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New Two-Photon Absorbing Fluorene Derivatives: Synthesis and Nonlinear Optical Characterization

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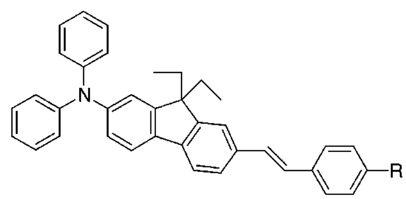
ABSTRACT



R = $P(O)(OCH_2CH_3)_2$ (**2**), NO_2 (**3**)

Efficient Pd-catalyzed Heck coupling methodology was employed to provide two new fluorene derivatives with phosphonate (2) and nitro (3) electron-withdrawing functionalities. Both derivatives exhibit two-photon absorption (2PA), as determined by nonlinear absorption measurements using a femtosecond pump/white light continuum probe "NLO spectrometer". Both fluorene derivatives have high 2PA cross sections (650 and 1300 $\times$ 10^{-50} cm^4 s photon^{-1} molecule^{-1} for compounds 2 and 3, respectively).

The quest for organic materials exhibiting high nonlinear optical (NLO) absorptivities has increased dramatically over the past several years.[1] One nonlinear absorption process, two-photon absorption (2PA), is the subject of fast-growing interest in the chemistry, photonics, and biological imaging communities. Several current and emerging technologies exploit the two-photon absorption phenomenon, including optical power limiting materials,[2] two-photon fluorescence imaging,[3] two-photon photodynamic cancer therapy,[4] and two-photon microfabrication.[5] The 2PA process considered here involves the simultaneous absorption of two photons, either degenerate or nondegenerate, at wavelengths well beyond the linear absorption spectrum of a particular molecule.[6] Though a subject of contemporary investigation, the simultaneous absorption of two quanta of energy was first predicted in 1931 by Goeppert-Mayer.[7] We report, herein, the synthesis and nonlinear optical characterization of two specific fluorene derivatives that exhibit relatively large 2PA cross sections, a measure of two-photon absorptivity. Nondegenerate 2PA spectra were recorded with our recently developed "NLO spectrometer".[8]

Why are two-photon absorbing materials so intensely pursued? Let us consider a major feature that distinguishes single-photon absorption (1PA) from two-photon absorption (2PA): the rate of energy (light) absorption as a function of incident intensity. In single-photon absorption, the rate of light absorption is directly proportional to the incident

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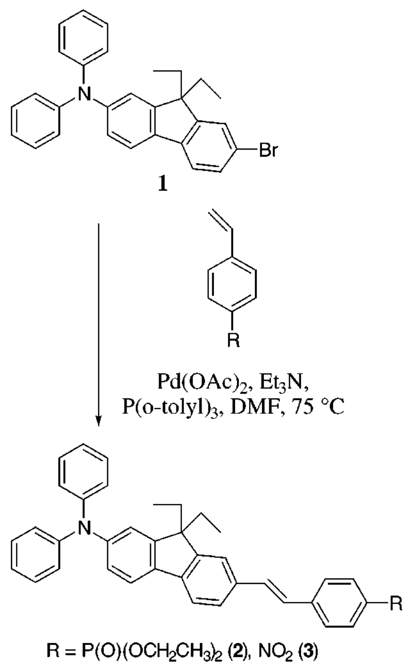
intensity ($dw/dt \propto I$), i.e., as the incident intensity is increased, the rate of photon absorption increases linearly for the molecule in question. By contrast, in simultaneous two-photon absorption, the rate of energy absorption is proportional to the square of the incident intensity ($dw/dt \propto I^2$).[1,6] This quadratic, or nonlinear, dependence has substantial implications. For example, in a medium containing one-photon absorbing chromophores, significant absorption occurs all along the path of a focused beam of suitable wavelength light. This can lead to, e.g., photodegradation or photobleaching. In 2PA, negligible absorption occurs except in the immediate vicinity of the focal point of a light beam of appropriate energy. This allows spatial resolution along the beam axis as well as radially and is the principal basis for two-photon fluorescence imaging.[3] The simultaneous absorption of two or more photons requires high peak power, which is now available from commercially available ultrafast pulsed lasers. Thus, certain materials can undergo nonresonant 2PA at wavelengths far beyond their linear absorption spectrum.

Two fluorene derivatives with different electron-withdrawing groups were synthesized via Heck coupling reactions, as illustrated in Scheme 1. The fluorenyl ring system was chosen to serve as a thermally and photochemically stable π-conjugated system that can be readily functionalized in the 2-, 7-, and/or 9-positions. Such functionalization facilitates the systematic preparation of derivatives with varying electronic character for molecular structure/nonlinear absorption relationships. Polarizable molecular structures with relatively long conjugation lengths may lead to large two-photon absorptivities.[1] In the current work, derivatives bearing electron-withdrawing groups (phosphonate and nitro) of different strengths were prepared and studied.

Scheme 1



Near-quantitative Pd-catalyzed Heck coupling[9] of 2-bromo-7-*N*,*N*-diphenylamino-9,9-diethylfluorene **1** (prepared in three steps from fluorene via dibromination, diethylation, and Ullmann-type coupling with diphenylamine as previously reported[10]) with either 4-vinylbenzene phosphonic acid diethyl ester or 4-nitrostyrene afforded novel fluorene dyes **2** and **3**, respectively. 4-Vinylbenzene phosphonic acid diethyl ester and 4-nitrostyrene were prepared from 4-bromoacetophenone and 4-nitroacetophenone, respectively, by established procedures.[11] The Heck coupling reactions were conducted with $Pd(OAc)_2$, tri-*o*-tolylphosphine, and Et_3N as base in DMF at 75 °C for 15 h. Phosphorylated fluorene derivative **2** was isolated in 92% yield as a fluorescent yellow solid and fully characterized.[12] The UV−visible absorption spectrum of **2** in CH_3CN extended out to about 480 nm with two λ_{max}, one at 308 nm and the other at 383 nm.

Nitro-containing fluorene derivative **3** was obtained in 90% yield as a fluorescent orange-red solid and fully characterized.[13] The visible absorption of **3** in CH_3CN extended out to about 550 nm with two λ_{max}, one at 309 nm and the other at 414 nm.

Linear and nonlinear absorption (nondegenerate 2PA) spectra for fluorene derivatives **2** and **3** are shown in Figures 1 and 2, respectively.

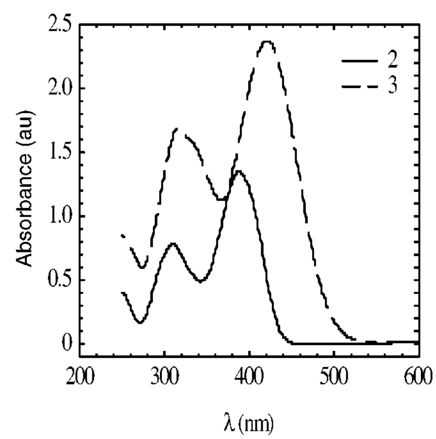


Figure 1. Linear absorption spectra (absorption units vs wavelength) for compounds **2** and **3**.

Details of the nonlinear absorption measurements and the "NLO spectrometer" have been described elsewhere.[8] Briefly, femtosecond pump probe experiments were performed in which the pump beam wavelength was selected to be at a low enough energy (long wavelength, 1210 nm) to prevent degenerate 2PA. The probe beam consisted of a femtosecond white light continuum (WLC) generated by irradiation of a sapphire window.

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The 2PA spectra illustrated in Figure 2 show the 2PA cross section (in units of cm^4 s $photon^{-1}$ $molecule^{-1}$). Fluorene **2**

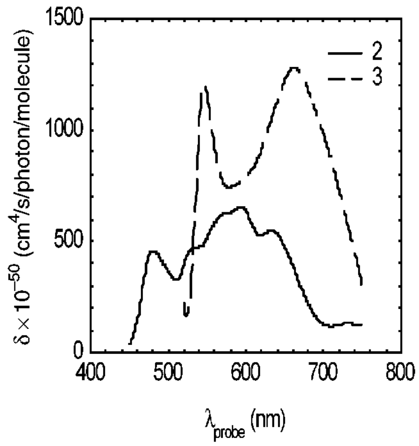

Figure 2. Two-photon absorption spectra [2PA cross section, δ (cm^4 s $photon^{-1}$ $molecule^{-1}$), vs probe wavelength] for compounds **2** and **3** using a 1210 nm pump beam.

exhibits a maximum 2PA cross section of ca. 650 $\times$ 10^{-50} cm^4 s $photon^{-1}$ $molecule^{-1}$ at WLC wavelength 605 nm. The 2PA cross section of fluorene **3** is significantly higher, ca. 1300 $\times$ 10^{-50} cm^4 s $photon^{-1}$ $molecule^{-1}$ at WLC wavelength 670 nm, and comparable to very large 2PA cross sections that were recently reported for another class of organic compounds (on the order of 500 to 1100 $\times$ 10^{-50} cm^4 s $photon^{-1}$ $molecule^{-1}$).[14]

Figures 3 and 4 display the linear and 2PA spectra of derivatives **2** and **3**, respectively, plotted as absorption vs

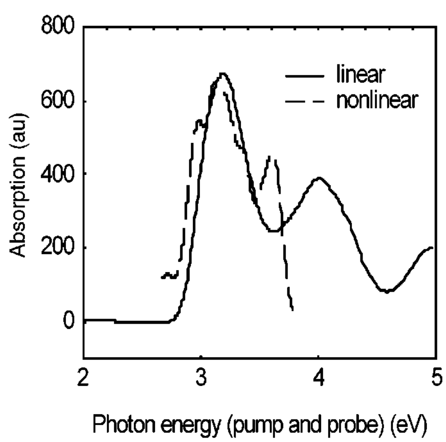

Figure 3. Linear and nonlinear absorption spectra of **2** (absorption units vs eV).

total photon energy in eV (the linear wavelengths were converted to photon energy while the wavelengths of the pump and probe beams were converted to photon energy and summed for the 2PA spectra). Relatively good correlation between the linear and nonlinear spectra was observed. This is to be expected for molecules having an extended π-conjugated system and permanent dipole moment. For these systems, the parity can mix such that the spectra of one- and two-photon allowed states overlap. Further overlap of the one- and two-photon spectra arise from the near degeneracy of one- and two-photon allowed states and the vibronic structure of the molecules.[6]

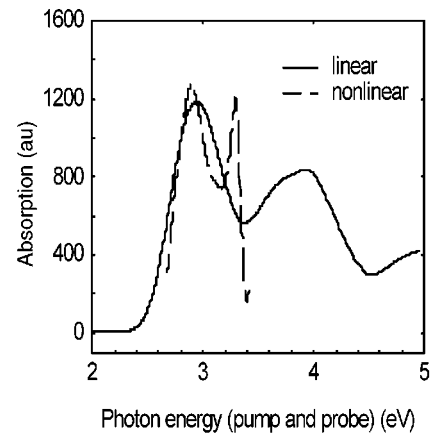

Figure 4. Linear and nonlinear absorption spectra of **3** (absorption units vs eV).

Thus, efficient Pd-catalyzed Heck coupling methodology afforded two new fluorene derivatives with phosphonate (**2**) and nitro (**3**) electron-withdrawing functionalities in at least 90% yield. Both derivatives exhibit two-photon absorption (2PA), as determined by nonlinear absorption measurements using a femtosecond pump/white light continuum probe "NLO spectrometer". The large 2PA cross sections for the two fluorene derivatives (650 and 1300 $\times$ 10^{-50} cm^4 s $photon^{-1}$ $molecule^{-1}$ for compounds **2** and **3**, respectively) open the door for potential applications of these chromophores in optical power limiting and multiphoton fluorescence imaging applications.

Acknowledgment. The authors would like to dedicate this work to Bruce A. Reinhardt (deceased) of the Air Force

(12) Characterization data for compound **2**: MS (EI) *m/z* 627 (M^+), 541 (M − $2(C_2H_5)$), 168 ($C_{12}H_{10}N^+$), 77 ($C_6H_5^+$); UV−vis (CH_3CN) λ_{max} = 308 and 383 nm; mp = 185−186 °C. Anal. Calcd: C = 78.45; H = 6.74; N = 2.23. Found: C = 78.22; H = 6.94; N = 1.85. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.85−6.98 (m, 20H, ArH), 7.12 (q, J = 7.4 Hz, 2H, *trans*-CH=CH), 4.14 (q, J = 7.0 Hz, 4H, OCH_2), 1.95 (m, J = 7.1 Hz, 4H, CH_2), 1.35 (t, J = 7.0 Hz, 6H, ester CH_3), 0.40 (t, J = 7.1 Hz, 6H, CH_3).

(13) Characterization data for compound **3**: MS (EI) *m/z* 536 (M^+), 490 (M − NO_2), 168 ($C_{12}H_{10}N^+$), 77 ($C_6H_5^+$); UV−vis (CH_3CN) λ_{maxima} = 309 and 414 nm; mp = 192−194 °C. Anal. Calcd: C = 82.81; H = 6.01; N = 5.22. Found: C = 82.75; H = 5.89; N = 4.90. ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.17 (d, J = 9.3 Hz, 2H, ArH *ortho* to NO_2), 7.60−6.93 (m, 18H, ArH), 7.05 (q, J = 8.0 Hz, 2H, *trans*-CH=CH), 1.88 (m, J = 7.0 Hz, 4H, CH_2), 0.30 (t, J = 7.0 Hz, 6H, CH_3).

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