Appl. Chem. Eng., Vol. 34, No. 1, February 2023, 94-97
https://doi.org/10.14478/ace.2022.1132

Article

Spirobifluorene 그룹을 포함하는 새로운 청색 발광 재료의 전계발광

박선우[1] · 이하윤[1] · 권혁민 · Godi Mahendra · 박상신 · 이승은 · 박종욱†

경희대학교 화학공학과 융합공학

(2022년 12월 28일 접수, 2023년 1월 5일 수정, 2023년 1월 6일 채택)

Electroluminescence Properties of Novel Blue-Emitting Materials Based on Spirobifluorene

Sunwoo Park[1], Hayoon Lee[1], Hyukmin Kwon, Godi Mahendra, Sangshin Park, Seungeun Lee and Jongwook Park†

Integrated Engineering, Department of Chemical Engineering, Kyung Hee University, Gyeonggi 17104, Korea

(Received December 28, 2022; Revised January 5, 2023; Accepted January 6, 2023)

초 록

BTPSF와 BDTSF는 유기발광다이오드용 스파이로플루오렌 모이어티를 기반으로 하는 새로운 청색 발광 물질로 성공적으로 합성되었다. BTPSF와 BDTSF는 촉매를 사용하지 않고 Diels-Alder 반응을 통해 합성하여 고순도를 얻었다. 합성된 물질의 광발광 스펙트럼은 용액 상태에서 약 381, 407 nm, 필름 상태에서 각각 395, 434 nm의 최대 발광 파장을 나타내어 자외선과 짙은 청색 발광색을 나타냈다. 합성된 BDTSF 물질은 non-doped 소자의 EML로 적용되었으며, 전류 효율은 0.61 cd/A이다.

Abstract

2,7-bis(3',6'-diphenyl-[1,1':2',1''-terphenyl]-4'-yl)-9,9'-spirobi[fluorene] (BTPSF) and 2,7-bis(1,4-diphenyltriphenylen-2-yl)-9,9'-spirobi[fluorene] (BDTSF) were successfully synthesized as novel blue-emission materials for organic light-emitting diodes (OLEDs) based on the spirobifluorene (SBF) moiety. BTPSF and BDTSF were obtained in high purity via a Diels-Alder reaction, without the use of a catalyst. Photoluminescence spectra of the synthesized materials showed maximum emitting wavelengths of approximately 381 and 407 nm in solution and 395 and 434 nm in the film state, for BTPSF and BDTSF, respectively, indicating ultra-violet and deep blue emission colors. BDTSF was applied as an emissive layer (EML) in non-doped devices and achieved a current efficiency of 0.61 cd/A and an external quantum efficiency (EQE) of 0.46%.

Keywords: *Organic light-emitting diodes (OLEDs), Blue, Spirobifluorene derivatives, Electroluminescence, Non-doped device*

1. Introduction

Organic light-emitting diodes (OLEDs) have received significant attention from industry and academia since their development was first reported in 1987 by Tang and Vanslyke[1]. OLEDs have been successfully applied to televisions, mobile phones, and lighting devices because of their low driving voltage, self-luminance, fast response, wide viewing angles, and excellent color purity[2-4]. As the OLEDs market grows, research and development on OLEDs light-emitting materials is being continuously conducted. In general, fluorescence has an internal quantum efficiency (IQE) of 25%, but for phosphorescence an IQE of 100% is theoretically possible. In the case of red and green phosphorescent materials, commercialization has been successful. However, blue phosphorescent materials have not been commercialized, owing to the wide intrinsic band gap and cost of heavy metals, as well as the unfavorable roll-off phenomenon. Therefore, there is a need for further research on blue fluorescent materials, with high efficiency and long lifetimes[5-11]. As shown in Scheme 1, blue light-emitting materials with high yield and high purity were synthesized using a catalyst-free Diels-Alder reaction. The synthesized materials contain a spirobifluorene (SBF) moiety, which possesses excellent luminous efficiency as a core emitting group. 3',6'-diphenyl-1,1':2',1'' -terphenyl (DPTP) and 1,4-diphenyltriphenylene (DPTPL) were employed as bulky side groups. Side groups with varied conjugation lengths were introduced into the SBF, to study the optical and electrical properties of the synthesized materials.

---

[1] Co-first authors

† Corresponding Author: Kyung Hee University
Integrated Engineering, Department of Chemical Engineering, Gyeonggi 17104, Korea
Tel: +82-31-201-3675 e-mail: jongpark@khu.ac.kr

pISSN: 1225-0112 eISSN: 2288-4505

2. Materials and methods

2.1. Synthesis

2.1.1. 2,7-bis(3',6'-diphenyl-[1,1':2',1''-terphenyl]-4'-yl)-9,9'-spirobi[fluorene] (BTPSF)

2,7-diethynyl-9,9'-spirobi[fluorene] (0.73 g, 2 mmol) and 2,3,4,5-tetraphenylcyclopenta-2,4-dienone (1.54 g, 4 mmol) were added to 50 mL xylene. The reaction mixture was heated under reflux at 180 °C for 24 h under an argon atmosphere. The solution was cooled to room temperature, and subsequently filtered and dried with MgSO$_4$. The crude product was purified by recrystallization from chloroform and ethanol to give 0.66 g (33%) of the compound BTPSF. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.62 (d, 2H), 7.56 (d, 2H), 7.41 (s, 2H), 7.21 (d, 2H), 7.08 (m, 13H), 6.86 (s, 6H), 6.78 (s, 6H), 6.73 (d, 5H), 6.70 (s, 2H), 6.64 (t, 8H), 6.57 (d, 4H), 6.41 (d, 2H), and 6.32 (s, 2H).

2.1.2. 2,7-bis(1,4-diphenyltriphenylen-2-yl)-9,9'-spirobi[fluorene] (BDTSF)

2,7-diethynyl-9,9'-spirobi[fluorene] (0.9 g, 2.5 mmol) and 1,3-diphenyl-2H-cyclopenta[l]phenanthren-2-one (1.93 g, 5 mmol) were added to 50 mL xylene. The reaction mixture was heated under reflux at 180 °C for 24 h under an argon atmosphere. The solution was cooled to room temperature, and subsequently filtered and dried with MgSO$_4$. The crude product was purified by recrystallization from chloroform and ethanol to give 1.15 g (43%) of the compound BDTSF. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 8.35 (d, 4H), 7.66 (d, 2H), 7.59 (t, 4H), 7.52 (s, 2H), 7.38 (m, 19H), 7.18 (d, 2H), 7.09 (t, 2H), 7.03 (t, 2H), 6.94 (m, 9H), 6.86 (d, 4H), 6.56 (d, 2H), and 6.23 (s, 2H).

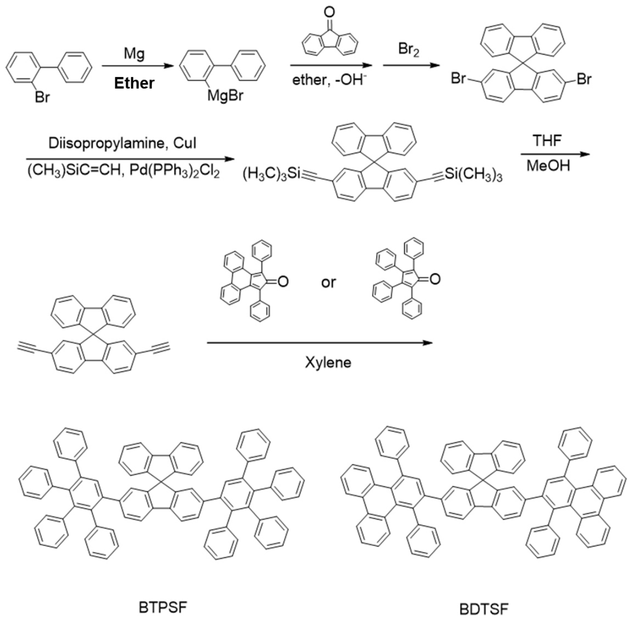
2.2. Measurements

The ^{1}H-NMR spectra were recorded on Bruker Advance 300 spectrometers. The optical UV-Vis absorption spectra were obtained using a Lambda 1050 UV/Vis/NIR spectrometer (Perkin Elmer). Perkin Elmer luminescence spectrometer LS55 (Xenon flash tube) was used for photo-luminescence (PL) spectroscopy. The photoluminescence quantum yield (PLQY) was obtained using Quantaurus-QY Absolute PL quantum yield spectrometer C11347 (Hamamatsu). For the EL devices, all organic layers were deposited under 10~6 torr, with a rate of deposition of 1 Å/s to give a deposition area of 4 mm^2. 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.

3. Results and discussion

3.1. Molecule design concept

The novel blue-emitting materials, BTPSF and BDTSF, were successfully synthesized, as shown in Scheme 1 and Figure 1. Spirobifluorene (SBF) exhibits high photoluminescence (PL) efficiency and a highly twisted structure achieved by sp3 bonding, which can be used as the main emitting moiety. In this study, we used sterically bulky side groups to prevent aggregation caused quenching (ACQ), which can occur in the film state due to the proximity of the molecules. DPTP and DPTPL were attached to the core of the molecules as bulky side groups. The two side groups have different rigidities, with DPTP having an open structure to rotate itself, while the triphenylene group of DPTPL has a fused ring system and, therefore, a relatively high rigidity. We believe that the two different side groups result in different electro-optical properties.



Scheme 1. Synthetic routes of BTPSF and BDTSF.

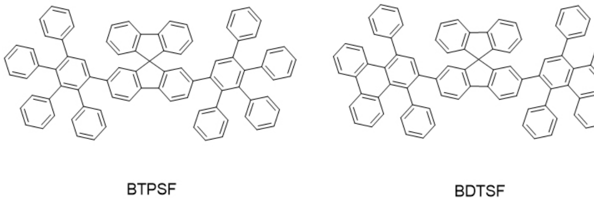


Figure 1. Chemical structures of BTPSF and BDTSF.

3.2. Optical properties of the synthesized compounds

Figure 2 and Table 1 show the ultraviolet-visible (UV-Vis) absorption spectra and PL spectra of the synthesized compounds. In the solution state UV-Vis spectra, BTPSF and BDTSF exhibited absorption wavelengths of 308 and 327 nm; and 308 and 339 nm, respectively. In the film state, BTPSF and BDTSF exhibited absorption maximum wavelengths of 311 and 329 nm; and 311 and 328 nm, respectively. For PL measurements recorded in the solution state, BTPSF and BDTSF exhibited ultraviolet and deep-blue emission at 381 and 407 nm, respectively, with full-width-at-half-maximum (FWHM) values of 54 nm. BTPSF and BDTSF exhibited high solution state photoluminescence quantum yield (PLQY) values of 88% and 93%, respectively. In the film state, BTPSF and BDTSF exhibited deep-blue emission at 395 and 434 nm, respectively. Compared with the solution state, the maximum emission values for the film state were redshifted

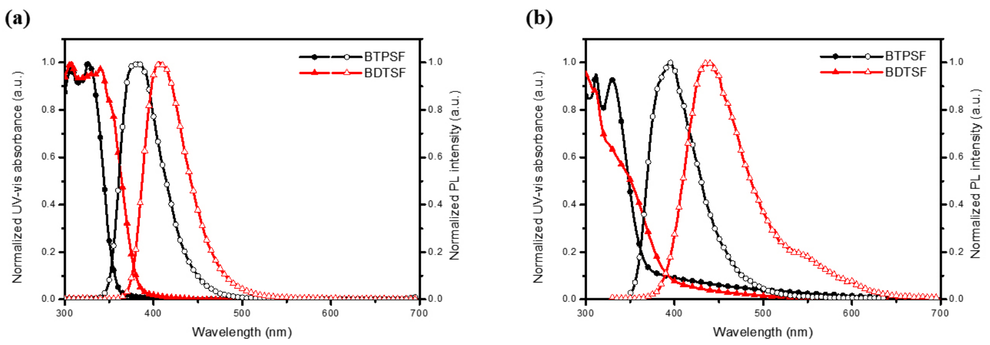


Figure 2. Normalized UV-visible absorption and PL spectra of newly synthesized compounds: (a) in solution state (1 × 10^{-5} M toluene), (b) in film state (vacuum-deposited film, 50 nm).

Table 1. Optical Properties of Synthesized Compounds

Compounds	Solution state[a]				Film state[b]			
	UV_{max} (nm)	PL_{max} (nm)	FWHM[c] (nm)	PLQY[d] (%)	UV_{max} (nm)	PL_{max} (nm)	FWHM[c] (nm)	PLQY[d] (%)
BTPSF	308/327	381	54	88	311/329	395	62	65
BDTSF	308/339	407	54	93	311/328	434	77	71

[a]: 1 × 10^{-5} M in toluene, [b]: vacuum-deposited film (50 nm), [c]: full width at half maximum, [d]: photoluminescence quantum yield

by 14 and 27 nm in BTPSF and BDTSF, respectively. FWHM values for BTPSF and BDTSF were 62 and 77 nm, respectively, 8 nm and 23 nm broader than solution state values. This means that the molecular packing of BDTSF in the film state is more efficient than that of BTPSF. Furthermore, for BDTSF, weak excimer emission of 549 nm was observed due to the proximity of the molecules. PLQY values for BTPSF and BDTSF in the film state were 65 and 71%, respectively. These values were approximately 23% and 22% lower than those observed in the solution state for BTPSF and BDTSF, respectively, owing to the ACQ effect[12]. The PLQY value for BDTSF was higher than that of BTPSF because the DPTPL side group is more rigid than the DPTP side group. It effectively prevents the intermolecular interaction compared to the DPTP side group.

3.3. Electroluminescence (EL) performance of the synthesized compounds

The synthesized compounds were used as emitting layers (EML) to fabricate non-doped OLEDs devices, and their EL performance was measured. The devices were structured as follows: ITO / 4,4',4''-Tris[2-naphthyl(phenyl)amino]triphenylamine (2-TNATA) (60 nm) / N,N'-Di(1-naphthyl)-N,N'- diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB) (15 nm) / BTPSF or BDTSF (30 nm) / Alq_3 (30 nm) / LiF (1 nm) / Al (200 nm). 2-TNATA was used as a hole injection layer, and NPB was used as both a hole transporting layer (HTL), and an electron blocking layer (EBL). Alq_3 was used as an electron transporting layer (ETL). The OLEDs properties of the non-doped devices using the synthesized EML materials are summarized in Figure 3 and Table 2. As shown in Figure 3, the BDTSF device exhibited typical OLEDs performance, such as current density (I)-voltage (V)-luminance (L) curve, current efficiency (CE) versus current density and external quantum efficiency (EQE) versus current density. However, for the BTPSF device, a normal EL spectrum was not observed because of the wide band gap of more than 3.4 eV. This was due to the wide band gap not allowing recombination for emission, as well as the worse electron and hole injections in the BTPSF device. The BDTSF device exhibited CE of 0.61 cd/A and EQE of 0.46%. In addition, no roll-off was observed for the BDTSF device, even at high current densities. Therefore, unlike the BTPSF device, the BDTSF device displays smooth charge injection. The BDTSF device exhibited an EL_{max} value of 437 nm, and the CIE color coordinates were (0.20, 0.17). The BDTSF device exhibited deep-blue region emission at the EL_{max} wavelength, but the CIE y-value was not as low. This is due to the weak excimer peak for BDTSF, which is derived from

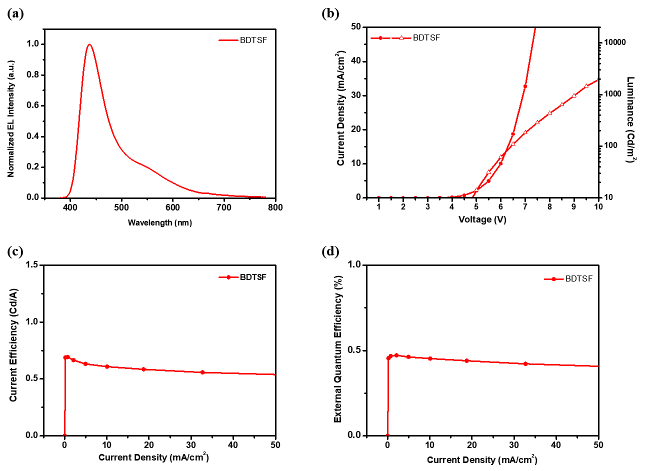


Figure 3. EL performances of non-doped devices using BDTSF as EML: (a) EL spectrum (b) I−V−L curve, (c) current efficiency versus current density, and (d) external quantum efficiency versus current density.

Table 2. EL Performances of Non-doped OLEDs Devices at 10 mA/cm^2. Device Structure: ITO / 2-TNATA (60 nm) / NPB (15 nm) / EML (synthesized materials / 30 nm) / Alq3 (30 nm) / LiF (1 nm) / Al (200 nm)

Compounds	Voltage (V)	CE[a] (cd/A)	EQE[b] (%)	CIE[c] (x, y)	PL$_{max}$[d] (nm)	EL$_{max}$ (nm)
BDTSF	6.0	0.61	0.46	(0.20, 0.17)	434	437

[a] Current efficiency, [b] external quantum efficiency, [c] commission International de l'Eclairage, [d] film state

the molecular packing in the device. However, this CIE *y*-value is close to the commercialized mobile phone specification of 0.15.

4. Conclusions

Two novel blue-emitting fluorescent compounds, BTPSF and BDTSF, were synthesized, based on the spirobifluorene moiety. BTPSF and BDTSF showed ultraviolet and deep-blue PL emission at 395 and 434 nm, respectively, in the film state. The EL performance of BDTSF based on a non-doped device showed a CE of 0.61 cd/A and an EQE of 0.46%. BDTSF exhibited deep-blue emission at an EL$_{max}$ wavelength of 437 nm, and exhibited a CIE color coordinates of (0.20, 0.17). The non-doped device displayed a relatively wide FWHM value owing to the molecular packing, but the CIE *y*-value of 0.17 for the BDTSF device was close to the commercialized mobile phone requirement (0.15) for blue emission.

Acknowledgements

This research was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (2020R1A6A1A03048004). This work was supported by the Technology Innovation Program (20017422, Development of raw materials and process for ArF-i photoresist) funded By the Ministry of Trade, Industry & Energy (MOTIE, Korea). This research was supported by Basic Science Research Capacity Enhancement Project through Korea Basic Science Institute (National research Facilities and Equipment Center) grant funded by the Ministry of Education (No. 2019R1A6C10 10052). This work was supported by the Korea Institute for Advancement of Technology (KIAT) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. P0017363).

References

1. C. W. Tang and S. A. VanSlyke, Organic electroluminescent diodes, *Appl. Phys. Lett.*, **51**, 913-915 (1987).
2. Y. Yu, C. Huang, J. Yeh, and P. Huang, Effect of methyl substituents on the N-diaryl rings of anthracene-9, 10-diamine derivatives for OLEDs applications, *Org. Electron.*, **12**, 694-702 (2011).
3. D. H. Ahn, S. W. Kim, H. Lee, I. J. Ko, D. Karthik, J. Y. Lee, and J. H. Kwon, Highly efficient blue thermally activated delayed fluorescence emitters based on symmetrical and rigid oxygen-bridged boron acceptors, *Nat. Photonics*, **13**, 540-546 (2019).
4. Y. Wang, W. Liu, S. Ye, Q. Zhang, Y. Duan, R. Guo, and L. Wang, Molecular engineering of anthracene-based emitters for highly efficient nondoped deep-blue fluorescent OLEDs, *J. Mater. Chem. C*, **8**, 9678-9687 (2020).
5. D. F. Pickup, H. Yi, H. Kun, A. Iraqi, M. Stevenson, and D. G. Lidzey, Alternating 2,7- and 3,6-linked carbazole copolymers as wide band gap energy transfer donors, *Thin Solid Films*, **517**, 2840-2844 (2009).
6. Q. Zhang, J. Ding, Y. Cheng, L. Wang, Z. Xie, X. Jing, and F. Wang, Novel heteroleptic CuI complexes with tunable emission color for efficient phosphorescent light emitting diodes, *Adv. Funct. Mater.*, **17**, 2983-2990 (2007).
7. H. Shin, B. Kim, H. Jung, J. Lee, H, Lee, S. Kang, J. Moon, J. Kim, and J. Park, Achieving a high-efficiency dual-core chromophore for emission of blue light by testing different side groups and substitution positions, *RSC Adv.*, **7**, 55582-55593 (2017).
8. J. Lee, H. Jung, H. Shin, J. Kim, D. Yokoyama, H. Nishimura, A. Wakamiya, and J. Park, Excimer emission based on the control of molecular structure and intermolecular interactions, *J. Mater. Chem. C*, **4**, 2784-2792 (2016).
9. M. Jung, J. Lee, H. Jung, S. Kang, A. Wakamiya, and J. Park, Highly efficient pyrene blue emitters for OLEDs based on substitution position effect, *Dyes Pigm.*, **158**, 42-49 (2018).
10. H. Jung, J. Ryu, S. Kang, H. Lee, and J. Park, Synthesis and electroluminescence property of green fluorescent dopant including anthracene and diphenylamine moiety, *J. Nanosci. Nanotechnol.*, **19**, 4799-4802 (2019).
11. H. Lee, S. Lee, H. Jung, S. Kang, and J. Park, Synthesis and electroluminescence properties of new dual-core derivatives, *J. Nanosci. Nanotechnol.*, **18**, 2166-2170 (2018).
12. Y. Jeon, J. Lee, J. Kim, C. Lee, and M. Gong, Deep-blue OLEDs using novel efficient spiro-type dopant materials, *Org. Electron.*, **11**, 1844-1852 (2010).

Authors

Sunwoo Park; M.Sc., Graduate Student, Integrated Engineering, Department of Chemical Engineering, Kyung Hee University, Yongin 17104, Korea; mdrafix@khu.ac.kr

Hayoon Lee; Ph.D., Researcher, Integrated Engineering, Department of Chemical Engineering, Kyung Hee University, Yongin 17104, Korea; kssarang1 @khu.ac.kr

Hyukmin Kwon; B.Sc., Graduate Student, Integrated Engineering, Department of Chemical Engineering, Kyung Hee University, Yongin 17104, Korea; hm531@khu.ac.kr

Sangshin Park; M.Sc., Graduate Student, Integrated Engineering, Department of Chemical Engineering, Kyung Hee University, Yongin 17104, Korea; mhdr0824@khu.ac.kr

Seungeun Lee; Ph.D., Researcher, Integrated Engineering, Department of Chemical Engineering, Kyung Hee University, Yongin 17104, Korea; demos815@khu.ac.kr

Jongwook Park; Ph.D., Professor, Integrated Engineering, Department of Chemical Engineering, Kyung Hee University, Yongin 17104, Korea; jongpark@khu.ac.kr