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SUBSTITUENT EFFECTS ON PHOTOPHYSICAL PROPERTIES OF *N*-THIENYLCARBAZOLES

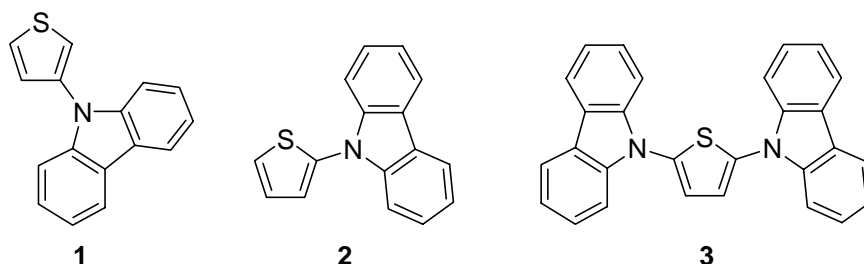
Hideyuki Shimizu, Atsushi Kobayashi, Shingo Itoi, Toshitada Yoshihara,
Seiji Tobita, Yosuke Nakamura,* and Jun Nishimura

Department of Chemistry and Chemical Biology, Graduate School of
Engineering, Gunma University, Tenjin-cho, Kiryu, Gunma 376-8515, Japan.

E-mail: nakamura@chem-bio.gunma-u.ac.jp

Abstract – The electronic and photophysical properties of a series of *N*-thienylcarbazoles were first clarified and compared to one another. The characters of both ground and excited states of carbazole moiety are much more affected by a 2-thienyl group than a 3-thienyl group.

Carbazole and thiophene are important heteroaromatic compounds from the aspects of constructing functional materials such as organic light-emitting materials, photoconductors, and so on.¹ For instance, these heterocycles have been used as building-blocks for hole-transport and light-emissive materials or host materials for triplet emitters in OLEDs.^{2,3} As one of the most fundamental compounds containing carbazole and thiophene, *N*-(2-thienyl)carbazole (**2**) has been prepared,⁴ but its photophysical properties are unknown. 2,5-Bis(*N*-carbazolyl)thiophene (**3**) is also known in the literature,⁵ but its photophysical properties are not clarified, although those of 5,5'-bis(*N*-carbazolyl)-2,2'-bithiophene are disclosed.⁶ Surprisingly, *N*-(3-thienyl)carbazole (**1**) has been unknown in the literature. Thus, we were prompted to investigate and compare the electronic and photophysical properties of **1–3** systematically. As a result, we have found that their photophysical properties remarkably depend on the substitution positions of thiophene.



N-(3-Thienyl)carbazole (**1**) was prepared by copper-catalyzed Ullmann condensation of 3-bromothiophene and carbazole, in a manner similar to **2** and **3**. It was characterized by ^1H and ^{13}C NMR and other spectroscopies. In the ^1H NMR spectrum of **1**, three sets of double doublets for the thiophene protons were observed in addition to the carbazole proton peaks, while the thiophene protons of **3** with a higher symmetry were observed as a singlet peak in contrast with **1** and **2**. The numbers of ^{13}C NMR peaks of **1** and **3** were 10 and 8, respectively, in consistent with their structures.

The absorption spectra of **1–3** in cyclohexane exhibit absorption bands characteristic of carbazole

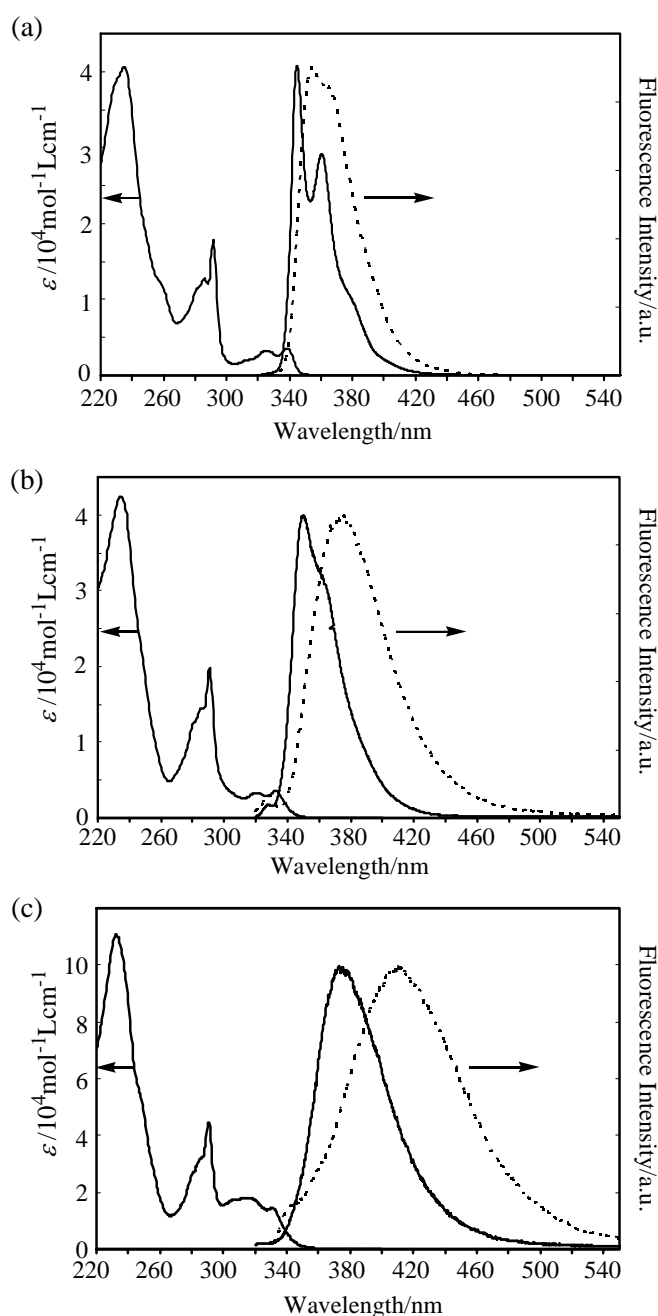


Figure 1. Absorption spectra in cyclohexane and fluorescence spectra ($\lambda_{\text{ex}} = 300$ nm) in cyclohexane (solid line) and acetonitrile (dotted line) of (a) **1**, (b) **2**, and (c) **3** at room temperature.

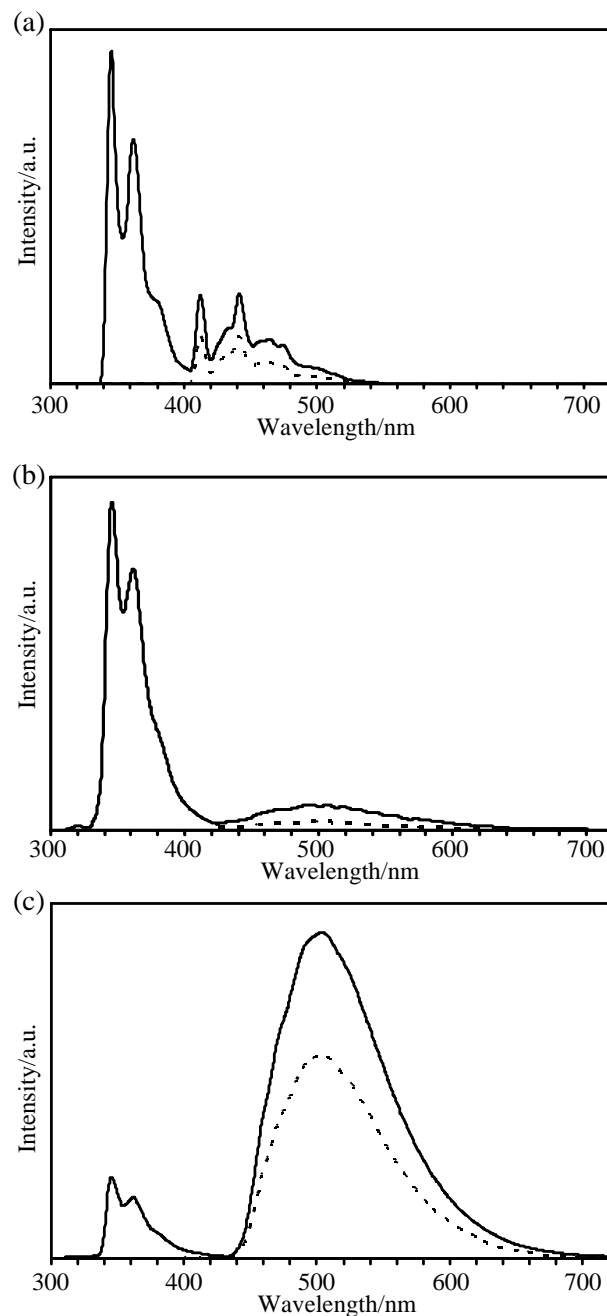


Figure 2. Total emission (solid line) and phosphorescence spectra (dotted line) of (a) **1**, (b) **2**, and (c) **3** in 3-methylpentane at 77 K ($\lambda_{\text{ex}} = 300$ nm).

derivatives, a sharp and intense band at ca. 295 nm and vibrational structures around 300–350 nm (Figure 1). Among **1–3**, the spectrum of **1** is considerably similar to that of *N*-ethylcarbazole. The spectrum of **2** is slightly broadened on the whole. This result suggests that the electronic property of ground state (S_0) of carbazole moiety is more perturbed by the 2-thienyl substitution than the 3-thienyl substitution. In **3**, the spectrum is further broadened and the spectral shape around 300–350 nm is rather different from the others. These observations may be partly due to the intramolecular interaction between the two carbazole moieties in a conjugated system. The absorption spectra of **1–3** in acetonitrile were quite similar to those in cyclohexane.

The fluorescence spectra of **1–3** in cyclohexane at room temperature are also shown in Figure 1. The spectrum of **1**, showing vibrational structures characteristic of carbazole derivatives, is quite similar to that of *N*-ethylcarbazole. The spectrum of **2** is slightly broadened. Noticeably, the spectrum of **3** is remarkably red-shifted and broadened without vibrational structures. The fluorescence spectra in polar acetonitrile are red-shifted and broadened relative to those in cyclohexane. This behavior suggests the CT character in the excited singlet state, as observed in some other *N*-arylcarbazoles.⁷ All the fluorescence excitation spectra were in good agreement with the corresponding absorption spectra, obviously indicating that these emissions originate from compounds **1–3**.

The fluorescence quantum yields and lifetimes of **1–3** are listed in Table 1. As seen from Table 1, both fluorescence quantum yields and lifetimes decrease in the order of *N*-ethylcarbazole, **1**, **2**, and **3**. These observations indicate that the property of excited singlet state (S_1) of carbazole moiety is also much more affected by the 2-thienyl substitution than the 3-thienyl substitution. Especially, the disubstitution at both 2- and 5-positions of thiophene drastically modifies the character of S_1 of carbazole. The decrease of fluorescence quantum yields in **1–3** relative to *N*-ethylcarbazole may be partially due to the effect of sulfur atom of thiophene, since the fluorescence quantum yield of *N*-phenylcarbazole (0.33 in hexane, 0.40 in acetonitrile)^{7c} is rather similar to that of *N*-ethylcarbazole.

Table 1. Fluorescence Quantum Yields (Φ_f) and Lifetimes (τ_f) of **1–3** in Cyclohexane at Room Temperature

Compound	Φ_f	τ_f / ps	k_f / 10^7 s ⁻¹ ^a
<i>N</i> -ethylcarbazole	0.43 ^b	14400 ^b	3.0
1	0.13	3210	4.03
2	0.014	381	3.67
3	0.0063	60.6	10.3

^a $k_f = \Phi_f / \tau_f$. ^b In MTHF. Ref. 8.

The phosphorescence spectra of **1–3** in 3-methylpentane at 77 K are entirely different from one another, as shown in Figure 2. Compound **1** provided a phosphorescence with vibrational structures similar to *N*-ethylcarbazole⁹ and a long lifetime ($\tau_p = 4.8$ s). The excited triplet state (T_1) of carbazole moiety is also relatively unaffected by the 3-thienyl group. In **2**, quite weak and broad phosphorescence was observed with a maximum around 500 nm.¹⁰ The phosphorescence lifetime of **2** ($\tau_p = 170$ μ s) was much shorter than those of **1** and **3**. A 2-thienyl group also remarkably modifies the character of T_1 state of carbazole. In **3**, similar broad phosphorescence was observed, and the lifetime ($\tau_p = 8$ ms) was much shorter than that of **1** but longer than that of **2**.

In summary, the electronic and photophysical properties of **1–3** were first clarified and compared to one another. 2-Thienyl groups more affect the characters of both excited singlet and triplet states of carbazole moiety than 3-thienyl groups. These results provide a guidance for the construction of new OLED materials and so on.

EXPERIMENTAL

***N*-(3-Thienyl)carbazole (1):** A mixture of 3-bromothiophene (0.50 g, 3.07 mmol), carbazole (0.34 g, 2.04 mmol), K_2CO_3 (0.71 g, 5.11 mmol), and Cu (0.20 g, 3.07 mmol) in nitrobenzene (7 mL) was stirred at 180 °C for 42 h. After cooling to rt, $CHCl_3$ (50 mL) was added, and the suspension was filtered through Celite. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography (silica gel, toluene/ hexane) to afford **3** (0.33 g, 1.32 mmol, 64%). Mp 79.9–80.2 °C; 1H NMR ($CDCl_3$, 500 MHz) δ 8.14 (2H, d, $J = 7.8$ Hz), 7.57 (1H, dd, $J = 3.4$ Hz, 1.8 Hz), 7.48 (1H, dd, $J = 1.8$ Hz, 1.4 Hz), 7.46–7.43 (4H, m), 7.34 (1H, dd, $J = 3.4$ Hz, 1.4 Hz), 7.31–7.28 (2H, m); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 140.9, 135.8, 126.2, 126.0, 125.4, 123.2, 120.2, 120.0, 119.4, 109.9; Anal. Calcd for $C_{16}H_{11}NS$: C, 77.07; H, 4.45; N, 5.62. Found: C, 77.07 ; H, 4.39 ; N, 5.56.

2,5-Bis(*N*-carbazolyl)thiophene (3): Compound **3** was prepared in a manner similar to **1**. Mp 227.2–227.4 °C; 1H NMR ($CDCl_3$, 500 MHz) δ 8.17 (4H, d, $J = 7.9$ Hz), 7.67 (4H, d, $J = 8.2$ Hz), 7.54 (4H, m), 7.38 (4H, m), 7.34 (2H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 141.70, 126.42, 124.55, 123.59, 123.18, 121.26, 119.98, 110.41; Anal. Calcd for $C_{28}H_{18}N_2S$: C, 81.13; H, 4.38; N, 6.76. Found: C, 80.76 ; H, 4.57 ; N, 6.73.

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- 10 With a rotating chopper, the emission of **2** at 77 K was not observed, but it is reasonable to assign the broad emission around 500 nm to the phosphorescence instead of the fluorescence, because its lifetime was 170 μ s, which is too long for fluorescence, and **3** also provided similar phosphorescence.