



# Photophysical properties and computational investigation on substituent effects on the structural and electronic properties of 3,6-di(thiophene-2-yl)-carbazole-based derivatives

Suwannee Sriyab<sup>a, b</sup>, Matthew Paul Gleeson<sup>a</sup>, Supa Hannongbua<sup>a, b</sup>,  
Songwut Suramitr<sup>a, b, \*</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand

<sup>b</sup> Center for Advanced Studies in Nanotechnology for Chemical, Food and Agricultural Industries, KU Institute for Advanced Studies, Kasetsart University, Bangkok 10900, Thailand

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## ABSTRACT

A series of 3,6-carbazole-based derivatives, **3,6-CzTh-(1)**, **3,6-CzTh-(2)**, **3,6-CzTh-(3)** and **3,6-CzTh-(4)**, were synthesized to investigate the influence of structural distortion on intramolecular charge transfer (ICT) complexation between the conjugation components and carbazole core unit of the 3,6-carbazole-based derivatives. The 3,6-carbazole-based derivatives were synthesized and analysed using UV-Visible, photoluminescence spectroscopy and DFT calculations. The electron-donating substituents on the carbazole core unit, which was linked by formyl and acetyl at the 3,6-positions of the carbazole core so as to directly involve the electron-donating edge substituents in backbone, exhibited conjugation breaks in the middle of the carbazole core units. The break lead to a planar structure with an extraordinary ability to stabilize on the excited state resulting in a strong fluorescence quantum yield ( $\Phi_{\text{fluor}} \approx 0.6-0.7$ ). The results of the Time-dependent density functional theory (TD-DFT) calculations were in agreement with the experimental results, and indicated that the low fluorescence of **3,6-CzTh-(1)** and **3,6-CzTh-(2)** is derived not only from intersystem crossing but also from internal conversion due to the proximity effect; this inference was also supported by the measurements of the photoluminescence spectra at low temperatures. In addition, factors leading efficiently to non-radiative processes were shown to be absent in **3,6-CzTh-(3)** and **3,6-CzTh-(4)**. This work deepens our understanding of 3,6-di(thiophen-2-yl)-carbazole-based derivatives and provides insight into the future design of novel materials for improved fluorescence efficiencies and optoelectronic devices.

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## 1. Introduction

Over the last two decades, a variety of organic carbazole-based compounds have been synthesized for use in organic light-emitting diodes (OLEDs), organic thin film transistors (OTFTs), organic and photovoltaic cells (OPVs) [1–4]. The carbazole-based compounds have been extensively used as donor materials, due to their excellent hole transporting ability, good thermal and oxidation stability [5]. These unique advantages result from the nitrogen atom on carbazole unit, which carries a lone pair of electrons, thereby

providing increased electron donating ability to the carbazole moiety. The planar structure of carbazole group and large band gap makes it and its derivatives good blue light emitters [6] and good hole-transporting materials and photoconductors [7]. The lone pair electrons can activate the 3,6-position of carbazole unit for electrophilic aromatic substitution, thus providing a straightforward and low-cost approach to produce functionalized carbazole derivatives [8]. Indeed, 3,6-carbazole-based compounds are promising candidates for various optoelectronic devices [9], light emitting diodes [10], electrochromic devices [11] due to their excellent thermal and photochemical stability, relatively high hole mobility and good solubility in common organic solvents. Modifications of 3,6-substituted carbazole by addition of functional groups with differing electronic and optical properties can be desirable [12]. Differences in the effective conjugation length and

\* Corresponding author. Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand.

E-mail address: [fsciswsm@ku.ac.th](mailto:fsciswsm@ku.ac.th) (S. Suramitr).

the electron-donating properties suggest that the linkage provides a handle for tuning intramolecular charge transfer (ICT) and, therefore, the electrochemical, optical, and electronic properties of the resulting polymers. Intramolecular charge transfer complexes may be formed using materials with alternating electron-rich carbazole derivatives (electron donor: D) and electron-deficient moieties (electron acceptor: A). Therefore, 3,6-linked carbazole derivatives was found to be very interesting for electrochemical and phosphorescence applications.

In this paper we describe a systematic study of the effective conjugation length of 3,6-carbazole-based derivatives focusing on the effect of conjugation breaks and steric hindrance. A series of 3,6-carbazole-based derivatives were prepared as shown in Fig. 1. Combinations of the various 4-thienyl groups substituted at the 3,6-positions of the carbazole were expected to produce V shape structures. The synthesis and characterization of the 3,6-carbazole-based derivatives and reported along with an investigation of the structural geometries using quantum mechanical calculations. The ground ( $S_0$ ) and first singlet excited ( $S_1$ ) state and optical properties of 9-octyl-3,6-di(thiophen-2-yl)-carbazole derivatives obtained using density functional theory (DFT) [13] and Time-dependent density functional theory (TD-DFT) [14] will help us to get a useful insight into the detailed information on the optical and electronics properties of the superior organic light-emitting compound.

## 2. Materials and methods

### 2.1. Synthesis and characterization

#### 2.1.1. Materials

All starting materials were purchased from Sigma Aldrich and used without further purification. Some reaction solvents were distilled before use (THF from sodium/benzophenone; diethyl ether from potassium/benzophenone;  $\text{CHCl}_3$  from  $\text{CaH}_2$ ; and MeOH from  $\text{CaH}_2$ ). Column chromatography was carried out on a silica gel (size 40–63  $\mu\text{m}$ , pore size 60  $\text{\AA}$ , Silicycle).  $^1\text{H}$  NMR spectra were recorded on a VARIAN UNITY INOVA spectrometer which operated at 400.00 MHz for  $^1\text{H}$  in deuterated chloroform ( $\text{CDCl}_3$ ) with tetramethylsilane (TMS) as an internal reference. UV analysis was done with a Perkin Elmer Lambda 35 UV-Vis spectrophotometer, using a quartz cell with 1 cm path length. Fluorescence analysis was obtained using a Perkin Elmer Instruments LS55 fluorescence spectrophotometer.

Fluorescence quantum yields were measured using a comparative method against a quinine sulfate standard. Quinine sulfate was dissolved in 0.1 N sulfuric acid and diluted such that its absorbance was approximately 0.5 at 400 nm. The absorbance was recorded. The solution was then accurately diluted tenfold. A fluorescence emission spectrum was taken, converted to the wavenumber scale, corrected, and integrated. The fluorescence quantum yield of all compounds ( $\varphi_{\text{dye}}$ ) were calculated according to [15].

$$\varphi_{\text{dye}} = \varphi_{\text{ref}} \frac{I_{\text{dye}} A_{\text{ref}}}{I_{\text{ref}} A_{\text{dye}}} \cdot \frac{n_{\text{dye}}^2}{n_{\text{ref}}^2} \quad (1)$$

where:  $\varphi_{\text{ref}}$  is fluorescence quantum yield of the reference (quinine sulfate;  $\varphi_{\text{ref}} = 0.55$ ) [16] sample in ethanol,  $A_{\text{dye}}$  and  $A_{\text{ref}}$  are the absorbances of the dye and reference at the excitation wavelength (400 nm).  $I_{\text{dye}}$  and  $I_{\text{ref}}$  are the integrated emission intensity for the dye and reference samples.  $n_{\text{dye}}$  and  $n_{\text{ref}}$  are the refractive indexes of the solvent use for the dye and reference, respectively.

### 2.1.2. General synthesis of 3,6-CzTh-(1)-(4)

All other compounds have been synthesized following the procedures described herein. A mixture of 3,6-dibromo-9-octyl-9H-carbazole (11.89 mmol), 2-thiopheneboronic acid derivatives (26.17 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.17 mmol), and 2.0 M  $\text{Na}_2\text{CO}_3$  aqueous solution (46 mmol) in THF (35 ml) was stirred at reflux under  $\text{N}_2$  atmosphere for 24 h. Water (150 ml) and  $\text{CH}_2\text{Cl}_2$  (150 ml) were added. The organic phase was separated, washed with water (150 ml), brine solution (100 ml), dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered, and the solvents removed to dryness. Purification by column chromatography using silica gel eluting with hexane gave light solids [17,18].

#### 2.1.3. 9-octyl-3,6-di(thiophen-2-yl)-carbazole, 3,6-CzTh-(1)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 0.88–0.98 (3H, m,  $-\text{CH}_3$ ), 1.27–1.47 (10H, m,  $-\text{CH}_2$ ), 2.07–2.11 (2H, m,  $-\text{CH}$ ), 4.16 (2H, dd,  $J = 7.8$  Hz,  $J = 1.8$  Hz,  $-\text{CH}_2-\text{N}$ ), 7.14 (2H, dd,  $J = 5.1$  Hz,  $J = 3.6$  Hz,  $-\text{CH}$ ), 7.29 (2H, dd,  $J = 5.1$  Hz,  $J = 1.2$  Hz,  $-\text{CH}$ ), 7.38–7.40 (4H, m), 7.75 (2H, dd,  $J = 8.4$  Hz,  $J = 1.8$  Hz,  $-\text{Ar}-\text{H}$ ), 8.36 (2H, d,  $J = 1.8$  Hz,  $-\text{Ar}-\text{H}$ ). UV-Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$ : 252 nm, 302 nm.

#### 2.1.4. 3,6-bis(5-methylthio-phen-2-yl)-9-octyl-9H-carbazole, 3,6-CzTh-(2)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 0.88 (3H, m,  $-\text{CH}_3$ ), 1.25–1.73 (12H, m,  $-\text{CH}_2$ ), 2.61 (6H, s,  $-\text{CH}_3$ ), 3.85 (2H, dd,  $-\text{CH}_2-\text{N}$ ), 6.60 (2H, d,  $-\text{CH}$ ), 6.70 (2H, d,  $-\text{CH}$ ), 7.34 (4H, m,  $-\text{Ar}-\text{H}$ ), 7.58 (2H, s,  $-\text{Ar}-\text{H}$ ). UV-Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$ : 298 nm.

#### 2.1.5. 1,1'-(5,5'-(9-octylcarbazole-3,6-diyl)-bis-(thiophene-5,2-diyl))-diethanone, 3,6-CzTh-(3)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 0.79 (3H, m,  $-\text{CH}_3$ ), 1.17 (8H, m,  $-\text{CH}_2$ ), 1.33 (2H, m,  $-\text{CH}_2-\text{CH}_3$ ), 1.73 (2H, m,  $-\text{CH}_2$ ), 2.49 (6H, s,  $-\text{CH}_3$ ), 4.24 (2H, t,  $-\text{CH}_2-\text{N}$ ), 7.00 (2H, d,  $-\text{CH}$ ), 7.34 (4H, m,  $-\text{Ar}-\text{H}$ ), 7.50 (2H, d,  $-\text{CH}$ ), 7.58 (2H, d,  $-\text{Ar}-\text{H}$ ). UV-Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$ : 318 nm, 356 nm, 365 nm.

#### 2.1.6. 5,5'-(9-octyl-carbazole-3,6-diyl)-dithiophene-2-carbaldehyde, 3,6-CzTh-(4)

$^1\text{H}$  NMR ( $\text{CDCl}_3$ ,  $\delta_{\text{ppm}}$ ): 0.79 (3H, m,  $-\text{CH}_3$ ), 1.29 (8H, m,  $\text{CH}_2$ ), 1.31 (2H, m,  $-\text{CH}_2-\text{CH}_3$ ), 4.16 (2H, t,  $-\text{CH}_2-\text{N}$ ), 7.34 (4H, m,  $-\text{Ar}-\text{H}$ ), 7.58 (2H, d,  $-\text{CH}$ ), 7.88 (2H, dd,  $-\text{CH}$ ), 7.91 (2H, d,  $-\text{CH}$ ), 7.99–8.00 (2H, d,  $-\text{CH}$ ), 9.84 (2H, s,  $\text{H}-\text{C}=\text{O}$ ). UV-Vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$ : 250 nm, 383 nm.

### 2.2. Computational details

The optimized structures of one of the 3,6-di(thiophen-2-yl)-carbazole-based derivatives are presented in Fig. 1. The ground and excited state structures of all molecules under investigation were fully optimized at the CAM-B3LYP level of theory [19] employing the 6-311G(d,p) basis set and were characterized as the true minima on the harmonic potential energy hypersurfaces. The long alkyl chains in N atom were replaced by the hydrogen atom to simplify the calculations. To obtain the fluorescence energies ( $E_{\text{Flu}}$ ), the first excited-state geometries were fully optimized by using the Time-dependent DFT method, employing the same exchange-correlation functional and basis set as was used in the ground-state structure optimization. The Time-dependent DFT method with the 6-311G(d,p) basis set and the Coulomb-attenuated CAM-B3LYP exchange-correlation functional was applied to get excitation energies ( $E_{\text{max}}$ ), and electronic transition of molecules. Solvent effects were simulated by employing a polarizable continuum model (PCM) [20] of dichloromethane. All calculations were carried out using the Gaussian 09 program [21].

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