

# Synthesis and two photon absorption of diphenylamino endcapped oligo(9,9-diphenyl)fluorenes with enhanced functional properties



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## ARTICLE INFO

### Article history:

Received 8 November 2015

Received in revised form 3 May 2016

Accepted 20 May 2016

Available online 5 June 2016

### Keywords:

Oligofluorene

9, 9-diphenyl derivatives

9, 9-diphenyl derivatives

Synthesis

Two photon absorption

## ABSTRACT

A homologous series of 9,9-diphenyl substituted oligofluorenes end-capped by diphenylamino groups, (Ph)-OF(*n*)-NPhs, *n* = 1–5, has been synthesized using Suzuki cross coupling reaction as a key step and were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS, and elemental analyses. The functional properties, including thermal stabilities, linear optical properties, fluorescence and electro-chemical properties, were investigated. The TPA cross sections of these newly synthesized oligofluorenes were measured by the TPF method. Compounds (Ph)-OF(4)-NPh and (Ph)-OF(5)-NPh exhibited larger two-photon absorption cross-sections, about 550 GM and 1390 GM at 800 nm, respectively.

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## 1. Introduction

Two-photon absorption (TPA) has been known for about four decades [1]. It is one of the very important third-order nonlinear optical (NLO) effects and can be defined as a simultaneous absorption of two photons via virtual states in a medium. The process requires high peak power that is available from pulsed lasers. Even though two-photon processes have been known for a long time, materials that exhibit two-photon absorption have not yet found widespread applications. The reason for this is that most materials have relatively low two-photon absorption cross sections,  $\delta$ . That is, applications of two-photon absorption, such as two-photon laser scanning microscopy [2], 3D optical data storage [3], optical power limiting [4], 3D micro- and nano-fabrication [5], and photo-dynamic therapy [6], depend critically on the availability of materials with high TPA cross sections and on the ability of these chromophores to perform specialized photo-physical, photochemical, or photobiological functions. So, development of novel molecular materials with large two-photon absorption cross-sections still remains attractive prospectus.

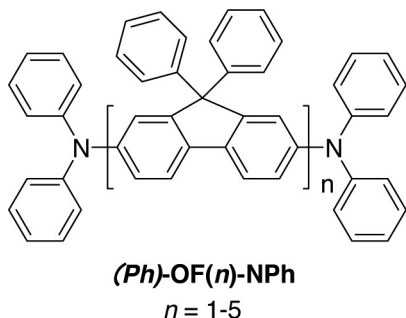
The research for molecules endowed with large two-photon absorption cross-sections has mainly focused on push-pull (D- $\pi$ -A) molecules [4b,7,8], pull-pull (A- $\pi$ -A), push-push (D- $\pi$ -D) or quadrupolar molecules [4b,7–10], where D is an electron-donating group, A is an electron-accepting group and  $\pi$  is a conjugated moiety. Otherwise, it has been observed that symmetrical conjugated molecules with two electron-donating (D) (or electron-withdrawing (A)) end groups exhibit highly nonlinear absorption properties [3], and large TPA cross-section values,  $\delta$  [11]. This enhancement in  $\delta$  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, will result in a large increase of  $\delta$  [8,12].

The fluorenyl  $\pi$ -system was chosen as TPA material candidates due to its inherently high thermal and photochemical stabilities [13–15]. More importantly, fluorene can be readily functionalized onto its 2-, 7-, and/or 9-positions. Recently, the synthesis and linear and nonlinear optical characterization of a number of fluorene derivatives with high two-photon absorptivities have been reported. [16–23] In our previous research [24], we have shown that the diphenylamino end-cap(s) can lower the first ionization potential which greatly reduces the energy barrier for the hole injection from ITO to the emissive oligofluorenes and does not perturb the planarity and alter the highly fluorescent nature of

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oligofluorene backbone. Furthermore, diphenylamino end-capped oligofluorenes showed enhanced thermal stability and exhibited superior amorphous morphological stability. However, the large difference ( $\sim 20$  nm) between the solution PL and thin film PL of (Bu)-OF(4)-NPh marked the presence of the intermolecular interaction among the quaterfluorene backbone [24a]. To prevent aggregation/excimer formation and induce amorphous state of fluorene-based molecular materials, a widely adopted approach is to introduce either spiro-linkage [25–27] or bulky substituent(s) or dendron(s) [28,29] at the C9-position of fluorene. In order to continuing our studies on the oligofluorene derivatives for optoelectronic applications [24], we herein describe the synthesis and two-photon absorption properties of a homologues series of



chromophores with symmetrical molecular structure of type D- $\pi$ -D, based on 9,9-diphenyl substituted oligofluorene end-capped with diphenylamino groups acting as an electron donor group (D), (Ph)-OF(*n*)-NPhs, *n* = 1–5.

## 2. Experimental

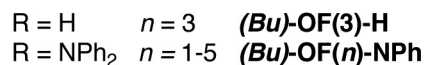
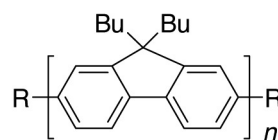
### 2.1. General procedures and requirements

All the solvents were dried by the standard methods wherever needed.  $^1\text{H}$  NMR spectra were recorded using either a JEOL JHM-EX270 FT NMR spectrometer or a Varian INOVA-400 FT NMR spectrometer and are referenced to the residual  $\text{CHCl}_3$  7.24 ppm or DMSO 2.5 ppm.  $^{13}\text{C}$  NMR spectra were recorded using a Varian INOVA-400 FT NMR spectrometer and are referenced to the  $\text{CDCl}_3$  77 ppm or DMSO- $\text{D}_6$  39.5 ppm. Mass spectroscopy (MS) measurements were carried using fast atom bombardment (FAB) on the API ASTAR Pulsar I Hybrid Mass Spectrometer. Elemental Analysis was carried on the CARLO ERBA 1106 Elemental Analyzer. Thermal stabilities were determined by thermal gravimetric analyzer (PE-TGA6) with a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$ . The glass transitions and melting transitions were extracted from the second run DSC traces which were determined by differential scanning calorimeter (PE Pyris Diamond DSC) with a heating rate of  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$ . All the physical measurements were performed in  $\text{CHCl}_3$  including electronic absorption (UV-vis) and fluorescence spectra. Electronic absorption (UV-vis) and fluorescence spectra were recorded using a Varian Cary 100 Scan Spectrophotometer and a PTI Luminescence Spectrophotometer, respectively. The fluorescence quantum yields in chloroform were determined by dilution method [ $^{31}\text{C}$ ] using quinine sulfate monohydrate ( $\lambda_{\text{exc}} = 313$  nm,  $\Phi = 48\%$ ) as a standard. The fluorescence decay curves were recorded at room temperature using nitrogen laser as excitation. The lifetimes were estimated from the measured fluorescence decay using iterative fitting procedure.  $E_{1/2}$  vs  $\text{Fc}^+/\text{Fc}$  was estimated by cyclic voltammetric method (Voltammetric Analyzer CV-50W) using platinum disc electrode as a working

electrode, platinum wire as a counter electrode, and SCE as a reference electrode with an agar salt bridge connecting to the oligomer solution dissolved in  $\text{CH}_2\text{Cl}_2$  using 0.1 M of  $\text{Bu}_4\text{NPF}_6$  as a supporting electrolyte with a scan rate of 100 mV/s and all the potentials were calibrated with ferrocene, ( $E_{1/2}(\text{Fc}/\text{Fc}^+) = 0.45$  V vs SCE) as an external. For two-photon-induced fluorescence method, fluorescein was used as a standard [38].

### 2.2. Synthesis

**(7-Bromo-9,9-diphenyl-9H-fluorene-2-yl) diphenylamine (2) and N,N,N',N',9,9-hexaphenyl-9H-fluorene-2,7-diamine [(Ph)-OF(1)-NPh].**



A single necked 100-mL round bottom flask was charged with diphenylamine (3.38 g, 20 mmol), sodium *tert*-butoxide (2.88 g, 30 mmol), palladium (II) acetate (0.11 g, 0.50 mmol), dry toluene (30 mL), 2,7-dibromo-9,9-diphenyl-9H-fluorene (**1**, 9.52 g, 20 mmol), [32] and tri-*o*-tolylphosphine (0.30 g, 1 mmol), and heated at  $110^\circ\text{C}$  for 24 h under a nitrogen atmosphere. After cooling, the reaction mixture was quenched with water and the solution was extracted with dichloromethane ( $3 \times 50$  mL). The combined organic extract was washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Evaporation of volatiles left a dark solid, which was separated by column chromatography using petroleum ether: dichloromethane ( $v/v = 8:1$ ) as eluent affording compound **2** in 45% yield as a light yellow solid and compound **(Ph)-OF(1)-NPh** in 52% yield as a yellow solid. **2**:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ) 7.47–7.60 (m, 4H), 7.14–7.30 (m, 16H), 7.00–7.10 (m, 6H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ) 152.6, 152.2, 147.8, 147.3, 145.0, 139.0, 133.1, 130.6, 129.3, 129.0, 128.2, 128.0, 126.7, 126.4, 124.2, 124.1, 122.9, 121.1, 120.7, 120.2, 65.6. MS (FAB)  $m/z$  564.6 ( $\text{M}^+$ ). **(Ph)-OF(1)-NPh**:  $^1\text{H}$  NMR (270 MHz,  $\text{CDCl}_3$ ,  $\delta$ ) 7.50 (d,  $J = 8.1$  Hz, 2H), 7.16–7.22 (m, 20H), 7.04–7.12 (m, 10H), 6.94–6.99 (m, 4H).  $^{13}\text{C}$  NMR (60 MHz,  $\text{CDCl}_3$ ,  $\delta$ ) 152.0, 147.5, 146.6, 145.5, 134.6, 129.0, 128.1, 127.9, 126.3, 123.9, 123.3, 122.5, 121.9, 120.0, 65.3. MS (FAB)  $m/z$  652.4 ( $\text{M}^+$ ).

**[7-(Diphenylamino)-9,9-diphenyl-9H-fluorene-2-yl] boronic acid (3)**. To a 100 mL two-necked flask containing the solution of **2** (1.13 g, 2.0 mmol) in 30 mL of dried THF equipped with a magnetic stirrer, a  $\text{N}_2$  purge and a  $-78^\circ\text{C}$  acetone-dry ice bath were added 1.5 M of *n*-butyl lithium/*n*-hexane (4.0 mL, 6.0 mmol) while maintaining a good stirring. After stirring for 0.5 h, the temperature was gradually lifted to room temperature for another 0.5 h, and then the reaction mixture was cooled to  $-78^\circ\text{C}$  again, trimethyl borate (0.70 mL, 6.0 mmol) was added. After stirring further 2 h, water was first added to the reaction mixture and then HCl (6 M) was added in a dropwise fashion until an acidic mixture was obtained. The reaction mixture was poured into water and extracted with dichloromethane ( $3 \times 50$  mL). The combined organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated to dryness. The crude product was purified by flash column

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