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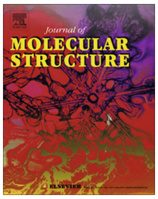

Synthesis, one and two-photon optical properties of two asymmetrical and symmetrical carbazole derivatives containing quinoline ring

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HIGHLIGHTS

- Novel carbazole derivatives containing quinoline were synthesized.
- Electronic transition of carbazole derivatives were theoretically studied by TD-DFT.
- Long fluorescence lifetime of carbazole derivatives was obtained.
- Two-photon absorption of compounds was measured by 120 fs pulse at 800 nm.

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ABSTRACT

The carbazole derivatives are suitable for two-photon absorption optical storage and photoluminescence material. Two carbazole derivatives, asymmetrical and symmetrical type molecules containing quinoline rings as electron acceptors and an N-ethylcarbazole group as electron donor, 9-ethyl-3-(2-quinolin)viny-carbazole (**4**) and 9-ethyl-3,6-bis(2-(quinolin)vinyl)-carbazole (**5**), had been synthesized by the Vilsmeier reaction of formylation and Knoevenagel condensation. The one-photon properties including absorption, fluorescence emission spectra, fluorescence quantum yields and fluorescence decay behaviors were investigated in N,N-dimethylformamide. Meanwhile, these compounds were theoretically surveyed by the density functional theory (DFT) and the time-dependent functional theory (TD-DFT). The two-photon excited fluorescence and two-photon absorption cross-sections were measured for the compounds by 120 fs pulse at 800 nm Ti: sapphire laser operating at 1 kHz repetition rate. The results showed that both of the two compounds **4** and **5** had higher fluorescence quantum yield (Φ) of 0.77 and 0.81 comparing with carbazole. Compounds **5** with symmetric π conjugated structure possessed longer fluorescence lifetime (τ) of 21.4 ns and larger two-photon absorption cross-sections (δ_{TPA}) of 364 × 10^{-50} cm^4 s/photon than those of compounds **4** with asymmetric π conjugated structure ($\tau = 10.03$ ns and $\delta_{TPA} = 81 \times 10^{-50}$ cm^4 s/photon). It was indicated that the one and two-photon optical properties of carbazole derivatives are influenced strongly by the symmetry and length of π conjugated structure.

1. Introduction

Two-photon absorption (TPA) is a phenomenon that involves the excitation of a molecule by simultaneous absorption of two-photons [1]. Therefore, two-photon absorption (TPA) holds a great potential for a number of industrial and medical applications such as optical power limiting [2–5], two-photon up-conversion lasing [6,7], two-photon fluorescence excitation microscopy [8–12], three-dimensional (3D) optical data storage and microfabrication [13–18]. For all the applications mentioned above, it is highly desirable to employ molecules with a large TPA cross section. For this requirement, research in both experimental and theoretical ways for obtaining the structure–property relation has been pushed forward [19–22]. In exploring strong TPA compounds, Albota et al. had focused on symmetric intramolecular charge transfer organic molecules and emphasized the importance of conjugation length, donor/acceptor strength, and molecular symmetry [23]. Meanwhile, Reinhardt et al. had also respectively studied the effects of the planarity of π-center, donor strength, and molecular asymmetry on asymmetric intramolecular charge transfer ones [24]. The available research results exhibited that the conjugation length, donor–acceptor functionalities, conformation, orientation of the molecule, the molecular dimensionality, molecular congregating effects, etc. are significant factors to be considered in the molecular design and synthesis [20,21].

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It is well known that carbazole is isoelectronic to diphenylamine, but it has a planar structure and it can be imagined as the bonded diphenylamine. The carbazole nucleus can be easily functionalized at 3-, 6-, 9-positions and covalently linked to other molecular groups [25]. Typical push–pull chromophores consist of a polar A–π–D system with a planar π-system end-capped by a strong electron donor (D) and a strong electron acceptor (A). In order to ensure intramolecular charge transfer (ICT) between the donor (D = N-alkyl group etc.) and the acceptor (A = cyano group etc.), double or triple bonds is the most common methods of linking the π-conjugated system between aromatic and hetero-aromatic rings [26,27]. Carbazole moiety being a rigid structure with a donor-rigidised residue improves π-electron delocalization resulting in better two-photon absorbing property [28]. Up to now, many research groups have reported the structures, optical and electronic properties of many carbazole derivatives because of their excellent advantages of chemical, thermal and photochemical stabilities as well as their ease adjustment of the electronic and optical properties [29–35]. It is very important for the applications of carbazole derivatives as optical materials to understand the relations between the optical properties and molecule structure, especially the effect of π-conjugated structure on the optical properties of carbazole derivatives. In this paper, two carbazole derivatives, asymmetrical and symmetrical type molecule containing quinoline rings as electron acceptors and an N-ethylcarbazole group as electron donor, 9-ethyl-3-(2-quinolin)viny-carbazole and 9-ethyl-3,6-bis (2-(quinolin)vinyl)-carbazole, have been synthesized by the Vilsmeier reaction of formylation and Knoevenagel condensation. Linear absorption spectra, one-photon excited fluorescence, fluorescence quantum yields and fluorescence decay behaviors of the compounds are investigated. Density functional theory (DFT) and time-dependent functional theory (TD-DFT) are utilized to survey theoretically the electron transition feature. The two-photon excited fluorescence of the compounds are studied by 120 fs pulse at 800 nm Ti: sapphire laser operating at 1 kHz repetition rate and two-photon absorption cross-section is measured. The effect of π-conjugated structure containing quinoline rings as electron acceptors and an N-ethylcarbazole group as electron donors on the one and two-photon optical properties of the carbazole derivatives is discussed as well.

2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE-300 MHz NMR instrument using TMS as internal standard. IR spectra were recorded using Perkin Elmer FT-IR System. The spectra of the solid compounds were performed in the form of KBr pellets. Mass spectra were obtained with a Bruker Agilent 6890-5973 MALDI-TOF mass spectrometer. Elemental analyses were performed using a PE2400 elemental analyzer. Melting points were determined on $x-5$ melting point detector.

2.2. Synthesis

2.2.1. Synthesis of materials

The synthetic route is outlined in Scheme 1. Carbazole was halogenated by bromobutane in alkaline condition. Compound 2 and 3 were synthesized by the Vilsmeier reaction of formylation from 9-alkyl-carbazole. 9-ethyl-3-(2-(quinolin-2-yl) vinyl)-carbazole (**4**) and 9-butyl-3,6-bis(2-(quinolin)vinyl)-carbazole (**5**) were synthesized using knoevenagel condensation. 9-ethyl-carbazole (**1**), 9-ethyl-3-formyl-carbazole (**2**) and 3,6-diformacy-9-ethyl-carbazole (**3**) were synthesized by the reported procedure [36]. The synthesized target compounds were identified by the measurements of ^{1}H NMR, IR and MS, and are in agreement with the chemical structures shown in Scheme 1.

2.2.2. Synthesis of 9-ethyl-3-(2-quinolin)viny-carbazole (*4*)

3-Formyl-9-ethyl-carbazole (1.784 g, 8 mmol) and 2-methylquinoline (1.144 g, 8 mmol) were added in 50 ml acetic anhydride. The reaction mixture was heated to 120 °C and refluxed for 36 h. After the reaction, when cooled it to room temperature, the reaction solution was poured into water, and adjusted its PH to neutral with alkaline solution. Then it was extracted with dichloromethane for three times to yield a rude sample. The product 4 was purified through column chromatography on silica gel using ethyl acetate–petroleum ether (1:4) as eluent.

9-ethyl-3-(2-quinolin)viny-carbazole (**4**), yield: 48.3%, M.P.286 °C. λ_{max} = 294 nm; ^{1}H NMR($CDCl_3$): δ(ppm) 1.3(t, 3H, CH_3), 4.5(m,2H, CH_2), 7.2(m, 2H, CH=CH), 7.4–8.4(m, 13H, carbazole); IR(KBr): 2950, 2925, 1610, 1496, 1465, 1424, 1381, 1327, 1213, 966, 820 cm^{-1}; Anal. calcd(%) for $C_{25}H_{20}N_2$: C, 86.21; H, 5.75; N, 8.04. Found: C, 85.67; H, 6.14; N, 8.19; LC–MS: m/z, 349.1(348.16) [M + 1].

2.2.3. Synthesis of 9-ethyl-3,6-bis(2-(quinolin)vinyl)-carbazole (*5*)

3,6-dicarbaldehyde-9-ethyl-carbazole (2.008 g, 8 mmol) and 2-methyl-quinoline (6.864 g, 48 mmol) were added in 100 ml acetic anhydride. The reaction mixture was heated to 120 °C and refluxed for 36 h. After the reaction, when cooled it to room temperature, the reaction solution was poured into water, and adjusted its PH to neutral with alkaline solution. Then it was extracted with dichloromethane for three times to yield a rude sample. The product 5 was purified through column chromatography on silica gel using ethyl acetate–petroleum ether (1:6) as eluent.

9-ethyl-3,6-bis(2-(quinolin)vinyl)-carbazole (**5**), yield 43.1%. M.P. 271 °C; λ_{max} = 296 nm; ^{1}H NMR($CDCl_3$): δ(ppm) 1.5 (t, 3H, CH_3), 4.4(m, 2H, CH_2), 7.2 (m, 4H, CH=CH), 7.4–8.4(m, 18H, carbazole); IR(KBr): 3037, 2955, 2929, 1589, 1501, 1483, 1426, 1381, 1312, 1232, 964, 819 cm^{-1}; Anal. calcd(%) for $C_{36}H_{27}N_3$: C, 86.23; H, 5.39; N, 8.38. Found: C, 85.46; H, 6.12; N,8 .42; LC–MS: m/z, 502.2(501.22) [M + 1].

2.3. One-photon optical properties measurements

The linear absorption spectra were measured in DMF at a concentration of $c = 1.0 \times 10^{-5}$ mol/dm^3, in which the solvent influence was not included. The linear absorption spectra of the compounds were obtained by a Perkin Elmer Lambda 900UV/Vis/NIR (SanJose, California, USA) spectrophotometer. One-photon fluorescence spectra were measured at room temperature. Fluorescence decay curves were recorded with the lifetime combined single-photon counting technique using a commercially available Edinburgh Instruments, model LS-55 spectrometer equipped with a 375 nm picosecond pulse diode laser made in Britain. The fluorescence quantum yield $\Phi_\chi = (A_s \times F_\chi \times n_\chi^2 \times \Phi_s)/(A_\chi \times F_s \times n_s^2)$ where A denotes the absorbance at the excitation wavelength, F means the area under the fluorescence curve and n is the refraction index. Subscripts s and χ refer to the standard and to the sample of unknown quantum yield, respectively. Rhodamine B in ethanol at 25 °C (Φ = 0.9) was made as the standard.

2.4. Two-photon fluorescence measurements

In order to explore the TPA properties of the target compounds, we use two-photon excited fluorescence method to measure the TPA cross section by laser [37,38]. The experimental setup is shown in Fig. 1. The two-photon fluorescence spectra of the compounds are investigated by a 120-fs 800-nm pulse Ti: sapphire