

# TWO-PHOTON ABSORPTION IN A NEW SYMMETRICAL SET OF DYPHENYLAMINOFLUORENE-BASED STRUCTURES

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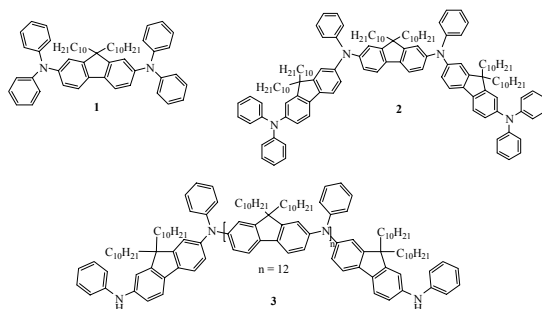
## Introduction

Organic molecules and polymers with specifically tuned chromophores are the subject of great interest owing to their numerous scientific and practical applications, including light-emitting diodes (LED's), two-photon absorption (TPA), and optical limiting devices. Two-photon absorption 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 an energy equal to the sum of the energies of the two photons absorbed [1]. Recently, the synthesis of multifunctional organic materials with increased multiphoton absorption cross-sections,  $\delta$ , and large upconverted fluorescence has opened a new area of research in the photonic and biophotonic fields, particularly in two-photon upconversion lasing, two-photon optical power limiting, 3D optical data storage, and photodynamic therapy [2-4]. Molecular structures used so far to develop efficient two-photon chromophores utilized either a symmetrically (terminating in two electron-donor or two electro-acceptor groups) or asymmetrically (terminating in a donor and an acceptor) substituted  $\pi$ -conjugation unit. Poly(fluorene)-based materials are of particular interest due to their thermal and chemical stability, and their high photoluminescence and electroluminescence properties. We report the synthesis, and linear and nonlinear characterization of new polymer-based dye, such as, amino fluorenyl polymer as well as a well-defined oligomer and a model compound via Ullmann amination condensation. Structural characterization along with photophysical properties, including linear absorption, quantum yield, single photon fluorescence, and TPA cross-section,  $\delta$  values measured in polar and nonpolar solvents are reported.

## Synthesis.

Diphenylaminofluorene was used as the basic structural motif as the  $\pi$ -electron donor in the series of symmetrical chromophores that we report. The model compound, oligomer, and polymer structures synthesized and studied 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*-diphenyl-fluorene-2,7-diamine (**2**), and poly-(9,9-didecyl-2,7-diphenylamino)fluorene (**3**), respectively (Figure 1). Compounds **1**, **2**, and **3** were synthesized via Cu-mediated Ullmann reaction from common intermediate 9,9-didecyl-2,7-diiodofluorene through facile functionalization at positions 2, 7, and 9 of the fluorene ring with the amine corresponding accomplished in *o*-dichlorobenzene using  $K_2CO_3$  as base, 18-crown-6 and copper bronze at reflux [5-7].

All compounds were highly soluble in a variety of organic solvents such as hexane, benzene, toluene, THF,  $CH_2Cl_2$ , and cyclohexanone.



**Figure 1.** Molecular structures of model compound **1**, oligomer **2**, and polymer **3**.

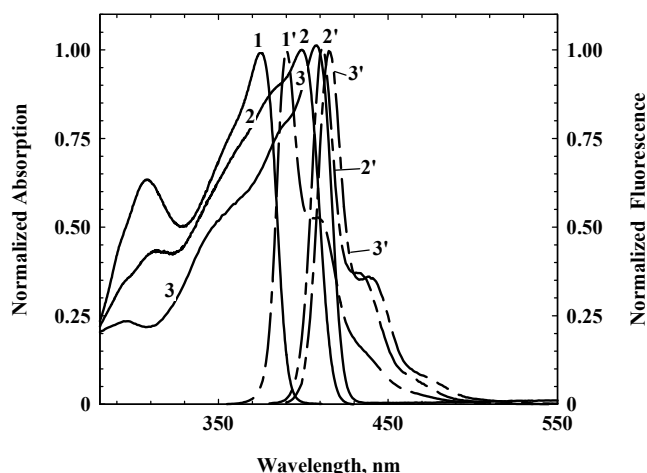
## Physical Measurement

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Gemini NMR spectrometer at 300 MHz and 60 MHz, respectively. FT-IR spectra were recorded on a Perkin Elmer spectrometer. Elemental analyses were performed at Atlantic Microlab. Thermal stability was assessed with a TA Instrument model 2050 thermogravimetric analyzer (TGA) under  $\text{N}_2$  at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  from room temperature to  $550\text{ }^\circ\text{C}$ . Phase and glass transitions were investigated using a TA Instrument model 2920 differential scanning calorimeter (DSC) at heating/cooling rates of  $10\text{ }^\circ\text{C}/\text{min}$  under  $\text{N}_2$ . The molecular weight for the oligomer (**2**) was confirmed by analysis elemental. For the polymer (compound **3**), the number-average molecular weight ( $M_n$ ), was evaluated by analysis elemental C, H, N, and estimated at 8800 Da., corresponds to about 14 fluorene units. UV-visible spectrophotometric measurements were recorded on Varian Cary 3 spectrophotometer in hexanes and cyclohexane with concentrations ca.  $2 \times 10^{-6}\text{ M}$  at room temperature in 10 mm quartz cuvettes. Steady-state fluorescence, and excitation spectra were recorded with a PTI Quantamaster spectrofluorimeter using a Xe lamp and excitation monochromator. Fluorescence quantum yields,  $Q$ , were measured for these compounds by a standard method relative to Rhodamine 6G in ethanol ( $Q \approx 0.94$ ). TPA cross-section values of the three compounds in solution were determined by nonlinear absorption measurements using a femtosecond pump/white light continuum probe “NLO spectrometer”. The experimental setup and data processing procedure can be found in References 8 and 9.

## Results and Discussion

TGA analysis, performed under  $\text{N}_2$  at a heating rate of  $20\text{ }^\circ\text{C}/\text{min}$  from room temperature to  $550\text{ }^\circ\text{C}$ , revealed **2** and **3** possess high thermal stability. Compound **2** exhibits high thermal stability up to  $395\text{ }^\circ\text{C}$  (2% weight loss) and **3** up to  $390\text{ }^\circ\text{C}$  (3% weight loss). The DSC analysis for **2** and **3** revealed a glass transition,  $T_g$ , near room temperature.

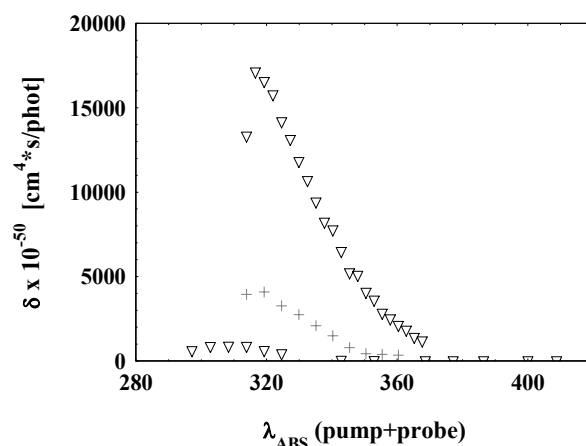
Figure 2 shows a comparison of the UV-visible absorption and one-photon emission spectra of **1-3** in nonpolar solvent. Most of these spectra exhibited a broad absorption band. This suggests a weak interaction between chromophores, with minimal perturbation of their electronic levels. In contrast, the absorption spectrum of **1** exhibited two strong absorption bands around 307 and 375 nm that were better resolved than the higher molecular weight analogs **2** and **3**.



**Figure 2.** UV-visible absorption spectra of **1**, **2**, and **3** solutions in hexane.

Emission spectra of **1-3** in hexane (Figure 2) obtained upon excitation at the maximum of the absorption band show the  $\lambda_{\text{max}}$  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's 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  $\lambda_{\text{exc}}$  in the entire absorption region. Fluorescence quantum yields,  $Q$ , for **1-3** were relatively high ( $Q \approx 0.4\text{-}1.0$ ). The values of quantum yield,  $Q$ , for **2** and **3** in polar and nonpolar solvents, for excitation in the maximum of the absorption band,  $\lambda_{\text{max}}$ , were near unity.

TPA cross-sections,  $\delta$ , values were calculated for the materials in hexane and cyclohexanone. Compound **1** exhibited a maximum TPA cross-section of ca.  $882 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$  at WLC wavelength 616 nm. The TPA cross-section of compound **2** (oligomer) was significantly higher, ca.  $4090 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$  at WLC wavelength 638 nm. Polymer **3** exhibited a very large TPA cross-section of ca.  $17125 \times 10^{-50} \text{ cm}^4 \text{ s photon}^{-1} \text{ molecule}^{-1}$  at WLC wavelength 632 nm (Figure 3). The values obtained in nonpolar solvent were larger than those obtained in polar solvent. Nevertheless, both values clearly indicated a relative increase of the nonlinear absorption cross-section as the number chromophore moieties increased (in a near linear fashion).



**Figure 3.** TPA cross-section,  $\delta$  for **1**, **2**, and **3** in hexanes.

## Conclusions

In conclusion, we have synthesized, using Ullmann condensation reactions, new set of materials with different numbers of chromophore moieties per molecule. All of the compounds exhibited very large two-photon absorption cross-sections as determined by the use of femtosecond pulses. The efficiency of synthesis, high two-photon absorptivity, and luminescence properties, make these compounds good candidates for two-photon based applications, such as optical power limiting and two-photon fluorescence imaging, aspects currently under investigation. Also, luminescence properties suggest possible application as blue light emitting diode hole-conducting materials.

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