry THF was then added to the ylide over a period of 15 min at 0 °C. The mixture turned orange-brown. The reaction mixture was allowed to warm to room temperature and was stirred for 24 h. Concentration under vacuum afforded a brown, gummy residue, which was washed repeatedly with a mixture of hexane/ CH_2Cl_2 (60:40). The combined organic washings were dried over MgSO_4 and concentrated to yield an orange-brown oil. The purification via column chromatography on silica gel, eluting with hexane/ CH_2Cl_2 (70:30), afforded 0.29 g of yellow oil (73% yield). Anal. Calcd for $\text{C}_{42}\text{H}_{55}\text{NS}$: C, 83.25%; H, 9.15%; N, 2.31%; S, 5.29%. Found: C, 83.21%; H, 9.17%; N, 2.36%; S, 5.26%. ^1H NMR (300 MHz, CDCl_3) δ : 8.08 (d, 2H), 8.02 (d, 1H), 7.90 (d, 1H), 7.76 (d, 1H), 7.69 (d, 1H), 7.50–7.34 (m, 4H), 6.81, (q, 1H), 5.85, 5.79 (d, 1H), 5.30, 5.26 (d, 1H), 2.03 (bs, 4H, CH_2), 1.12

(bd, 28H, CH_2), 0.81 (t, 6H, CH_3), 0.63 (bs, 4H, CH_2). ^{13}C NMR (75 MHz, CDCl_3) δ : 168.8, 154.3, 152, 143.9, 140.1, 137.5, 137.4, 135.1 (sp^2 carbon of $\text{RHC}=\text{CH}_2$), 132.3, 127.2, 126.5, 125.5, 125.2, 123.1, 121.7, 120.8, 120.5, 120.3, 113.8 (sp^2 carbon of $\text{RHC}=\text{CH}_2$), 55.7, 40.7, 32.3, 30.4, 30, 29.9, 29.7, 24.2, 23.1, 14.6.

Synthesis of {7-[2-(7-Benzothiazol-2-yl)-9,9-didecylfluorene-2-yl]vinyl}-9,9-didecylfluorene-2-yl}diphenylamine (2). (7-Bromo-9,9-didecylfluorene-2-yl)diphenylamine (**A**; 0.28 g, 0.54 mmol), 2-(9,9-didecyl-7-vinyl-fluorene-2-yl)benzothiazole (**E**; 0.3 g, 0.49 mmol), $\text{Pd}(\text{OAc})_2$ (36 mg, 0.16 mmol), tri-*o*-tolylphosphine (0.08 g, 0.26 mmol), and Et_3N (3 mL) were combined in a screw cap vial and heated at reflux for 72 h. The mixture was cooled to room temperature and filtered. The solvent was removed under reduced pressure, and the residue was dissolved in CH_2Cl_2 . The organic layer was washed with distilled water, dried over MgSO_4 , filtered, and concentrated. The crude product was purified by column chromatography on silica gel eluting first with hexane/ EtOAc (90:10), followed by hexane/toluene (90:10), resulting in 0.29 g of yellow oil (53% yield). Anal. Calcd for $\text{C}_{87}\text{H}_{114}\text{N}_2\text{S}$: C, 85.66%; H, 9.42%; N, 2.30%; S, 2.63%. Found: C, 85.78%; H, 9.36%; N, 2.40%; S, 2.56%. ^1H NMR (300 MHz, CDCl_3) δ : 8.10, 8.04 (dd, 3H), 7.91 (d, 1H), 7.74 (t, 2H), 7.51 (complex multiplet, aromatic protons, 6H), 7.37 (d, 1H), 7.24 (t, 6H, aromatic protons), 7.12 (d, 5H), 6.99 (d, 4H), 2.1, 1.92 (dd, 8H, CH_2), 1.13 (bt, 56H, CH_2), 0.82 (m, 20H, CH_3 , CH_2).

Synthesis of 9,9-Didecyl-2,7-divinylfluorene (F). *n*-BuLi (7 mL, 1.6 M) was added over 15 min to methyltriphenylphosphonium iodide (2.73 g, 6.75 mmol) in dry THF (50 mL) at 0 °C under Ar, and the solution was stirred at 0 °C for 45 min. A solution of 9,9-didecylfluorene-2,7-dicarbaldehyde (**C**; 1.75 g, 3.48 mmol) in dry THF (40 mL) was then added to the ylide over a period of 20 min at 0 °C via syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 24 h. Concentration under vacuum afforded a brown-orange gummy residue, which was washed repeatedly with a mixture of hexane/THF (60:40). The combined organic washings were dried and concentrated to obtain orange oil. The product was purified via column chromatography on silica gel eluting first with hexane/THF (90:10), followed by hexane resulting in 1.20 g of colorless oil (70%). Anal. Calcd for $\text{C}_{35}\text{H}_{54}$: C, 89.09%; H, 10.91%. Found: C, 88.85%; H, 10.88%. ^1H NMR (300 MHz, CDCl_3) δ : 7.6, 7.58 (d, 2H), 7.37, 7.34 (d,

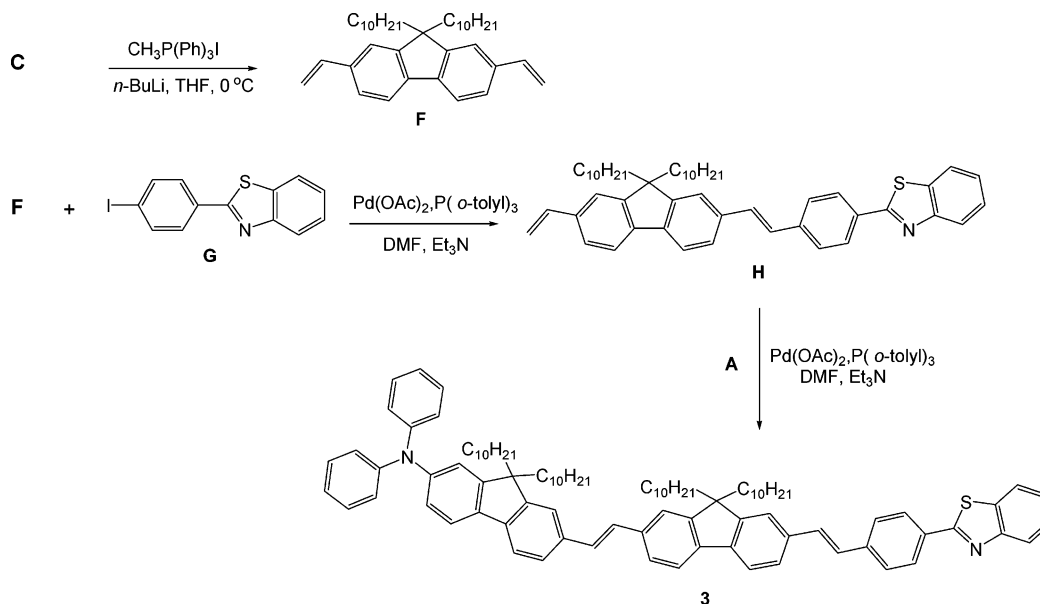


Figure 4. Synthesis of fluorene 3.

2H), 7.32 (s, 2H), 6.76 (q, 2H), 5.80, 5.74 (d, 2H), 5.25 (d, 2H), 1.94 (m, 4H, CH₂), 1.15 (bm, 28H, CH₂), 0.86 (t, 6H, CH₃), 0.61 (bs, 4H, CH₂). ¹³C NMR (75 MHz, CDCl₃) δ: 151.4, 140.8, 137.5 (sp² carbon of RHC=CH₂), 136.5, 125.3, 120.6, 119.8, 113.2 (sp² carbon of RHC=CH₂), 55.2, 40.8, 32.3, 30.4, 30.0, 29.9, 29.7, 29.6, 24.1, 23.1, 14.6.

Synthesis of 2-{4-[2-(9,9-Didecyl-7-vinylfluorene-2-yl)vinyl]-phenyl}benzothiazole (H). 9,9-Didecyl-2,7-divinylfluorene (F; 0.35 g, 0.701 mmol), 2-(4-iodophenyl)benzothiazole (G; 0.260 g, 0.77 mmol), Pd(OAc)₂ (13 mg, 0.057 mmol), tri-*o*-tolylphosphine (26 mg, 0.085 mmol), and Et₃N (5 mL) were combined in a screw cap vial and heated to 100 °C for 84 h. The reaction mixture was cooled to room temperature and dissolved in CH₂Cl₂. The mixture was poured into water and extracted with CH₂Cl₂, dried over MgSO₄, and concentrated. The crude product was purified by column chromatography eluting first with hexane/EtOAc (90:10), followed by hexane/EtOAc (95:5), resulting in a yellow solid mp = 96–97 °C (0.16 g, 32% yield). Anal. Calcd for C₅₀H₆₁NS: C, 84.81%; H, 8.68%; N, 1.98%; S, 4.53%. Found: C, 84.80%, H, 8.81%; N, 1.99%; S, 4.40%. ¹H NMR (75 MHz, CDCl₃) δ: 8.07 (t, 3H), 7.9 (d, 1H), 7.65 (t, 4H, olefinic protons 2H, aromatic protons 2H), 7.48 (t, 3H, aromatic protons), 7.36 (m, 3H, aromatic protons), 7.28 (s, 1H), 7.23 (d, 1H), 6.8 (q, 1H), 5.82, 5.77 (d, 1H), 5.27, 5.23 (d, 1H), 2.0 (bs, 4H, CH₂), 1.1 (bd, 28H, CH₂), 0.8 (bt, 6H, CH₃), 0.6 (bs, 4H, CH₂). ¹³C NMR (300 MHz, CDCl₃) δ: 163.7, 154.3, 151.7, 151.5, 141.2, 140.7, 140.4, 137.5 (sp² carbon of RHC=CH₂), 136.7, 135.9, 135.1, 132.5, 131.2, 128, 127, 126.9, 126.5, 126, 125.5, 125.3, 123.3, 121.7 (sp² carbon of RCH=CHR), 121.1 (sp² carbon of RCH=CHR), 120.7, 120.1, 119.9, 113.3 (sp² carbon of RHC=CH₂), 55.3, 40.9, 32.3, 30.5, 30, 29.9, 29.7, 24.2, 23.1, 14.6.

Synthesis of [7-(2-{7-[2-(4-Benzothiazol-2-ylphenyl)vinyl]-9,9-didecylfluoren-2-yl}vinyl)-9,9-didecylfluoren-2-yl]diphenylamine (3). (7-Bromo-9,9-didecylfluoren-2-yl)diphenylamine (A; 0.17 g, 0.33 mmol), 2-{4-[2-(9,9-didecyl-7-vinylfluorene-2-yl)vinyl]-phenyl}benzothiazole (G; 0.20 g, 0.28 mmol), Pd(OAc)₂ (27 mg, 0.11 mmol), tri-*o*-tolylphosphine (57 mg, 0.18 mmol), and Et₃N (3 mL) were combined in a screw cap vial and heated at 90 °C for 112 h. The mixture was cooled to room temperature and filtered. The solvent was removed under reduced pressure, and the residue was dissolved in CH₂Cl₂. The organic layer was washed with

distilled water, dried over MgSO₄, filtered, and concentrated. The crude product was purified by column chromatography on silica gel eluting first with hexane/CH₂Cl₂ (90:10), followed by hexane/EtOAc (95:5), affording 0.15 g of yellow oil (42% yield). HR-MS (EI): *m/z* = 1319.92 (M⁺, 100% relative abundance); calcd for C₉₅H₁₁₈N₂S, 1320.03. ¹H NMR (300 MHz, CDCl₃) δ: 8.06 (t, 3H), 7.9 (d, 1H), 7.65–7.44 (complex multiplets; olefinic protons 4H, aromatic protons 6H), 7.36 (m, 2H, aromatic protons), 7.27–7.20 (complex multiplets, aromatic protons 8H), 7.12 (d, aromatic protons, 6H, *J* = 7.5 Hz), 7.01 (t, aromatic protons, 4H), 1.92 (bm, 8H, CH₂), 1.18 (bd, 56H, CH₂), 0.8 (bt, 12H, CH₃), 0.6 (bs, 8H, CH₂). ¹³C NMR (75 MHz, CDCl₃) δ: 167.2, 153.7, 152.0, 150.8, 147.5, 146.8, 140.9, 139.9, 135.8, 134.6, 134.5, 131.9, 130.7, 129.3, 128.7, 127.5, 126.4, 126.1, 126, 125.6, 124.7, 123.5, 123.1, 122.7 (sp² carbon of RCH=CHR), 122.2 (sp² carbon of RCH=CHR), 121.2, 120.4, 120.1, 118.9, 118.8, 54.8, 40.2, 31.8, 29.9, 29.5, 29.4, 29.3, 29.2, 23.8, 22.6, 14.1.

Results and Discussion

Synthesis. A series of dipolar chromophores with extended conjugation length and different acceptor groups were prepared. The structures of the compounds {7-[2-(9,9-didecyl-7-nitrofluoren-2-yl)vinyl]-9,9-didecylfluoren-2-yl}-diphenylamine (1), {7-[2-(7-benzothiazol-2-yl-9,9-didecylfluoren-2-yl)vinyl]-9,9-didecylfluoren-2-yl}diphenylamine (2), and [7-(2-{7-[2-(4-benzothiazol-2-ylphenyl)vinyl]-9,9-didecylfluoren-2-yl}vinyl)-9,9-didecylfluoren-2-yl]diphenylamine (3) are shown in Figure 1. Compounds 1 and 2 have D-π-π-π-A architectures. Molecule 3 has an additional styryl group attached to the fluorene possessing an extended D-π-π-π-π-A conjugated architecture. The synthetic strategy employed involved the preparation of key intermediates from fluorene that were readily adaptable for diverse functionalization. As illustrated in Figure 1, the three novel fluorene dyes (1–3), with nitro or benzothiazole as terminal groups, were synthesized via efficient Heck coupling reactions between vinylfluorene and brominated fluorene derivatives. The vinyl moiety was obtained via Wittig reaction of a carboxaldehyde fluorene derivative (C and D) with *n*-BuLi

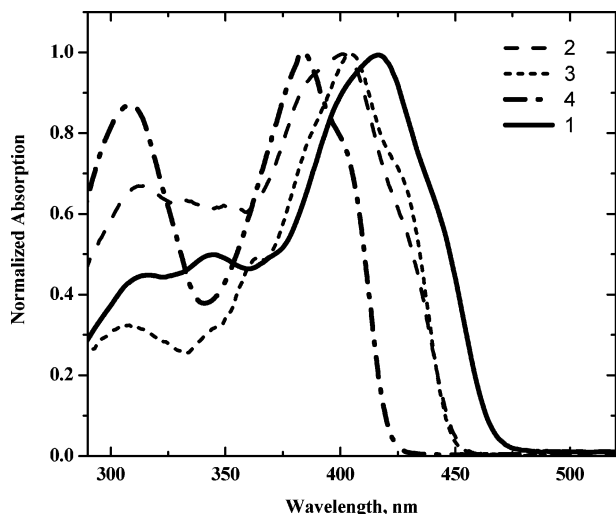


Figure 5. Normalized absorption spectra of **1–4** in hexane at 10^{-6} M concentrations.

and methyltriphenylphosphonium iodide. Heck coupling reactions were carried out with palladium acetate/tri-*o*-tolylphosphine as the catalyst and triethylamine as the base in dimethylformamide under reflux.

Thus, our molecular design was focused on extending the conjugation of the π bridge via addition of a second fluorene moiety, where the NO_2 group was utilized as an electron-withdrawing moiety. 7-[2-(9,9-Didecyl-7-nitrofluoren-2-yl)-vinyl]-9,9-didecylfluoren-2-yl)diphenylamine (**1**) was produced by the palladium-catalyzed Heck reaction of 7-bromo-9,9-didecylfluoren-2-yl)diphenylamine (**A**) with 9,9-didecyl-2-nitro-7-vinylfluorene (**B**) as depicted in Figure 2. The FT-IR spectrum displayed the presence of the asymmetric $\nu_{\text{as}}(\text{NO}_2)$ and symmetric $\nu_{\text{s}}(\text{NO}_2)$ stretching at 1522 and 1337 cm^{-1} , respectively. Confirmation of the product composition was secured by CHN analysis, along with ^1H and ^{13}C NMR spectra.

The synthesis of {7-[2-(7-benzothiazol-2-yl-9,9-didecylfluoren-2-yl)vinyl]-9,9-didecylfluoren-2-yl}diphenylamine (**2**) involved the preparation of two new intermediates: 2-(7-carbaldehyde-9,9-didecylfluoren-2-yl)benzothiazole (**D**) and 2-(9,9-didecyl-7-vinyl-fluoren-2-yl)benzothiazole (**E**). Different strategies were attempted to synthesize **D**. However, not all the strategies were successful. The first attempt to obtain the desired product **D** involved the direct condensation of **C** with 2-aminothiophenol in a 1:1.1 molar ratio. Under these conditions, it was found that the major product isolated was the disubstituted adduct (2,7-bis-(benzothiazol-2-yl)-9,9-didecylfluorene) and compound **D** in very low yield. However, using 2-aminothiophenol as the limiting reagent and **C** in large excess (1:2.2), intermediate **D** was obtained as the major product as a yellow oil in 68% yield (Figure 3). Intermediate **E** was prepared using a general Wittig procedure.⁴¹ Hence, **D** underwent Wittig reaction with *n*-BuLi and methyltriphenylphosphonium iodide in THF, affording 2-(9,9-didecyl-7-vinyl-fluoren-2-yl)benzothiazole (**E**) as a yellow oil purified in 73% yield (Figure 3). The ^1H NMR spectrum of **E** clearly showed the complete disappearance

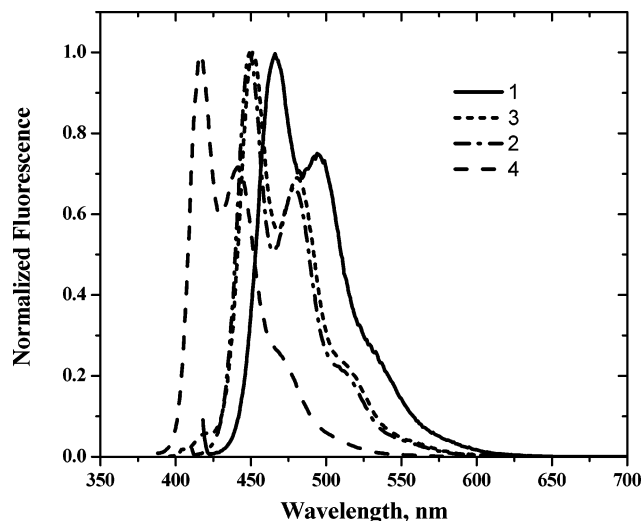


Figure 6. Normalized emission spectra of **1–4** in hexane at 10^{-6} M concentrations.

of the carbonyl proton of the aldehyde at 10.06 ppm, observed in **D**, and clearly displays the signals of the three mutually coupled nonequivalent vinyl protons H_A , H_B , and H_C (three-spin ABC system). The H_C and H_B protons each produce a doublet at 5.8 and 5.3 ppm, with coupling constants of about $J_{AC} = 17.1$, $J_{CB} = 1.8$, and $J_{AB} = 11.1$ Hz, respectively, while the H_A proton gave a quartet at 6.8 ppm, with $J_{AB} = 11.1$ and $J_{AC} = 17.1$ Hz, respectively.

The Pd-catalyzed Heck coupling reaction between (7-bromo-9,9-didecylfluoren-2-yl)diphenylamine (**A**) and 2-(9,9-didecyl-7-vinyl-fluoren-2-yl)benzothiazole (**E**) afforded {7-[2-(7-benzothiazol-2-yl-9,9-didecylfluoren-2-yl)vinyl]-9,9-didecylfluoren-2-yl}diphenylamine (**2**) as a yellow oil in 53% yield (Figure 3). Clearly evident in the ^1H NMR spectrum of **2** was the complete disappearance of the vinyl proton resonances at ≈ 5.3 –6.8 ppm, respectively, observed in **E**. Also notable was the appearance of two doublets at 1.91 and 2.1 ppm, attributable to CH_2 protons α to C9 of the two fluorene ring systems.

Fluorene **3** was designed to possess a large conjugation length to maximize the charge density distribution via the incorporation of a styryl–benzothiazole group directly connected to the π -bridge moiety, resulting in a D– π – π – π –A molecular architecture. To synthesize **3**, two intermediates, **F** and **H**, were required (Figure 4). 9,9-Didecylfluorene-2,7-dicarbaldehyde (**C**) was subjected to a Wittig reaction with *n*-BuLi and methyltriphenylphosphonium iodide in THF. The strategy afforded 9,9-didecyl-2,7-divinylfluorene (**F**) in good yield (70%) after purification (Figure 4). The symmetrical intermediate **F** was fully characterized via conventional methods. Subsequently, a Pd-catalyzed Heck coupling reaction was performed between **F** and 2-(4-iodophenyl)benzothiazole (**G**; Figure 4). 2-{4-[2-(9,9-Didecyl-7-vinylfluoren-2-yl)vinyl]phenyl}benzothiazole (**H**) was obtained as a yellow solid in 32% purified yield. Thus, **H** underwent a Pd-catalyzed Heck coupling with (7-bromo-9,9-didecylfluoren-2-yl)diphenylamine (**A**) to produce [7-(2-{7-[2-(4-benzothiazol-2-yl-phenyl)vinyl]-9,9-didecylfluoren-2-yl}vinyl)-9,9-didecylfluoren-2-yl]diphenylamine (**3**) as a bright yellow viscous oil in 42% yield after column

(41) Leopold, E. J. *Org. Synth.* **1986**, *64*, 164.

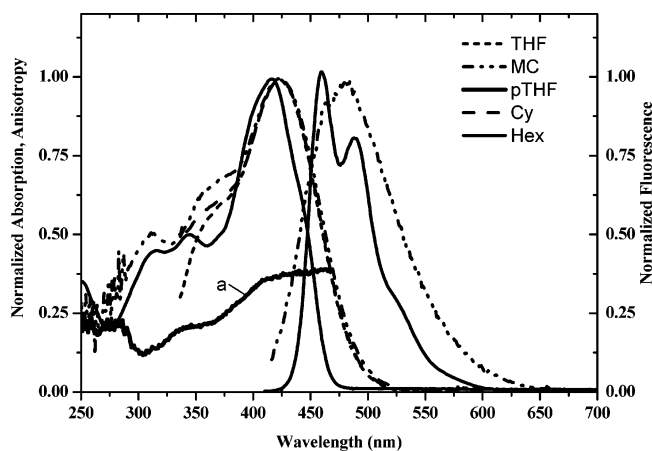


Figure 7. Normalized absorption and emission spectra for **1** in different solvents at 10^{-6} M concentrations and excitation anisotropy spectrum in pTHF (a).

chromatographic purification (Figure 4). The presence of the base peak (m/z) = 1319.92 (M^+) in the HR-MS of **3** supported its structure along with ^1H and ^{13}C NMR spectra.

All three compounds (**1–3**) had high solubility (10^{-2} M) in a number of common organic solvents, including cyclohexanone, hexane, THF, and CH_2Cl_2 . They exhibited high thermostability, as demonstrated by their thermogravimetric analyses; the thermograms revealed high thermal stability up to 395°C (6% weight loss).

Linear Photophysical Properties. To understand their nonlinear properties (2PA) and energetics of their electronically excited states, as well as their potential for a number of applications, a comprehensive photophysical study was undertaken for **1–3**. Each compound showed somewhat different trends in their linear and nonlinear properties in various solvents. Linear properties, such as absorption, steady-state fluorescence, excitation, and excitation anisotropy were investigated. The detailed investigation presented here is an important step to establish relationships between molecular structure and the corresponding optical properties of this set of compounds. Photophysical results are compared to and analyzed with those obtained for {7-[2-(4-benzothiazol-2-yl-phenyl)-vinyl]-9,9-didecylfluoren-2-yl}diphenylamine (**4**), previously reported, to evaluate the effect of extended conjugation (**4**). Compound **4** represents a variation of molecule **2** with a shorter conjugation length.

As shown in Figure 5, the novel chromophores **1**, **2**, **3**, and **4** exhibit an intense absorption band in the UV–blue region (≈ 400 nm) and display high transparency in the visible region. The dipolar molecules **1–4** possess absorption spectra with two distinct peaks, one lying within the range 380–410 nm and the second positioned between 280 and 310 nm. The nature of the absorption bands over the spectral range 250–460 nm was revealed from the excitation anisotropy measurements for compounds **1** and **2** (Figures 7 and 8, curve a). Extending the conjugated length by the addition of a second fluorene as a core in **2** resulted in a slight red shift of the absorption band compared to compound **4**, indicative of improved electronic conjugation. A considerable shift of the emission band was also observed for chromophores **1–4** (Figure 6). As illustrated in Figures 7

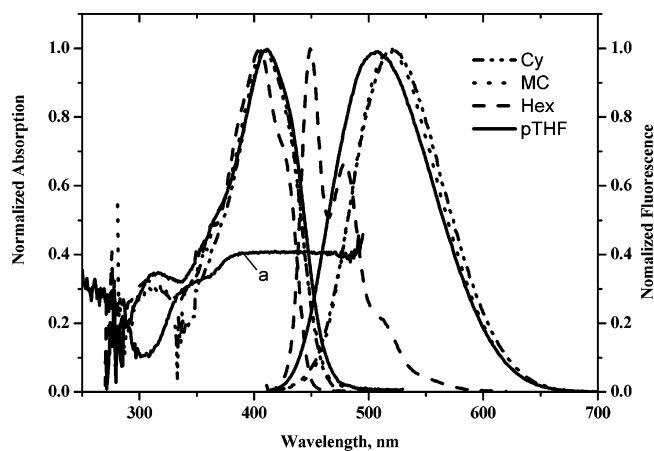


Figure 8. Normalized absorption and emission spectra for **2** in different solvents at 10^{-6} M concentrations, and excitation anisotropy spectrum in pTHF (a).

Table 1. Photophysical Parameters for Fluorenes 1, 2, 3, and 4

com- pound	parameter	hexane	CH_2Cl_2	THF	cyclo- hexanone	pTHF
1	$\lambda_{\text{abs}}^{\text{max}}$, nm	415	425	420	422	
	$\lambda_{\text{em}}^{\text{max}}$, nm	466	475	469	482	
	$\Delta\lambda_{\text{st}}$, nm	51	50	49	60	
	Q	0.60	0.02			
	ϵ^{max} ($\text{M}^{-1}\text{cm}^{-1}$)	38 260	46 950	56 920	62 680	
2	$\lambda_{\text{abs}}^{\text{max}}$, nm	405	409		409	411
	$\lambda_{\text{em}}^{\text{max}}$, nm	449	519		521	508
	$\Delta\lambda_{\text{st}}$, nm	44	110		112	97
	Q	0.86	0.56		0.52	0.52
	ϵ^{max} ($\text{M}^{-1}\text{cm}^{-1}$)	102 600	92 700		85 000	
3	$\lambda_{\text{abs}}^{\text{max}}$, nm	402				
	$\lambda_{\text{em}}^{\text{max}}$, nm	451				
	$\Delta\lambda_{\text{st}}$, nm	49				
	Q	0.77				
	ϵ^{max} ($\text{M}^{-1}\text{cm}^{-1}$)	107 600				
4	$\lambda_{\text{abs}}^{\text{max}}$, nm	384	386		386	388
	$\lambda_{\text{em}}^{\text{max}}$, nm	416	479		484	472
	$\Delta\lambda_{\text{st}}$, nm	32	93		98	84
	Q	0.93	0.63		0.64	0.92
	ϵ^{max} ($\text{M}^{-1}\text{cm}^{-1}$)	42 400	63 460			

and 8, compounds **1** and **2** displayed pronounced positive solvatochromism (i.e., bathochromic shift with increasing solvent polarity) in their emission spectra, whereas only a slight red shift was observed in the absorption spectra. Large values of the Stokes shift ($\Delta\lambda_{\text{st}}$) were observed for **1** and **2** in CH_2Cl_2 (Figures 7 and 8) due to strong solvent–solute dipole–dipole interactions, a manifestation of the large dipole moment and orientational polarizability in CH_2Cl_2 ($\Delta f \approx 0.209$). Because compounds **1** and **2** contain an electron-donating group and an electron-withdrawing group they exhibit a significant dipole moment in the ground state, which depends on charge separation in the fluorophore. In the excited state, it is likely that this charge separation increases, resulting in a larger dipole moment than in the ground state.³⁵ Thus, such an increase in dipole moment would explain the sensitivity of the emission spectra of these dipolar compounds to solvent polarity. The main photophysical properties of **1–4** are listed in Table 1.

Fluorescence quantum yields, Q , were determined,³⁵ exciting at the absorption maximum, $\lambda_{\text{abs}}^{\text{max}}$ of each molecule. Nearly all molecules exhibited a high Q , in hexane, CH_2Cl_2 , and cyclohexanone, with the exception of compound **1**.

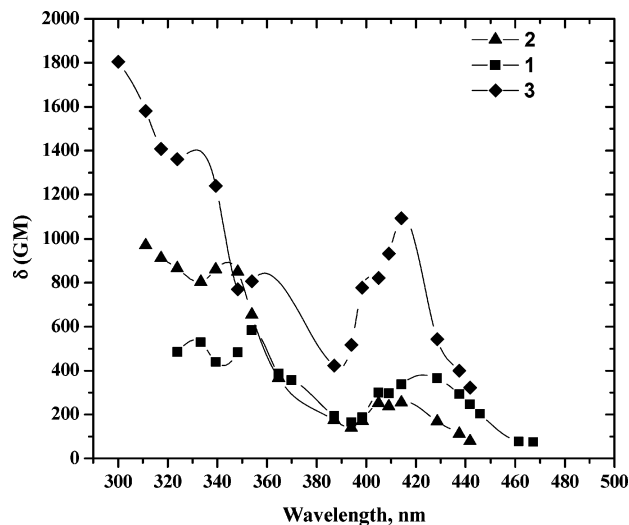


Figure 9. 2PA spectra for fluorenes **1** (■), **2** (▲), and **3** (◆) determined by the femtosecond WLC pump–probe method in hexane. The wavelength plotted is one-half of the actual excitation wavelength to allow comparison with the corresponding linear absorption.

The low Q of **1** in CH_2Cl_2 is attributed to strong solvent interaction of the NO_2 moiety in the charge-transfer excited state with the polar solvent, and subsequent nonradiative decay. This was consistent with the other polar solvents studied (THF and cyclohexanone) in which no fluorescence from **1** was detectable. Consistent with dipolar molecules, the Q values were solvent dependent (see Table 1). Because fluorenylbenzothiazole derivatives **2** and **4** exhibited decreases in Q of a similar magnitude (hexane vs CH_2Cl_2), determination of Q in CH_2Cl_2 was not deemed necessary, as it is expected to follow the same trend as **2** and **4**.

The excitation anisotropy spectra and anisotropy values, r , for **1** and **2** in pTHF, are shown in Figures 7 and 8, curve a, along with the linear absorption spectra. Compound **1** displayed a constant value of $r \approx 0.38$, for excitation in the spectral range $\lambda \approx 410\text{--}468$ nm (Figure 7, curve a), corresponding to the first electronic transition $S_0 \rightarrow S_1$. A higher electronic transition, for example, $S_0 \rightarrow S_2$, was observed in the wavelength range $\lambda \approx 340\text{--}365$ nm. The minimum of the anisotropy value in the short wavelength region ($\lambda \approx 298\text{--}310$ nm) was assigned to the $S_0 \rightarrow S_3$ transition. Electronic transitions were also observed for compound **2** (Figure 8, curve a). The first electronic transition, $S_0 \rightarrow S_1$, was observed in the long wavelength region at $\lambda \approx 380\text{--}450$ nm, exhibiting the maximum r value (0.40). The $S_0 \rightarrow S_2$ transition was assigned to the wavelength range $\lambda \approx 345\text{--}360$ nm. Also, **2** exhibited a high intensity shoulder in the absorption spectrum (Figure 9, curve a) near 312 nm, likely associated with the $S_0 \rightarrow S_3$ transition. Excitation anisotropy proved to be a powerful technique to experimentally determine wavelength ranges (energies) of important electronic transitions.

Nonlinear Photophysical Properties. The 2PA spectra for compounds **1**, **2**, and **3** in hexane are shown in Figure 9. The 2PA cross sections δ (given in $\text{GM} = 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$) are plotted versus the sum of the energies of the two photons involved in the nondegenerate process (this energy has been converted to wavelength for

reference). All of these spectra were acquired using the femtosecond WLC pump–probe technique.^{28,40} The 2PA cross-sectional values for compound **4** were previously reported.²⁷ The 2PA for **1–4** at about 410 nm (corresponding to the $S_0 \rightarrow S_1$ transition) was lower than the maxima exhibited at about 340 nm (attributed to the $S_0 \rightarrow S_2$ transition, a 2PA allowed transition). Compound **1** exhibited an enhancement of the 2PA cross section, δ , ($365 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ at 858 nm) by nearly 1.5 times relative to compound **2** (see Figure 9). The maximum 2PA cross section of about $254 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ at 828 nm for molecule **2** exhibited a definitive enhancement of 1.4 times when compared to **4** (δ of ca. $183 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ at 828 nm) into the $S_0 \rightarrow S_1$ electronic transition. Comparison of δ between compound **3** ($1093 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ at 828 nm) and compound **2** ($254 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ at 828 nm) reveals an over fourfold enhancement of δ . As expected, the longer conjugated systems show considerable enhancement relative to the shorter conjugated dipolar substituted compounds in their maximum 2PA cross section. A clear example was compound **3**, which exhibited the largest enhancement of this series by an increase of nearly six times compared to **4**. It can be seen that the 2PA correlates quite well with the $S_0 \rightarrow S_2$ transition, identified by the maxima of the linear absorption spectra and excitation anisotropy shown in Figures 7 and 8. The slight red-shifting of the linear absorption spectrum for compound **1** (nitro end group) with respect to the two other systems was also apparent in the nonlinear absorption spectra. As discussed previously, these trends are typical of dipolar systems. Symmetrical fluorene derivatives exhibit negligible 2PA into the first excited state (S_1) but strong absorption into the first two-photon allowed state, similar to centrosymmetric systems.²⁷ However, the dipolar derivatives due to the relaxed molecular symmetry clearly indicate that significant 2PA is possible into a number of excited states, regardless of parity.

Conclusions

The synthetic methodology employing Heck and Wittig reaction conditions facilitated a systematic variation of functional groups of differing electronic character, providing compounds with high thermal stabilities, high fluorescence quantum yields, and high 2PA. In this paper, the 2PA peak cross-section was explored by extending the conjugation in dipolar type compounds: vinyl–fluorene extension and styryl groups attached to a fluorene unit. Molecules **1–3** demonstrate that as conjugation length is increased in the molecule the peak nonlinear absorption into S_1 intensifies. Interestingly, the use of the vinyl–fluorene moiety in **3** gives promise of possible cooperative enhancement of the nonlinearity, showing a sixfold improvement in δ relative to **4**, a subject of further investigation. The 2PA cross section of fluorene **3** was over 1000 GM for the lower energy transition ($S_0 \rightarrow S_1$) at about 830 nm, a wavelength particularly useful in two-photon fluorescence imaging. In fact, the three new fluorene derivatives (**1–3**) all have useful δ in the 820–840 nm range, making these compounds quite well-suited for two-photon fluorescence imaging.

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