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Synthesis and Electroluminescence of Novel Pyrene-Fused Chromophores

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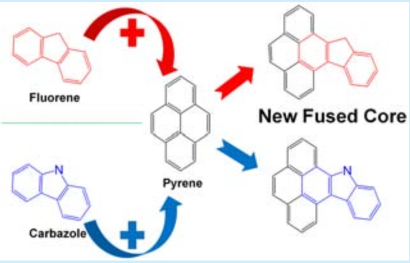
Supporting Information

ABSTRACT: Using 4,9-dibromopyrene as a key intermediate, two new fused-core compounds, TP-PFF and TP-PFC-TP, were synthesized. These compounds not only exhibited excellent thermal stability but also yielded superior electroluminescence (EL) devices with a lower turn-on voltage, over 50% greater efficiency, and over 3 times longer lifetime than did a similar compound lacking a fused core. This new core-forming method can be applied in various applications with many different core groups.



The range of applications of organic functional compounds has recently expanded rapidly, with especially innovative uses for optoelectronics.[1] Researchers have begun to report how the properties of these compounds can be modified by varying their core and side groups.[2] The development of new core and side groups and the study of how they combine to form desired organic functional compounds are thus key research areas. Since the core component is the key factor that determines the final physical properties of materials, and diverse organic compounds can be proposed based on varying the core, it is more important in terms of novelty and performance to develop new core groups than to develop new side groups.[2] Therefore, the demand for new core groups is increasing as the need for new organic functional groups is increasing in optoelectronics applications such as organic light-emitting diodes (OLEDs),[3] organic thin film transistors (OTFTs),[4] and organic photovoltaics (OPVs).[5] This paper proposes a new core structure, for use in OLEDs, and reports excellent characteristics of its derivatives. The method proposed to synthesize this new core structure can be applied to various groups, such as anthracene, phenanthrene, and chrysene, and would hence also be of significant interest in other applications, such as OTFT and OPV.

OLEDs, having potential applications in large full-color displays and lighting, are currently the subject of extensive research, with great efforts underway for the development of fluorescent emitters of blue light for high-performance devices.[6] While derivatives of diverse core groups such as anthracene, phenanthrene, and chrysene are well-known as blue light fluorescent emitters, pyrene and its derivatives have received the spotlight in this regard as they provide high quantum efficiency and thermal and chemical stabilities.[7] Researchers have modified pyrene in various ways in order to improve device performance, using approaches such as (1) changing the functional group substituted into the pyrene,[8] (2) changing the number of such functional groups and their positions on pyrene,[9] and (3) substituting various numbers of pyrenes as side groups into another moiety used as the core.[10] Many studies have focused on the 1, 3, 6, and 8 positions of pyrene, which can be synthetically accessed with ease when using any of these three methods.[8−10] However, the use of pyrene as an efficient emitter in OLEDs has been limited because its planar structure strongly tends to form excimers in the solid state, resulting in long wavelength excimer emissions with low fluorescence quantum yield and emission quenching.[11]

In this study, we designed and synthesized novel fused-core systems based on pyrene and other groups for blue OLED emitters without using the conventional methods mentioned above.[12] Instead, fluorene and carbazole units, known for not only high quantum efficiency as emitters in the field of OLEDs but also having carrier transport properties,[13] were combined with pyrene into a fused-core system to design a new core group. This new core was designed with an asymmetric structure as such structures have been shown to enhance the electronic properties of OLED emitters.[3e] Furthermore, we were able use the 4 and 9 positions of pyrene, despite their rare use in the past due to synthesis difficulties. Figure 1 shows the structures of the newly synthesized derivatives. To produce 5′-([1^1,2^1:2^3,3^1-terphenyl]-2^5-yl)spiro[fluorene-9,9′-indeno[1,2-*e*]pyrene] (TP-PFF), spirofluorene, which has a highly twisted structure, was synthesized with the pyrene core in the form of a

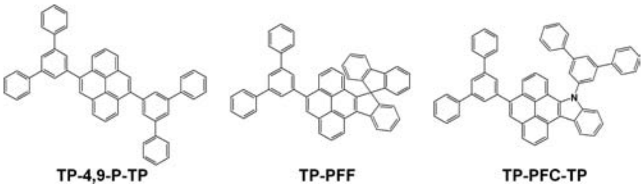


Figure 1. Chemical structures of synthesized compounds.

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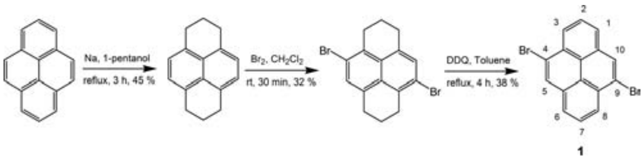
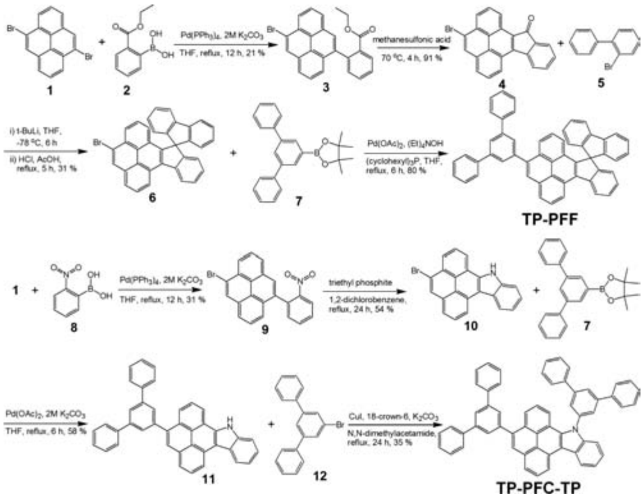
PFF core. In addition, 5,9-bis([1^1,2^1:2^3,3^1-terphenyl]-2^5-yl)-phenanthro[4,5-*abc*]carbazole (TP-PFC-TP) was synthesized using carbazole in the form of a PFC core. 4,9-Bis[1,1′;3′,1″]-terphenyl-5′-yl-pyrene (TP-4,9-P-TP) was synthesized using the 4 and 9 positions of pyrene to compare the new PFF core and PFC core to the pyrene core (Figure 1).

In these reactions, 4,9-dibromopyrene is a key intermediate but cannot be synthesized from the direct bromination of pyrene due to its lack of regioselectivity. It was instead synthesized from pyrene in three steps (Scheme 1).[14] The new TP-PFF and TP-PFC-TP compounds, whose synthetic routes are shown in Scheme 2, were successfully synthesized using reactions such as Suzuki coupling, acid-catalyzed intramolecular Friedel−Crafts acylation,[15] reductive Cadogan ring closure,[16] and Ullmann coupling.[17] In addition, synthetic routes to TP-4,9-P-TP are outlined in Scheme S2. Although to date the overall yields achieved for these reactions have not been high, there is a strong likelihood that future work focused on optimizing the structure and reaction conditions will lead to higher yields. The synthesized compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, and high-resolution mass spectrometry (HRMS), as well as elemental analysis (see the Supporting Information).

Scheme 1. Preparation of 4,9-Dibromopyrene



Scheme 2. Synthetic Routes of TP-PFF and TP-PFC-TP



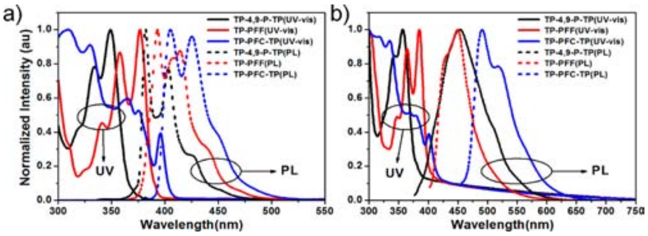


Figure 2. UV−vis absorption and PL spectra of TP-4,9-P-TP, TP-PFF, and TP-PFC-TP: (a) in 1×10^{-5} M THF and (b) in films.

Figure 2 shows UV−vis (UV−vis) absorption and photoluminescence (PL) spectra of the synthesized compounds in THF solution and vacuum-deposited film states, and Table 1 summarizes the optical, energy levels of molecular orbitals and thermal properties of these compounds. In THF, TP-4,9-P-TP showed absorption maxima at 334 and 349 nm (Figure 2a). TP-PFF showed values of 358 and 377 nm, which are red-shifted relative to TP-4,9-P-TP due to the increased π-conjugation length of the PFF core group. TP-PFC-TP exhibited the longest wavelength absorption peaks, at 375 and 396 nm, due to the lengthy π-conjugation in the PFC core group and the effect of the nitrogen atom in the carbazole unit. The peak at about 396 nm could be assigned to the n−π* transitions of the carbazole moiety.[18] PL$_{max}$ in THF was 382 and 403 nm for TP-4,9-P-TP and red-shifted to 393, 414 nm for TP-PFF and to 405, 425 nm for TP-PFC-TP. PL spectra of the three compounds were observed to have vibronic peaks, which can be interpreted as the effects of planar and rigid core structures. As for the film state, UV−vis absorption was slightly red-shifted, by 5−8 nm, compared to in solution (Figure 2b). Whereas PL$_{max}$ in the film state was 454 nm for TP-4,9-P-TP, it was blue-shifted to 449 nm for TP-PFF. This shift can be explained by the difference between their torsion angles. According to the molecular structures optimized using density functional theory (DFT) calculations at the B3LYP/6-31G(d) level (see Figure 3), the torsion angle between the core and terphenyl side group (α position) in TP-4,9-P-TP was 59.3° and that in the corresponding (β) position of TP-PFF was 58.3°. In contrast, the torsion angle at the γ position of TP-PFF that corresponds to the pyrene-spirofluorene bond was 74.7°, indicative of an orthogonal connection. Such a highly twisted structure prevents intermolecular packing or aggregation in film. Therefore, whereas TP-4,9-P-TP showed a greater bathochromic effect in film compared to solution, TP-PFF had a relatively small bathochromic effect due to the large torsion angle. TP-PFC-TP had angles of δ = 59.5° and ε = 64.5° and the longest PL$_{max}$ wavelength, at 491 nm, because of the electron-donating effect of the carbazole unit in the PFC core. Due to the influence of such a torsional angle, the fwhm of TP-PFF and of TP-PFC-TP, with their fused cores, were decreased to 56 and 64 nm relative to the 86 nm fwhm for TP-4,9-P-TP. In addition, the absolute photoluminescence quantum yields (Φ_f) of TP-PFF and TP-PFC-TP, at 61% and 59%, were higher than the 44% for TP-4,9-P-TP (Table 1).

The calculated electron density distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) for TP-4,9-P-TP, TP-PFF, and TP-PFC-TP are shown in Figure 3. For TP-4,9-P-TP, the HOMO and LUMO electron densities were distributed only at the pyrene core. However, TP-PFF and TP-PFC-TP showed different electron density distributions at their fused-core ring structure than did the pyrene core. This difference implies that the fused fluorene group as well as the fused carbazole group combined with pyrene to form two new core chromophores.

Decomposition temperatures (T_d) and glass transition temperatures (T_g) of the synthesized compounds were determined using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 1). The T_d values of TP-4,9-P-TP, TP-PFF, and TP-PFC-TP were measured to be 453, 458, and 472 °C, respectively, whereas

Table 1. Physical Properties of TP-4,9-P-TP, TP-PFF, and TP-PFC-TP

compd	$\lambda_{max,abs}$ (nm) solns^a/films^b		$\lambda_{max,PL}$ (nm) solns^a/films^b		$\Phi_f{}^c$ (%)	fwhm^d	$E_{HOMO}{}^e$ (eV)	$E_{LUMO}{}^f$ (eV)	T_g (°C)	T_d (°C)
TP-4,9-P-TP	334, 349	344, 357	382, 403	454	44	86	−5.81	−2.58	118	453
TP-PFF	358, 377	364, 385	393, 414	429, 449	61	56	−5.70	−2.62	187	458
TP-PFC-TP	375, 396	380, 401	405, 425	491, 517	59	64	−5.51	−2.55	176	472

[a] Measured in 1 × 10^{-5} M THF. [b] Measured in neat films (thickness: 50 nm). [c] Absolute photoluminscence quantum yield in neat films. [d] Full width at half-maximum of PL in neat films. [e] Ultraviolet photoelectron spectroscopy (Riken-keiki, AC-2). [f] LUMO obtained from the HOMO and the optical band gap.

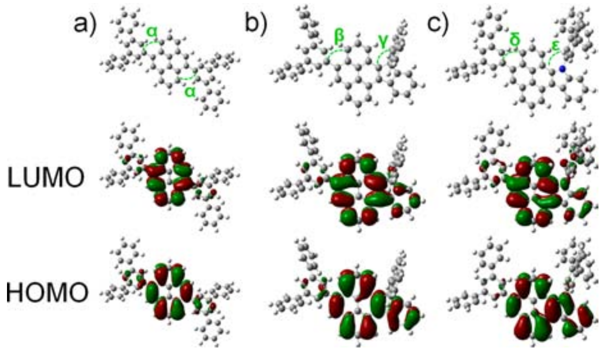


Figure 3. Optimized geometries and HOMO/LUMO electron density distributions of (a) TP-4,9-P-TP, (b) TP-PFF, and (c) TP-PFC-TP.

the T_g of TP-4,9-P-TP was 118 °C and the T_g values of TP-PFF and TP-PFC-TP were, respectively, 187 and 176 °C, indicative of their high thermal stabilities. In general, when an organic compound is applied to an OLED device, the device lifetime can be reduced by the joule heating effect during its operation, and thermal stability is highly correlated with device lifetime.[19] Therefore, a device that includes a fused-core derivative can be expected to have a longer lifetime than that with a single pyrene core derivative.

The synthesized compounds were used as nondoped emitting layers (EMLs) in OLEDs with the following structures: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized compounds (35 nm)/Alq_3 or TPBi (15 nm)/LiF (1 nm)/Al (200 nm). The OLED properties are summarized in Table 2.

Table 2. EL Performance of Synthesized Compounds

compd	$V_{on}{}^a$ (V)	$\eta_c{}^b$ (cd/A)	$\eta_p{}^c$ (lm/W)	$\lambda_{max}{}^d$ (nm)	CIE$_{(x,y)}{}^d$
TP-4,9-P-TP	5.4	2.11	0.87	455	(0.16, 0.14)
TP-PFF	4.5	3.24	1.41	457	(0.15, 0.13)
TP-PFC-TP	3.1	3.99	2.18	490, 518	(0.23, 0.50)

[a] Turn-on voltage measured at 1 cd/m^2. [b] Current efficiency at 10 mA/cm^2. [c] Power efficiency at 10 mA/cm^2. [d] Measured at 10 V.

At 10 mA/cm^2, the operating voltages of the devices with the fused-core TP-PFF and TP-PFC-TP compounds were 7.9 and 6.5 V, respectively—less than the 8.4 V for the device with the pyrene core containing TP-4,9-P-TP (Figure 4a). While the LUMO energy levels of these three compounds were similar, the HOMO energy levels of TP-PFF and TP-PFC-TP, at −5.70 and −5.51 eV, were higher than the −5.81 eV of TP-4,9-P-TP (Table 1 and Figure S19). These results imply that hole injection from NPB acting as a hole-transporting layer (HTL) to the EML is relatively easy. In addition, as structural characteristics of the fused-core, fluorene and carbazole with hole-transporting functions are fused with pyrene. The improved hole transporting abilities of TP-PFF and TP-PFC-TP probably helped the performances of their devices compared to TP-4,9-P-TP. For such reasons, turn-on voltages were also improved, i.e., reduced, in the fused-core TP-PFF and TP-PFC-TP devices to 4.5 and 3.1 V from 5.4 V for TP-4,9-P-TP.

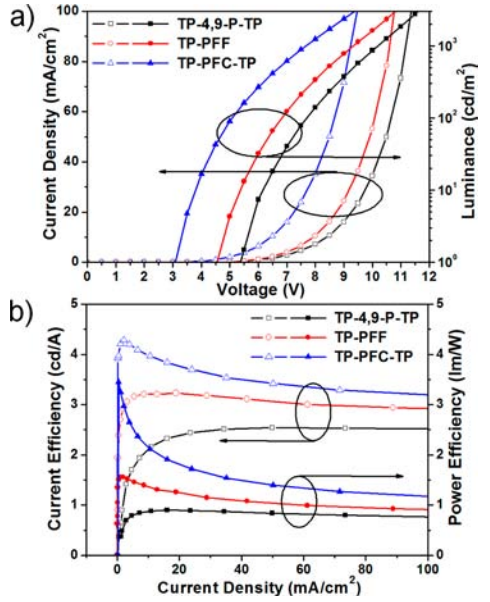


Figure 4. (a) Current density−voltage-luminance characteristics. (b) Current and power efficiency as a function of current density.

Figure 4b, Figure S20, and Table 2 show the current efficiency, power efficiency, EL spectra and CIE color coordinates of each device. TP-4,9-P-TP yielded efficiencies of 2.11 cd/A and 0.87 lm/W and a blue emission of (0.16, 0.14). TP-PFC-TP showed efficiencies of 3.99 cd/A and 2.18 lm/W, with a greenish-blue emission of (0.23, 0.50). TP-PFF yielded values of 3.24 cd/A, 1.41 lm/W, and (0.15, 0.13). The current and power efficiency values of TP-PFF were about 50% and 60% greater, respectively, than those of TP-4,9-P-TP, and slightly deeper blue color coordinates were shown. However, considering that the PL$_{max}$ in the film state was 449 nm, these color coordinates were inappropriate. The commonly used Alq_3 ETL material had to be replaced in order to adjust the emission range. The 453 nm EL$_{max}$ value of the TP-PFF device that used TPBi as the ETL was closer to the PL$_{max}$ in film than was the EL$_{max}$ value of the device that used Alq_3. Also, the TP-PFF device showed a relatively deep blue emission with color coordinates of (0.15, 0.12) and efficiencies of 3.53 cd/A and 1.65 lm/W (Figure S21). This improvement resulted from the greater hole-blocking effect of TPBi than Alq_3.[10a]

Figure S22 shows the lifetime of each device. When measured at 1000 cd/m^2, the lifetime was 9.9 h for TP-4,9-P-TP and 40.8 and 30.4 h for TP-PFF and TP-PFC-TP, i.e., a 3−4 times longer lifetime for the fused-core than for the pyrene-core derivative. These increased lifetimes resulted from their high current efficiencies and excellent thermal stabilities.

In this study, a new approach for forming fused-core structures was introduced: compounds using the 4 and 9 positions of pyrene were synthesized with derivatives having PFF and PFC cores. In this way, new fused-core chromophores were synthesized by using a pyrene core and fluorene or carbazole groups. In addition, their optical and EL properties were characterized: a large internal torsion angle in film, especially for TP-PFF, led to a blue-shifted $\mathrm{PL_{max}}$ compared to that of TP-4,9-P-TP, creating a blue chromophore with a 30 nm narrower fwhm; also, the TP-PFF EL device showed a reduced turn-on voltage, roughly 50% increase in current efficiency, and 4-fold increase in lifetime.

The new compounds showed excellent characteristics in the field of blue light-emitting materials for OLEDs. Moreover, the new approach can be used to design and synthesize new fused aromatic systems, based on combining chromophores other than pyrene, such as anthracene, phenanthrene, and chrysene, and hence find use in other applications such as OTFT and OPV. Introduction of diverse side groups can also produce many new organic functional materials and should result in the development of organic materials with outstanding characteristics in the future.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01793.

Synthetic and experimental procedures, NMR, energy diagrams, EL spectra, and additional references (PDF)

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Notes

The authors declare no competing financial interest.

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