

Scientific paper

Two-Photon Absorption and Optical Limiting Properties of a New 9-Branched Fluorene Derivative

Guohui Zhang,^a Duxia Cao,^{a,*} Zhiqiang Liu^b and Guozhong Li^a

^aSchool of Materials Science and Engineering, University of Jinan, Jinan 250022, China

^bState Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

* Corresponding author: E-mail: duxiacao@ujn.edu.cn

Tel.: +86-531-89736751; Fax: +86-531-87974453

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Abstract

A new trisubstituted fluorene derivative, 4,4'-[4-(diethylamino)benzylidene]-9H-fluorene-2,7-diyl]di-2,1-ethenediyl]bis(N,N-diphenyl)benzeneamine (**1**), with electron-donating N,N-diphenyl-4-vinylaniline group at the 2- and 7-positions, and a N,N-diethyl-4-vinylaniline group as a branch at the 9-position, has been synthesized by a route involving Heck reaction. The photophysical properties of this compound in six different solvents were examined in detail and compared with its non-branched analogue to establish structure-properties relationships. The two-photon absorption coefficient β of the sample was found to be $1.32 \times 10^{-2} \text{ cm GW}^{-1}$, determined by a direct nonlinear optical transmission (NLT) method, when pumped by Ti-sapphire laser at 775 nm, which indicates its potential as an optical limiting material.

Keywords: Fluorene, two-photon absorption, optical limiting

1. Introduction

Fluorene features greatly increased planarity and rigidity, compared to its biphenyl analogue. Its derivatives often possess enhanced chemical, thermal, and photochemical stability. Consequently, fluorenyl-containing conjugated backbones are popularly adapted as intramolecular charge-transfer bridges in the design and synthesis of novel materials suitable for electronic and photonic applications.^{1,2} For example, many novel fluorenyl-containing two-photon absorbing (TPA) materials have been reported recently.^{2–7}

Among these fluorenyl-containing chromophores, the π -conjugated substituents are usually located on the phenyl rings, often at the 2 and 7 positions of fluorene. Substitutions at the 9-position usually involve two alkyl or aryl groups, such that the carbon atom at the 9-position remains sp^3 hybridized. These groups therefore lie out of the conjugation plane and will efficiently reduce intermolecular interactions. However, they are not conjugated with the rest of the molecule and therefore do not influence the intramolecular charge transfer and related optoelectronic properties. As a representative compound, 4,4'-[[9,9-Bis

(ethyl)-9H-fluorene-2,7-diyl]di-2,1-ethenediyl]bis(N,N-diphenyl)benzeneamine (**2**) exhibits high fluorescence quantum yields, good solubility in common organic solvents, excellent thermo- and photo-stability, and outstanding TPA properties.^{5–7}

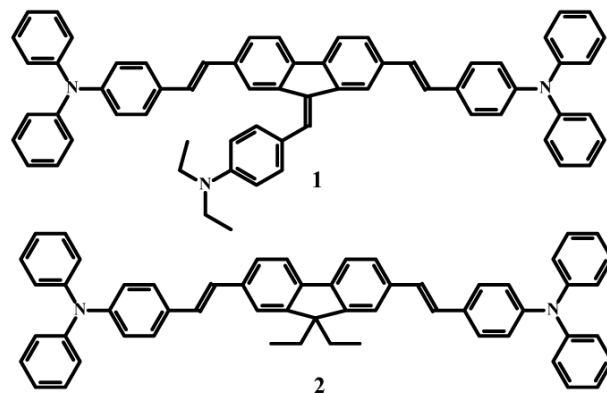


Figure 1. Molecular structures of branched and linear fluorene derivatives **1** and **2**.

With our ongoing interests in TPA active fluorene derivatives,⁸ we synthesized a new derivative (**1**) of compound **2** by introducing a *N,N*-diethyl-4-vinylaniline group as a branch on the 9-position of fluorene and investigated its photophysical properties. The molecular structures of **1** and **2** are shown in Figure 1. Compared with the strongly single- and two-photon fluorescent compound **2**, **1** inherits its large TPA cross section but is only weakly fluorescent. This compound could be a good candidate suitable for optical limiting applications.

2. Experimental

2.1. Chemical and Instruments

Nuclear magnetic resonance spectra were recorded on a Varian Mercury Plus 400 NMR spectrometer. MALDI-TOF mass spectra were obtained on an Agilent 5973N MSD spectrometer. Elemental analyses were carried out on a PE 2400 autoanalyzer. 4-(diethylamino)benzaldehyde was synthesized according to the literature procedure.⁹ Fluorene, palladium (II) acetate, tri-*o*-tolyl phosphine, and other key chemicals were obtained from Acros Ltd and used without further purification.

2.2. Synthesis

The synthetic strategy for the title compound is shown in Scheme 1. Strong base catalysed condensation between the starting material 2,7-diiodo-9*H*-fluorene (**S-1** prepared from fluorene via diiodination) and one equivalent of 4-(diethylamino)benzaldehyde afforded compound **S-2** as a yellow powder. Further double Heck coupling re-

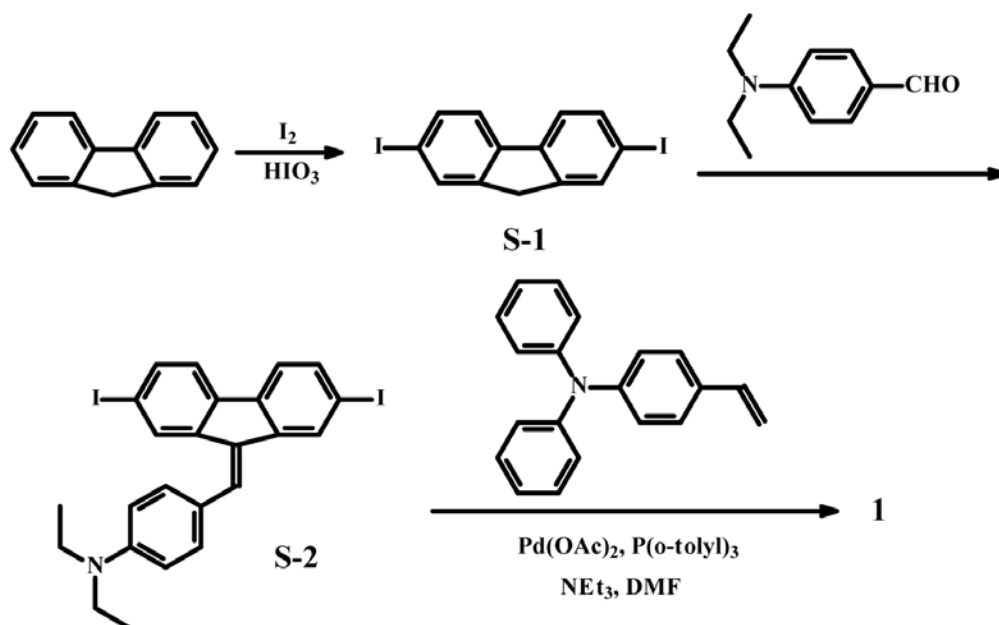
action between **S-2** and two equivalents of *N,N*-diphenyl-4-vinylaniline resulted in the title compound **1**.

2,7-diiodo-9*H*-fluorene (**S-1**)

6.0 g (36 mmol) fluorene, 3 mL carbon tetrachloride, 13 mL distilled water, 6.9 g (27 mmol) iodine, 3.0 g (17 mmol) iodic acid, 2 mL concentrated sulfuric acid and 250 mL acetic acid were added into a flask equipped with a condenser. The mixture was heated under reflux for 4h with stirring. After cooling to room temperature, a great deal of white precipitate formed and the precipitate was filtered. The product was obtained as a white solid in 80% yield by recrystallization from anhydrous ethanol. ¹H NMR (CDCl₃, 400MHz): δ 3.71 (s, 2 H), 7.36 (d, 2 H, *J* = 7.8 Hz), 7.61 (t, 2 H, *J* = 8.8 Hz), 7.76 (s, 2 H).

N,N-diethyl-4-[(2,7-diiodo-9*H*-fluorene-9-yl)methylene]benzeneamine (**S-2**)

3.3 g (8.0 mmol) 2,7-diiodo-9*H*-fluorene (**S-1**) was added into a flask with 150 mL of anhydrous ethanol containing 1.0 g EtONa, and the mixture was continuously stirred at room temperature for 1 h. Then 3.7 g (21 mmol) of 4-(diethylamino)benzaldehyde was added and the mixture was heated under reflux for 6 h before cooling to room temperature. A yellow precipitate was purified by column chromatography on silica gel using petroleum ether as the eluent to give the product as a yellow solid in 70% yield. ¹H NMR (CDCl₃, 400 MHz): δ 1.25 (t, 6 H, *J* = 7.3 Hz), 3.46 (q, 4 H, *J* = 7.1 Hz), 6.74 (d, 2 H, *J* = 8.7 Hz), 7.46 (t, 2 H, *J* = 7.2 Hz), 7.53 (d, 2 H, *J* = 8.7 Hz), 7.60–7.64 (m, 3 H), 8.08 (s, 1 H), 8.44 (s, 1 H).



Scheme 1. Synthetic strategy for the title compound **1**.

4,4'-{[9-[4-(diethylamino)benzylidene]-9H-fluorene-2,7-diyl]di-2,1-ethenediyl}bis(N,N-diphenyl)benzene-amine (**1**)

1.15 g (2.0 mmol) of **S-2**, 0.029 g (0.15 mmol) of palladium (II) acetate, 0.091 g (0.30 mmol) of tri-*o*-tolylphosphine and 20 mL of redistilled DMF were added to a 100 mL three-necked flask. The mixture was heated to 80 °C for 0.5 h, and then 1.09 g (4 mmol) of N,N-diphenyl-4-vinylaniline and 4 mL redistilled triethylamine were added into the system. The reaction mixture was continuously stirred at 90 °C overnight. After cooling to room temperature, the crude product was condensed and purified by column chromatography on silica gel using chloroform/petroleum ether (1:2) as the eluent. The product was obtained as a red powder in 60% yield. ¹H NMR (CDCl₃, 400 MHz): δ 1.24 (t, 6 H, *J* = 7.0 Hz), 3.46 (q, 4 H, *J* = 7.0 Hz), 6.78 (d, 2 H, *J* = 7.6 Hz), 6.95 (d, 2 H, *J* = 6.0 Hz), 7.02–7.15 (m, 22 H), 7.24–7.28 (m, 4 H), 7.33 (d, 2 H, *J* = 7.2 Hz), 7.43 (d, 3 H, *J* = 7.2 Hz), 7.48 (d, 1 H, *J* = 6.8 Hz), 7.63 (d, 2 H, *J* = 7.2 Hz), 7.67–7.69 (m, 2 H), 7.71 (s, 1 H), 7.90 (s, 1 H), 8.25 (s, 1 H). ¹³C NMR (CDCl₃, 100 MHz): δ 147.6, 141.1, 139.8, 137.7, 136.1, 131.7, 129.3, 127.4, 124.4, 123.7, 123.0, 121.6, 119.7, 44.5, 29.7, 12.7. MALDI-TOF MS *m/z* calcd for [M + H]⁺ 864.14, found 863.00. Anal. Calcd. for C₆₄H₅₃N₃: C, 88.96; H, 6.18; N, 4.86. Found: C, 88.89; H, 6.20; N, 4.81.

2. 3. Measurements

Linear absorption spectra with $c = 1.0 \times 10^{-5}$ mol/L were recorded on a PE Lambda 35 UV/VIS spectrometer. Fluorescence spectra with $c = 1.0 \times 10^{-5}$ mol/L were measured on an Edinburgh FLS920 fluorescence spectrometer. The fluorescence quantum yields Φ for the compound in various solvents were determined relative to the fluorescein using a standard method.¹⁰

Nonlinear absorption phenomena were investigated by a direct nonlinear transmission (NLT) method.^{11–13} Intensity-dependent transmission was measured at 775 nm using the laser pulses with 150 fs duration. The laser beam passed through a 10 mm path quartz cuvette filled with the solution of **1** and the intensities of transmitted beam were recorded as a function of incident intensity.

2. 4. Theoretical Calculations

We performed DFT (density functional theory) quantum chemical calculations on compound **1** by using Gaussian 03.¹⁴ The functional used includes Becke's three parameter hybrid functional¹⁵ in conjunction with the Lee–Yang–Parr correlation functional.¹⁶ The used basis set was 6-31G. The electron density distribution of the frontier molecular orbitals (HOMO and LUMO) was obtained using the visualization package Gauss View.¹⁷

3. Results and Discussion

Table 1. Absorption and fluorescence properties of the title compound **1** in various solvents.

Solvents	$\lambda_{\max}^{\text{abs}}/\text{nm}$	$\epsilon_{\max}/10^4 \text{ cm}^{-1} \text{ mol L}^{-1}$	$\lambda_{\max}^{\text{SPEF}}/\text{nm}$	Φ
Hexane	397	8.19	447 ? 472	0.003
Toluene	401	7.31	459 ? 487	0.003
THF	401	7.65	486	0.016
Acetone	400	8.17	500	0.005
DMF	401	8.04	501	0.023
CH ₃ CN	401	8.04	511	0.004

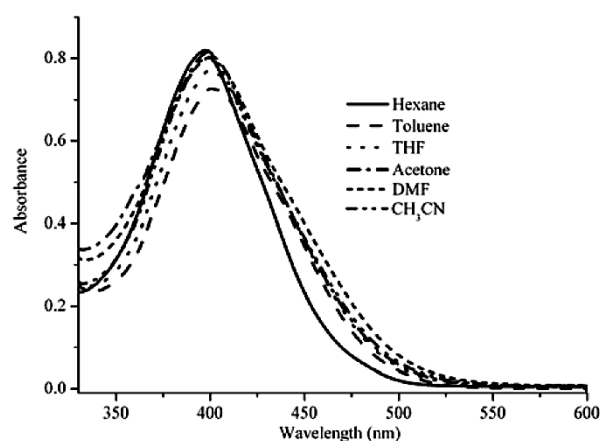


Figure 2. Linear absorption spectra of **1** in various solvents with $c = 1.0 \times 10^{-5}$ mol/L.

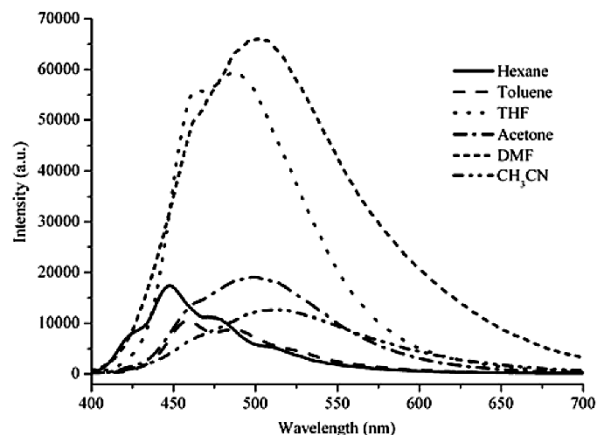


Figure 3. Fluorescence spectra of **1** in various solvents with $c = 1.0 \times 10^{-5}$ mol/L.

The linear absorption and fluorescence spectra of **1** in various solvents with different polarity are shown in Figure 2 and Figure 3, respectively, and the comprehensive photophysical properties are listed in Table 1. As shown in Table 1 and Figure 2, linear absorption properties including peak positions and absorbance exhibit little

dependence on solvent polarity, which indicates that the molecule possesses low polarity in the ground state. With the increase of solvent polarity, the fluorescence peak positions are lightly red-shifted, which means that there is some intramolecular charge transfer process taking place, and the molecular polarity increases slightly in the excited state relative to that in the ground state. The fluorescence quantum yields are very low and there is no obvious correlation with the increase in solvent polarity.

Compound **2** has been studied as a typical single and two-photon active fluorescence emitter^{5–7} and electro-luminescent material.^{18–20} The maximum linear absorption peaks of **1** and **2** are quite similar (both around 400 nm). Recently, a derivative of 4-branched **2** was reported, which exhibits remarkable single- and two-photon absorption properties.⁶ Comparing the structures and properties of these compounds, the weak fluorescence of **1** seems to result from the N,N-diethyl-4-vinylaniline embranchment.

Quantum chemical calculations on compound **1** by using Gaussian 03 package were performed to obtain the charge transfer mode and equilibrium geometry for this compound and to understand of the reasons for the weak fluorescence. As shown in Figure 4, symmetric charge transfer from the two terminal diphenylamino groups to the central fluorenyl moiety occurs upon excitation from the HOMO to the LUMO. Although the diethylamino group is a strong electron-donor, the diethylaminophenyl and fluorene centre are not effectively conjugated with each other because of the lack of co-planarity between them.

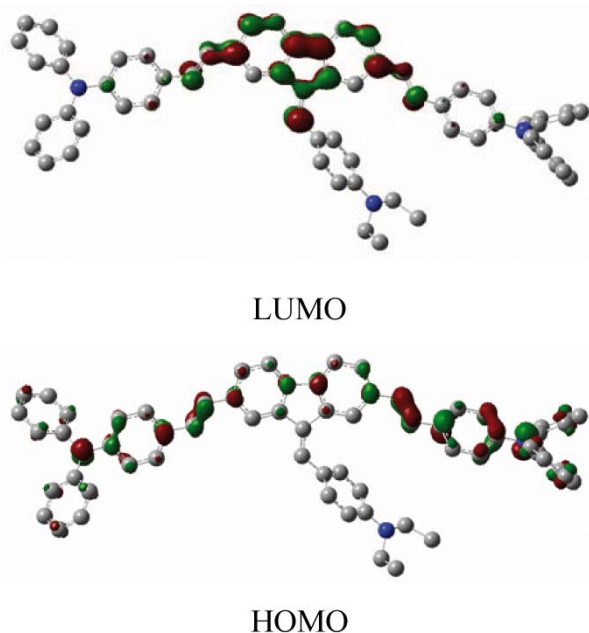


Figure 4. The electron density distribution of the frontier molecular orbitals (HOMO and LUMO) of compound **1**.

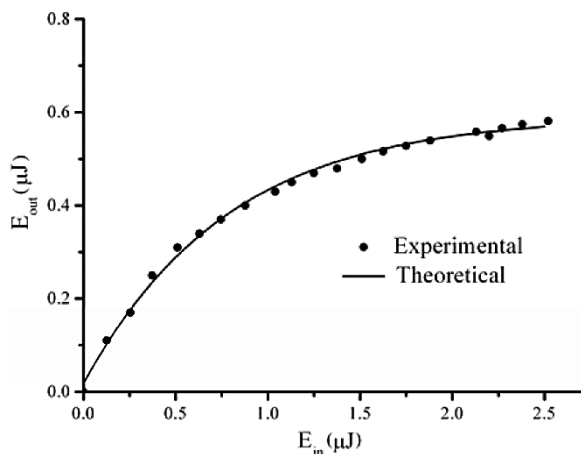


Figure 5. Nonlinear transmission of **1** in THF with $c = 5.0 \times 10^{-3}$ mol/L.

Considering the strong two-photon absorption properties of **2** and the relative weak fluorescence of **1**, we assumed that **1** may be useful as optical limiting material. A laser transmission experiment was carried out, where the laser beam (775 nm) passed through a 10 mm path quartz cuvette filled with a THF solution of **1** and the energy of the transmitted beam was recorded as a function of incident light. As shown in Figure 5, at very low irradiance, the compound responds linearly to the incident intensity, obeying Beer's law. However, under stronger irradiance, the curve obviously departs from Beer's law and the sample solution becomes less transparent as the irradiance increases. From these phenomena, one can readily see the optical limiting effects of the title compound.

Since a fs pulse laser was used as the light source, we can assume that two-photon absorption (TPA) is the predominant process causing the observed intensity dependence in the non-linear transmission measurement. Then, according to the basic theoretical consideration, the TPA induced transmissivity change for a Gaussian transverse distribution laser beam will be expressed as:¹²

$$T(I_0) = [\ln(1 + I_0 L \beta)] / I_0 L \beta \quad (1)$$

where I_0 is the incident intensity, L is the thickness of the sample, and β is the TPA coefficient of the solution. The solid curve in Figure 5 was fitted with Eq. (1) and a TPA coefficient β of the sample was calculated to be 1.32×10^{-2} cm GW⁻¹.

4. Conclusions

A new 9-branched fluorene derivative was synthesized and examined as two-photon absorption material. Due to the introduction of the embranchment at 9-position of fluorene, a special fluorescence quenching takes place.

Combining a large TPA cross section and a low quantum yield, this compound was believed to be a good candidate for optical limiting application, which has been preliminarily indicated from the nonlinear optical transmission experiment. The search is currently underway to find their application.

5. Acknowledgments

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Povzetek

V prispevku je podana priprava novega trisubstituiranega fluorena **1** z elektrondonorsko N,N-difenil-4-vinilnilinsko skupino na mestih 2 in 7, in z N,N-dietil-4-vinilnilinsko skupino na mestu 9, preko Heckove reakcije. Avtorji so na pripravljeni spojini {tudirali fotofizikalne lastnosti v {estih različnih topilih in njene lastnosti primerjali z analogno, na mestu 9, nerazvejano spojino, da bi ugotovili zvezo med strukturo in lastnostjo spojine. Z neposredno nelinearno optično prepustnostno metodo (NLT metoda, Ti-safirni laser, $\lambda = 775$ nm) zmerjeni dvo-fotonski absorpcijski koeficient β (1.32×10^{-2} cm GW⁻¹) kaže na njeno možno uporabo kot materiala za optično omejevanje.