Synthesis and Photoluminescent Properties of Violet Emitting 5,6-Diphenylfuro[2,3-*d*]pyrimidine Derivatives

Eun Jee Hwang, Chan Seong Cheong, Hyoyoung Lee,[†] Sang Woo Lee,[‡] In Tae Kim,[‡,*] and So Ha Lee[*]

Life Sciences Division, Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul 130-650, Korea
[*]E-mail: LSH6211@kist.re.kr
[†]Future Technology Research Division, New Functional Device Team, Electronics and Telecommunications Research Institute, Daejeon 305-350, Korea
[‡]Department of Chemistry, Kwangwoon University, Seoul 139-701, Korea
Received March 25, 2005

Key Words : Photoluminescent, 5,6-Diphenylfuro[2,3-*d*]pyrimidine, Organic light-emitting diode, Fluorescent dye

Furopyrimidines have known to possess antitumor,[1] analgesic,[2] antihypertensive,[3] anti-inflammatory activity,[4] and to inhibit adenosine kinase in very low concentration.[5] Recently, we found that various furopyrimidine derivatives had optical properties to apply for organic light-emitting diodes (OLED) or fluorescent dye.

Organic electroluminescent diode has undergone dramatic improvement since pioneering work of Tang and VanSlyke.[6] Much progress has made especially in recent year, including the development of device fabrication, good material, and construction of manufacture infrastructure.

It is necessary to have a set of red,[7] green,[8] and blue[9] emitting materials with excellent luminous efficiency, proper chromaticity and the photochemical stability of emitters for an emitting layer for OLED. Though many organic, polymeric and inorganic emitting materials have been reported, many breakthroughs have to be achieved on the field of materials for excellent efficiency of OLEDs. Therefore, we report the synthesis of furopyrimidine derivatives and their photoluminescent properties.

Furopyrimidines (**1**-**9**) were obtained in high yield in five steps, starting from the reaction of furoin with malonitrile in the presence of diethyl amine, as shown in Scheme 1.[5,10]

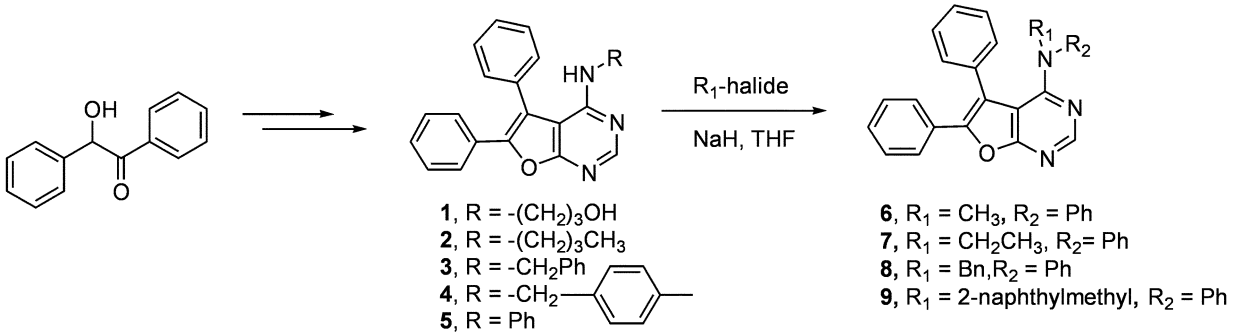
The absorption spectra and photoluminescent spectra of the compounds (**1**-**9**) were monitered using dichloromethane on the concentration of 50 μM by UV/Vis spectroscopy and luminescent spectroscopy, and their results were showed in Table 1 and typical example of spectrum was shown in Figure 1 for **1**, **5** and **7**. The full widths at half maximum value of all compounds were between 59 and 91 nm, showing generally good color purity. Thermogravimetric analysis (TGA, 50-500 °C, 20 °C/min, N_2) of **5** showed an onset of weight loss at 243 °C, 10% weight loss at 270 °C, and over 90% weight loss 382 °C. The onset temperature of weight loss of compounds **1**-**4** and **6**-**9** were between 210 and 250 °C.

Table 1. The λ_{max} value for compounds (**1**-**9**)

Compound	UV λ_{max} (nm)[a]	PL λ_{max} (nm)[a]	FWHM[b] (nm)
1	321	385	59
2	323	386	60
3	321	387	59
4	324	402	87
5	334	400	62
6	339	478	90
7	342	479	91
8	340	460	86
9	342	462	81

[a]in CH_2Cl_2 solution on 50 μM concentration. [b]The full widths at half maximum value.

All furopyrimidine derivatives (**1**-**9**) displayed intenser photoluminescence (PL) in concentration of 50 μM CH_2Cl_2



Scheme 1. Synthesis of furopyrimidine derivatives (**1**-**9**).

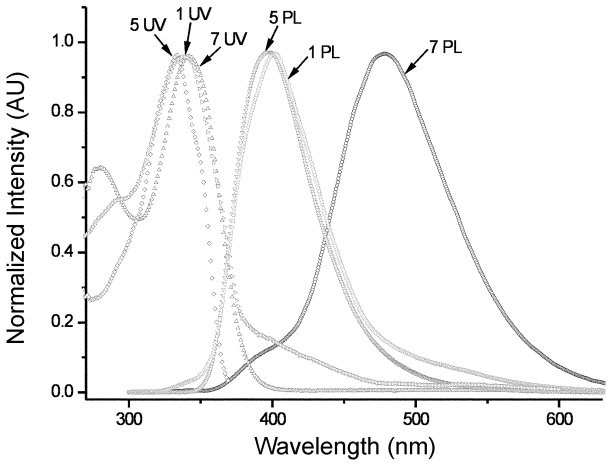


Figure 1. UV and PL spectra of **1**, **5**, and **7**.

solution than that of 4,4'-bis(2,2-diphenyl-1-ethen-1-yl)-biphenyl made from Idemitsu Kosan, Ltd. Co., in comparison with intensity of luminescence emitted when irradiated with UV light. Compound **1** showed a maximum photoluminescence of 385 nm near violet region. A comparison of the influences of the different groups on N-position of compounds showed analogous effects on the photoluminescent spectra, though the size of group was unlike in going from **1** to **3**. The absorption and emission maximum of **4** showed a bathochromic shift due to *p*-methylphenyl group on N position, showing the emission difference of 15 nm, when compared with compound **3**. The luminescent spectra of **4** and **5** are nearly identical. In compounds **6** and **7**, the strong auxochrome effects on the additional methyl and ethyl groups at N-position were shown and these groups of compounds **6** and **7** shifted the maximum emission to considerable low energies about 78 and 79 nm, by comparison with emission of compound **5**, respectively. The results showed that there were 18 and 16 nm more hypsochromic shifts for emission spectra of compound **8** and **9** than that of compound **6**.

In summary, we have accomplished the synthesis of luminescent furopyrimidine derivatives with high thermal stability and studied their photoluminescent properties, and future work will focus on the fine tuning of emitting properties through measurement of their electrophysical characteristics.

Experimental Section

All reactions were carried out under an atmosphere of nitrogen and solvents were distilled from the corresponding reagents before use. Column chromatography was performed on Merck Silica Gel 60 (230-400 mesh). TLC was carried out using glass sheets precoated with silica gel 60 F_{254} prepared by E. Merck. All the commercially available reagent chemicals were obtained from Aldrich, Fluka and Tokyo Kasei Chemical Company and generally used without further purification. ^{1}H (300 MHz) and ^{13}C NMR spectra (75 MHz) were recorded on a Varian Gemini 300 MHz spectrometer with TMS as internal reference. IR spectra were recorded on a MIDAC 101025 FT-IR spectrometer and melting points were determined by Thomas Hoover Capillary melting point apparatus and are uncorrected. UV spectra were determined by Pharmacia Biotech Ultraspec 2000 UV/Vis spectrometer and photoluminescent spectra were recorded on Jobin Yvon Horiba Fluoromax-3.

Synthesis of *N*,5,6-triphenylfuro[2,3-*d*]pyrimidin-4-amine (5). 4-Chloro-5,6-diphenylfuro[2,3-d]pyrimidine (10 g, 32.6 mmol) was dissolved in 1-propanol (50 mL), followed by aniline (8.9 mL, 97.8 mmol) and the mixture was refluxed for 24 hours. After the completion of reaction, the mixture was evaporated in vacuo and poured in 2% HCl solution, and then the solid was formed. The solid was poured in the saturated $NaHCO_3$ solution, filtered and was recrystallized in the mixed solvent of diethylether and methylene chloride to give the pure product.

Yield 70%; m.p 198-198.5 °C (diethylether + methylene chloride); ^{1}H NMR (300 MHz, $CDCl_3$); δ 8.56 (s, 1H), 7.63-7.58 (m, 7H), 7.41 (d, J = 10.4 Hz, 2H), 7.32-7.17 (m, 5H), 7.05 (t, J = 7.3 Hz, 1H), 6.56 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$); 165.2, 155.0, 153.8, 147.5, 138.5, 132.2, 130.1, 130.0, 129.4, 129.3, 129.0, 128.8, 128.6, 126.5, 123.5, 119.9, 114.4, 104.3; IR (KBr); 3406, 1616, 1570, 1498, 1452, 1296, 1212, 1072, 758, 692 cm^{-1}.

Typical procedure for the synthesis of compounds **6-9**.

Synthesis of *N*-methyl-*N*,5,6-triphenylfuro[2,3-*d*]pyrimidin-4-amine (6). *N*,5,6-triphenylfuro[2,3-d]pyrimidin-4-amine (50 mg, 0.14 mmol) in THF (5 mL) was cooled to 0 °C and then added NaH (14 mg, 0.35 mmol) and iodomethane (0.09 mL, 1.4 mmol). The solution was refluxed under N_2 for 3 h. After cooling, the mixture was quenched with water and the solution extracted with methylene chloride. The organic extract was dried with $MgSO_4$ and then evaporated to dryness. The product was recrystallized from *n*-hexane (31 mg).

Yield 59%; mp 155-158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.7 (s, 1H), 7.3-6.5 (m, 15H), 3.4 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.81, 159.36, 152.98, 147.95, 147.74, 132.17, 129.52, 129.47, 129.00, 128.51, 128.31, 128.24, 127.01, 126.90, 123.96, 123.40, 116.29, 107.73, 126.90, 123.96, 123.40, 116.29, 107.73, 41.06; IR (KBr) 3046, 2917, 1591, 1501, 1396, 704 cm^{-1}.

Synthesis of *N*-ethyl-*N*,5,6-triphenylfuro[2,3-*d*]pyrimidin-4-amine (7). Yield 51%; mp 162-164 °C (*n*-hexane + ethyl acetate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.6 (s, 1H), 7.3-6.4 (m, 15H), 4.0 (q, J = 6.98 Hz, 2H), 1.2 (t, J = 6.98 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.99, 158.53, 152.92, 146.11, 132.18, 129.51, 128.88, 128.44, 128.21, 126.88, 123.85, 116.40, 47.72, 13.12; IR (KBr) 2917, 1591, 1556, 1471, 1391, 1117, 773 cm^{-1}.

Synthesis of *N*-benzyl-*N*,5,6-triphenylfuro[2,3-*d*]pyrimidin-4-amine (8). Yield 24%; mp 169-171 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.7 (s, 1H), 7.4-6.5 (m, 20H), 5.2 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.08, 158.49, 152.89, 148.16, 147.39, 138.81, 132.07, 129.62, 129.45, 128.95, 128.57, 128.26, 128.00, 127.05, 127.00, 126.89, 123.81,

123.12, 116.28, 108.32, 99.14, 56.16; IR (KBr) 3056, 1591, 1551, 1456, 1391, 1147, 704 cm^{-1}.

Synthesis of *N*-((naphthalene-2-yl)methyl)-*N*,5,6-triphenylfuro[2,3-*d*]pyrimidin-4-amine (9). Yield 59%; mp 170-172 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.7 (s, 1H), 7.9-6.5 (m, 23H), 5.4 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.51, 152.91, 148.22, 147.49, 136.45, 129.63, 129.01, 128.58, 128.30, 128.27, 127.98, 127.71, 127.68, 127.03, 126.89, 126.60, 126.21, 126.07, 125.67, 123.89, 123.11, 116.27, 108.38, 56.26; IR (KBr) 3026, 1566, 1526, 1491, 1448, 1371, 1247, 1142, 1057, 769 cm^{-1}.

Acknowledgements. Financial support from Ministry of Science and Technology is gratefully acknowledged and this work was partly supported by a research grant of Kwangwoon University (2004) and by the Information Technology Research Center (ITRC) Support Program.

References

1. Hand, E. S.; Baker, D. C. *Can. J. Chem*. **1984**, *62*, 2570.
2. Noda, K.; Nakagawa, A.; Nakajima, Y.; Ide, H. *JP Patent 85194*, 1997.
3. Cannitro, A.; Pemmsin, M.; Lnu-Due, C.; Hoguet, F.; Gaultier, C.; Narcisse, J. *Eur. J. Chem*. **1990**, *25*, 635.
4. Nega, S.; Aionso, J.; Diazj, A.; Junqquere, F. *J. Heterocyclic Chem*. **1990**, *27*, 269.
5. Bischoff, E.; Hauswald, M.; Nell, P.; Rohrig, S.; Schlemmer, K.-H.; Steinhagen, H.; Stoltefub, J.; Weigand, S. *DE 10141212 A1*, 2003.
6. Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett*. **1987**, *51*, 913.
7. Ma, C.-Q.; Liang, Z.; Wang, X.-S.; Zhang, B.-W.; Cao, Y.; Wang, L.-D.; Qiu, Y. *Synth. Met*. **2003**, *138*, 537.
8. Mishra, A.; Nayak, P. K.; Periasamy, N. *Tetrahedron Lett*. **2004**, *45*, 6265.
9. Kim, D. Y.; Cho, H. N.; Kim, C. Y. *Prog. Poly. Sci*. **2000**, *25*, 1089.
10. (a) Prousek, J.; Jurasek, A.; Kovac, J. *Collection Czechoslov. Chem. Commun*. **1980**, *45*, 1581. (b) Shishoo, C. J.; Devani, M. B.; Bhati, V. S. *J. Heterocyclic Chem*. **1990**, *27*, 119. (c) Eisaku, H.; Takeo, H.; Chihoko, I.; Etsuo, O.; Hirokazu, M.; Toshio, I.; Fusako, Y.; Yoko, Y.; Yoshihisa, I. *Yakugaku Zasshi* **1977**, *97*, 1022. (d) Pyo, J. I.; Hwang, E. J.; Cheong, C. S.; Lee, S.-H.; Noh, T.; Kim, I. T.; Lee, S. H. *Synth. Met*. **2005**, Submitted. (e) Pyo, J. I.; Lee, S. H.; Cheong, C. S. *J. Heterocyclic Chem*. **2005**, submitted.