

Linear and Two-Photon Photophysical Properties of a Series of Symmetrical Diphenylaminofluorenes

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A series of linear, symmetrical, diphenylaminofluorene-based materials are reported. The series investigated was model 9,9-didecyl-2,7-bis(*N,N*-diphenylamino)fluorene (**1**), oligomer 9,9-didecyl-*N,N*-bis(9,9-didecyl-7-*N,N*-diphenylaminofluorene-2-yl)-*N,N*-diphenyl-fluorene-2,7-diamine (**2**), and poly(9,9-didecyl-2,7-diphenylaminofluorene) (**3**). Structural characterization and photophysical properties, including linear absorption, quantum yields, single photon fluorescence, and two-photon absorption (2PA) spectra, were studied in polar and nonpolar solvents. 2PA spectra were determined by two independent methods: a nonlinear transmission method employing a femtosecond white-light continuum (WLC) and a two-photon fluorescence (2PF) method. Polymer **3**, a low-molecular-weight polymer with fourteen fluorene units, exhibited a very large two-photon absorption cross-section of $17\,200$ and 6800×10^{-50} cm⁴ s photon⁻¹ molecule⁻¹ as estimated from the WLC and 2PF methods, respectively.

Introduction

Nonlinear optical materials are of interest for the applications of fast processing of information and dynamic or permanent optical data storage, among others. Among the various classes of nonlinear optical materials, multiphoton absorbing materials have been the subject of growing interest. Although the first theoretical prediction of simultaneous two-photon absorption (2PA) was made by Maria Göppert-Mayer in 1931,¹ the field of research and development of multiphoton absorbing materials received increased interest after the invention of the laser in 1960. In particular, compounds with large 2PA cross sections, δ , have been receiving greater attention, mainly in the developing fields of multiphoton fluorescence imaging,^{2–8} optical data storage, optical power limiting,^{9,10} 3-D microfabrica-

tion,^{11–14} lasing materials,^{2,15–17} and photodynamic therapy.^{18,19}

Systematic studies have shown that conjugated organic molecules with large delocalized π electron systems often exhibit large nonlinear optical effects.^{3,7,8,14,20–25} Therefore, it is important to understand the nature of the relationship between chromo-

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phore structure and 2PA properties to provide guidelines for the development of new materials for a number of emerging technologies. The effects of attachment of functional groups with electron-accepting and -donating character at opposite ends of the π -conjugation bridge, introducing additional groups in the π -conjugation bridge to vary the charge distribution, and varying the effective π -conjugation length have been studied to understand design criteria for producing structures with enhanced 2PA activity.^{22,26} Large 2PA cross sections have been reported for fluorene derivatives with a donor-acceptor substituent pattern.^{4,7,8,23,27}

Until recently, most interest has focused on nonlinear materials belonging to the group of π -conjugated polymers because of their extended delocalization of π -electrons along the polymer backbone. In general, the extension of the electron delocalization remains a key point in designing materials with enhanced third-order optical nonlinearity, even if the latter does not continuously increase with the π -conjugation length.^{28,29} The properties of these polymers still present a challenge to theoreticians and experimentalists because of a variety of new properties brought about by their quasi-one-dimensional structure and complications due to intermolecular interactions when in the solid state (ordering of chains, interchain charge, and energy transfer). However, as is usual in the field of organic materials, substantial knowledge of polymer properties can be gained by studying the properties of model molecules resembling sections of a polymer backbone.

Poly(fluorene)-based materials are of particular interest because of their thermal and chemical stability, along with their desirable photoluminescence and electroluminescence properties. In addition, polyfluorenes are known to have large two-photon absorptivity.^{30,31} Facile substitution of the fluorene monomeric unit at the nine-position facilitates the grafting of various functional groups.

Symmetrical molecular designs that have been explored involve substituted systems having a general structure D- π -D or A- π -A, where D is an electron-donating group, A is an electron-accepting group, and π is a conjugating moiety. However, the criteria for the design of appropriate materials with large 2PA cross sections remain a matter of active investigation. Recently, we reported a study on the steady-state fluorescence properties of fluorene derivatives in order to understand chromophore-chromophore interactions in compounds containing multiple fluorene units.³² As a result, it was concluded that the general steady-state

fluorescence properties were nearly independent of the number of fluorenyl units in a molecule.

Herein, we report the enhancement of 2PA in symmetrical diphenylaminofluorene-based chromophores of the type D- π -D. We describe the synthesis of poly-(9,9-didecyl-2,7-diphenylaminofluorene), which involved Ullmann condensation reactions, as well as linear and nonlinear optical properties measured in solvents of differing polarity. Linear and nonlinear photophysical results are compared to and analyzed with those obtained for a model compound (**1**) and a well-defined oligomer (**2**).

Experimental Section

Materials and Methods. 9,9-Didecyl-2,7-diiodofluorene (**A**), 9,9-didecyl-2,7-bis(*N,N*-phenylamino)-fluorene (**1**), 9,9-didecyl-2,7-bis(*N*-phenylamino)-fluorene (**B**), and 9,9-didecyl-*N,N*-bis(9,9-didecyl-7-*N,N*-diphenylaminofluorene-2-yl)-*N,N*-diphenyl-fluorene-2,7-diamine (**2**) were prepared as described previously.^{27,32} Reactions were carried out under N₂. All other reagents and solvents were used as received from commercial suppliers.

¹H and ¹³C NMR spectra were recorded in C₆D₆ on a Varian Mercury NMR spectrometer at 300 and 75 MHz, respectively. FTIR spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer. Elemental analyses were performed by Atlantic Microlab, Inc. Thermal stability was assessed with a TA Instruments model 2050 thermogravimetric analyzer (TGA) under N₂ at a heating rate of 20 °C/min from room temperature to 550 °C. Phase and glass transitions were investigated using a TA Instruments model 2920 differential scanning calorimeter (DSC) at heating/cooling rates of 10 °C/min under N₂. Gel permeation chromatography (GPC) analysis was performed at room temperature with THF as the carrier solvent at a flow rate of 1 mL/min using a Waters model 600 pump, and a Waters 410 differential refractometer detector calibrated with polystyrene standards. Polymer molecular weights were also estimated from elemental (C, H, N) and ¹H NMR spectroscopic analyses.

Synthesis of Poly(9,9-Didecyl-2,7-diphenylaminofluorene) (3). Iodofluorene intermediate **A** (1.0 g, 1.44 mmol) was dissolved in 15 mL of 1,2-dichlorobenzene at room temperature under N₂. To this was added K₂CO₃ (1.58 g, 11.43 mmol), 18-crown-6 (0.11 g, 0.41 mmol), and copper bronze (0.45 g, 7.07 mmol) at room temperature. Aminofluorene intermediate **B** (0.91 g, 1.44 mmol) was added, and the mixture was degassed. The reaction mixture was heated to 180 °C under nitrogen. After 12 days, TLC indicated that the condensation was complete. Upon completion, the brown mixture was filtered through a short silica gel plug and the yellow solution was concentrated resulting in brown-yellow oil. 1,2-Dichlorobenzene was removed under reduced pressure. The crude product was further purified by column chromatography on silica gel with hexane/CH₂Cl₂ (70:30) as the eluent, followed by hexane/THF (85:15), providing a yellow solid 0.65 g (72 wt % yield). FTIR (KBr, cm⁻¹): 2956, 2854 (ν alCH), 1465 (ν ArC=C). ¹H NMR δ : 7.19 (d, 5H), 6.93 (d, 5H), 6.63 (s, 1H), 1.48 (bd, 4H), 0.85 (bm, 38H). ¹³C NMR δ : 151.17, 147.66, 145.83, 135.30, 128.30, 122.91, 122.39, 121.49, 119.04, 112.89, 59.10, 39.19, 31.00, 29.22, 28.82, 28.75, 28.61, 28.45, 23.32, 21.74, 13.03. Anal. Calcd for C₁₃₅H₁₇₄N₄: C, 87.51%, H, 9.46%, N, 3.02%. Found: C, 87.37, H, 9.53%, N, 3.02%.

Techniques. Steady-state absorption and fluorescence spectra were investigated for **1**, **2**, and **3** in hexane and cyclohexanone at room temperature. Absorption spectra were measured with a Cary-3 UV-visible spectrophotometer. Steady-state fluorescence spectra were obtained at room temperature with a PTI Quantmaster spectrofluorimeter using 10-mm quartz cuvettes. The concentrations for the solutions did not exceed 5 \times 10⁻⁶ M, and processes of reabsorption were negligible. Quantum yields (Φ) were calculated from the

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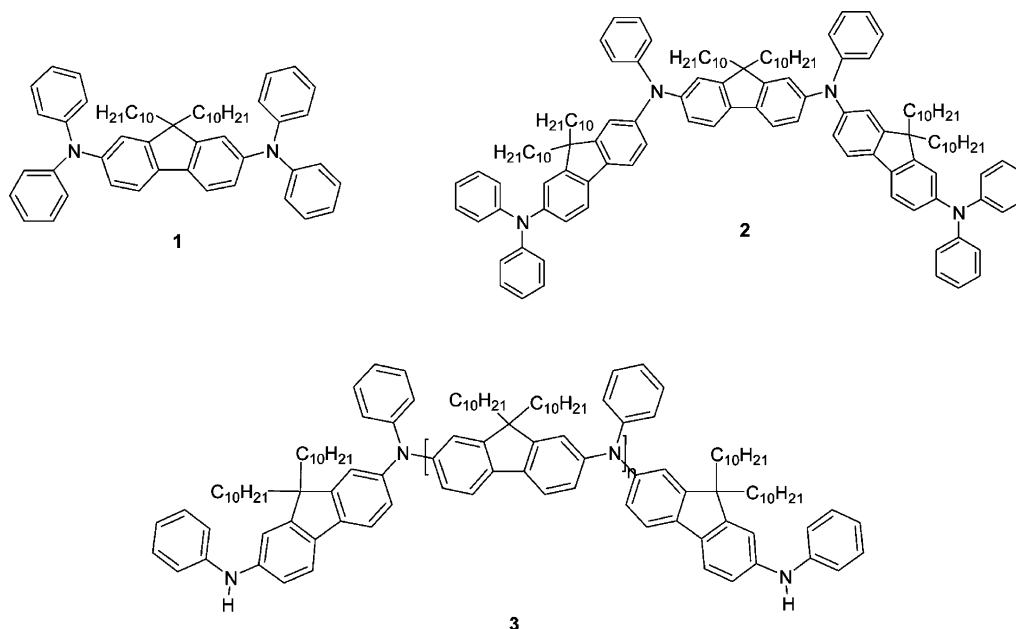


Figure 1. Structures of compound **1**, oligomer **2**, and polymer **3**.

corrected fluorescence spectra by a standard method,³³ relative to Rhodamine 6G in ethanol ($\Phi \approx 0.94$).³⁴

The 2PA spectra of **1**, **2**, and **3** were determined through two independent nonlinear characterization techniques: a degenerate two-photon induced fluorescence (2PF) method and a femtosecond white-light continuum (WLC) pump-probe method. The source used for these two methods was a fiber ring oscillator, Ti:sapphire based regenerative amplifier laser system (CPA-2001, CLARK-MXR), providing laser pulses at 775 nm of 150 fs duration at a 1 kHz repetition rate. This laser in turn pumped two identical optical parametric amplifier (OPA) systems (TOPAS, Light Conversion) which could produce pulses of 110–150 fs over a broad range in the near-IR and/or visible.

In the 2PF method a strong, tunable pump beam excited the chromophore via 2PA and the total integrated fluorescence was monitored as a function of input frequency. One of the OPA systems generated the pump beam which was tuned from 570 to 950 nm and provided the 10–150 nJ energy range necessary to produce 2PF in the materials under investigation. The samples were prepared in hexane and cyclohexanone solutions at concentrations of ca. 1×10^{-4} M, in 1-cm path length quartz cuvettes. The sample holder compartment was housed within the PTI Quantamaster spectrofluorimeter. Following excitation of the sample via the pump beam, the full 2PA-induced fluorescence spectrum was recorded to make certain that the up-converted fluorescence spectrum was independent of pump frequency (not always the case in all materials).³⁵ The spectrum was integrated over the entire emission range to obtain the total integrated fluorescence for the particular pump wavelength. Finally, varying the pump wavelength allowed the construction of the full 2PA spectrum. This can be a very time-consuming endeavor and so the fluorescence measurement made was a relative one.²⁶ The 2PF results obtained for the chromophores under investigation were calibrated against well-known reference standards: fluorescein in water (pH = 11)³⁶ and 1,4-bis(2-methylstyryl)-benzene in cyclohexane.^{36,37} The collection geometry inside the fluorimeter apparatus was kept constant for all samples. The

quadratic dependence of 2PF on the pump irradiance was verified for multiple excitation wavelengths.

For the WLC pump-probe method one OPA provided the strong pump beam and the other OPA generated a weak, broadband WLC beam. The WLC probe was generated by focusing 1–2 μ J of 1300 nm radiation into a 2-mm thick piece of calcium fluoride. A pump wavelength of 1200 nm was chosen with corresponding irradiances ranging from 10 to 70 GW/cm². The 2PA process requires simultaneous absorption of one photon from both the pump and probe beams and so the outcome is the nondegenerate 2PA spectrum of the sample, unlike the 2PF technique which generates a degenerate 2PA spectrum. The WLC probe was chirped in time (i.e., different spectral components arrive at the sample at different times) which required us to delay the pump pulse with respect to the probe pulse 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. A full description of this method can be found in ref 38.

Results and Discussion

In this paper, diphenylaminofluorene was selected as the basic structural motif providing the D- π -D architecture. The respective single chromophore model, oligomer, and polymer were 9,9-didecyl-2,7-bis(*N,N*-diphenylamino)fluorene (**1**), 9,9-didecyl-*N,N*-bis(9,9-didecyl-7-*N,N*-diphenylamino)fluorene-2-yl)-*N,N*-diphenylfluorene-2,7-diamine (**2**), and poly(9,9-didecyl-2,7-diphenylamino)fluorene (**3**), respectively. Their structures are shown in Figure 1. This series provided for the direct comparison of photophysical properties as a function of the number of chromophore units in the molecule. One- and two-photon absorption properties were experimentally measured.

The synthetic route to polymer **3** is shown in Figure 2. The versatility of the Ullmann condensation reaction provided access to **1**, **2**, and key intermediates in reasonable yield.^{27,32} Thus, efficient synthesis of 9,9-didecyl-2,7-diiodofluorene (intermediate **A**) and 9,9-didecyl-2,7-bis(*N*-phenylamino)fluorene (intermediate

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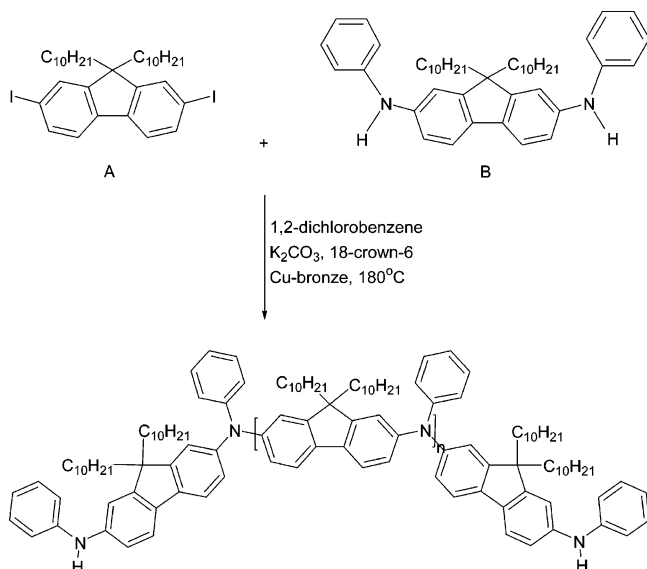


Figure 2. Synthesis of poly(9,9-didecyl-2,7-diphenylaminofluorene), **3**.

B) was accomplished by conducting the reaction in dichlorobenzene using K_2CO_3 as base, 18-crown-6, and copper bronze at reflux for 12 days. The resulting poly-(9,9-didecyl-2,7-diphenylaminofluorene) (**3**) was isolated in 72 wt % yield as a yellow solid. The polymer was purified by repeated column chromatography, affording isolation in high purity (>99.5%). All dyes are highly soluble in a variety of organic solvents such as hexanes, benzene, toluene, THF, CH_2Cl_2 , and cyclohexanone. Compounds **2** and **3** appeared fluorescent blue in the solid state. CHN analysis was in excellent agreement with calculated values, and the FTIR spectrum of **3** revealed weak NH stretching vibrations, indicating that the polymer possessed aminofluorene terminal units. Weight-average molecular weight (M_w) of poly-(9,9-didecyl-2,7-diphenylaminofluorene) **3** was 7680 Da and had a polydispersity of 1.24 (determined by GPC analysis) corresponding to about 14 fluorene units. Molecular weights determined by 1H NMR, GPC, and CHN were in close agreement with each other. Molecular weight determination of polymer **3** by 1H NMR was accomplished by comparing integration of the total aliphatic proton signals to the total aromatic proton signals (3.7: 1), a value consistent with the chain length determined by GPC and CHN analyses. The ^{13}C NMR spectrum of **3** provided additional confirmation of the expected polymer structure.

Thermal analyses were performed on **3** to determine its thermal stability and properties. TGA analysis, performed under N_2 , revealed **3** to exhibit high thermal stability up to 390 °C (3% weight loss). A weight loss of 50% was subsequently observed between 390 and 550 °C, leaving a residue corresponding to 50% of the original sample weight. Repeated DSC scans with controlled heating and cooling were performed on **3**, and revealed a glass transition, T_g , onset at 20 °C and midpoint at 23 °C. The DSC analysis indicated **3** is amorphous, in which no melting or crystallization transitions were detected between -40 and 325 °C.

Figures 3 and 4 show the linear absorption spectra of the diphenylaminofluorene series (**1–3**) in hexane and cyclohexanone. Most of these spectra exhibited a

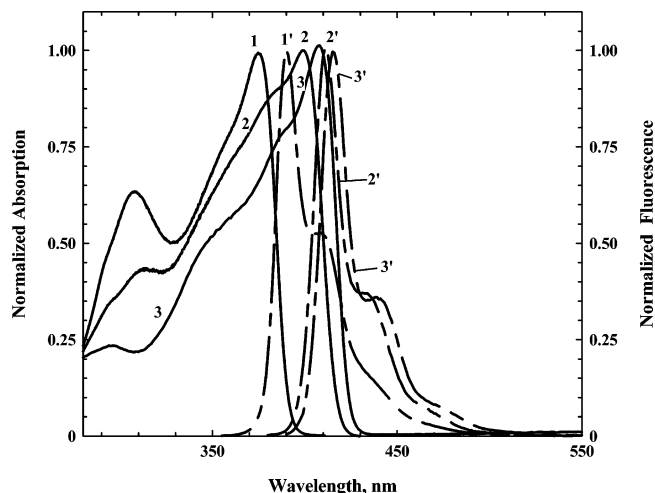


Figure 3. Normalized absorption (1, 2, 3) and fluorescence spectra (1', 2', 3') for **1** (1, 1'), **2** (2, 2'), and **3** (3, 3') in hexane at 10^{-6} M concentrations.

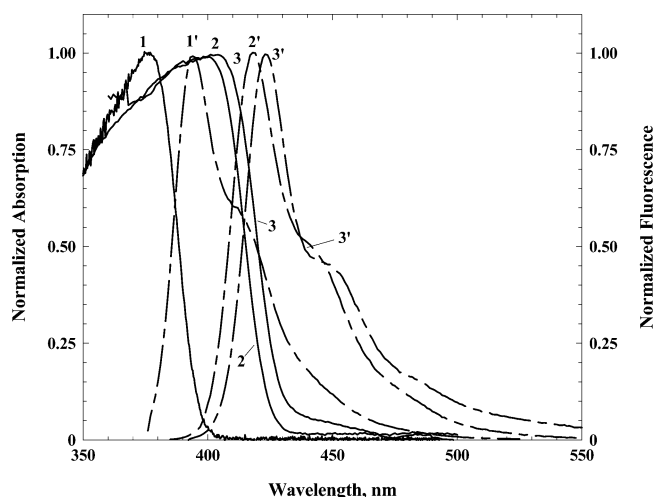


Figure 4. Normalized absorption (1, 2, 3) and fluorescence spectra (1', 2', 3') for **1** (1, 1'), **2** (2, 2'), and **3** (3, 3') in cyclohexanone at 10^{-6} M concentrations.

broad absorption band. This suggests a weak interaction between chromophores, with minimal perturbation of their electronic levels.³² The position of the main peak in the absorption spectrum in hexane, $\lambda_{max}^{(1)}$, exhibited a bathochromic shift with increasing number of fluorene units, and varied over the range of 375 nm (for **1**) to 408 nm (for **3**). The differences between $\lambda_{max}^{(1)}$ in a polar solvent, such as cyclohexanone, for **1–3** did not exceed 3 nm.

One-photon emission spectra of **1–3** in nonpolar and polar solvents, obtained upon excitation at the maximum of the absorption band, show the λ_{max} values of emission shift from 390 nm for **1** to 411 nm for **2** and 416 nm for **3**. Thus, the same trend was observed in the UV–visible absorption and the emission spectra as the content of the chromophore moiety per molecule increased. Absorption and emission spectra exhibited a weak dependence on solvent polarity. In all compounds, a small Stokes shift was observed, which can be explained by a small change in the molecular dipole moment upon electronic excitation. All fluorescence spectra obtained for this series were independent of the excitation wavelength λ_{exc} in the entire absorption region.

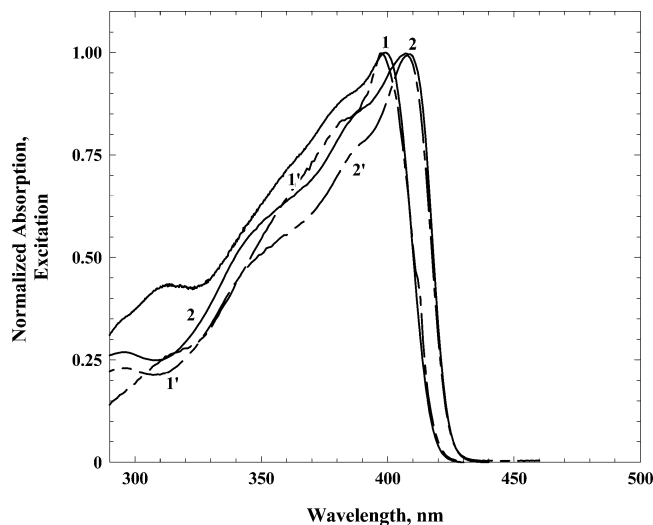


Figure 5. Absorption (1, 2) and excitation spectra (1', 2') for **2** (1, 1') and **3** (2, 2') in hexane. Observation wavelengths correspond to the fluorescence λ_{\max} .

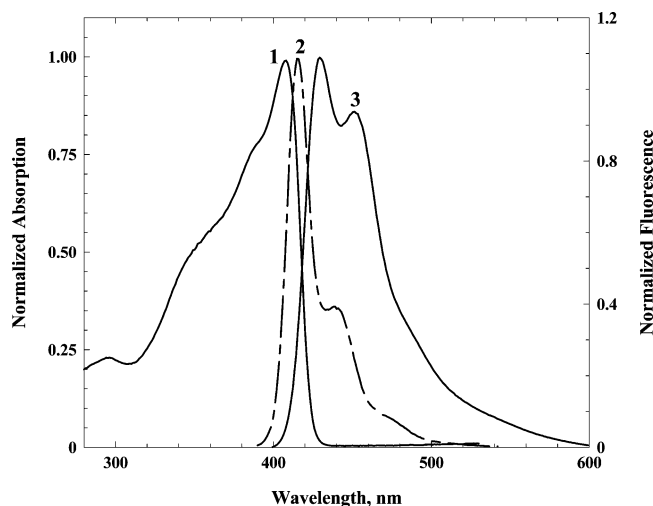


Figure 6. Normalized absorption and fluorescence spectra for **3** at room temperature: (1) absorption in hexane, (2) fluorescence emission in hexane, and (3) photoluminescence of neat thin film.

The fluorescence quantum yield, Φ , was determined by exciting at the absorption maximum, λ_{\max} , for each dye. The values of Φ for **2** and **3** in hexane and cyclohexanone were near unity, whereas for **1** it was 0.4 in hexane and 0.63 in cyclohexanone. The excitation spectra for **2** and **3** were quite similar to the absorption spectrum (Figure 5). This indicates that the emitting species is the one responsible for the absorption spectrum. One can see the fluorescence intensity for all compounds at $\lambda_{\text{exc}} \geq 380$ nm correspond to the main absorption band. However, for short wavelength excitation ($\lambda_{\text{exc}} < 340$ nm), the fluorescence intensity decreased to a greater degree than the corresponding absorption value. As previously described, this decrease at short wavelengths corresponds to excitation to the second electronic excited-state $S_0 \rightarrow S_2$.³⁹

The solid-state luminescence of a spin-cast thin film of neat **3** is shown in Figure 6, along with absorption and emission spectra in hexane. As expected for a

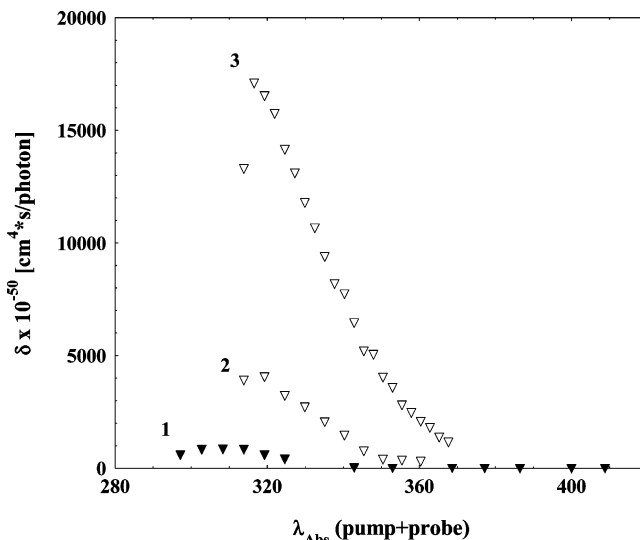


Figure 7. Comparison of nondegenerate 2PA spectra for **1** (1), **2** (2), and **3** (3) in hexane determined by the WLC method.

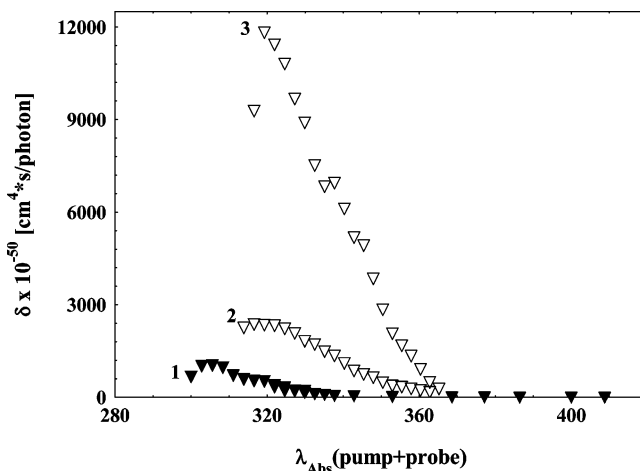


Figure 8. Comparison of nondegenerate 2PA spectra for **1** (1), **2** (2), and **3** (3) in cyclohexanone determined by the WLC method.

concentrated solution or neat sample, the emission spectrum was red shifted, but maintained the general spectral features of the solution-phase spectrum. Polymer **3** exhibited maxima of emission in solution and film at 415 and 429 nm, with shoulders at 439 and 451 nm, respectively.

The nondegenerate 2PA spectra (via the WLC method) for **1–3** in nonpolar (hexane) and polar (cyclohexanone) solvents are shown in Figures 7 and 8, respectively. Here, the cross-sections (given in $10^{-50} \text{ cm}^4 \text{ sec photon}^{-1} \text{ molecule}^{-1}$) 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). Figures 9 and 10 show the degenerate 2PA spectra (via the 2PF method) for **1–3** in hexane and cyclohexanone, respectively. In these graphs, δ is plotted versus half of the value of the pump wavelength used in the 2PF process. For each of these methods, the experimental error of the absolute value of the 2PA cross-section is 20%. For comparison, the single-photon absorption spectrum of compound **1** (in the appropriate solvent) is given in Figures 9 and 10 as a solid line. As can be seen by comparing Figure 7 with 8 and Figure 9 with 10, the values obtained in nonpolar solvents were

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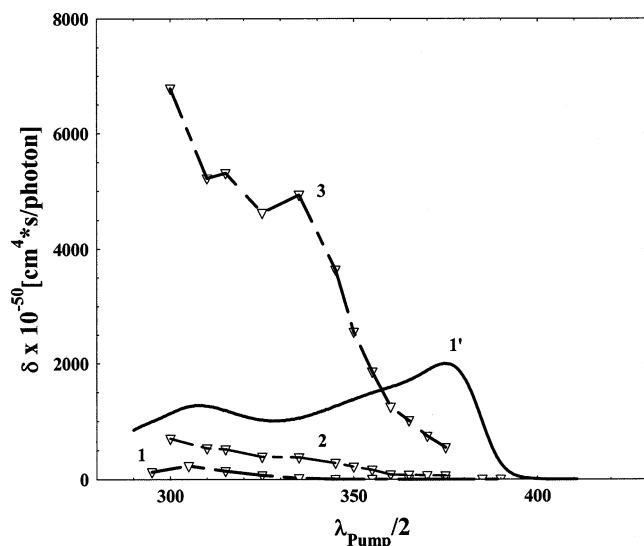


Figure 9. Comparison of degenerate 2PA spectra for **1** (1), **2** (2), and **3** (3) in hexane at 10^{-4} M concentrations determined by the two-photon fluorescence method. Linear absorption spectrum of **1** (1') is shown for reference.

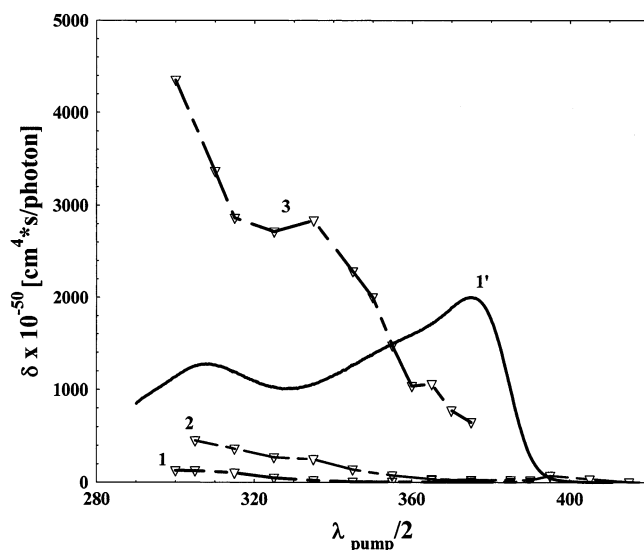


Figure 10. Comparison of degenerate 2PA spectra for **1** (1), **2** (2), and **3** (3) in cyclohexanone at 10^{-4} M concentrations determined by the two-photon fluorescence method. Linear absorption spectrum of **1** (1') is shown for reference.

larger than those obtained in polar solvents. Nevertheless, despite this solvent dependency on the nonlinearity, both values clearly indicate a relative increase of the 2PA cross-section as the number of chromophore moieties increased.

To explain the strong 2PA enhancement observed when comparing oligofluorene (**2**, $N = 3$) and polyfluorene (**3**, $N = 14$), a model compound (**1**, $N = 1$) was also studied. No appreciable red shift of the 2PA resonance from 610 nm (for **1**) to 600 nm (for **3**) was observed due to the use of the amino group as the functionality linking the fluorenyl units, indicating only a weak electronic coupling between fluorenyl moieties in the polymer. Examination of the nondegenerate 2PA spectrum of compound **1** in hexane (Figure 7) revealed a maximum 2PA cross-section of ca. $1000 \times 10^{-50} \text{ cm}^4 \text{ sec photon}^{-1} \text{ molecule}^{-1}$ at 610 nm. The 2PA cross-section of oligo **2** (oligomer) displayed a moderate enhancement,

ca. $4100 \times 10^{-50} \text{ cm}^4 \text{ sec photon}^{-1} \text{ molecule}^{-1}$ at 600 nm. Compound **3** exhibited a very large 2PA cross-section of ca. $17\,200 \times 10^{-50} \text{ cm}^4 \text{ sec photon}^{-1} \text{ molecule}^{-1}$ at 600 nm.

The 2PA cross-sections for **1–3** in hexane as determined by the 2PF method (Figure 9) exhibited trends similar to those of the nondegenerate data. Compounds **1**, **2**, and **3** exhibited peak 2PA cross-section values of ca. 240 , 710 , and $6800 \times 10^{-50} \text{ cm}^4 \text{ sec photon}^{-1} \text{ molecule}^{-1}$, respectively. The magnitudes of the 2PA spectra for **1–3** measured via the WLC method were larger than those determined by the fluorescence method. This is due to the inherent enhancement of the nondegenerate 2PA cross-section with respect to the commonly measured degenerate 2PA cross-section.⁴⁰ However, this enhancement is present for all of the compounds examined by the WLC method, and, therefore, the trends (i.e., strength of the nonlinearity as a function of the number of chromophores) observed are independent of the method used to study them.

The strong 2PA for **1–3** (at ca. $\lambda_{2PA} = 600$ nm) can be attributed to a transition from the ground state to the lowest-lying two-photon allowed state. This transition is expected and allowed for highly centrosymmetric molecules. We also note that this transition is very nearly degenerate with the one-photon forbidden $S_0 \rightarrow S_2$ transition (ca. $\lambda_{1PA} = 300$ nm), which was verified through steady-state fluorescence anisotropy measurements.^{32,39,41} Also apparent is very weak 2PA for the $S_0 \rightarrow S_1$ transition (360–390 nm for linear or single-photon absorption), a transition forbidden for two-photon absorption. These results are consistent with quantum mechanical selection rules.

The value of $\delta_{\text{max}}/\text{MW}$ for **1–3** increases from 0.3 to 0.38 to 0.88 in hexane (from 2PF data) with increasing number of chromophore moieties, indicating that the magnitude of the 2PA cross-section exhibits a near linear increase with the number of chromophore units. Furthermore, from the WLC data for the compounds in hexane, model **1** and polymer **3** show a δ_{max}/N of ca. 1000, where N = the number of fluorene units, also consistent with a linear increase with the number of chromophore units. A similar enhancement in δ has been reported in a triphenylamine-based multibranch structure, attributed, partly, to the electronic coupling between the branches,⁴² though a theoretical study revealed that the vibronic effects are the primary cause for such an enhancement.⁴³ The electronic coupling is weak in the fluorenyl molecules because the amino group links the fluorene units, limiting the conjugation length. Furthermore, increasing the number of chromophores of the system will increase the density of states, providing more effective coupling channels, which would in turn increase the 2PA cross-section.^{42,44} The large enhancement in δ observed for this series of chromophores (**1–3**) may be due to a similar effect.^{42,44}

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Additionally, the enhancement in δ observed here can be correlated with intramolecular charge transfer from the terminal groups to the π -bridge (because the charge is transferred over a longer distance).²² Hence, the 2PA cross-section increases monotonically with the extent of charge transfer.

Conclusions

A series of materials varying in the number of aminofluorenyl units has been synthesized using Ullmann condensation reactions. The 2PA spectra of this series were measured with two independent characterization techniques: a WLC pump-probe method and the familiar 2PF method. Compounds **2** and **3** exhibited very large two-photon absorption cross-sections, nearly $7000 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$ for **3** (as measured by the 2PF technique). Analysis of the experimental data shed light on understanding some molecular structure/nonlinear optical property relationships for this series of chromophores. The 2PA spectra, determined in solvents of different polarity, indicated that the 2PA cross-sections measured in nonpolar solvents were noticeably larger than the values measured in a polar solvent. This type of solvatochromic behavior has been observed for fluorescent dyes, where

the fluorescence intensity of a molecule in solution is reduced via solvation by a polar solvent.⁴⁵ The synthetic efficiency, high photochemical⁴⁶⁻⁴⁸ and thermal stability, high two-photon absorptivity, and desirable luminescence properties make these compounds good candidates for two-photon based applications, such as optical power limiting and two-photon fluorescence imaging, the aspects of which are currently under investigation.

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