Synthesis, Characterization, and Optical Properties of New Two-Photon-Absorbing Fluorene Derivatives

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Received January 22, 2004. Revised Manuscript Received May 11, 2004

The synthesis of a series of four new compounds containing fluorenyl chromophores is presented, along with the results of spectroscopic and photochemical studies aimed at understanding the two-photon absorption properties and energetics of their electronically excited states. The molecular structures of the compounds were systematically varied to allow comparison of molecules possessing high and low molecular symmetry, short and long alkyl chains, and a fluorenyl conjugated π-system. Solvent-dependent absorption and emission were investigated along with π-conjugation length. Preliminary measurements of two-photon absorption (2PA) using a two-photon fluorescence method indicate that these chromophores exhibit high two-photon absorptivity. A symmetrical molecule (**3**), possessing a relatively large π-conjugated system, flanked on either side by electron-withdrawing groups (benzothiazole), exhibited a peak 2PA cross section (δ) of 6000×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 600 nm. Excitation anisotropy studies revealed the position of the $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ electronic transitions. Consistent with quantum mechanical selection rules, the two-photon allowed transition ($S_0 \rightarrow S_2$) was dominant.

Introduction

Two-photon absorption (2PA) has been known for about four decades.[1] Over the past decade, 2PA has become the subject of numerous research efforts, leading to a number of significant technological developments. Due in no small part to the pioneering work of Denk, Strickler, and Webb,[19] molecules with high 2PA cross-sections, δ, are now of great interest because of their application in various fields. In addition to the burgeoning field of multiphoton fluorescence imaging,[2−8] other applications of 2PA materials have emerged, including optical data storage,[9,10] optical power limiting,[11,12] three-dimensional (3-D) microfabrication,[13−16] and photodynamic therapy.[17,18] Molecular excitation by the simultaneous absorption of two photons has several advantages, including a capacity for highly confined excitation, intrinsic three-dimensional resolution, and the possibility of imaging at an increased penetration depth in tissue with reduced photodamage and background fluorescence.[19,20]

It has been observed recently that symmetrical conjugated molecules with two electron-donating (D) (or electron-withdrawing (A)) end groups exhibit high nonlinear absorption properties,[21,22] and large 2PA cross-

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10.1021/cm049872g CCC: $27.50

section values, δ.[12,23] This enhancement in δ was correlated to an intramolecular charge redistribution that occurs between the ends and the center of the molecule. Increasing the conjugation length of the molecule or increasing the extent of symmetrical charge from the ends to the middle, or vice versa, results in a large increase of δ.[12,24,25]

As part of a study to establish an empirical relationship of nonlinear absorptivity as a function of molecular structure, and prepare efficient two-photon-absorbing chromophores, a series of compounds with systematic variation in molecular structure have been synthesized and characterized. To better understand their nonlinear properties and their potential for a number of applications, a comprehensive investigation of their photophysics was undertaken.

The fluorenyl π-system was chosen due to its inherently high thermal and photochemical stabilities.[26−28] Importantly, fluorene can be readily functionalized in the 2-, 7-, and/or 9-positions. Joint efforts of Reinhardt (Air Force Research Laboratory), Prasad (SUNY—Buffalo), and our laboratory have reported the synthesis and linear optical and nonlinear optical characterization of a number of fluorene derivatives with high two-photon absorptivities.[29−31] Herein, we describe the synthesis, structural characterization, and photophysical study of a series of chromophores with symmetric and asymmetric molecular structure of types A−π−A, A−π−π−A, and D−π−π−A, based on substituted fluorene derivatives containing a benzothiazole motif as an electron acceptor group (A) and diphenylamine as an electron donor group (D), to attempt to determine certain molecular structure/linear and nonlinear absorption property correlations. To prepare this series of chromophores, efficient preparation of key, common intermediates was regarded using synthetic methodology that would be readily adaptable for rapid functionalization. Structural confirmation data for the new compounds are presented. Linear absorption, steady-state fluorescence, excitation, and excitation anisotropy spectral properties, as well as the fluorescence quantum yield, of these fluorene-based compounds were measured in solvents of different polarities to investigate solvatochromic effects. Preliminary investigation of the two-photon absorptivity was performed using the well-known two-photon fluorescence (2PF) method, over a broad spectral range. Results from excitation anisotropy experiments facilitated the assignment of electronic transitions (i.e., $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$). 2PA cross-section, δ, data indicate that this class of compounds may be useful as two-photon fluorophores.

Experimental Section

General Procedures. 2,7-Dibromo-9,9-diethylfluorene (**A**),[32] 2-(4-iodophenyl)benzothiazole (**7**),[33] and 2-(tri-*n*-butylstannyl)-benzothiazole (**5**)[34] were prepared according to literature procedures. 2,7-Dibromo-9,9-didecylfluorene (**B**) and (9,9-didecyl-7-iodofluoren-2-yl)diphenylamine (**9**) were prepared as described previously.[35,36] All the reagents and solvents were purchased from Acros Organics and Aldrich and used as received, unless otherwise note. THF, DMSO, and DMF were dried using standard procedures.[37] Reactions were carried out under N_2. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Mercury-300 NMR spectrometer at 300 and 75 MHz, respectively. FT-IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer. Elemental analyses were performed by Atlantic Microlab Inc. Thermal stability was assessed with a TA Instruments model 2050 thermogravimetric analyzer, under N_2 at a heating rate of 20 °C/ min, from room temperature to 550 °C.

Synthesis of 9,9-Diethylfluorene-2,7-dicarbaldehyde (6). To a solution of 2,7-dibromo-9,9-diethylfluorene (**A**) (10 g, 26.3 mmol) in dry THF (110 mL), cooled in a dry ice/acetone bath, was added *n*-BuLi (50 mL of a 1.6 M solution in hexane, 78 mmol) dropwise over 25 min. After 20 min, DMF (6.1 mL, 78 mmol) in THF (12 mL) was added, and the mixture was stirred in the cooling bath for 1.5 h and outside the bath for 3 h. The reaction was then cooled to 5 °C and treated with aqueous HCl (4 mL of concentrated HCl diluted and 32 mL of water). The mixture was then diluted with 120 mL of toluene. The combined organic phase was washed with dilute $NaHCO_3$ solution, dried over $MgSO_4$, and concentrated. The residual solid was recrystrallized from hexane, affording a white solid (67% yield, mp 140−141 °C). Anal. Calcd for $C_{19}H_{18}O_2$: C, 81.99; H, 6.52; O, 11.50. Found: C, 81.69; H, 6.53; O, 11.88. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.07 (s, 2H), 7.91 (br d, 6H), 2.16 (br q, 4H), 0.30 (br m, 6H).

Synthesis of 2-(4-Vinylphenyl)benzothiazole (12). 7 (2.40 g, 7.11 mmol), tributyl(vinyl)tin (2.35 g, 7.41 mmol), Pd(dppf)$Cl_2 \cdot CH_2Cl_2$ (0.087 g, 0.106 mmol), and CuI (0.04 g, 0.21 mmol) were dissolved in 25 mL of dry THF at room temperature under N_2. The reaction mixture was heated at reflux for 28 h. Upon completion the dark brown mixture was cooled to room temperature. The mixture was filtered and concentrated under reduced pressure. The product was poured into water and extracted with CH_2Cl_2, dried over $MgSO_4$, and concentrated to obtain a yellow oil. Purification was accomplished by column chromatography using hexane/CH_2Cl_2 (70:30) as eluent, providing 1.7 g of a colorless oil (82% yield). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, 3H), 7.89 (d, 1H), 7.43 (m, 3H), 7.36 (t, 1H), 6.76 (q, 1H), 5.88 (d, 1H), 5.37 (d, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 167.9, 154.3, 140.4, 136.2, 135.2, 133.1, 128.0, 127.0, 126.6, 125.4, 123.4, 121.8, 115.9.

Synthesis of 2,7-Bisbenzothiazole-9,9-diethylfluorene (1). A mixture of **6** (0.16 g, 0.59 mmol), 2-aminothiophenol (0.18 g, 1.48 mmol), and DMSO (3 mL) was heated in an oil bath to a bath temperature of 195 °C, held at that temperature

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for 2.5 h, and then poured into water. The solids were collected, reslurried in 1:4 acetic acid/water (50 mL), filtered, and washed with water and dilute $NaHCO_3$ solution. Further purification was accomplished using a Si gel column eluting first with hexane/toluene (60:40), followed by hexane/EtOAc (90:10), resulting in 0.21 g of a yellow solid (71% yield, mp 199−200 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08, (q, 6H), 7.92, 7.86 (dd, 4H), 7.50 (t, 2H), 7.38 (t, 2H), 2.22 (m, 4H), 0.38 (t, 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 167.9, 153.7, 151.1, 143.1, 134.6, 132.7, 126.9, 126, 124.8, 122.7, 121.3, 121.2, 120.3, 56.8, 32.6, 8.6.

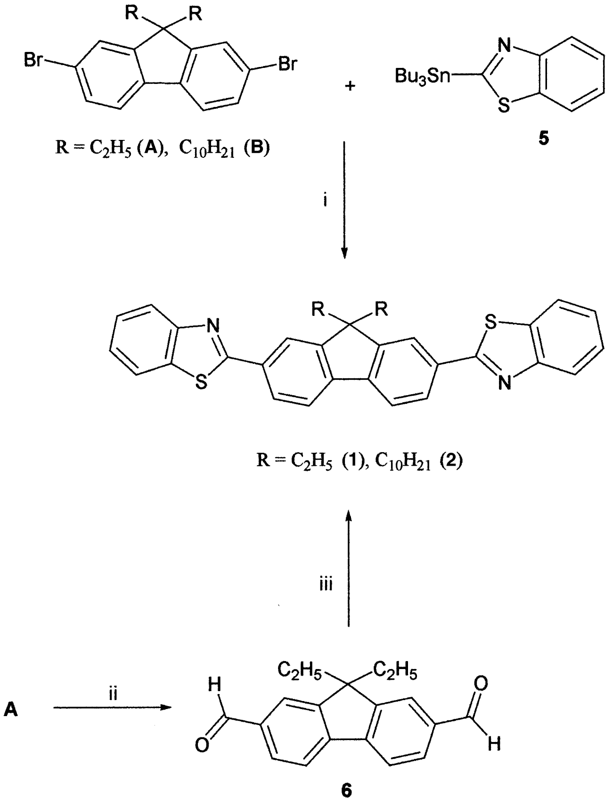
General Synthetic Procedure for 2,7-Bisbenzothiazole-9,9-dialkylfluorenes 1 and 2. Synthesis of 2,7-Bisbenzothiazole-9,9-didecylfluorene (2). 2,7-Dibromo-9,9-didecylfluorene (**B**) (2 g, 3.3 mmol) and **5** (5.25 g, 12.37 mmol) were dissolved in 75 mL of toluene and degassed under vacuum and Ar. $Pd(PPh_3)_4$ (0.12 g, 0.1 mmol) was added, and the mixture was degassed. The reaction mixture was heated to reflux under Ar for 72 h. TLC revealed a very slow reaction; at the end the mixture was black in coloration. Toluene was removed in vacuo, and the resulting dark brown oil was passed through a Si gel column eluting first with hexane/EtOAc (90:10), followed by hexane/toluene (85:15), affording 0.65 g of a light yellow solid (28% yield, mp 77−78 °C). Anal. Calcd for $C_{47}H_{56}N_2S_2$: C, 79.16; H, 7.92; N, 3.93. Found: C, 78.95; H, 7.82; N, 3.86. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.12 (q, 6H), 7.93 (d, 2H), 7.85 (d, 2H), 7.50 (t, 2H), 7.40 (t, 2H), 2.16 (br s, 4H), 1.11 (br d, 28H), 0.79 (t, 6H), 0.68 (br s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 167.9, 153.7, 151.8, 142.5, 134.6, 132.6, 126.8, 126, 124.8, 122.7, 121.3, 121.2, 120.4, 55.7, 40.1, 31.7, 29.8, 29.4, 29.3, 29.1, 23.7, 22.5, 14.

Synthesis of 1 via Stille Coupling. A yellow solid was obtained after column chromatographic purification (26% yield, mp 216−217 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (m, 6H), 7.86 (dd, 4H), 7.5 (t, 2H), 7.38 (t, 2H), 2.22 (m, 4H), 0.35 (m, 6H). Anal. Calcd for $C_{31}H_{24}N_2S_2$: C, 76.20; H, 4.95; N, 5.73. Found: C, 76.34; H, 5.18; N, 5.82.

Synthesis of 2,7-Bis[4-(9,9-didecylfluoren-2-yl)vinyl]-phenylbenzothiazole (3). 2,7-Dibromo-9,9-didecylfluorene (**B**) (1.1 g, 1.81 mmol), 2-(4-vinylphenyl)benzothiazole (**8**) (1.4 g, 4.16 mmol), $Pd(OAc)_2$ (0.04 g, 0.18 mmol), and P(*o*-tolyl)$_3$ (0.1 g, 0.032 mmol) were dissolved in 30 mL of a DMF/Et_3N (5:1) mixture degassed with N_2 for 15 min. The reaction mixture was heated at 90 °C for 96 h, cooled to room temperature, and filtered. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The crude product was purified by column chromatography on silica gel using toluene/CH_2Cl_2 (95:5) as eluent to afford a yellow solid (0.34 g, 31% yield, mp 143−144 °C). Anal. Calcd for $C_{63}H_{70}N_2S_2$: C, 82.30; H, 7.67; N, 3.05; S, 6.98. Found: C, 82.16; H, 7.45; N, 3.09; S, 7.3. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.1 (t, 6H), 7.9 (d, 2H), 7.6 (m, 6H), 7.5 (t, 6H), 7.4 (t, 3H), 7.3 (s, 1H), 7.2 (d, 2H), 2.03 (m, 4H), 1.1 (m, 28H), 0.8 (m, 6H), 0.7 (br s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 167.9, 154.4, 151.9, 141.3, 140.5, 136.2, 135.2, 132.6, 131.2, 128.2, 127.2, 126.6, 126.2, 125.4, 123.4, 121.9, 121.2, 120.3, 55.3, 40.8, 32.1, 30.3, 29.8, 29.7, 29.5, 24.0, 22.9, 14.3.

Synthesis of {7-[2-(4-Benzothiazol-2-ylphenyl)vinyl]-9,9-didecylfluoren-2-yl}diphenylamine (4). **9** (0.324 g, 0.437 mmol), **8** (0.135 g, 0.568 mmol), $Pd(OAc)_2$ (9 mg, 0.0437 mmol), and tri-*o*-tolylphosphine (0.026 g, 0.0874 mmol) were dissolved in 6 mL of a DMF/Et_3N (5:1) mixture. The reaction mixture was degassed and heated at 90 °C under nitrogen for 62 h, cooled to room temperature, and filtered. The solvent was removed under reduced pressure and the residue dissolved in CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The product was purified by column chromatography on silica gel using a hexane/C_6H_6 mixture as eluent to afford 0.22 g of a yellow solid (61% yield). Anal. Calcd for $C_{60}H_{68}N_2S$: C, 84.85; H, 8.07; N, 3.29; S, 3.77. Found: C, 84.59; H, 8.17; N, 3.33; S, 3.91. ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.29 (s, 1H), 8.13 (d, 1H), 7.94 (t, 2H), 7.65 (d, 1H), 7.46 (m, 6H), 7.38 (t, 3H), 7.27 (t, 4H), 7.14 (d, 5H), 7.01 (s, 3H), 1.91 (m, 4H), 1.07 (br d, 28H), 0.85 (t, 6H), 0.693 (br s, 4H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 167.7, 154.9, 152.9, 151.5, 148.5, 147.8, 141.5, 138.8, 136.4, 135.9, 135.5, 134.6, 130.9, 129.5, 129.4, 129, 127, 126.7, 126.4, 126.3, 125.6, 125.2, 124.3, 123.8, 123.7, 122.9, 121.7, 121.2, 121, 119.7, 119.4, 55.3, 40.6, 32.1, 30.4, 29.9, 29.8, 29.7, 29.6, 24.3, 22.9,14.2.

Scheme 1. Synthetic Route for 2,7-Bisbenzothiazolyl-9,9-diethylfluorene (1) and 2,7-Bisbenzothiazolyl-9,9-didecylfluorene (2)



Techniques. Steady-state absorption and fluorescence spectra were investigated for **1**−**4** in hexane, CH_2Cl_2, and cyclohexanone at room temperature. Absorption spectra were measured with a Cary-3 UV−vis spectrophotometer. Steady-state fluorescence excitation anisotropy, excitation, and emission spectra were recorded with a PTI Quantamaster spectrofluorimeter at room temperature using 10 mm quartz cuvettes. Quantum yields, Φ, were calculated from the corrected fluorescence spectra by a standard method,[35] relative to that of Rhodamine 6G in ethanol ($\Phi \approx 0.94$).[39]

Results and Discussion

We considered symmetrical and asymmetrical substituted architectures, wherein the electron density shifts upon excitation, from the ends toward the center of the molecule or from the center to the periphery through the use of electron-donor and electron-acceptor moieties. In this paper, the following compounds were investigated: 2,7-bisbenzothiazole-9,9-diethylfluorene (**1**), 2,7-bisbenzothiazole-9,9-didecylfluorene (**2**), 2,7-bis[4-(9,9-didecylfluoren-2-yl)vinyl]phenylbenzothiazole (**3**), and {7-[2-(4-benzothiazol-2-ylphenyl)vinyl]-9,9-didecylfluoren-2-yl}diphenylamine (**4**). Pd-catalyzed Stille and Heck coupling methodologies were employed to provide this series of pull−pull (A−π−A) and push−pull

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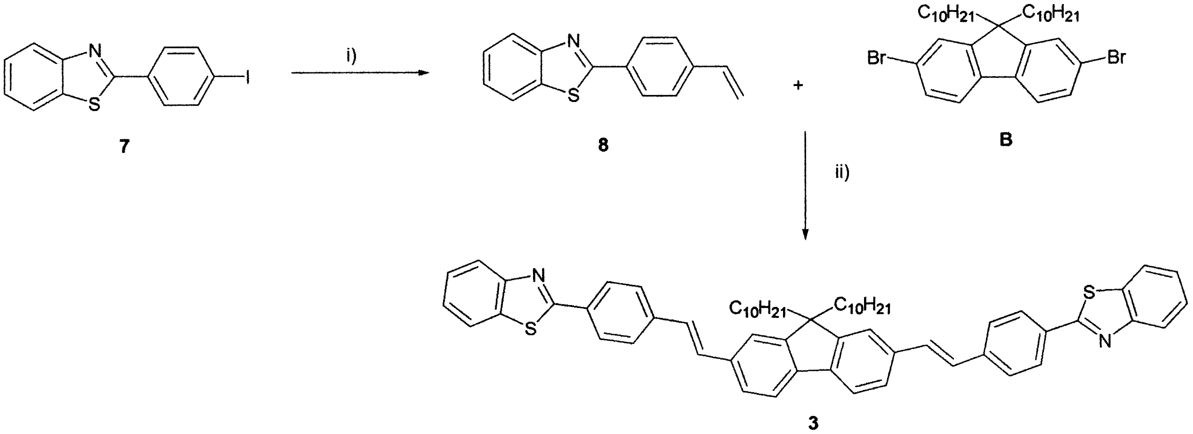
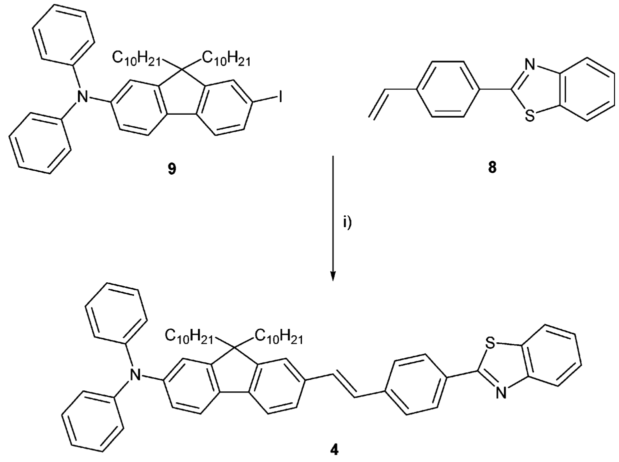
Scheme 2. Synthesis of 2,7-Bis[4-(9,9-didecylfluoren-2-yl)vinyl]phenylbenzothiazole (3)



Scheme 3. Synthesis of {7-[2-(4-Benzothiazol-2-ylphenyl)vinyl]-9,9-didecylfluoren-2-yl}diphenylamine (4)



i) $Pd(OAc)_2$, P(Tolyl)$_3$, DMF/Et_3N

(D−π−A) molecules containing benzothiazole electron-withdrawing and diphenylamino electron-donating groups coupled with a fluorene bridge. The synthetic schemes are shown in Schemes 1−3.

Symmetrical chromophores **1** and **2** were synthesized by two different routes. The first synthetic strategy, via Stille coupling methodology, involved the reaction of 2,7-dibromo-9,9-diethylfluorene (**A**), which was easily synthesized from bromination of the corresponding dialkylfluorene and the stannylbenzothiazole derivative **5**. 2-(Tri-*n*-butylstannyl)benzothiazole (**5**) was prepared as previously reported.[34] Pd-catalyzed Stille coupling was subsequently performed between 2,7-dibromo-9,9-diethylfluorene and 2-(tri-*n*-butylstannyl)benzothiazole in refluxing toluene with $Pd(PPh_3)_4$ (Scheme 1). **1** was obtained as a light yellow solid in 26% isolated yield after column chromatography.

2,7-Dibromo-9,9-didecylfluorene (**B**) was subjected to similar conditions discussed above with **5**, affording **2** as a yellow solid in 28% yield (Scheme 1). It was observed that, although this route did produce **1** and **2**, purification was difficult. Thus, an alternate route to form **1** was pursued via the intermediate 9,9-diethylfluorene-2,7-dicarbaldehyde (**6**). The dialdehyde was derived from 2,7-dibromo-9,9-diethylfluorene (**A**), upon halogen−metal exchange reaction with *n*-BuLi, followed by reaction with DMF and acidic aqueous workup, and produced in 67% yield. 9,9-Diethylfluorene-2,7-dicarbaldehyde, on reaction with 2-aminothiophenol in DMSO at reflux, afforded **1** in 71% yield (see Scheme 1). The synthesis of **2** by this second route will be reported elsewhere.

A compound belonging to the D−π−D type was designed to have increased conjugation length via the incorporation of a styryl group directly connected to the π-bridge motif to obtain a D−π−π−π−D molecular structure. 2,7-Bis[4-(9,9-didecylfluoren-2-yl)vinyl]phenylbenzothiazole (**3**) was prepared via palladium-catalyzed coupling of 2,7-dibromo-9,9-didecylfluorene (**B**) with 2-(4-vinylphenyl)benzothiazole (**8**) (Scheme 2). Compared to the chromophores **1** and **2**, the synthesis of compound **3** is somewhat more laborious because of its more complex structure. Intermediate **8** was prepared from Pd-catalyzed Stille coupling between 2-(4-iodophenyl)benzothiazole (**7**) and tri-*n*-butyl(vinyl)tin. The Heck coupling reaction between **B** and **8** was conducted with $Pd(OAc)_2$, tri-*o*-tolylphosphine, and Et_3N as base in DMF at reflux. The fluorene derivative **3** was isolated in 31% yield as a fluorescent yellow solid.

An additional chromophore was designed to have an asymmetric structure of the type D−π−π−A, containing diphenylamino as an electron-donating group and benzothiazole as an electron-acceptor group. The conjugation length was increased via the addition of a polarizable π-system (styryl) between the bridging unit and the benzothiazole acceptor. 7-[2-(4-Benzothiazol-2-yl-phenyl)vinyl]-9,9-didecylfluoren-2-yl-diphenylamine (**4**) was synthesized via efficient Pd-catalyzed Heck coupling reaction between (9,9-didecyl-7-iodofluoren-2-yl)diphenylamine (**9**) and **8**. The Heck coupling reaction was conducted with $Pd(OAc)_2$, tri-*o*-tolylphosphine, and Et_3N as base in DMF at 90 °C for 62 h (Scheme 3). Compound **4** was isolated in 61% yield as a fluorescent yellow solid.

Key intermediates were readily isolated and purified. However, the Heck reaction used to form **3** and **4** was not straightforward and produced several byproducts, making the purification difficult. The compounds were highly soluble in a variety of organic solvents such as hexane, CH_2Cl_2, $CHCl_3$, THF, and cyclohexanone. C, H, N analyses were in excellent agreement with calculated values for all new compounds, with additional structural confirmation provided by ^1H and ^{13}C NMR spectroscopic analyses. This series of compounds, **1**−**4**, exhibited high

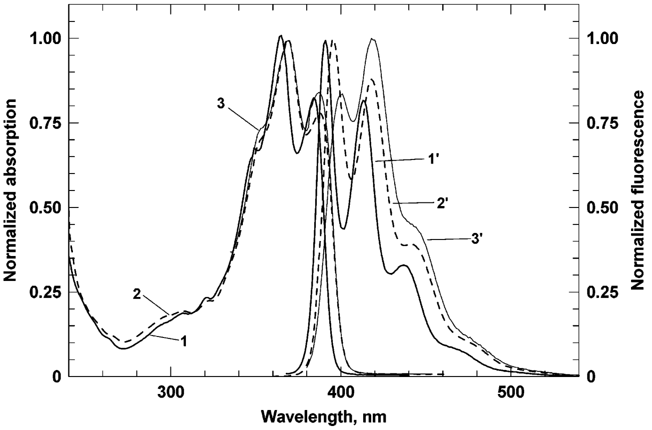


Figure 1. Normalized absorption (1−3) and fluorescence (1′−3′) spectra for **1** in hexane (1, 1′), CH_2Cl_2 (2, 2′), and cyclohexanone (3, 3′) at 10^{-6} M concentration.

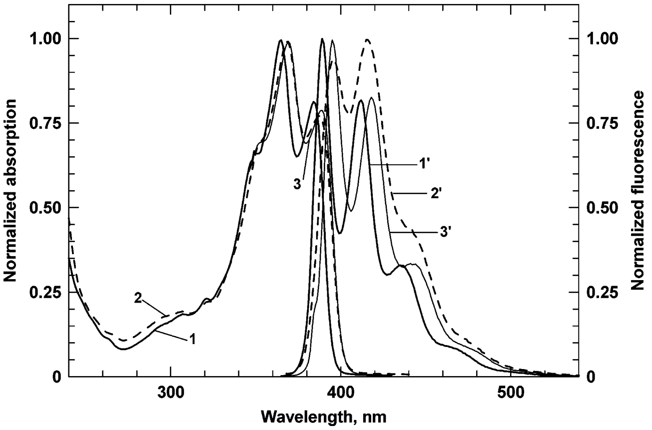


Figure 2. Normalized absorption (1−3) and fluorescence (1′−3′) spectra for **2** in hexane (1, 1′), CH_2Cl_2 (2, 2′), and cyclohexanone (3, 3′) at 10^{-6} M concentration.

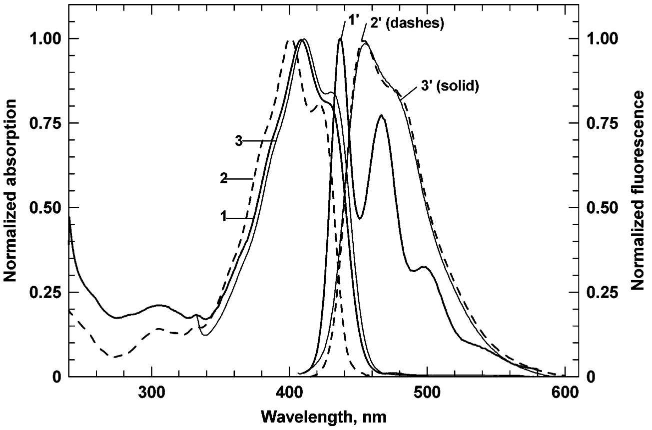


Figure 3. Normalized absorption (1−3) and fluorescence (1′−3′) spectra for **3** in hexane (1, 1′), CH_2Cl_2 (2, 2′), and cyclohexanone (3, 3′) at 10^{-6} M concentration.

thermal stability up to 390 °C, determined by thermogravimetric analysis (TGA).

Possible solvent influence on the linear absorption behavior was investigated. The absorption spectra of **1**−**4** in three different solvents, hexane, CH_2Cl_2, and cyclohexanone, at a concentration of 10^{-6} M are shown in Figures 1−4. The compounds have strong linear absorption at ca. 400 nm. The absorption spectra and shapes of the absorption spectra in hexane, for **1**−**4**, consist of two partially overlapping bands (see Figures 1−4, curve 1). The maximum absorption bands are located at 365, 363, 400, and 383 nm for **1**−**4**, respectively. A second absorption band was observed for **1** and **2** at ca. 383 nm, and **3** exhibited a shoulder at 421 nm. The absorption maxima and shapes of the spectra exhibited weak solvent polarity dependencies. The increase in conjugation of the π-system from **1** and **2** to **3** is reflected in the shift of the long-wavelength absorption band (Table 1). Asymmetrical molecule **4** exhibited a bathochromic shift relative to **1** and **2** (see Table 1). None of the absorption spectra of the four compounds exhibited vibrational fine structure in any solvent studied.

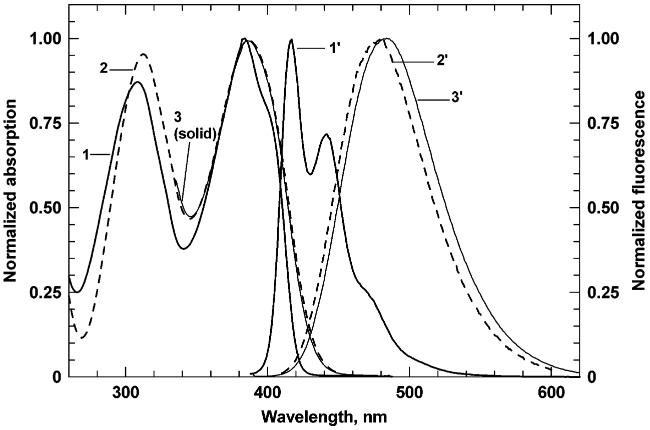


Figure 4. Normalized absorption (1−3) and fluorescence (1′−3′) spectra for **4** in hexane (1, 1′), CH_2Cl_2 (2, 2′), and cyclohexanone (3, 3′) at 10^{-6} M concentration.

The emission spectra in hexane for **1**−**3** displayed vibrational structure with a maximum at 391, 389, and 437 nm, respectively, and a shoulder at 411, 410, and 466 nm, respectively (see Figures 1−4, curve 1′). In polar solvents, the same spectral profile was observed for **1**−**3**; the emission maximum was situated at 396, 395, and 456 nm (see Figures 1−3, curves 2′ and 3′). As expected, for **1**−**3** (molecules of high molecular symmetry) small Stokes shifts were observed, due to only a small change in the molecular dipole moment upon electronic excitation.

In contrast to absorption, fluorescence spectra for the asymmetrical (D−π−A) compound **4** exhibited a strong solvent dependence, Δf (Table 1). A linear correlation between the Stokes shifts of emission spectra and Δf, predicted by the Lippert equation,[8,40] indicated the absence of the specific solute−solvent interactions for **4** in aprotic solvents.[41] In the nonpolar solvent hexane, **4** exhibited a well-resolved vibrational structure with a maximum at 416 nm (see Figure 4, curve 1′). In polar solvents, this vibrational structure was absent, replaced by a broad band, the maximum of which shifted to longer wavelengths (484 nm) in a solvent of higher polarity (see Figure 4, curves 2′ and 3′). This spectral behavior is typical for molecules that undergo a large change in dipole moment upon electronic excitation.[41] All fluorescence spectra obtained for this series were independent of the excitation wavelength, λ_{exc}, over the entire absorption region.

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Table 1. Photophysical Parameters for Compounds 1−4

compd	param	hexane	CH_2Cl_2	cyclohexanone	pTHF
1	λ^{ab}_{max}, nm	365	369	369	371
	λ^{em}_{max}, nm	391	396	400	400
	$\Delta\lambda_{St}$, nm	26	27	31	29
	Q	0.91 ± 0.05	0.76 ± 0.05	0.94 ± 0.05	0.72 ± 0.05
	r_{max}, $S_0 \rightarrow S_1$				0.36
	λ^{ab}_{max}, nm ($S_0 \rightarrow S_2$)				298 ± 5
	r_{max}, $S_0 \rightarrow S_2$				0.13
2	λ^{ab}_{max}, nm	365	369	369	371
	λ^{em}_{max}, nm	389	395	395	400
	$\Delta\lambda_{St}$, nm	24	26	26	29
	Q	0.9 ± 0.05	0.74 ± 0.05	0.92 ± 0.05	0.70 ± 0.05
	r_{max}, $S_0 \rightarrow S_1$				0.39
	λ^{ab}_{max}, nm ($S_0 \rightarrow S_2$)				298 ± 5
	r_{max}, $S_0 \rightarrow S_2$				0.16
3	λ^{ab}_{max}, nm	401	408	408	410
	λ^{em}_{max}, nm	437	453	454	486
	$\Delta\lambda_{St}$, nm	36	45	46	76
	Q	1.0 ± 0.05	0.91 ± 0.05	0.99 ± 0.05	0.98 ± 0.05
	r_{max}, $S_0 \rightarrow S_1$				0.37
	λ^{ab}_{max}, nm ($S_0 \rightarrow S_2$)				343 ± 5
	r_{max}, $S_0 \rightarrow S_2$				0.24
4	λ^{ab}_{max}, nm	384	386	386	388
	λ^{em}_{max}, nm	416	479	484	472
	$\Delta\lambda_{St}$, nm	32	93	98	84
	Q	0.93 ± 0.05	0.63 ± 0.05	0.64 ± 0.05	0.92 ± 0.05
	r_{max}, $S_0 \rightarrow S_1$				0.37
	λ^{ab}_{max}, nm ($S_0 \rightarrow S_2$)				296 ± 5
	r_{max}, $S_0 \rightarrow S_2$				0.05

Quantum yields, Q, were determined using a fluorescence method,[38] exciting at the absorption maximum, λ_{max}, of each chromophore. Nearly the same values of quantum yield, Q, for **1** and **2** in hexane, CH_2Cl_2, and cyclohexanone were obtained. The quantum yield for **3** was near unity in all of the solvents. In contrast to the symmetrical compound **3**, the values Q for **4** were solvent dependent (see Table 1).

Compounds **1** and **2** were chosen to verify the alkyl chain played no role in the photophysical properties. The photophysical properties of **1** and **2** were indeed similar. They both absorb and emit in the same wavelength region and exhibited similar solvent dependency. Therefore, the role of the pendant alkyl chain, increasing from ethyl (**1**) to n-decyl (**2**), imposed no influence on the linear optical properties.

Through steady-state excitation anisotropy, the spectral positions and orientation of the transition dipole moments from the ground state to the first and higher excited states $S_0 \rightarrow S_n$ ($n = 1-3$) relative to the emission dipole moment orientation can be determined. The angular displacement of the chromophore that occurs between absorption and subsequent emission of a photon is dependent upon the rate and extent of rotational diffusion during the lifetime of the excited state. The excitation anisotropy spectrum, r, was calculated as a function of the excitation wavelength, λ, at a fixed emission wavelength (usually near a fluorescence maximum). r is defined as

$$r = \frac{I_{VV} - GI_{VH}}{I_{VV} + 2GI_{VH}}$$

where the G factor is the ratio of the sensitivities of the detection system for vertically and horizontally polarized light and can be calculated using

$$G = \frac{I_{HV}}{I_{HH}}$$

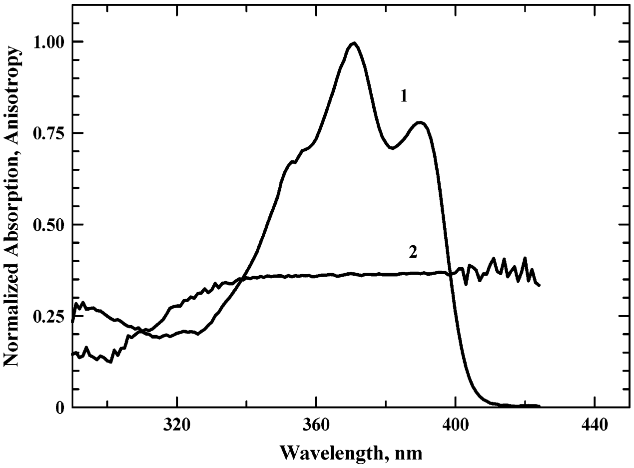

Figure 5. Absorption (1) and excitation anisotropy (2) spectra for **1** in pTHF.

The two subscripts indicate the orientation of the emission and excitation polarizations. For example, I_{HV} corresponds to horizontally polarized excitation and vertically polarized emission. Excitation anisotropy spectra were obtained using high-viscosity solvents to avoid rotational diffusion. The solutions must be optically dilute to avoid depolarization due to radiative reabsorption or emission.[38] The anisotropy excitation spectra, r, for **1**−**4** in polytetrahydrofuran (pTHF) are presented in Figures 5−8. For comparison, the absorbance is plotted together with the anisotropy. In a viscous solvent, the rate of reorientational motion in the excited state is much slower than in solvents of low

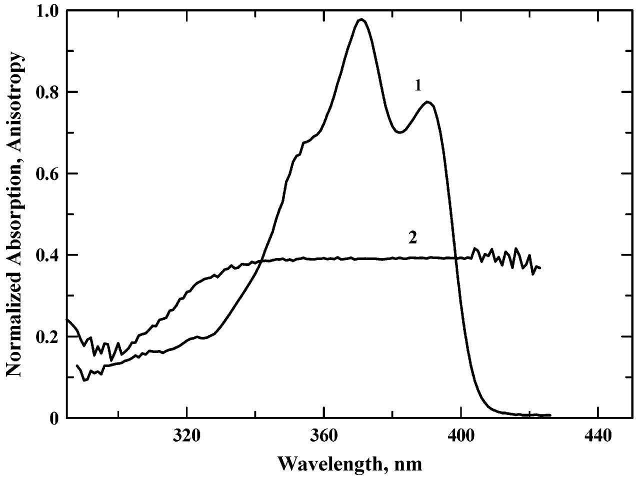

Figure 6. Absorption (1) and excitation anisotropy (2) spectra for **2** in pTHF.

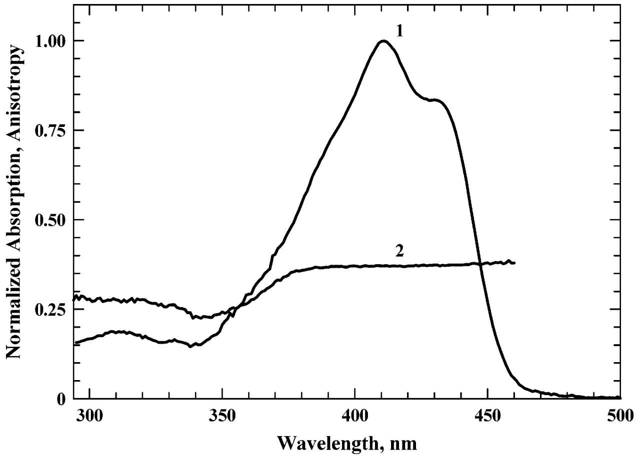

Figure 7. Absorption (1) and excitation anisotropy (2) spectra for **3** in pTHF.

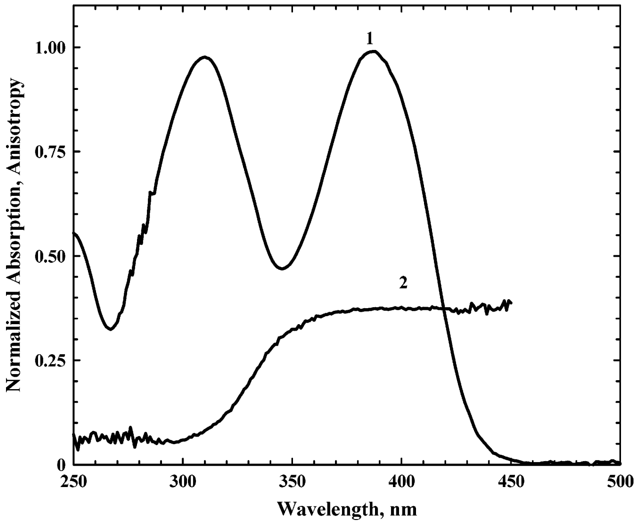

Figure 8. Absorption (1) and excitation anisotropy (2) spectra for **4** in pTHF.

viscosity, and anisotropy values within the first absorption band should be equal to 0.4 in the case of a parallel orientation of the dipole moments in absorption $S_0 \rightarrow S_1$ and emission $S_0 \rightarrow S_1$. For these curves (see Figures 5−8), a constant value of *r*, for excitation in the spectral range $\lambda_{exc} \approx 350-400$ nm, was observed, corresponding to the first electronic transition $S_0 \rightarrow S_1$. The minimum of the anisotropy value in the short-wavelength region, $\lambda_{exc} \approx 300-310$ nm, corresponded to the position of the transition $S_0 \rightarrow S_2$, and the next maximum near $\lambda_{exc} \approx 260-280$ nm corresponded to the transition $S_0 \rightarrow S_3$.

The values of excitation anisotropy, *r*, for compounds **1**−**4** in the main absorption band were constant. Compounds **1** and **2** showed the same positions in anisotropy peaks, but **1** exhibited a smaller anisotropy value than its analogue **2** (see Table 1), even though both molecules have a similar structure. The shorter pendant alkyl chain length (ethyl) induced a faster rotational diffusion in the rate of emission for **1**. Therefore, the emission was depolarized, and the anisotropy value decreased. Compounds **3** and **4** exhibited high anisotropy values, $r \approx 0.38$.

2PA cross-section, δ, measurements are currently ongoing using two different methods, a nonlinear transmission method employing a femtosecond white light continuum (WLC) and a 2PF method. Preliminary data using the 2PF method in a polar solvent (CH_2Cl_2) indicate that these chromophores exhibited high two-photon absorptivity. Compound **1** exhibited a maximum 2PA cross-section, δ, of ca. 370×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 600 nm and 53×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 700 nm. As expected, compound **2** exhibited almost the same 2PA cross-section, δ, values as **1**, ca. 420×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 600 nm and 45×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 700 nm. Compound **3** exhibited a large 2PA cross-section of ca. 6000×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 600 nm and 1185×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 800 nm. The 2PA cross-section of **4** was ca. 1530×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 610 nm and 525×10^{-50} cm^4 s photon^{-1} molecule^{-1} at 790 nm.

The 2PA cross-section, δ, data are consistent with steady-state excitation anisotropy measurements and quantum mechanical selection rules. The maximum 2PA for **1**−**4** at ca. 600 nm (corresponding to a one-photon absorption at ca. 300 nm) can be attributed to the two-photon allowed $S_0 \rightarrow S_2$ transition, according to the selection rules. The low 2PA value at ca. 700−800 nm (350−400 nm for one-photon absorption) was assigned to $S_0 \rightarrow S_1$ (forbidden transition for 2PA). The details of nonlinear absorption spectroscopic analysis of the series of chromophores described herein will be reported elsewhere.

Conclusions

The spectral properties were obtained for a series of D−π−D and D−π−A fluorene derivatives in solvents of different polarities. Steady-state excitation anisotropy spectra allowed us to assign the position of the electronic transitions, which were in good correlation with the location of 2PA peaks. All compounds have very high fluorescence quantum yields; this combined with the relatively high 2PA suggests their potential use as fluorescent probes for two-photon microscopy. Upon extending the π-conjugation length of the fluorene bridge by inserting styryl moieties in compound **3**, the position of the 2PA band is shifted toward the red, moving from 600 nm for **1** and **2** to 800 nm for **3**. The

2PA cross-section at 800 nm increased 4-fold for symmetrical **3** relative to unsymmetrical **4**. This behavior may be due to increased planarity of the conjugated π-system of compound **3**. Electronic transitions deduced from excitation anisotropy experiments, along with the two-photon cross-sections over a large wavelength range, revealed strong quantum-mechanically allowed two-photon $S_0 \rightarrow S_2$ transitions and weak quantum-mechanically forbidden two-photon $S_0 \rightarrow S_1$ transitions.

Acknowledgment. The National Science Foundation (Grants ECS-9970078, ECS-0217932, and DMR-9975773), the National Research Council (COBASE), the Research Corp., and the donors of the Petroleum Research Fund, administerd by the American Chemical Society, are gratefully acknowledged for support of this work.

CM049872G