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Suzuki Coupling Approach for the Synthesis of Phenylene–Pyrimidine Alternating Oligomers for Blue Light-Emitting Material

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ABSTRACT

Conjugated oligomers with an alternating phenylene–pyrimidine structure have been synthesized by the successive Suzuki coupling reaction starting from 2-bromo-5-iodopyrimidine. The photoluminescence properties and quasi-reversible redox behavior of these oligomers make them applicable as an active material for a light-emitting device. Blue light-emitting electroluminescent devices with an external quantum efficiency up to 1.8% have been fabricated.

Since the pioneering work1 of Tang and VanSlyke in the thin film OLED device, conjugated organic materials with high morphological stability have received considerable attention due to their promising potential for the industrial manufacture of light-emitting displays.2 However, most of the organic solids used for OLED exhibit several orders higher of hole mobility than electron mobility. Therefore, the poor quantum efficiency of the OLED device can be primarily ascribed to the imbalance of electron–hole recombination in the active layer. To create an efficient device, new materials with high electron transporting capability are demanded. Over the past decade, many activities have been carried out on this issue, resulting in great contributions to the molecular design for fulfilling the requirements of high electron affinity, high electron mobility, and morphology stability. The electronic properties of organic solids now can be finely tailored by modifying the main chain structure with highly electronegative groups3 or introducing the heteroaryl moiety as a functional subunit. For example, 1,3,4-oxadiazole-containing molecules4 have been extensively investigated as an electron transporting material in OLED. Moreover, benzimidazole,5 phenanthroline,6 pyridine,7 pyrazine,8 quinoline,9 quinoxaline,10 pyrazolopyridine,11 silole,12 thiophene-
The selective coupling reaction of 1 on the iodo-substituted carbon with aryl boronic acids was carried out under standard aqueous Suzuki coupling conditions to afford 2a–c in excellent yields. However, a second Suzuki coupling on the bromo-substituted carbon of 2 with diboronic acid was promoted by adding a bulky trialkyphosphine, P(tBu)₃, as a cocatalyst. The corresponding oligomers 3a–c were isolated in good yields and characterized with satisfactory spectral analyses.

To investigate the electronic properties of the phenylene–pyrimidine alternating oligomers, 3a–c, we first examined the absorption spectra for each oligomer in dilute solution (CHCl₃). The vacuum-deposited thin films of 3a–c were also inspected for comparison. Two absorption bands were observed, which were red-shifted when compared to those of the analogous pentaphenylene. The resultant bathochromic shift is presumably due to the intramolecular charge transfer in our oligomers with a donor–acceptor alternating arrangement. In the solid film, the relative intensity of the long wavelength absorption is increased and distinctly red-shifted while the short wavelength absorption stays almost unchanged. The red-shifted absorption could result from the molecules with a more coplanar conformation in the solid film. The terminal substituents of oligomers 3a–c have no substantial influences on the absorption wavelength; the oligomers terminated with electron-donating butoxy groups (3b) only exhibit a slightly bathochromic shift (ca. 17 nm) in short wavelength absorption when compared to that of 3a. The ʎ_max for oligomers 3a–c are summarized in Table 1.

Oligomers 3a–c exhibit strong blue fluorescence in dilute solution with emission maximum centered at 419 nm irrespective of the nature of the terminal substituents. The quantum yields are 0.37, 0.54, and 0.37 for 3a, 3b, and 3c, respectively. It is worth noting that, in the solid film, 3a and 3b exhibit PL spectra without a distinct red shift when compared to those in solution. The identity of the emission behavior suggests that the excited state of 3a and 3b could have a similar conjugation length in dilute solution and in the solid film. A comparison of the photoluminescence spectrum of 3c in solution and in the solid film is shown in Figure 1. For 3c, the most intensive emission peaks in the solid film are almost overlapped with the emission peak in solution. In addition, three weak emission peaks at 461, 495, and 545 nm were also detected. The long wavelength emission peaks could be possibly attributed to the intermo-
molecular interactions occurring in the solid state or the formation of excimer.

Figure 2a provides views of the crystal packing diagram of 3a. The terminal phenyl ring and pyrimidine ring are in a coplanar plane (with angles between the least-squares planes of <3.3°) due to the lack of ortho-ortho interactions, while the central phenyl ring is rotated by 42.5° with respect to the pyrimidine ring. The 3a crystals stack each other in such a way that the coplanar phenyl-pyrimidine segments are closely lined up, but in opposite direction, with the same segment of the neighboring molecule. Although these coplanar segments could overlap to a large extent, the closest interatomic (least-squares interplane) distance between the terminal phenyl ring in one molecule and the pyrimidine ring in another molecule is calculated to be 3.49 Å (3.55 Å), which is expected to have intermolecular interactions. In contrast to 3a, 3c crystallized in a different manner. The crystal packing diagram for 3c is shown in Figure 2b. The five aryl rings of 3c are not coplanar to one another. The tBu-substituted phenyl ring is twisted by -19.2° to the adjacent pyrimidine ring, while the central phenyl ring is rotated by 25.2° with respect to the pyrimidine ring. 3c stacks in such a way that the pyrimidine rings from different molecules are closely packed to one another as the dipolar orientation is in opposite direction. The crystal packing is driven by this dipole-dipole interaction between the pyrimidine rings. However, the packing between the terminal phenyl ring and the central phenyl ring may also contribute to the crystallization. Due to the large terminal groups in 3c, the weak intermolecular interactions are characterized by inspecting the shortest intermolecular contact distance, 3.66 Å, between the nitrogen in one molecule and the C4 carbon in the pyrimidine of neighboring molecule.

The electrochemical properties of oligomers 3a–c were investigated by cyclic voltammetry in THF. The data are summarized in Table 1. Two quasi-reversible cathodic reduction couples were observed with the potential difference (ΔE = E1pc − E2pc) 180 mV, 170 mV, and 200 mV for 3a, 3b, and 3c, respectively. These two reductions were believed to occur at the pyrimidine rings successively. The large potential difference between the two reductions indicates that the first radical anion, as it was formed, could efficiently delocalize along the π-conjugation in the molecule, resulting in the difficult formation of the dianion species. Figure 3 shows a comparison of the cyclic voltamogram of oligomers 3a–c. The electron-donating butoxy group in 3b slightly increased the first reduction potential by 0.08 V when compared to that of 3a. 3c, with the less electron-donating tBu groups, exhibits a reduction potential between that of 3a and 3b. These results indicate that the pyrimidine moiety

| Table 1. Physical Properties of Phenylene–Pyrimidine Alternating Oligomers 3a–c |
|-----------------|--------|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| compound  | λmaxa | λmaxb | θmaxa | θmaxb | E1pc E1pa | E2pc E2pa | ΔE (mV) | Td (°C) |
| 3a  | 290, 352 | 292, 362 | 419 | 423 | −2.00, −1.73 | −2.18, −1.91 | 180 | 444 |
| 3b  | 307, 352 | 307, 392 | 419, 430 | 417, 434 | −2.04, −1.77 | −2.21, −1.95 | 170 | 457 |
| 3c  | 296, 352 | 299, 370 | 419 | 410, 428 | −2.08, −1.83 | −2.28, −2.04 | 200 | 441 |

* In nm, 5.0 × 10−5 M in CHCl3. * In nm, vacuum deposited thin film. * V vs Ag/AgCl in THF with n-Bu4NClO4 as a supporting electrolyte. * ΔE = E1pc − E2pc. * Detected by the DSC analysis of liquid N2 quenched melt sample, heating rate = 10 °C/min. * Detected by TGA analysis.

Figure 1. A comparison of the absorption and emission spectra of 3c in solution (5.5 × 10−5 M in CHCl3) and thin film.

Figure 2. The molecular packing diagram of 3a (a) and 3c (b). The long octyl chains are omitted for clarity.
could serve as an electron-accepting center once it was incorporated into a $\pi$-conjugated system. In addition, the reduction potential could be finely tuned by introducing substituents with different electronic nature at the terminal position.

The thermal property and the morphological stability of 3a–c were investigated by the TGA and DSC analysis, respectively. 3a–c exhibited high thermal stability; the TG thermograms revealed that no weight loss was detected below 380 °C for 3a–c. The temperature corresponding to the completed weight loss of 3a–c is summarized in Table 1. The DSC analysis of the liquid nitrogen quenched melt-samples of 3a–c showed that only 3a and 3c exhibited a relatively low glass transition temperature ($T_g$) at 27.7 and 31.5 °C, respectively. DSC analysis also indicated that there were several phase transitions of 3a–c before the crystalline sample completely melted. Oligomers 3a and 3b melt at 150.5 and 160.2 °C, respectively, while 3c with bulky terminal groups showed a higher melting temperature at 194.7 °C. The low $T_g$ and low melting temperature are presumably due to the introduction of two octyloxyl side chains at the central phenylene ring as a solubilizing group.

We have studied the electroluminescent (EL) properties of these pyrimidine-containing oligomers. The typical device structure was ITO/PEDT-PSS (300 Å)/NCB (450 Å)/3b or 3c (500 Å)/Mg:Ag (10:1)/Ag. It was found that 3b and 3c function well as the electron-transport layer in the device. It is consistent with the electrochemical results since it is found that these pyrimidine derivatives in general have a strong electron-accepting reduction tendency. Their electron affinities estimated from electrochemical results are about 3.0 eV, comparable or even slightly larger than that of Alq3, a widely used electron-transport material. Among the compounds studied (3b and 3c), the 3c device exhibits substantially lower operation voltage than the 3b device (10 vs 15 V at 100 cd/m²); this may be due to the higher morphological stability and lower reduction potential of 3c. Oligomers 3b and 3c also function as efficient blue emitters in the devices, exhibiting blue EL similar to their PL with external EL quantum efficiencies of 1.3–1.8% (photon/electron) and brightness over 2000 cd/m². These results are rather encouraging since these devices are nondoped; optimization of device structures and material properties may further enhance the blue-emitting device performance.

In conclusion, a series of phenylene–pyrimidine alternating oligomers with interesting photophysical and electronic properties have been successfully synthesized using the Suzuki coupling reaction. Further modification of the central linkage by introducing a rigid skeleton for creating pyrimidine-containing glassy materials is currently under investigation and will be reported in due course.

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Supporting Information Available: $^1$H and $^{13}$C NMR spectra of 3a, 3b, and 3c and detailed experimental procedures, full characterization, X-ray crystallographic data (CIF) for 3a and 3c. UV–vis and PL spectra for 3a and 3b. OLED device characteristics of 3b and 3c. This material is available free of charge via Internet at http://pubs.acs.org.

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