Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

New carbazole derivatives including coumarin moiety for blue emitting materials

Hayoon Lee, Hyocheol Jung, Minjin Jo, Dong-Hee Shin, Kwang-Yol Kay & Jongwook Park

To cite this article: Hayoon Lee, Hyocheol Jung, Minjin Jo, Dong-Hee Shin, Kwang-Yol Kay & Jongwook Park (2017) New carbazole derivatives including coumarin moiety for blue emitting materials, Molecular Crystals and Liquid Crystals, 654:1, 34-39, DOI: 10.1080/15421406.2017.1355197

To link to this article: https://doi.org/10.1080/15421406.2017.1355197

Published online: 22 Nov 2017.

Submit your article to this journal

Article views: 1

View related articles

View Crossmark data

Full Terms & Conditions of access and use can be found at
http://www.tandfonline.com/action/journalInformation?journalCode=gmcl20

Download by: [Gothenburg University Library] **Date:** 24 November 2017, At: 19:55

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2017, VOL. 654, 34–39
https://doi.org/10.1080/15421406.2017.1355197

Taylor & Francis
Taylor & Francis Group

Check for updates

New carbazole derivatives including coumarin moiety for blue emitting materials

Hayoon Lee[a], Hyocheol Jung[a], Minjin Jo[b], Dong-hee Shin[c], Kwang-Yol Kay[c,d], and Jongwook Park[a]

[a]Department of Chemical Engineering, Kyung Hee University, Gyeonggi-do, Korea; [b]Department of Chemistry, The Catholic University of Korea, Bucheon, Korea; [c]R&D Center, G-OLED Co., Ltd., Yeongtong-gu, Suwon, Korea; [d]Department of Molecular Science and Technology, Ajou University, Suwon, Korea

ABSTRACT
New carbazole derivatives including coumarin moiety, 7-(3-Carbazol-9-yl-phenyl)-chromen-2-one (C-PCa), 7-(9-Phenyl-9H-carbazol-3-yl)-chromen-2-one (PCa-C), 7-[9-(3-Carbazol-9-yl-phenyl)-9H-carbazol-3-yl]-chromen-2-one (PDCa-C) were synthesized by Suzuki reaction. A non-doped OLED was fabricated using the synthesized material as emitting materials. Among the three synthesized compounds, PDCa-C showed the highest efficiency with current efficiency of 1.34 cd/A and C.I.E of (0.18, 0.23) in the current density 10 mA/cm^2.

KEYWORDS
Blue emitting materials; carbazole; coumarin; fluorescence; OLEDs

Introduction

Organic lighting emitting diodes (OLEDs) have received much attention because of its advantages such as lower current drive voltage, less power consumption, and full-color display [1, 2]. In order to fabricate full-color OLED display, red, green, and blue emitters with high-efficiency, good thermal property and pure color coordinate are necessary [3–5]. Especially, blue emitter requires a wide band gap compared to red, green emitters, so, it is very difficult to be well-matched with highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of blue emitter and the other layer such as hole transporting layer (HTL) and electron transporting layer (ETL). Thus, development of blue emitting materials with a pure color and high efficiency is still required.

The emitting materials can be divided into fluorescent materials and phosphorescent materials. In the case of a blue-emitting material, many fluorescent materials have been synthesized to improve the efficiency and the long lifetime [6]. The phosphorescent blue-emitting material should use a lower triplet energy level (T1) than the singlet energy level (S1) of the fluorescent material, and it is difficult to develop a phosphorescent blue emitting material because of the limits in achieving a molecular structure with a high T1 level.

Most fluorescent material studies have tested using anthracene, pyrene, carbazole, which are blue emitters with high luminous efficiency [7–9]. Also, coumarin has been used in various areas such as fluorescence probe, charge-transfer agents due to its characteristics such as high photo-stability and good solubility [10].

CONTACT Prof. Jongwook Park jongpark@khu.ac.kr Department of Chemical Engineering, Kyung Hee University, 1732, Deogyeong-daero, Giheung-gu, Yongin-si, Gyeonggi-do, 17104, Korea(ROK); Kwang-Yol Kay kykay@ajou.ac.kr Department of Molecular Science and Technology, Ajou University, Suwon 16499, Korea.

© 2017 Taylor & Francis Group, LLC

Downloaded by [Gothenburg University Library] at 19:55 24 November 2017

Downloaded by [Gothenburg University Library] at 19:55 24 November 2017

In this study, coumarin was substituted in carbazole, which shows high luminous efficiency, and 7-(3-Carbazol-9-yl-phenyl)-chromen-2-one (C-PCa), 7-(9-Phenyl-9H-carbazol-3-yl)-chromen-2-one (PCa-C), and 7-[9-(3-Carbazol-9-yl-phenyl)-9H-carbazol-3-yl]-chromen-2-one (PDCa-C) were synthesized. The three synthesized compounds were applied to OLED devices as emitting layers and EL performance of devices were measured.

Experimental

Measurements

The ^{1}H NMR spectra were recorded on Bruker Avance 400. The optical absorption spectra were obtained by HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo-luminescence (PL) spectroscopy. The current–voltage-luminance (I-V-L) characteristics of the fabricated EL devices were obtained by Keithley 2400 electrometer, and light intensity was obtained by Minolta CS-1000A.

Synthesis

Synthesis of 2-oxo-2H-chromen-7-yl trifluoromethanesulfonate (1)

Trifluoromethanesulfonic anhydride (20 ml, 119 mmol) was added to a solution of umbelliferon (21.35 g, 132 mmol) in pyridine (500 ml) at 0 °C. The mixture was stirred at 0 °C for 5 minutes and then at room temperature for 24 hours. The reaction mixture was poured into water (400 ml) and extracted with toluene (400 ml). The organic extracts were washed with 10% HCl solution (100 ml) and then with saturated NaCl solution (100 ml). The organic layer was dried over Na_2SO_4, filtered and evaporated to dryness to give 33.8 g (96%) in a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.71 (d, 1H), 7.60 – 7.58 (d, 1H), 7.27 – 7.20 (m, 2H), 6.48 (d, 1H). Anal. Calcd. for $C_{10}H_5F_3O_5S$ (294.2 g/mol): C, 40.82%; H, 1.71%. Found: C, 40.74%; H, 1.82%.

Synthesis of 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-chromen-2-one (2)

A mixture of 2-oxo-2H-chromen-7-yl-trifluoromethanesulfonate (I) (2.13 g, 7.24 mmol), bis(pinacolato)diboron (2.22 g, 8.74 mmol), [1,1'-bis(diphenylphosphino)ferrocene] dichloropalladium(II) (0.18 g, 0.22 mmol), 1,1'-bis(diphenylphosphino)ferrocene (0.13 g, 0.23 mmol) and potassium acetate (2,2 g 22.4 mmol) in 1,4-dioxane (80 ml) was stirred at 80 °C for 18 hours. The reaction mixture was cooled to room temperature, reduced to a small volume and extracted with dichloromethane (500 ml). The organic extracts were dried over $Na_2SO_{4,}$ filtered and evaporated to dryness. The crude product was then chromatographed on silica gel with ethanol/hexane (1:9) to produce 1.0 g (61%) in a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 – 7.67 (m, 3H), 7.47 (d, 1H), 6.45 (d, 1H), 1.36 (s, 12H). Anal. Calcd. for $C_{15}H_{17}BO_4$ (272.1 g/mol): C, 66.21%; H, 6.30%. Found: C, 65.98%; H, 6.46%.

Synthesis of 7-(3-(9H-carbazol-9-yl)phenyl)-2H-chromen-2-one (C-PCa)

9-(3-Bromophenyl)-9H-carbazole(0.59 g, 1.83 mmol), 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-chromen-2-one (0.57 g, 2.09 mmol), tetrakis(triphenylphosphine) palladium(0) (0.11 g, 0.09 mmol) and potassium carbonate (0.76 g, 5.49 mmol) were added to a solution of toluene (40 ml), ethanol (15 ml) and water (15 ml). The reaction mixture

Downloaded by [Gothenburg University Library] at 19:55 24 November 2017

was refluxed for 18 hours and then cooled to room temperature, reduced to a small volume and extracted with dichloromethane (600 ml). The organic extracts were dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was then chromatographed on silica gel with dichloromethane to afford 0.4 g (56%) in a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 (d, 2H), 7.84 (s, 1H), 7.75 – 7.72 (m, 3H), 7.62 – 7.56 (m, 4H), 7.48 – 7.42 (m, 4H), 7.33 – 7.31 (m, 2H), 6.45 (d, 1H). Anal. Calcd. for $C_{27}H_{17}NO_2$ (387.43 g/mol): C, 83.70%; H, 4.42%; N, 3.62%. Found: C, 83.47%; H, 4.60%; N, 3.51%.

Synthesis of 8-(9-phenyl-9H-carbazol-3-yl)-2H-chromen-2-one (PCa-C)

3-Bromo-9-phenyl-9H-carbazole (0.44 g, 1.38 mmol), 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-chromen-2-one (0.38 g, 1.38 mmol), tetrakis(triphenylphosphine) palladium(0) (0.08 g, 0.07 mmol) and potassium carbonate (0.57 g, 4.12 mmol) were added to a solution of toluene (40 ml), ethanol (15 ml) and water (15 ml). The reaction mixture was refluxed for 18 hours, cooled to room temperature, reduced to a small volume and extracted with dichloromethane (600 ml). The organic extracts were dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was then chromatographed on silica gel with dichloromethane to give 0.21 g (40%) in a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (s, 1H), 8.20 (d, 1H), 7.75 – 7.73 (d, 2H), 7.66 – 7.61 (m, 4H), 7.58 – 7.54 (m, 3H), 7.49 – 7.43 (m, 3H), 7.35 – 7.33 (m, 2H), 6.41 (d, 1H). Anal. Calcd. for $C_{27}H_{17}NO_2$ (387.43 g/mol): C, 83.70%; H, 4.42%; N, 3.62%. Found: C, 83.54; H, 4.64%; N, 3.58.

Synthesis of 7-(9-(3-(9H-carbazol-9-yl)phenyl)-9H-carbazol-3-yl)-2H-chromen-2-one (PDCa-C)

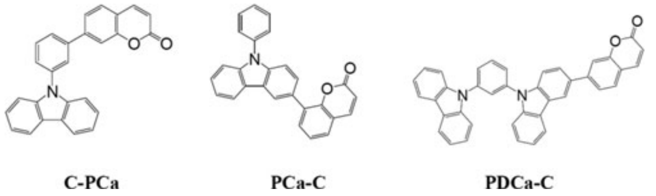
9-(3-(9H-carbazol-9-yl)phenyl)-3-bromo-9H-carbazole (1.43 g, 2.93 mmol), 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2H-chromen-2-one (1.20 g, 4.41 mmol), tetrakis (triphenylphosphine)palladium(0) (0.17 g, 0.15 mmol) and potassium carbonate (1.21 g, 8.75 mmol) were added to a solution of toluene (40 ml), ethanol (15 ml) and water (15 ml). The reaction mixture was refluxed for 18 hours, cooled to room temperature, reduced to a small volume and extracted with dichloromethane (600 ml). The organic extracts were dried over Na_2SO_4, filtered and evaporated to dryness. The crude product was then chromatographed on silica gel with dichloromethane to give 0.75 g (46.3%) in a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.40 (s, 1H), 8.16 (d, 3H), 7.88 (s, 1H), 7.73 – 7.71 (m, 4H), 7.69 – 7.63 (m, 4H), 7.58 – 7.53 (m, 4H), 7.48 – 7.43 (m, 4H), 7.33 – 7.31 (m, 2H), 6.45 (d, 1H). Anal. Calcd. for $C_{39}H_{24}N_2O_2$ (552.62 g/mol: C, 84.76%; H, 4.38%; N, 5.07%. Found: C, 84.62%; H, 4.51%; N, 5.26%.

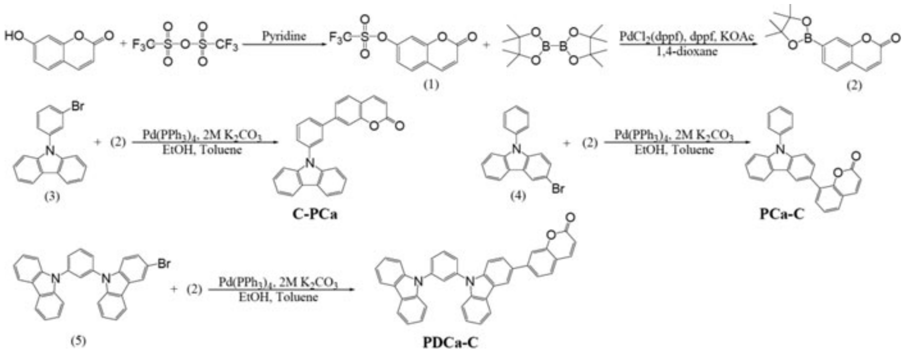
Results and discussion

The chemical structures and synthetic routes of compounds are shown in Scheme 1 and 2. Compounds (3), (4) and (5) were synthesized according to the literature [11]. In film state, maximum UV-Vis absorption (UVmax) of three synthesized compounds, C-PCa, PCa-C and PDCa-C appeared in the range 331 to 345 nm. As observed for maximum photoluminescence (PLmax), C-PCa, PCa-C and PDCa-C showed 449, 467 and 467 nm, respectively. (Figure. 1) The UVmax values of PCa-C and PDCa-C were red-shifted about 20 nm compared to that of C-PCa. This trend was similar to that seen in the PLmax values of PCa-C and PDCa-C because PCa-C and PDCa-C had coumarin substituted para position in carbazole, increasing

Downloaded by [Gothenburg University Library] at 19:55 24 November 2017



Scheme 1. Chemical structures of the synthesized compounds.



Scheme 2. Synthetic routes of the synthesized compounds.

conjugation length [12, 13]. In contrast, C-PCa had coumarin substituted in meta position to prevent conjugation length from increasing. In the case of PDCa-C, UVmax and PLmax were observed in the region similar to PCa-C, and this is also because the two carbazoles substituted in phenyl were connected in meta position. This connection does not affect the conjugation length [13].

The three synthesized compounds were used as the emitting layer (EML), and non-doped OLED was fabricated with the following structure: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized compounds (35nm) /TPBi (20 nm)/LiF (1 nm)/Al(200 nm). Here, 2-TNATA was used as the hole injection layer (HIL), and NPB was used as the hole transporting layer (HTL). TPBi was used as the electron transporting layer (ETL), LiF as the electron

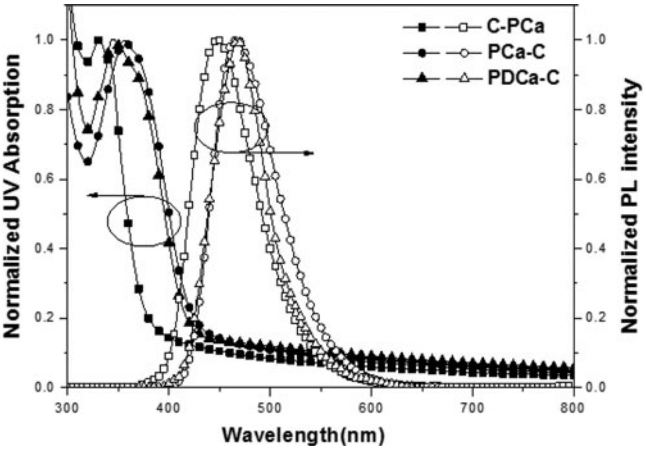


Figure 1. UV&PL spectra of C-PCa, PCa-C, and PDCa-C in film state.

Downloaded by [Gothenburg University Library] at 19:55 24 November 2017

Table 1. EL performances of multilayered devices with the synthesized compound at 10 mA/cm^2.

EML	Volt[a] (V)	C.E.[b] (cd/A)	P.E.[c] (lm/W)	C.I.E.[d] (x, y)
C-PCa	7.13	1.20	0.59	(0.26, 0.34)
PCa-C	6.30	1.13	0.62	(0.19, 0.27)
PDCa-C	6.97	1.34	0.66	(0.18, 0.23)

[a]: turn on voltage,
[b]: current efficiency,
[c]: power efficiency,
[d]: Commission International de l'Eclairage.

injection layer (EIL), and ITO and Al were respectively used as anode and cathode. The EL performance is summarized in Table 1 and Figure 2 at 10mA/cm^2.

C-PCa showed white emission of current efficiency of 1.16 cd/A and C.I.E of (0.26, 0.33). (Figure. 3) The original emission peak of C-PCa showed at 466 nm in film state. However, as shown EL spectrum of C-PCa, it can be seen that new emission peak has occurred about 520 nm. It probably means that exciplex has occurred within the device so, non-doped OLED using C-PCa as EML exhibited white emission. C-PCa showed power efficiency of 0.59 lm/W, which is the lowest power efficiency among three synthesized compounds because C-PCa had the highest turn on voltage for 7.13 V.

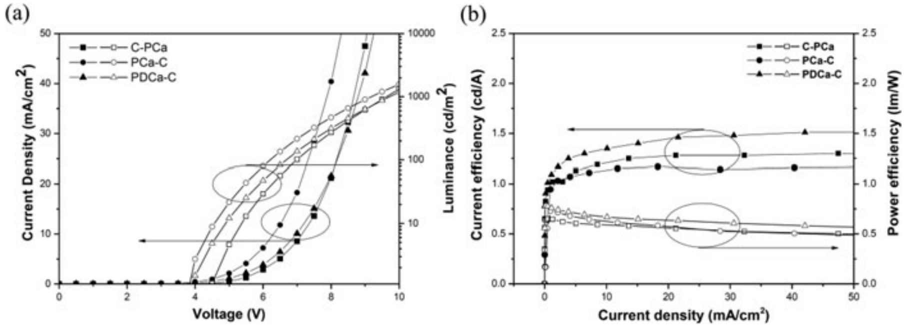


Figure 2. EL characteristics of devices: (a) I-V-L curve (b) Current efficiency and power efficiency versus current density.

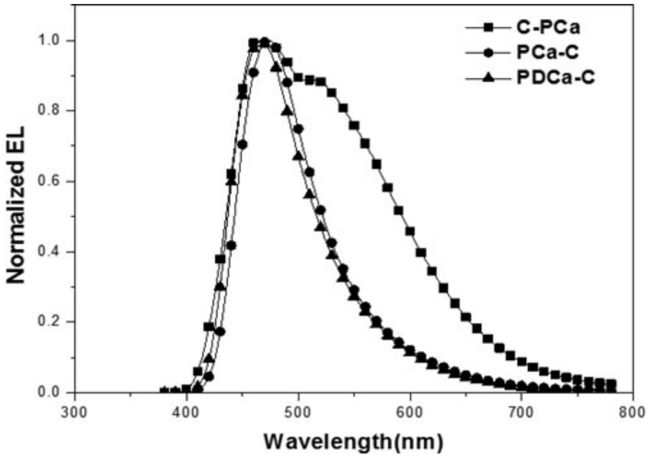


Figure 3. Normalized EL spectra of C-PCa, PCa-C, and PDCa-C.

PCa-C showed current efficiency of 1.13 cd/A, power efficiency of 0.62 lm/W and C.I.E of (0.19, 0.27). PDCa-C showed the highest current efficiency of 1.34 cd/A, power efficiency of 0.62 and C.I.E of (0.18, 0.23). PCa-C and PDCa-C have emission in the blue region as in film state. PDCa-C showed the highest current efficiency because carbazole, which is a chromophore with high luminous efficiency, was substituted one more than C-PCa and PCa-C. In other words, efficiency of final emitter might be found to increase with increasing efficiency of the substituted group [14, 15].

Conclusion

Using coumrain and carbazole, chromophores with high luminous efficiency, new blue fluorescent compounds of C-PCa, PCa-C and PDCa-C were synthesized. This was applied to non-doped OLED as the emitting layer, showing current efficiency of 1.16, 1.13 and 1.34 cd/A, respectively. Among the three synthesized compounds, PDCa-C showed the highest efficiency maintaining emission in blue region. This is because the substituent was maintained at meta-position to avoid conjugation length from increasing, and a lot of chromophores with high luminous efficiency were substituted.

Funding

This research was supported by a grant from the Technology Development Program for Strategic Core Materials funded by the Ministry of Trade, Industry & Energy, Republic of Korea (Project No. 10047758). This research was also supported by National R&D Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Science & ICT (No. 2017M3A7B4041699).

References

[1] Tang, C. W., & Vanslyke, S. A. (1987). *Appl. Phys. Lett.*, *51*, 913.
[2] Zhao, Z., Deng, C., Chen, S., Lam, J. W. Y., Qin, W., Lu, P., Wang, Z., Kwok, H. S., Ma, Y., Qiu, H., & Tang, B. Z. (2011). *Chem. Commun.*, *47*, 8847.
[3] Giridhar, T., Han, T. H., Cho, W., Saravanan, C., Lee, T. W., & Jin, S. H. (2014). *Chem. Eur. J.*, *20*, 8260.
[4] Uoyama, H., Goushi, K., Shizu, K., Nomura, H., & Adachi, C. (2012). *Nature*, *492*, 234.
[5] Yu, Y., Wu, Z., Li, Z., Jiao, B., Li, L., Ma, L., Wang, D., Zhou, G., & Hou, X. (2013). *J. Mater. Chem. C*, *1*, 8117.
[6] Kuma, H., & Hosokawa, C. (2014). *Sci. Techol. Adv. Mater.*, *15*, 034201.
[7] Hu, J. Y., Pu, Y. J., Satoh, F., Kawata, S., Katagiri, H., Sasabe, H., & Kido, J. (2014). *Adv. Funct. Mater.*, *24*, 2064.
[8] Zhang, R., Zhao, Y., Zhang, T., Xu, L., & Ni, Z. (2016). *Dyes and Pigments*, *130*, 106.
[9] Uoyama, H., Goushi, K., Shizu, K., Nomura, H., & Adachi, C. (2012). *Nature*, *492*, 234.
[10] Zhang, H., Chai, H., Yu, T., Zhao, Y., & Fan, D. (2012). *J. Fluoresc.*, *22*, 1509.
[11] Jeon, S. O., & Lee, J. Y. (2012). *J. Mater. Chem.*, *22*, 7239.
[12] Yan, M. K., Tao, Y., Chen, R. F., Zheng, C., An, Z. F., & Huang, W. (2012). *RSC Adv.*, *2*, 7860.
[13] Wagner, D., Hoffmann, S. T., Heinemeyer, U., Münster, I., Köhler, A., & Strohriegl, P. (2013). *Chem. Mater.*, *25*, 3758.
[14] Lee, H., Park, Y. I., Kim, B., Lee, J. H., & Park, J. (2014). *Optical. Mater. Express.*, *4*, 924.
[15] Niko, Y., Kawauchi, S., Otsu, S., Tokumaru, K., & Konishi, G. I. (2013). *J. Org. Chem.*, *78*, 3196.

Downloaded by [Gothenburg University Library] at 19:55 24 November 2017