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#### New 9-(fluoren-2-yl)anthracene derivatives with combined blue-light-emitting and hole-transporting characteristics have been developed that exist in a stable amorphous state and deliver high fluorescence quantum yields.





# **FULL PAPER**

#### **Blue Light-Emitting Diodes**

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## Synthesis and Characterization of 9-(Fluoren-2-yl)anthracene Derivatives as **Efficient Non-Doped Blue Emitters for Organic Light-Emitting Diodes**

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Keywords: Donor-acceptor systems / Molecular electronics / Thin films / Solid-state structures / Nonlinear optics / Organic light-emitting diodes

A series of 9-(fluoren-2-yl)anthracene derivatives bearing either thiophene (FATh), triphenylamine (FAT and FATT) or pyrene (FATP) moieties as substituents have been designed, synthesized, and characterized as non-doped blue emitters for organic light-emitting diodes (OLEDs). Their optical, electrochemical and thermal properties have been investigated, and their molecular structure-property relationships were evaluated. All FAT, FATT and FATP compounds possess combined blue-light-emitting and hole-transporting characteristics, and showed stable amorphous states with high fluorescence quantum yields in solution (up to 89%) and strong

## Introduction

Since the ground-breaking works on the first organic light-emitting diodes (OLEDs) by Tang and co-workers in 1987,<sup>[1]</sup> OLEDs have attracted enormous attention from the scientific community due to their high technological potential for the next generation of full-color-flat-panel displays<sup>[2]</sup> and lighting applications.<sup>[3]</sup> In today's developments of OLED technologies, trends of OLED studies are mainly focused on the optimization of device structures and on developing new emitting materials. Clearly, the key point of OLED development for full-color flat displays is to find materials that emit pure colors of red, green and blue (RGB) with excellent emission efficiency and high stability. The performance of blue OELDs is usually inferior to that of green and red OLEDs due to poor carrier injection into the emitters,<sup>[4]</sup> and hence the electroluminescent (EL) properties of blue devices need to be improved, particularly in

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luminance in the OLED devices, whereas FATh showed poor photoluminescent and electroluminescent properties. Efficient, non-doped blue and Alg3-based green OLEDs were fabricated and characterized. The blue and green devices with maximum luminance efficiencies and CIE coordinates of 3.17 cd A<sup>-1</sup> and (0.13, 0.14), and 3.81 cd A<sup>-1</sup> and (0.28, 0.50) were achieved, respectively, with FATT having 4-{bis[4'-(diphenylamino)biphenyl-4-yl]amino}phenyl substituents as emitting layer and hole-transporting layer, respectively. These devices also showed considerably low turn-on voltages of 3.0 and 2.6 V, respectively.

terms of EL efficiencies and color purity. Therefore, one area of continuing research in this field is the pursuit of a stable, blue-emitting material.<sup>[5]</sup> Although many fluorescent blue emitters have been reported, such as anthracene derivatives,<sup>[6]</sup> phenylene derivatives,<sup>[7]</sup> pyrene derivatives,<sup>[8]</sup> fluorene derivatives,<sup>[9]</sup> carbazole derivatives,<sup>[10]</sup> aromatic hydrocarbons.<sup>[11]</sup> triarylamine derivatives.<sup>[12]</sup> and phosphorescent iridium complexes,<sup>[13]</sup> there is still a clear need for further improvements in terms of efficiency and color purity compared to red and green emitters. Due to its unique chemical and electron-rich structure, low electronic band gap and strong blue fluorescence, anthracene has been used as a building block to form many emissive materials.<sup>[6,14]</sup> It has also been reported that incorporation of anthracene and its 9,10-substituted derivatives into polymer main-chains<sup>[15]</sup> or linked as pendent groups<sup>[16]</sup> has helped to solve the problem of preparation of films with good optical quality or to suppress excimer formation. To date, many kinds of anthracene-functionalized materials have been synthesized and considered for several applications,<sup>[17]</sup> and some of them were found to be promising blue emitters for OLEDs.<sup>[18]</sup> Recently, we have reported on the development of anthracene derivatives with the combined characteristics of blue-light-emitting and hole-transporting materials.<sup>[19]</sup> Non-doped blue OLEDs with a maximum efficiency of 1.65 cd A<sup>-1</sup> was attained. However, new classes of anthracene-based blue-light emitters with improvements in terms of efficiency and color purity remain to be explored.

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#### 9-(Fluoren-2-yl)anthracene Derivatives

In this work, we prepared a series of blue-light-emitting small molecules based on 9-(fluoren-2-yl)anthracene bearing thiophene, triphenylamine and pyrene moieties as substituents. Their physical and photophysical properties were investigated with the aim of understanding their structure-property relationships and developing novel molecular  $\pi$ -conjugated materials. The introduction of planar thiophene would allow a long  $\pi$ -conjugation system to be achieved, whereas integration of the bulky triphenylamine could suppress aggregation of the planar anthracene ring, as well as improve the hole-carrier injection ability and thermal stability of the anthracene.<sup>[20]</sup> Incorporation of a pyrene unit, which is a highly blue fluorescent chromophore, into the cruciform of this platform is an effective way to maintain the high blue emissive ability of pyrene in the solid state, which significantly impacts the emission behavior of materials and devices. Fluorene also has a number of advantages, including its capability to emit in the blue part of the visible spectrum, and its chemical and photochemical stability.<sup>[9,21]</sup> Investigations on OLED device fabrication and characterization of these materials are also described.

## **Results and Discussion**

#### Synthesis and Quantum Chemical Calculations

The target anthracene derivatives were synthesized as illustrated in Scheme 1. 9-Bromo-10-(9,9-dihexylfluoren-2yl)anthracene (2) obtained from the reaction of 2-iodo-9,9dihexylfluorene (1) and (10-bromoanthracen-9-yl)boronic

acid was cross-coupled with either [4-(diphenylamino)phenyl]boronic acid or (thiophen-2-yl)boronic acid in the presence of [Pd(PPh<sub>3</sub>)<sub>4</sub>] as catalyst and 2 M Na<sub>2</sub>CO<sub>3</sub> as base in tetrahydrofuran (THF) to give 9-(9,9-dihexylfluoren-2yl)-10-[4-(diphenylamino)phenyl]anthracene (FAT) and 9-(9,9-dihexylfluoren-2-yl)-10-(thiophen-2-yl)anthracene (FATh), respectively, as light-yellow solids in good yields. From FAT, the triphenylamine- and pyrene-functionalized molecules, namely 9-(4-{bis[4'-(diphenylamino)biphenyl-4yl]amino}phenyl)-10-(9,9-dihexylfluoren-2-yl)anthracene (FATT) and 9-(4-{bis[4-(pyren-1-yl)phenyl]amino}phenyl)-10-(9,9-dihexylfluoren-2-yl)anthracene (FATP), respectively, were synthesized in two steps. Bromination of FAT with N-bromosuccinimide (NBS) in THF provided 9-{4-[bis(4-bromophenyl)amino]phenyl}-10-(9,9-dihexylfluoren-2-yl)anthracene (3) in 96% yield followed by cross-coupling of the resulting dibromo derivative 3 with either (pyren-2yl)boronic acid or [4-(diphenylamino)phenyl]boronic acid catalyzed by [Pd(PPh<sub>3</sub>)<sub>4</sub>]/Na<sub>2</sub>CO<sub>3</sub> afforded FATP and FATT in good yields (54-69%) as yellow and light-yellow solids, respectively. The chemical structures and purities of these materials were characterized unambiguously by NMR and IR spectroscopy and mass spectrometry. All had good solubility in most organic solvents at room temperature, resulting from their bulky structures and the presence of *n*hexyl groups at C-9 of the fluorene ring. As a result, no crystallization thin film should be obtained from solution casting.

The optimized structures of FATh, FAT, FATT and FATP calculated by the TDDFT/B3LYP/6-31G(d,p) method<sup>[22]</sup> revealed that all molecules adopted noncoplanar



Scheme 1. Synthesis of the 9-(fluoren-2-yl)anthracene derivatives.

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Table 1. Physical data of the materials.

Compd.	$\lambda_{\mathrm{abs}}^{\mathrm{[a]}}$ [nm]	λ <sub>em</sub> <sup>[a]</sup> [nm]	λ <sub>e</sub> <sup>[b]</sup> [nm]	$\Phi_{\mathrm{F}}^{\mathrm{[c]}}$	Stokes shift [nm] <sup>[d]</sup>	$T_{\rm g}/T_{\rm c}/T_{\rm m}/T_{\rm 5d}$ [°C] <sup>[e]</sup>	<i>E</i> <sub>1/2</sub> vs. Ag/Ag <sup>+</sup> [V] <sup>[f]</sup>	E <sup>OX</sup> onset [V] <sup>[f]</sup>	$E_{g}$ [eV] <sup>[g]</sup>	$E_{\rm g}$ calcd. [eV] <sup>[h]</sup>	HOMO/LUMO [eV] <sup>[i]</sup>
FATh	359, 378, 398	439	439	0.12	41	-/115/209/330	1.20, 1.45	1.12	2.96	3.11	-5.56/-2.60
FAT	359, 380, 399	484	458	0.73	85	79/_/_/390	0.95, 1.21	0.88	2.90	2.93	-5.32/-2.44
FATT	365, 381, 401(sh)	525	471	0.80	125	147/_/_/401	0.73, 0.93, 1.11, 1.27	0.66	2.88	2.92	-5.10/-2.22
FATP	364, 379, 400(sh)	489	469	0.89	89	212///434	0.74 (E <sub>pc</sub> ), 0.90, 1.14, 1.66	0.86	2.90	3.10	-5.30/-2.40

[a] Measured in CH<sub>2</sub>Cl<sub>2</sub>. [b] Measured in thin film on quartz substrate. [c] Measured in CH<sub>2</sub>Cl<sub>2</sub> with quinine sulfate as a standard. [d] Calculated from the difference of  $\lambda_{abs}^{max}$  and  $\lambda_{em}^{max}$ . [e] Measured by DSC/TGA at a heating rate of 10 °C min<sup>-1</sup>. [f] Obtained from CV at a scan rate of 50 mV s<sup>-1</sup>. [g] Estimated from the optical absorption edge,  $E_g = 1240/\lambda_{onset}$ . [h] Obtained from quantum calculations by using TDDFT/B3LYP/6-31G(d,p). [i] Calculated by HOMO = -(4.44 +  $E^{OX}_{onset}$ ), and LUMO = HOMO  $E_g$ , where  $E^{OX}_{onset}$  is the onset potential of the oxidation.

conformations. Particularly, the planar anthracene unit was twisted nearly perpendicular to the adjacent thiophene, fluorene, and triphenylamine moieties because of steric repulsion between the anthracene peri-hydrogen atoms (1,8and 4,5-positions) and hydrogen atoms of those aromatic rings. Such structural characteristics can influence some of their electronic and physical properties such as a suppression of the conjugation. As depicted in Figure 1 (see also the Supporting Information), in the lowest unoccupied molecular orbitals (LUMO) of all compounds, the excited electrons locate only on electron-rich and electron-deficient anthracene moieties. In the highest occupied molecular orbitals (HOMO) of FATh and FAT,  $\pi$ -electrons locate on the anthracene and thiophene/triphenylamine moieties, whereas in the HOMO orbitals of FATT and FATP,  $\pi$ -electrons are delocalized mainly over the donor triphenylamine/triphenylamine and triphenylamine/pyrene peripheries, respectively. Participation of the fluorene ring in the  $\pi$ -conjugation system was diminished in all cases. The HOMO-LUMO energy gaps ( $E_{g}$  calcd.) were calculated, and the values deviated slightly from those obtained from the experimental results estimated from the optical edge (Table 1).



Figure 1. The HOMO and LUMO orbitals calculated by the TDDFT/B3LYP/6-31G(d,p) method.

Factors responsible for the discrepancies include the fact that the orbital energy difference between HOMO and LUMO is still an approximate estimation of the transition energy, because the transition energy also contains significant contributions from some two-electron integrals. The real situation is that an accurate description of the lowest singlet excited state requires a linear combination of a number of excited configurations.

### **Optical Properties**

Optical properties of FATh, FAT, FATT and FATP were investigated in  $CH_2Cl_2$  solution and thin film coated on quartz substrates. The results are presented Figure 2 and summarized in Table 1.



Figure 2. (a) UV/Vis absorption spectra in  $CH_2Cl_2$ . (b) PL spectra in  $CH_2Cl_2$  (line + symbol) and in thin film on quartz substrates (line).

Their UV/Vis spectra showed two absorption bands, which were assigned in terms of the strong absorption band in the region of 250–320 nm corresponding to the  $\pi$ - $\pi$ \* local electron transition of the individual aromatic units, and the absorption bands at longer wavelengths (350-425 nm) attributed to the characteristic  $\pi$ - $\pi$ \* electron transition of the anthracene. The intensities of the latter bands of FATT and FATP are more intense than those of FATh and FAT. The energy gaps  $(E_g)$  of the triphenylamine-substituted anthracenes FAT and FATT estimated from the optical onset were found to be identical (2.90 eV), whereas the  $E_{\rm g}$  of FATP was slightly lower (2.89 eV), and the  $E_g$  of FATh was as high as 2.96 eV. These compounds fluoresced in solution from bright-blue to blue-green with featureless photoluminescence (PL) spectra, which is similar to what has been observed for most 9,10-diphenylanthracenes.<sup>[6]</sup> The solution PL spectra of FAT and FATP redshifted with respect to that of FATh, whereas the PL spectra of FATT were further redshifted. These observations were in agreement with the results of theoretical and UV/Vis experiments. These materials showed a slight Stokes shift (41-125 nm), suggesting

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#### 9-(Fluoren-2-yl)anthracene Derivatives

less energy loss during the relaxation process and efficient fluorescence. The thin-film PL emission spectrum of FATh, shown in Figure 2b, was similar to its solution PL spectrum in terms of line shape, emission  $\lambda_{max}$  and full-width at halfmaximum, thus indicating that less, if any, solid-state packing occurred in this case due to its bulky molecular structure. In the cases of FAT, FATT and FATP, having more bulky structures, their thin-film PL spectra exhibited hypsochromic shifts of 20-54 nm compared with their corresponding solution spectra. This result may also be attributed to the aforementioned solid-state packing force, which prohibits the electron-vibration coupling between the triphenylamine substituent and the anthracene photoactive unit. The solution fluorescence quantum yields ( $\Phi_{\rm F}$ ) of FATh, FAT, FATT and FATP were 0.12, 073, 0.80 and 0.89, respectively. The results indicated that direct attachment of the thiophene ring to the luminous anthracene moiety in FATh lowered the  $\Phi_{\rm F}$  of the anthracene ( $\Phi_{\rm F}$  = 0.35-0.40).<sup>[23]</sup> The decrease of  $\Phi_{\rm F}$  with increasing numbers of thiophene units is usually observed in most of the thiophene oligomers as the molecule becomes more planar and likely to undergo fluorescence quenching by intermolecular  $\pi$ - $\pi$  stacking.<sup>[24]</sup> In contrast, replacing the thiophene ring with electron-donating triphenylamine in FAT and FATT significantly increased the  $\Phi_{\rm F}$  and the value was even higher in FATP, having highly fluorescent pyrene as peripheral substituents.

#### **Electrochemical and Thermal Properties**

The electrochemical behavior of all compounds was investigated by cyclic voltammetry (CV); the resulting data are shown in Figure 3 and summarized in Table 1.



Figure 3. (a) CV curves, and multiple-scan CV curves of (b) FATh, (c) FATT, and (d) FATP measured in  $CH_2Cl_2/nBu_4NPF_6$  at a scan rate of 50 mV s<sup>-1</sup>.

The CV curve of FATh showed two irreversible oxidation processes and identical CV curves under multiple scans, demonstrating the stability of the molecule (Figure 3b). The first oxidation wave corresponded to the removal of electrons from the terminal thiophene ring to form a radical cation. No oxidation peak at lower potential due to a dimerization coupling of such species was detected, unlike what is observed in most cases of  $\alpha$ -unsubstituted short oligothiophenes such as FTh,<sup>[25]</sup> which, under repeated CV scans, suffered an electrochemical oxidative dimerization reaction of the thiophene ring. In our case, this electrodimerization reaction could be prevented by steric hindrance generated by the nearby anthracene moiety. The CV curves of the triphenylamine-substituted anthracenes FAT and FATT were found to exhibit two and four well-separated (quasi-) reversible oxidation processes at 0.95 and 1.21 V, and 0.73, 0.93, 1.11 and 1.27 V, respectively, whereas the CV curve of FATP showed three irreversible processes at 0.90, 1.14, and 1.66 V, with an additional peak at a lower potential (0.74 V) on the cathodic scan  $(E_{pc})$ . The first oxidation wave was assigned to the removal of electrons from the triphenylamine moiety resulting in the formation of triphenylamine radical cations (TPA+·). This oxidation potential was found to decrease from 0.95 (FAT) to 0.90 (FATP) and to 0.73 V (FATT) due to the extended delocalization of the  $\pi$ -electrons between the triphenylamine and pyrene in FATP, and the two triphenylamines in FATT, as observed in the TDDFT calculation results. The multiple CV scans of both FAT and FATT revealed identical CV curves, indicating that no oxidative coupling (or a weak oxidative coupling if any) at the *p*-phenyl rings of the peripheral triphenylamine led to electropolymerization and that they are electrochemically stable molecules. Usually, this type of electrochemical coupling reaction is detected in triphenylamine derivatives with an unsubstituted para position of the phenyl ring such as 2,7-bis{2-[4-(diphenylamino)phenyl]-1,3,4-oxadiazol-5-yl}-9,9-bis(n-hexyl)fluorene.<sup>[26]</sup> In the cases of FAT and FATT, the steric bulk and resultant stability of the radical cation formed play an important role in preventing both molecules from undergoing such an electrochemical reaction. The radical cations TPA<sup>+</sup> of FAT and FATT are stabilized by electron delocalization from TPA<sup>+-</sup> through the adjacent anthracene ring and triphenylamine moiety, respectively, as depicted in Figure 4. The significant steric effects on the radical center formed prevent such a radical from undergoing radical-radical dimerization coupling. However, the radical cation of FATP is stabilized by electron delocalization through the substituted electron-rich pyrene ring to form a pyrene radical cation (Py<sup>+</sup>), which is relatively less stable compared with the TPA<sup>+-</sup> of FAT and FATT. The Py<sup>+-</sup> readily undergoes a radical-radical dimerization coupling to form a stable neutral pyrene dimer, as indicated by the presence of the cathodic peak at 0.74 V in their first CV scan and an increasing change in the CV curves under repeated CV scans (Figure 3d). However, this type of radical-radical coupling reaction will become inactive in nondiffusion systems or the solid state. Moreover, under these CV experiment condi-

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Figure 4. Proposed oxidation and electrochemical reaction of the triphenylamine and pyrene moieties.

tions, no distinct reduction process was observed in any case.

The HOMO and LUMO energy levels of FATh, FAT, FATT and FATP were calculated from the oxidation onset potentials ( $E_{onset}$ ) and energy gaps ( $E_g$ ), and the results are summarized in Table 1. The HOMO levels of these materials ranged from 5.10 to 5.56 eV, matching well with the work functions of the gold (Au) or indium tin oxide (ITO) electrodes and hence favoring the injection and transport of holes.

The thermal properties of FATh, FAT, FATT and FATP were investigated by thermal gravimetric analysis (TGA) and by differential scanning calorimetry (DSC) (Table 1 and Figure S3). These results suggest that all compounds are thermally stable materials with 5% weight loss temperatures  $(T_{5d})$  well over 330 °C. The DSC thermogram of FATh showed a broad exothermic peak due to crystallization  $(T_c)$  at 115 °C followed by an endothermic melting peak (T<sub>m</sub>) at 209 °C. Compounds FAT, FATT and FATP, bearing triphenylamine moieties as substituents, exhibited different thermal behavior. The asymmetric and bulky nature of this group may play an additional role in molecular packing. Their DSC thermograms revealed only an endothermic baseline shift owing to glass transition  $(T_g)$  with no crystallization and melting peaks at higher temperature. The  $T_{\rm g}$  values increase from 79 °C for FAT to 147 °C for FATT and to 212 °C for FATP. The ability of these materials to form a molecular glass with the possibility of preparing thin films both by evaporation and by solution casting is highly desirable for applications in electroluminescent devices.

#### **Electroluminescence Properties**

To investigate the electroluminescence properties of FATh, FAT, FATT and FATP, blue OLED devices were fabricated with the following device structure: ITO/ PEDOT:PSS/EML(50 nm)/BCP(40 nm)/LiF(0.5 nm):Al-

(150 nm), in which the materials developed here were used as the blue emitting layer (EML). Conductive polymer poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate)



Figure 5. EL (line + symbol) and PL (line) spectra of the materials and their OLED devices.



Figure 6. (a) *J-V-L* characteristics and (b) variation in luminance efficiency with current density of the fabricated blue OLEDs.



Table 2. Device characteristics of the fabricated OLEDs.
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Device	EML/HTL	$V_{\rm on}  [V]^{[c]}$	V <sub>100</sub> [V] <sup>[d]</sup>	λ <sub>max</sub> [nm] <sup>[e]</sup>	$L_{\rm max}$ [V] (V [cd m <sup>-2</sup> ]) <sup>[f]</sup>	$J[\mathrm{mAcm^{-2}}]^{\mathrm{[g]}}$	$\eta  [cd  A^{-1}]^{[h]}$	CIE $(x, y)^{[i]}$
$I^{[a]}$	FATh	5.2	6.9	440, 463sh	504 (9.4)	237	0.48	0.15, 0.13
$II^{[a]}$	FAT	3.8	5.2	457	2621 (8.6)	436	1.28	0.14, 0.13
III <sup>[a]</sup>	FATT	3.0	3.9	471	8459 (8.8)	618	3.17	0.13, 0.14
IV <sup>[a]</sup>	FATP	3.3	4.5	472	6404 (9.6)	672	1.42	0.13, 0.23
$V^{[b]}$	FATT	2.6	3.8	511	19246 (9.6)	1385	3.81	0.28, 0.50
VI <sup>[b]</sup>	FATP	3.5	4.4	517	16667 (9.8)	1268	2.11	0.27, 0.46
VII <sup>[b]</sup>	NPB	2.8	3.8	515	24803 (10.2)	1517	3.52	0.28, 0.53
VIII <sup>[b]</sup>	_	4.2	5.4	518	4961 (10.0)	693	0.91	0.30, 0.54

[a] ITO/PEDOT:PSS/EML/BCP/LiF:Al. [b] ITO/PEDOT:PSS/HTL/Alq3/LiF:Al. [c] Turn-on voltage at 1 cd m<sup>-2</sup>. [d] Voltage at luminance of 100 cd m<sup>-2</sup>. [e] Emission maximum. [f] Maximum luminance at applied voltage. [g] Current density at maximum luminance. [h] Luminance efficiency. [i] CIE coordinates.

(PEDOT:PSS) as hole injection layer and 2,9-dimethyl-4,7diphenyl-1,10-phenanthroline (BCP) as hole-blocking layer were also used to enable high-performance devices. The electroluminescent (EL) spectra and current density-voltage-luminance (*J-V-L*) characteristics of the devices are shown in Figures 5 and 6, and their electrical parameters are summarized in Table 2.

The results revealed that FAT, FATT and FATP, having the electron-donating triphenylamine group attached to the 9-(fluoren-2-yl)anthracene moiety, had far better EML properties in the OLEDs than FATh, having thiophene as the substituent, both in terms of turn-on voltage and luminance efficiency ( $\eta$ ). The device performance of the blue OLED devices (maximum luminance and  $\eta$ ) matched the observed PL quantum efficiencies of these materials (Table 1). Fluorescence quantum yields ( $\Phi_F$ ) of FAT, FATT and FATP were significantly higher than that of FATh.

It has been demonstrated that the efficiency of an OLED depends both on the balance of electrons and holes and the  $\Phi_{\rm F}$  of the emitter.<sup>[27]</sup> Device III, having FATT as EML, showed the best performance with a high maximum brightness of 8459 cd m<sup>-2</sup> at 8.8 V, an  $\eta$  of 3.17 cd A<sup>-1</sup> and a low turn-on voltage of 3.0 V, which is considered to be one of the lowest turn-on voltages seen for blue OLEDs. Devices II and IV, using FAT and FATP as EML, respectively, exhibited lower device performance with maximum brightness, turn-on voltage and  $\eta$  of 2621 cd m<sup>-2</sup>, 3.8 V and 1.28 cd A<sup>-1</sup>, and 6404 cd m<sup>-2</sup>, 3.3 V and 1.42 cd A<sup>-1</sup>, respectively. These results can be explained by analysis of band energy diagrams of all devices. It is found that the HOMO levels of all compounds (5.32–5.56 eV) fell between those of PEDOT:PSS (5.00 eV) and BCP (6.50 eV) (Figure 7). However, there is a barrier of around 0.1 eV for holes to migrate from the PEDOT:PSS/EML interface in device III, whereas such energy barriers are wider in devices II and IV (0.30-0.32 eV) and even larger in device I (0.56 eV). This suggests that migration of the hole from the PEDOT:PSS to the EML layer is more effective in device III, resulting in the charge efficiently recombining in the emitting layer and better device performance compared with both devices II and IV. Under applied voltage, devices I-IV emitted a bright blue emission with peaks centered at 404, 457, 471, and 472, respectively (Figure 5). The electroluminescence (EL) spectra of all diodes matched their corresponding thin-film

PL spectra. Device I, having FATh as EML, displayed a shoulder emission peak at the longer wavelength (463 nm) owing to excimer and exciplex species formed at the interface of EML and HBL materials, which often occurs in devices fabricated from EML with planar molecular structure. However, no such emission shoulder was observed in devices II–IV. In these cases, the formation of those species could be prevented by the steric bulk of FAT, FATT and FATP. Additionally, stable emission was obtained from all devices, with the EL spectra not changing much over the entire drive voltages.



Figure 7. Schematic energy-level diagram of each material in the devices.

As the HOMO levels of both FATT and FATP match well with the work function of ITO (4.8 eV), these compounds may potentially serve as hole-transporting materials (HTM). To test this hypothesis, double-layer green OLED with the structure of ITO/PEDOT:PSS/ devices HTL(40 nm)/Alq3(50 nm)/LiF(0.5 nm):Al(150 nm) were fabricated, in which the materials developed here were used as hole-transporting layers (HTL) and tris(8-hydroxyquinoline)aluminum (Alq3) as the green-light-emitting (EML) and electron-transporting layers (ETL). The reference devices (devices VII and VIII) with and without a commonly used commercial HTM, N,N'-bis(naphthalen-2-yl)-N,N'-diphenylbenzidine (NPB), as HTL was made for comparison. By comparison with the reference device VIII, it was found that the incorporation of FATT and FATP in the devices (V and VI) as HTL not only increased the device efficiencies, but also significantly decreased the turn-on voltages of both diodes. Furthermore, their EL spectra were nearly identical. Moreover, the device characteristics in terms of luminous efficiency clearly demonstrated that the HTM

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abilities of these materials were greater than a commonly used HTM, NPB (device VII). Both devices (V and VI) exhibited light turn-on voltage at 1 cd m<sup>-2</sup> in the range 2.6-3.5 V and operating voltages at 100 cd m<sup>-2</sup> in the range 3.8-4.4 V, indicating a good performance for all devices (Figure 8 and Table 2). Device V, having FATT as HTL, exhibited the best performance, with a high maximum brightness of 19246 cd m<sup>-2</sup> for green OLED at 9.6 V, an  $\eta$  of  $3.81 \text{ cd } \text{A}^{-1}$  and a low turn-on voltage of 2.6 V, which is considered to be one of the lowest turn-on voltages found for green OLEDs. A slightly lower device performance was observed for device VI (FATP as HTL) (Table 2). Under applied voltage, both devices V and VI exhibited a bright green emission with peaks centered at 511 and 517 nm, and CIE coordinates of (0.28, 0.50) and (0.27, 0.46), respectively (Figure 5b). The EL spectra of these diodes matched the PL spectrum of Alq3, the EL of the reference devices VII and VIII, and also other reported EL spectra of Alq3-based devices.<sup>[28]</sup> No emission at longer wavelength owing to exciplex species formed at the interface of HTL and ETL materials, which often occurs in devices fabricated from HTL with planar molecular structure, was detected.<sup>[29]</sup> From these results and in view of the fact that a barrier for electron migration at the Alq3/HTL interface (0.60-0.78 eV) is higher than those for hole migration at the HTL/Alq3 interface (0.50-0.70 eV); hence, under the present device configuration of ITO/PEDOT:PSS/HTL/Alq3/LiF:Al, FATT and FATP would act only as HTL, and Alq3 would act preferably as an electron blocker more than as a hole blocker, with charge recombination thus confined to the Alq3 layer. More importantly, a stable emission was obtained from both diodes, with the EL spectra and CIE coordinates not changing over the entire applied voltage range. Although, many blue-emitting and hole-transporting materials have been reported, in terms of the amorphous morphology, high  $T_{g}$ and device efficiency, FATT is among the better bifunc-



Figure 8. (a) *J-V-L* characteristics and (b) variation in luminance efficiency with current density of the fabricated green OLEDs.

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## Conclusions

Blue-fluorescent materials based on 9-(fluoren-2-yl)anthracene, having either thiophene, triphenylamine and pyrene moieties as substituents, were successfully synthesized and characterized. All were thermally stable, with degradation temperatures well above 330 °C. By the inclusion of triphenylamine and pyrene as substituents, we were able to maintain the high emissive ability of anthracene in the solid state, and improve the amorphous stability of these materials. Molecules having electron-donating triphenylamine groups attached to the 9-(fluoren-2-yl)anthracene moiety displayed a combined light-emitting and hole-transporting characteristic for OLED. These materials also exhibited strong blue emission with fluorescent quantum efficiency over 89% in solution and strong electroluminescence in the solid state, whereas anthracene bearing thiophene as substituent showed poor photoluminescent and electroluminescent properties. Efficient non-doped blue and Alq3based green OLEDs with maximum luminance efficiencies and CIE coordinates of  $3.17 \text{ cd } \text{A}^{-1}$  and (0.13, 0.14), and 3.81 cd  $A^{-1}$  and (0.28, 0.50), respectively, were achieved with FATT having 4-{bis[4'-(diphenylamino)biphenyl-4-yl]amino}phenyl substituents as emitting layer and hole-transporting layer, respectively. Both devices also showed low turn-on voltages of 3.0 and 2.6 V, respectively, which are considered among the lowest turn-on voltages for blue and green OLEDs. According to these characteristics, these materials, especially FATT, have sufficient potential for use in fluorescence OLED applications.

### **Experimental Section**

Materials and Instruments: All reagents were purchased from Aldrich, Acros or Fluka, and used without further purification. All solvents were supplied by Thai companies and used without further distillation. THF was heated to reflux with sodium and benzophenone, and distilled prior to use. CH<sub>2</sub>Cl<sub>2</sub> for electrochemical measurements was washed with concd. H<sub>2</sub>SO<sub>4</sub> and distilled twice from calcium hydride. Chromatographic separations were carried out on Merck silica gel 60 (0.0630-0.200 mm). <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer with TMS as the internal reference by using CDCl<sub>3</sub> as solvent in all cases. Infrared (IR) spectra were measured as potassium bromide (KBr) discs with a Perkin-Elmer FTIR RXI spectrometer. UV/Vis spectra were recorded as dilute solutions in CH<sub>2</sub>Cl<sub>2</sub> with a Perkin-Elmer UV Lambda 25 spectrometer. Photoluminescence spectra and fluorescence quantum yields ( $\Phi_{\rm F}$ ) were recorded as dilute solutions in CH<sub>2</sub>Cl<sub>2</sub> and thin films obtained by thermal evaporation with a Perkin-Elmer LS 50B Luminescence Spectrometer. Quinine sulfate solution in 0.01 M H<sub>2</sub>SO<sub>4</sub> ( $\Phi_{\rm F}$  = 0.54) was used as a reference standard.<sup>[30]</sup> DSC and TGA were performed with a Mettler DSC823e thermal analyzer and a Rigaku TG-DTA 8120 thermal analyzer, respectively, under nitrogen with heating rates of 10 °C min<sup>-1</sup>. CV was carried out with an Autolab potentiostat

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PGSTAT 12 with a three-electrode system (platinum counter electrode, glassy carbon working electrode and  $Ag/Ag^+$  reference electrode) at a scan rate of 50 mV s<sup>-1</sup> in the presence of  $nBu_4NPF_6$  as a supporting electrolyte in CH<sub>2</sub>Cl<sub>2</sub> under argon. Melting points were measured with an Electrothermal IA 9100 series digital melting point instrument and are uncorrected. High-resolution mass spectrometry (HRMS) analysis was performed by the Mass Spectrometry Unit, Mahidol University, Thailand.

Fabrication and Characterisation of DSSCs: Blue OLED devices using FATh, FAT, FATT and FATP as EML with structure ITO/ PEDOT:PSS/EML(50 nm)/BCP(40 nm)/LiF(0.5 nm):Al(150 nm) and double-layer green OLED devices using FATT, FATP and NPB as HTL with structure ITO/PEDOT:PSS/HTL(40 nm)/ Alq3(50 nm)/LiF(0.5 nm):Al(150 nm) were fabricated and characterized as follows. The patterned indium tin oxide (ITO) glass substrate with a sheet resistance of  $14 \Omega sq^{-1}$  (purchased from Kintec Company) was cleaned and dried at 60 °C in a vacuum oven. A 50 nm thick PEDOT:PSS layer was spin-coated on top of ITO from a 0.75 wt.-% dispersion in water at a spin speed of 3000 rpm for 20 s and dried at 200 °C under vacuum for 15 min. Thin films of each organic EML or HTL were then deposited on top by evaporation from resistively heated alumina crucibles at an evaporation rate of 0.5-1.0 nm s<sup>-1</sup> in a vacuum evaporator for deposition (ES280, ANS Technology) under a base pressure of ca.  $10^{-5}$  mbar. The film thickness was monitored and recorded with a quartz oscillator thickness meter (TM-350, Maxtek). A 40 nm thick layer of BCP or a 50 nm thick layer of Alq3 was then deposited on the organic EML or HTL, respectively, without breaking the vacuum chamber. The chamber was then vented with dry air to load the cathode materials and pumped back; a 0.5 nm thick layer of LiF and a 150 nm thick layer of aluminum were then subsequently deposited through a shadow mask on top of the EML/HTL film without braking vacuum to form active diode areas of 4 mm<sup>2</sup>. The measurement of device efficiency was performed according to M. E. Thomson's protocol, and the external quantum efficiencies of the device was calculated by using the procedure reported previously.<sup>[31]</sup> Current density-voltage-luminescence (J-V-L) characteristics were measured simultaneous with a Keithley 2400 source meter and a Newport 1835C power meter equipped with a Newport 818-UV/CM calibrated silicon photodiode. The EL spectra were acquired with an Ocean Optics USB4000 multichannel spectrometer. All the measurements were performed under ambient atmosphere at room temperature.

**Quantum Chemical Calculations:** The ground-state geometries of all molecules were fully optimized by using density functional theory (DFT) at the B3LYP/6-31G(d,p) level, as implemented in Gaussian 09.<sup>[22]</sup> TDDFT/B3LYP calculation of lowest excitation energies were performed at the optimized geometries of the ground states.

**9-Bromo-10-(9,9-dihexylfluoren-2-yl)anthracene (2):** A mixture of 2-iodo-9,9-bis(*n*-hexyl)fluorene (1)<sup>[32]</sup> (1.28 g, 2.79 mmol), (10-bromoanthracen-9-yl)boronic acid (0.84 g, 2.79 mmol),  $[Pd(PPh_3)_4]$  (0.065 g, 0.12 mmol), and a 2 M Na<sub>2</sub>CO<sub>3</sub> (8 mL) aqueous solution in THF (12 mL) was degassed with N<sub>2</sub> for 5 min. The reaction mixture was stirred at reflux under N<sub>2</sub> for 18 h. After cooling to room temperature, water (50 mL) was added, and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL). The combined organic phases were washed with water (50 mL) and brine solution (50 mL), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were removed to dryness. Purification by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>/hexane, 1:4) followed by recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) afforded the product (0.66 g, 52%) as a light-yellow solid

(m.p. 158 °C). FTIR (KBr):  $\tilde{v} = 2928$ , 1462, 1438, 1344, 1260, 1020, 890 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.76-0.88$  (m, 10 H), 1.09–1.14 (m, 12 H), 1.95–2.01 (m, 4 H), 7.34–7.40 (m, 7 H), 7.59 (t, J = 8.8 Hz, 2 H), 7.72 (d, J = 9.0 Hz, 2 H), 7.81 (dd, J = 3.3, 2.7 Hz, 1 H), 7.89 (d, J = 7.5 Hz, 1 H), 8.62 (d, J = 8.7 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 13.99$ , 22.47, 23.85, 29.60, 31.52, 40.37, 55.26, 119.62, 119.83, 122.92, 124.87, 125.46, 125.91, 126.54, 126.92, 127.32, 127.44, 129.73, 130.30, 131.20, 136.90, 140.81, 150.95 ppm. HRMS: calcd. for C<sub>39</sub>H<sub>42</sub>Br [M<sup>+</sup>] 589.2432; found 589.3042.

**9-(9,9-Dihexylfluoren-2-yl)-10-(thiophen-2-yl)anthracene** (FATh): FATh (0.51 g, 76%) was synthesized from **2** and (thiophen-2-yl)boronic acid in a manner similar to that for **2** and obtained as a light-yellow solid (m.p. 186 °C). FTIR (KBr):  $\tilde{v} = 2930$ , 1458, 1440, 1380, 1224, 1028, 824 cm<sup>-1.</sup> <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.78$ – 0.82 (m, 10 H), 1.12–1.18 (m, 12 H), 2.03 (t, J = 9.0 Hz, 4 H), 7.34–7.47 (m, 11 H), 7.66 (d, J = 4.8 Hz, 1 H), 7.79 (d, J = 8.7 Hz, 2 H), 7.84 (d, J = 7.8 Hz, 1 H), 7.92–7.98 (m, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 14.03$ , 22.51, 23.89, 29.66, 31.55, 40.45, 55.27, 119.64, 119.82, 122.92, 125.10, 125.57, 126.03, 126.73, 126.91, 127.03, 127.20, 127.26, 128.66, 129.50, 129.75, 131.65, 137.40, 139.17, 139.31, 140.87, 141.05, 150.91, 151.02 ppm. HRMS: calcd. for C<sub>43</sub>H<sub>45</sub>S [M<sup>+</sup>] 593.3197; found 593.3186.

**9-(9,9-Dihexylfluoren-2-yl)-10-[4-(diphenylamino)phenyl]anthracene** (FAT): FAT (0.52 g, 79%) was synthesized from **2** and [4-(diphenylamino)phenyl]boronic acid in a manner similar to that for **2** and obtained as a light-yellow solid (m.p. 146 °C). FTIR (KBr):  $\tilde{v} = 2929$ , 1590, 1494, 1380, 1273, 1019, 823, 746 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.75-0.80$  (m, 10 H), 1.09–1.16 (m, 12 H), 1.98–2.03 (m, 4 H), 7.07–7.12 (t, J = 7.0 Hz, 2 H), 7.26–7.46 (m, 21 H), 7.77–7.95 (m, 6 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 14.02$ , 22.51, 23.89, 31.55, 40.47, 55.26, 119.61, 119.78, 122.91, 123.10, 123.13, 124.71, 124.97, 126.16, 126.88, 127.10, 127.19, 129.40, 129.89, 130.10, 130.15, 132.14, 132.69, 136.92, 137.70, 140.54, 141.00, 147.17, 147.84, 150.86, 150.98 ppm. HRMS: calcd. for C<sub>57</sub>H<sub>56</sub>N [M<sup>+</sup>] 754.4407; found 754.4386.

10-{4-[Bis(4-bromophenyl)amino]phenyl}-10-(9,9-dihexylfluoren-2yl)anthracene (3): To a solution of FAT (0.30 g, 0.39 mmol) in THF (25 mL) was added NBS (0.15 g, 0.83 mmol) in small portions. Soon after, the starting material was completely consumed, water (10 mL) was then added, and the mixture was extracted with  $CH_2Cl_2$  (2 × 50 mL). The combined organic phases were washed with water (50 mL) and brine (50 mL), dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvents were removed to dryness. Purification by recrystallization (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) gave the product (0.35 g, 97%) as a light-yellow solid (m.p. 194 °C). FTIR (KBr): v  $= 2990, 2686, 2520, 2410, 2360, 1726, 1586, 1422, 1266, 896 \text{ cm}^{-1}.$ <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.75–0.80 (m, 10 H), 1.09–1.26 (m, 12 H), 2.00-2.05 (m, 4 H), 7.09-7.16 (m, 4 H), 7.22-7.47 (m, 17 H), 7.58–7.67 (m, 2 H), 7.78–7.83 (m, 3 H), 7.93–7.96 (m, 1 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.00, 22.50, 23.89, 29.66, 31.55, 40.46, 55.41, 115.92, 116.30, 119.58, 119.63, 119.79, 119.96, 122.28, 122.95, 123.33, 123.71, 124.99, 125.11, 125.92, 126.17, 126.87, 127.15, 127.22, 127.68, 128.62, 129.86, 130.10, 131.31, 132.48, 132.58, 132.65, 133.96, 136.40, 137.58, 137.84, 140.35, 140.54, 140.60, 140.97, 146.24, 146.27, 146.84, 150.89, 150.97 ppm. HRMS: calcd. for C<sub>57</sub>H<sub>53</sub>Br<sub>2</sub>N [MH<sup>+</sup>] 911.2524; found 912.3551.

**9-(4-{Bis|4-(pyren-1-yl)phenyl]amino}phenyl)-10-(9,9-dihexylfluoren-2-yl)anthracene (FATP):** FATP (0.11 g, 69%) was synthesized from **3** and (pyren-1-yl)boronic acid in a manner similar to that for **2** and obtained as a yellow-green solid (m.p. 188 °C). FTIR (KBr):  $\tilde{v} = 2990, 2684, 2520, 2408, 2360, 1726, 1588, 1266, 896 cm<sup>-1</sup>. <sup>1</sup>H$ 

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NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.76-0.80$  (m, 10 H), 1.10–1.16 (m, 12 H), 1.99–2.02 (m, 4 H), 7.34–7.55 (m, 11 H), 7.63 (d, J = 8.4 Hz, 6 H), 7.72 (d, J = 8.4 Hz, 4 H), 7.83 (d, J = 8.4 Hz, 3 H), 7.97 (d, J = 8.4 Hz, 3 H), 8.04 (t, J = 7.5 Hz, 2 H), 8.11 (d, J = 9.3 Hz, 8 H), 8.21 (t, J = 6.0 Hz, 4 H), 8.28 (d, J = 7.8 Hz, 2 H), 8.42 (d, J = 9.3 Hz, 2 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 14.03$ , 22.52, 23.91, 29.68, 31.57, 40.48, 55.28, 119.65, 119.80, 122.92, 124.11, 124.33, 124.77, 124.81, 125.03, 125.10, 125.44, 126.03, 126.18, 126.90, 127.13, 127.37, 127.47, 127.71, 128.56, 129.91, 130.16, 130.20, 130.51, 131.57, 132.47, 133.53, 135.87, 136.84, 137.44, 137.68, 137.73, 140.58, 141.01, 146.99, 147.03, 150.90, 150.99 ppm. HRMS: calcd. for C<sub>89</sub>H<sub>71</sub>N [MH<sup>+</sup>] 1153.5587; found 1154.5370.

**10-(4-{Bis**[4'-(diphenylamino)biphenyl-4-yl]amino}phenyl)-10-(9,9dihexylfluoren-2-yl)anthracene (FATT): FATT (0.09 g, 54%) was synthesized from **3** and [4-(diphenylamino)phenyl]boronic acid in a manner similar to that for **2** and obtained as a yellow-green solid (m.p. 148 °C). FTIR (KBr):  $\tilde{v} = 2990$ , 2686, 2360, 1726, 1588, 1422, 1266, 894 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta = 0.76-0.81$  (m, 5 H), 1.11 (m, 6 H), 2.02 (m, 2 H), 7.02–7.07 (m, 2 H), 7.16 (d, J =7.8 Hz, 6 H), 7.30 (d, J = 7.8 Hz, 4.5 H), 7.36–7.45 (7.5 H, m), 7.48–7.53 (2.5 H, m), 7.59 (d, J = 8.7 Hz, 2 H), 7.79–7.96 (m, 3 H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 14.03$ , 22.51, 23.90, 29.67, 30.92, 31.56, 40.48, 55.27, 119.63, 119.80, 122.89, 124.08, 124.39, 124.80, 125.03, 126.18, 126.17, 126.90, 127.10, 127.38, 127.54, 129.28, 129.91, 130.13, 132.26, 134.68, 136.87, 137.65, 137.70, 140.56, 141.01, 146.88, 147.74, 150.88, 150.99 ppm. HRMS: calcd. for C<sub>93</sub>H<sub>81</sub>N<sub>3</sub> [MH<sup>+</sup>] 1240.6464; found 1241.6255.

**Supporting Information** (see footnote on the first page of this article): Quantum chemical calculation results, multiple CV scans, DSC/TGA thermograms, and <sup>1</sup>H and <sup>13</sup>C NMR spectra.

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