Asymmetric anthracene-based blue host materials: synthesis and electroluminescence properties of 9-(2-naphthyl)-10-arylanthracenes[†]

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A series of bulky aryl-substituted asymmetric anthracene blue host materials, 9-(2-naphthyl)-10-(3-(1-naphthyl)phenyl)anthracene, where phenyl was varied from H (**5a**), Me (**5b**), Ph (**5e**), and 1-Naph (**5f**) at the 6-position and Me (**5c**) at the 2-position, was synthesized by Suzuki coupling reaction between 10-(2-naphthyl)anthracene-9-boronic acid and 1-(3-iodophenyl)naphthalene derivatives. A less bulky aryl-substituted anthracene, 9-(2-naphthyl)-10-(2,5-diphenyl)phenyl)anthracene (**5d**), was also synthesized for comparison. All asymmetric anthracenes showed high glass transition temperatures in the range of 84–153 °C. The photophysical and electrochemical properties in solution showed that the substituent at the 10-positions of the anthracene unit did not influence the blue emission of 420 nm and HOMO–LUMO energy level (5.5–2.5 eV). However, a gradual decrease of bathochromic shift in solid state PL was observed from the increaseg of the substituent bulkiness, exhibiting **5e** (18 nm) ≤ **5f** (19 nm) < **5c** (25 nm) ≤ **5b** (26 nm) < **5a** (30 nm) < **5d** (41 nm), respectably. When **5a** was used as a blue host material in the multilayered device structure of ITO/DNTPD/NPD/host:dopant (9%)/PyPySPyPy/LiF/Al, enhanced OLED device performance was observed, showing a luminous current efficiency of 9.9 cd A⁻¹, power efficiency of 6.3 lm W⁻¹ at 20 mA cm⁻², deep blue color coordinates of (0.14, 0.18), and a 932 h device lifetime at $L_0 = 3000$ cd m⁻².

Introduction

Since the pioneering report of Tang et al., organic light emitting devices (OLEDs) have attracted enormous interest because of their high efficiency, pure color reproduction, fast response, and wide viewing angle.1 Full-color displays require red, green, and blue emission of relatively equal stability, efficiency, and color purity. Although significant improvements in OLED performance have been achieved over the past decades, further improvement is required. In particular, the performance of blue OLEDs is relatively poor compared with red and green OLEDs; thus, it is necessary to improve their performance for display or lighting applications.² Recently, a number of fluorescent blue emitting materials, such as styrylarylene,3 fluorene,4 fluoranthene,5 quinoline,6 quinoxaline,7 triarylamines,8 pyrene,9 and diarylanthracence¹⁰ derivatives have been reported. Among these, anthracene and its derivatives has been the subject of investigation because of their excellent photoluminescence, electroluminescence, and electrochemical properties.11 However, they fail to provide dense films, and the thin films tend to be crystallized producing rough surfaces, grain boundaries, or pin holes that lead to current leakage.¹² To prevent such problems and improve device lifetime with highly efficient electroluminescence properties, we carefully designed asymmetric anthracene materials, containing a bulky aryl group substituted at the 10position, as shown in Chart 1. To achieve amorphous films based

on anthracenes, several issues need to be resolved. It is important to avoid strong intermolecular forces, such as hydrogen bonding or π - π stacking, between the molecules in the film state.¹³ Accordingly, we expected that the introduction of the bulky substituent leads to larger intermolecular distances and is a hindrance in packing and, therefore, produces amorphous behavior. Another strategy for designing amorphous materials is the synthesis of asymmetric molecules, enabling an increase in the number of conformers. This approach comes from the assumption that increasing the number of conformers necessitates high energy for crystallization, favoring the stability of amorphous films.¹⁴ As a result, the asymmetric nonplanar anthracene structure provides a steric hindrance to the close-packing of the molecules, with low crystallization behavior in the solid state; thus, it enables formation of smooth and pinhole-free thin films.

In this study, we report the synthesis and characterization of a series of asymmetric anthracene derivatives, 9-(2-naphthyl)-10-arylanthracene (**5a–5f**), as blue host materials for OLEDs. These



Chart 1 Structures of the asymmetric and bulky aryl-substituted anthracene derivatives (5a-5f).

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film forming capability with moderate fluorescence quantum yields. Based on using these asymmetric anthracenes as host materials, blue fluorescence OLEDs have been fabricated with a 6,12-bis(di(3,4-dimethylphenyl)amino)chrysene dopant. The **5a**-based device exhibits highly efficient blue emission (0.14, 0.18) with luminous current efficiency of 9.9 cd A^{-1} , power efficiency of 6.3 lm W⁻¹ at 20 mA cm⁻² and reduced efficiency roll off at high luminance and a stable device lifetime. **Results and discussion**

compounds show high thermal stability and good amorphous

Synthesis

The synthesis of asymmetric anthracene derivatives, 5a-5f, was accomplished according to the synthetic routes given in Scheme 1. Initially, 2,3,6-substituted nitrobenzenes, 2a-2f, were obtained *via* Pd(0)-mediated Suzuki–Miyaura coupling reactions between 1a-1d and phenylboronic acid or 1-naphthylboronic acid. Compounds 2a, 2b, and 2c were prepared by reacting 1-naphthylboronic acid and 1a-1c, respectively; compounds 2d, 2e, and 2f were obtained in moderate yields by reacting 1d and different equivalents of phenylboronic acid or 1-naphthylboronic acid. Hydrogenation of 2a-2f with hydrogen gas in the presence of a catalytic amount of Pd/C afforded 2,3,6-substituted anilines, 3a-3f, in quantitative yields. The subsequent Sandmeyer reaction using 3a-3f with *p*-toluenesulfonic acid and NaNO₂ produced the desired 2,3,6-substituted iodobenzenes, 4a-4f, in 51-68%yield.



Scheme 1 Synthetic route towards 9-(2-naphthyl)-10-arylanthracene derivatives (5a-5f).

Finally, a series of bulky aryl-substituted asymmetric 9-(2-naphthyl)-10-phenylanthracene derivatives, **5a–5f**, where phenyl was varied with methyl, phenyl, and naphthyl at the 2,3,6-position, was obtained by Suzuki–Miyaura coupling using **4a–4f** and 10-(2-naphthyl)anthracene-9-boronic acid. The details of this synthesis are given in the experimental section. All **5a–5f** compounds were isolated by flash column chromatography with yields ranging from 70 to 87%, and further purified by train sublimation. Their compositions were confirmed based on elemental and high resolution mass analyses. The structures were authenticated based on functional group analysis of the ¹H and ¹³C NMR spectra.

Thermal properties

The thermal properties of 5a-5f were determined by differential scanning calorimetry (DSC) analysis as listed in Table 1. A heating rate of 10 °C min⁻¹ was used after the first melting, which was followed by rapid cooling to room temperature. As shown in Fig. 1, the first heating cycle revealed a $T_{\rm m}$ for 5a, 5b, 5c, 5d, 5e, and 5f in the order of 288, 294, 164, 219, 242, and 292 °C, respectively. In subsequent heating cycles, weak endothermic transitions associated with T_g were found in the order of 116, 125, 84, 123, 126, and 153 °C for 5a, 5b, 5c, 5d, 5e, and 5f, respectively. It was noted that the $T_{\rm g}$ of the anthracene derivatives increase in proportion to the size of the substituent groups at the 10-position of the anthracene molecules, except for compound 5c. In particular, no distinct crystallization temperature was observed in this series when the temperature was swept continuously between 30 and 350 °C with the exception of 5f. These experiments demonstrate that it is possible to get stable glasses from these materials. Therefore, a stable device lifetime can be expected for OLEDs using these asymmetric anthracenes since it has been demonstrated that high $T_{\rm g}$ materials lead to enhanced device stability and lifetime.15

Photophysical properties

The photophysical properties of each anthracene compound were examined by UV-vis absorption and photoluminescence (PL) in the solution and film states. Table 1 summarizes the spectroscopic data. The UV-vis absorption spectrum (Fig. 2a) shows that all of the anthracene derivatives exhibited the characteristic vibronic structure at approximately 397, 376, and 358 nm, which was attributed to the anthracene molecule. The

Table 1 Photophysical properties of 9-(2-naphthyl)-10-phenylanthracene derivatives (5a-5f)

Compound	λ_{abs} (nm)	$\lambda_{\rm em}$ [FWHM] (nm)				
	Sol^a	Film^{b}	Sol^a	Film ^b	${\pmb \Phi_{\mathrm{f}}}^c$	$T_{g}/T_{c}/T_{m}^{d}$ (°C)
5a	396.8, 376.2, 358.5	401.7, 380.6, 359.5	421.1 [54]	451.0 [53]	0.81	116/—/288
5b	396.7. 376.2. 357.8	400.3, 379.5, 360.4	416.4 52	441.9 [53]	0.78	125//294
5c	396.9, 376.2, 357.7	402.0, 382.5, 358.5	417.4 52	441.8 [53]	0.78	84//164
5d	399.3, 378.6, 359.5	402.3, 381.1, 359.4	420.0 [53]	461.1 [42]	0.82	123//219
5e	399.6, 378.6, 359.4	403.4, 382.3, 362.2	421.0 53	438.8 [60]	0.84	126/—/242
5f	399.5, 378.6, 359.7	405.1, 383.5, 364.1	425.0 54	443.9 [57]	0.82	153/194/292

^{*a*} In CH₂Cl₂. ^{*b*} Prepared by a vapor deposition method. ^{*c*} Relative to 9,10-diphenylanthracene as standards in CH₂Cl₂ at room temperature. ^{*d*} Determined by differential scanning calorimetry (DSC).



Fig. 1 DSC traces of **5a–5f** were recorded at a heating rate of 10 $^{\circ}$ C min⁻¹.



Fig. 2 (a) UV/vis absorbance, (b) photoluminescence spectra of 5a-5f in CH_2Cl_2 solution. (Inset: film PL spectrum of 5e).



Fig. 3 6,12-Bis(di(3,4-dimethylphenyl)amino)chrysene dopant UV/vis (red line) and PL (blue line) spectrum in solution. (dashed line: **5a** PL spectrum).

PL wavelengths of all compounds were similar to those found in 9,10-diphenylanthracene,¹⁶ which could be assigned unambiguously to the lowest π - π * transition of the anthracene chromophore in the molecule, as shown in Fig. 2b. This suggests there is little or negligible electronic communication between the anthracene and periphery group because the twisted bulky aryl unit blocks the extending π -conjugation of the 9,10-diarylanthracene.

Moreover, the PL emission spectrum of these anthracenes was sufficiently overlapped with the UV-vis absorption of the dopant materials of 6,12-bis(di(3,4-dimethylphenyl)amino)chrysene¹⁷ (DACrs), as shown in Fig. 3. Therefore, efficient energy transfer from the anthracene host to the blue dopant through a Förster energy transfer was expected, suggesting that anthracenes act as a good host material in OLED devices using chrysene dopant materials.¹⁸

The PL spectra of the anthracenes (5a-5f) in thin solid film on quartz plates are shown in Fig. S1[†] and the inset of Fig. 2b. The maximum emission peaks of 5a-5f in thin films were slightly red-shifted, but not significantly, compared to those acquired in a dilute solution, exhibiting values in the range of 18 to 41 nm. The reduced spectral shifts in the solid state spectra imply that the intermolecular interactions were weak due to the twisted asymmetrically bound aryl groups. Furthermore, a gradual decrease of red-shift effects was observed with an increase of the substituent bulkiness, exhibiting 5e (18 nm) \leq 5f (19 nm) < 5c (25 nm) \leq 5b (26 nm) < 5a (30 nm) < 5d (41 nm), respectively. As a result, the introduction of a twisted bulky aryl group at the 10-position of the anthracene not only prevents red-shifted emissions in the solid state due to molecular interactions, but also enables the formation of stable amorphous thin films.

Electrochemical properties

The electrochemical properties of **5a–5f** were examined by cyclic voltammetry (CV). Table 2 summarizes the CV results, which were obtained in CH₂Cl₂ containing 0.1 M tetrabutylammonium perchlorate (TBAP) at a scan rate of 0.1 V s⁻¹. All scans are shown in Fig. 4. The potential values of the first redox wave in both the positive and negative directions represent E_{ox} and E_{red} , respectively. All anthracenes exhibited reversible oxidation peaks. Moreover, a distinct cathodic reduction process was recorded when the electrode potential was swept continuously between 0.0 and -2.5 V.

Table 2 Oxidation and reduction potentials of 5a-5f in CH₂Cl₂ solution containing 0.1 M TBAP

Entry	Oxidatio	Oxidation (V) ^{<i>a</i>}			Reduction (V) ^a			
	$E_{\rm pa}$	$E_{\rm pc}$	$E_{\rm on}^{\rm ox}$	$E_{\rm pc}$	$E_{\mathrm{on}}^{\mathrm{red}}$	$E_{\rm g}^{\rm opt} \left({\rm eV} \right)^b$	HOMO $(eV)^c$	LUMO (eV) ^c
5a	0.84	0.75	0.70	-2.50	-2.36	3.02	-5.50	-2.48
5b	0.82	0.75	0.70	-2.50	-2.36	3.02	-5.50	-2.48
5c	0.81	0.74	0.69	-2.52	-2.37	3.03	-5.49	-2.46
5d	0.81	0.74	0.69	-2.52	-2.37	3.01	-5.49	-2.48
5e	0.80	0.74	0.70	-2.52	-2.37	3.00	-5.50	-2.50
5f	0.79	0.72	0.68	-2.53	-2.39	3.00	-5.48	-2.48

^{*a*} E_{pa} = anodic peak potential; E_{pc} = cathodic peak potential; E_{onset} = onset potential. ^{*b*} Optical bandgap $E_{\text{g}}^{\text{opt}}$ from the absorption edge. ^{*c*} The HOMO and LUMO levels were determined using the following equations: E_{HOMO} (eV) = $-e(E_{\text{onset}}^{\text{ox}} + 4.8)$, E_{LUMO} (eV) = $-e(E_{\text{HOMO}} - E_{\text{g}}^{\text{opt}})$.



Fig. 4 Cyclic voltammetry of **5a–5f** in CH_2Cl_2 solution containing 0.1 M TBAP.

The HOMO and LUMO energy levels of these anthracene derivatives were determined by CV experiments. From the first oxidation onset potential, the HOMO energy levels of **5a–5f** were estimated to be *ca.* -5.48 to -5.50 eV. The LUMO energy levels were calculated to be in the range of -2.46 to -2.50 eV from the absorption edge of the optical absorption spectra of **5a–5f**. All compounds of anthracene derivatives have wide optical energy band gaps (E_g) of 3.0–3.1 eV, as determined from the edge of the UV-vis absorption spectra. As expected, CV experiments suggest that there is no significant electronic communication between the anthracene and the periphery group. The photophysical and electrochemical properties of **5a–5f** indicate that the bulky substituent at the 10-positions of the anthracene core without significant excimer emission in the solid state.

Theoretical calculations

The electronic structure of these compounds was further investigated by performing quantum chemical calculations at the Density Functional Theory (DFT) level, as implemented in the $Dmol^{\beta}$ package.¹⁹ The HOMO–LUMO levels of **5a–5f** were calculated using double numerical plus d-functions (DND), and the geometries were optimized under the same conditions. No atom was omitted from the detailed study of the bond lengths and angles of the optimized structure. Fig. 5 and Fig. 6



Fig. 5 Representative HOMO–LUMO orbital diagrams of 5a-5f obtained from the *Dmo^F* calculation.



Fig. 6 HOMO–LUMO energy levels obtained from the $Dmol^3$ calculation.

summarize the calculated results and representative HOMO and LUMO diagrams for **5a–5f**. The calculated geometries of **5a–5f** show that the 9-(2-naphthyl)anthracene and phenyl units at the 10-position of anthracene are significantly twisted against each other because of the bulky 2,3,6-substituted phenyl group, resulting in a three-dimensional structure in each molecule. These geometric characteristics can effectively prevent intermolecular interactions, such as hydrogen bonding or π - π stacking between the molecules.

The electron densities of the HOMO and LUMO are mostly localized on the anthracene unit, implying that the absorption and emission processes can only be attributed to the π - π * transition at the anthracene unit. Molecular orbital analysis clearly indicates that the substituent at the 10-positions of the anthracene unit does not alter the energy level of the anthracene unit.

Electroluminescent properties

The asymmetric anthracenes, **5a**, **5b**, **5e**, and **5f** were evaluated as blue host materials by fabricating multi-layer OLED devices with DACrs dopant. As shown in Fig. 7, all devices were fabricated with the following configuration: ITO/DNTPD (65 nm)/NPB (20 nm)/host:DACrs (9%) (35 nm)/PyPySPyPy (20 nm)/LiF (1 nm)/Al (100 nm), where ITO (indium tin oxide) was the anode, DNTPD (N,N-[p-di(m-tolyl)aminophenyl]-N,N-diphenylbenzidine) served as a hole-injection layer, NPB (N,N-bis-(naphthalen-1-yl)-N,N-bis(phenyl)benzidine) as a hole transport layer, host (MADN, **5a**, **5b**, **5e**, and **5f**) and dopant (DACrs) as an emitting layer, PyPySPyPy (2,5-bis(2',2''-bipyridin-6-yl)-1,1dimethyl-3,4-diphenylsilacyclopentadiene) as an electron transport layer, and LiF:Al as the composite cathode.



Fig. 7 The device structure and materials used in this study.



Fig. 8 The I-V-L curve of the 5a (a), 5b (b), 5e (c), and 5f (d) based device. (The insets denote the current efficiency and EL spectrum).

Fig. 8 show the current–voltage–luminance (I-V-L) characteristics of the anthracene host based devices with a 9% ratio of dopant; their device characteristics at 20 mA cm⁻² are listed in Table 3.

The EL spectra for all devices were featureless with the maximum peak at 467 nm with CIE coordinates of x = 0.14 and $v = \sim 0.18$. The similarity of the PL of DACrs and EL spectra suggests that the EL was attributed to emissions from the radiation decay of the excited singlet state of the DACrs dopant. In addition, negligible EL color shift was observed when the driving voltage was increased from 3 to 11 V. It also suggests that the electron-hole pairs for recombination are well confined in the blue emitter region. In the I-V-L curves, the bulky arylsubstituted anthracene (5a, 5b, 5e, and 5f) based device showed better performance than that of a common blue host material, 2methyl-9,10-di(2-naphthyl)anthracene²⁰ (MADN). In particular, as shown in Fig. 8a, a 5a-based device showed promising performance compared with previous blue devices,²¹ exhibiting a turn-on potential of 3.0 V and a maximum brightness of 49360 cd m⁻² at 555 mA cm⁻² (11 V), as well as maximum current and power efficiencies of up to 10.1 cd A^{-1} and 6.4 lm W^{-1} , respectively. Moreover, the device efficiency showed no significant fall-off from low current density to a higher current density. This result might be due to less intermolecular interaction of anthracenes in the solid state.

The operational lifetime of the four blue devices under an initial brightness of 3000 cd m^{-2} was examined after encapsulation in the nitrogen-purged glove box. A MADN based device was also examined for comparison. As shown in Fig. 9, bulky



Fig. 9 Device operational stability for the lifetime of the ref (MADN), 5a, 5b, 5e, and 5f based device at 3000 cd m^{-2} brightness.

aryl-substituted asymmetric anthracene based devices showed a more stable lifetime than that of the MADN based device. For example, the 5a based device under a constant current density of 38 mA cm^{-2} with $L_0 = 3000 \text{ cd m}^{-2}$ dropped to about 2450 cd m⁻² after operating continually for 215 h and with the driving voltage increased by 1.1 V, while the MADN based device dropped to about 2040 cd m^{-2} after operating continually for 215 h. Assuming the scalable law of Coulombic degradation²² and by estimation of its extrapolated profile, driving at a normalized L_0 value of 3000 cd m⁻², the $t_{1/2}$ values for the MADN and 5a based device without considering any accelerating factor²³ for a blue device, are projected to be 429 h and 932 h, respectively. The longer lifetime of bulky aryl-substituted asymmetric anthracene based devices may be attributed to the better thermal stability and no significant intermolecular interaction in the solid state.

Conclusions

In summary, a series of asymmetric anthracene blue host materials, 9-(2-naphthyl)-10-arylanthracene, **5a–5f**, was synthesized and characterized. By employing these asymmetric anthracenes as a host material of DACrs-based blue OLEDs, the reduced efficiency roll-off at high luminance and stable lifetime were observed. This results suggest that the introduction of a sterically bulky unit at the 10-position of the anthracene provides an effective handle to prevent the close-packing of the molecules in the solid state and thus enables formation of stable amorphous thin films. Further studies, focusing on additional structural tuning of the anthracene series with the aim of improving the amorphous properties and high quantum efficiency, as well as device optimization, are currently underway.

Table 3 EL performance of an anthracene host with a 9% doping ratio at 20 mA $\rm cm^{-2}$

9% doping	$V_{\rm on}{}^a$	V	$\eta_{\mathrm{ex}}{}^b$	$\eta_{ ext{lum}}{}^c$	${\eta_{\mathrm{pw}}}^d$	L_{\max}^{e}	CIE (<i>x</i> , <i>y</i>)
MADN (ref)	2.7	5.6	5.8	7.2	4.3	50 080	0.14, 0.18
5a	2.9	5.0	7.3	9.9	6.3	49 360	0.14, 0.18
5b	3.0	5.2	5.9	7.6	4.5	36 410	0.14, 0.18
5e	2.9	5.5	6.9	8.7	5.3	39 400	0.14, 0.17
5f	2.9	5.4	7.1	9.2	5.8	38 710	0.14, 0.17

^{*a*} Turn-on voltage (V). ^{*b*} External quantum efficiency (%). ^{*c*} Luminance efficiency (cd A⁻¹). ^{*d*} Power efficiency (lm W⁻¹). ^{*e*} Maximum luminance (cd m⁻²).

Experimental

General procedures

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. The ¹H and ¹³C spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1 and 75.4 MHz, respectively. All proton and carbon chemical shifts were measured relative to the internal residual benzene and chloroform from the lock solvent (99.5% C₆D₆, 99.9% CDCl₃). The elemental analyses were performed using a Carlo Erba Instruments CHNS-O EA 1108 analyzer. High Resolution Tandem Mass Spectrometry (Jeol LTD JMS-HX 110/110A) was performed by the Seoul Branch of the Korean Basic Science Institute. The absorption and photoluminescence spectra were recorded on a SHIMADZU UV-3101PC UV-VIS-NIR scanning spectrophotometer and a VARIAN Cary Eclipse fluorescence spectrophotometer, respectively. The absorption spectra of the solution were measured in CH₂Cl₂ and the corresponding fluorescence emissions were determined at each excitation wavelength (λ_{abs}^{max}/nm) . 9,10-Diphenylanthracene ($\Phi_f = 0.90$) was used as the standard for determining the quantum yields (1 to 4 \times 10^{-6} M in CH₂Cl₂). The thermal stability of the compound was measured by differential scanning calorimetry (Q20, TA). A heating rate of 10 °C min-1 was used after first melting the compound followed by rapid cooling to room temperature. Cyclic voltammetry (CV) was performed in an electrolyte containing 1 mM of the electro-active compounds and 0.1 M tetrabutylammonium perchlorate (TBAP) at room temperature under a N₂ atmosphere using a BAS 100B electrochemical analyzer. Platinum, platinum wire, and Ag|AgNO₃ (0.1 M) were used as the working, counter, and reference electrodes, respectively. All potentials were calibrated to the ferrocene/ ferrocenium (Fc|Fc⁺) redox couple. 3-Bromonitrobenzene, 4bromo-1-methyl-2-nitrobenzene, 1-bromo-2-methyl-3-nitrobenzene, 1,4-dibromo-2-nitrobenzene, phenylboronic acid and 1-naphthylboronic acid were purchased and used as received. 10-(2-Naphthyl)anthracene-9-boronic acid was prepared using the method reported in the literature.²⁴

Synthesis

1-(3-Nitrophenyl)naphthalene (2a). 3-Bromonitrobenzene (2.00 g, 9.90 mmol), 1-naphthylboronic acid (1.88 g, 10.88 mmol), Pd(PPh_3)_4 (0.34 g, 3 mol%), and K_2CO_3 (4.10 g, 29.66 mmol) were added to a mixture of DME (100 mL). After adding deionized water (25 mL), the resulting mixture was refluxed for 12 h under an inert atmosphere. The mixture was cooled to room temperature and quenched with H₂O. The organic layer was extracted with CH_2Cl_2 (3 × 30 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue purified by silica gel column chromatography using CH_2Cl_2 /hexane (1:2) as the eluent. 2a was obtained as a yellow solid (2.34 g, 95%). ¹H NMR (CDCl₃) δ 8.39 (s, 1H), 8.32 (d, 1H), 7.97-7.93 (m, 2H), 7.86 (d, 1H), 7.79 (d, 1H), 7.70-7.66 (m, 1H), 7.59-7.53 (m, 2H), 7.51-7.44 (m, 2H). Anal. calcd. for C₁₆H₁₁NO₂: C, 77.10; H, 4.45; N, 5.62; O, 12.84. Found: C, 77.04; H, 4.42; N, 5.63.

1-(4-Methyl-3-nitrophenyl)naphthalene (2b). A procedure analogous to the preparation of **2a** was used, but starting from 4-bromo-1-methyl-2-nitrobenzene (2.14 g, 9.90 mmol). **2b** was obtained as a pale yellow powder. Yield: 62% (0.92 g).¹H NMR (CDCl₃) δ 8.13 (s, 1H), 7.95–7.90 (m, 2H), 7.81 (d, 1H), 7.64 (d, 1H), 7.57–7.41 (m, 5H), 2.71 (s, 3H). Anal. calcd. for C₁₇H₁₃NO₂: C, 77.55; H, 4.98; N, 5.32; O, 12.15. Found: C, 77.52; H, 4.95; N, 5.30.

1-(2-Methyl-3-nitrophenyl)naphthalene (2c). A procedure analogous to the preparation of **2a** was used, but starting from 1-bromo-2-methyl-3-nitrobenzene (2.14 g, 9.90 mmol). **2c** was obtained as a pale yellow oil. Yield: 62% (0.92 g). ¹H NMR (CDCl₃) δ 7.94–7.92 (m, 3H), 7.58–7.49 (m, 3H), 7.46–7.41 (m, 2H), 7.37–7.31 (m, 2H), 2.16 (s, 3H). C₁₇H₁₃NO₂: C, 77.55; H, 4.98; N, 5.32; O, 12.15. Found: C, 77.50; H, 4.97; N, 5.31.

1,4-Diphenyl-2-nitrobenzene (2d). A procedure analogous to the preparation of **2a** was used, but starting from 1,4-dibromo-2-nitrobenzene (2.78 g, 9.90 mmol) and 2.2 equiv. phenylboronic acid (2.66 g, 21.78 mmol). **2d** was obtained as a pale yellow powder. Yield: 92% (2.50 g). ¹H NMR (CDCl₃) δ 8.08 (s, 1H), 7.84 (d, 1H), 7.65 (d, 2H), 7.53–7.49 (m, 3H), 7.46–7.42 (m, 4H), 7.39–7.35 (m, 2H). Anal. calcd. for C₁₈H₁₃NO₂: C, 78.53; H, 4.76; N, 5.09; O, 11.62. Found: C, 78.52; H, 4.74; N, 5.08.

1-Phenyl-4-(1-naphthyl)-2-nitrobenzene (2e). A stirred mixture of 1,4-dibromo-2-nitrobenzene (2.78 g, 9.90 mmol), 1 equiv. phenylboronic acid (1.22 g, 10.00 mmol), Pd(PPh₃)₄ (0.34 g, 3 mol%), and K₂CO₃ (4.10 g, 29.66 mmol) in toluene (160 nm) were added to a mixture of toluene (160 nm) and deionized water (40 mL) was refluxed for 12 h under an inert atmosphere. The mixture was cooled to room temperature and quenched with H₂O. The organic layer was extracted with CH₂Cl₂ (3×30 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue purified by silica gel column chromatography. After the first coupling was complete, a procedure analogous to the preparation of 2a was used to obtain 2e as a pale yellow powder. Yield: 81% (2.61 g). ¹H NMR (CDCl₃) δ 8.00 (s, 1H), 7.97–7.89 (m, 3H), 7.76 (d, 1H), 7.60–7.42 (m, 10H). Anal. calcd. for C₂₂H₁₅NO₂: C, 81.21; H, 4.65; N, 4.30; O, 9.83. Found: C, 81.20; H, 4.64; N, 4.27.

1,4-Di(1-naphthyl)-2-nitrobenzene (2f). A procedure analogous to the preparation of **2a** was used, but starting from 1,4-dibromo-2-nitrobenzene (2.78 g, 9.90 mmol) and 2.2 equiv. of 1-naphthylboronic acid (3.76 g, 21.78 mmol). **2f** was obtained as a pale yellow powder. Yield: 94% (3.49 g).¹H NMR (CDCl₃) δ 8.26 (s, 1H), 8.03–7.96 (m, 6H), 7.86 (d, 1H), 7.69–7.49 (m, 9H). Anal. calcd. for C₂₆H₁₇NO₂: C, 83.18; H, 4.56; N, 3.73; O, 8.52. Found: C, 83.17; H, 4.54; N, 3.73.

Aniline derivatives (3a–3f). Nitrobenzene derivatives (2a–2f), ethanol (150 ml), ethyl acetate (100 ml), and 10% palladium on charcoal (1.0 g) were placed in a 500 mL Parr bottle. The bottle was then placed on a Parr hydrogenation apparatus. The sample was evacuated and filled with hydrogen, and the process repeated three times. The tank and bottle were then filled with hydrogen to 30 psi. The shaker was started, and hydrogenation was allowed

Downloaded by Pennsylvania State University on 26 June 2012 Published on 22 November 2010 on http://pubs.rsc.org | doi:10.1039/C0JM02877K to proceed for five hours. After safely venting the hydrogen from the bottle, the resulting solution was filtered through celite and the catalyst washed carefully with 20 mL of ethanol. The filtrate was transferred to a flask and solvent was removed under reduced pressure. After dissolving in CH_2Cl_2 , the solution was filtered again through silica gel and the resulting solvent was removed under reduced pressure to obtain **3a–3f** as a white powder in quantitative yield.

3-(1-Naphthyl)aniline (3a). ¹H NMR (CDCl₃) δ 8.03 (d, 1H), 7.87 (d, 1H), 7.67–7.39 (m, 6H), 7.25 (d, 1H), 6.78 (d, 1H), 6.71 (s, 1H), 3.56 (s, -N*H*₂-). Anal. calcd. for C₁₆H₁₁NO₂: C, 77.10; H, 4.45; N, 5.62; O, 12.84. Found: C, 77.11; H, 4.44; N, 5.59.

2-Methyl-5-(1-naphthyl)aniline (3b). ¹H NMR (CDCl₃) δ 7.96 (d, 1H), 7.88 (d, 1H), 7.83 (d, 1H), 7.58–7.41 (m, 4H), 7.19 (d, 1H), 6.92–6.88 (m, 2H), 3.78 (s, -N*H*₂-), 2.32 (s, 3H). Anal. calcd. for C₁₇H₁₃NO₂: C, 77.55; H, 4.98; N, 5.32; O, 12.15. Found: C, 77.52; H, 4.95; N, 5.30.

2-Methyl-3-(1-naphthyl)aniline (3c). ¹H NMR (CDCl₃) δ 7.91 (d, 1H), 7.87 (d, 1H), 7.55–7.46 (m, 3H), 7.41–7.34 (m, 2H), 7.14 (t, 1H), 6.83 (d, 1H), 6.76 (d, 1H), 3.67 (s, -N*H*₂-), 1.84 (s, 3H). Anal. calcd. for C₁₇H₁₃NO₂: C, 77.55; H, 4.98; N, 5.32; O, 12.15. Found: C, 77.54; H, 4.97; N, 5.31.

2,5-Diphenylaniline (3d). ¹H NMR (CDCl₃) δ 7.62 (d, 2H), 7.51 (d, 2H), 7.46–7.43 (m, 4H), 7.37–7.32 (m, 2H), 7.24 (d, 1H), 7.13 (d, 1H), 7.08 (s, 1H), 3.77 (s, -N*H*₂-). Anal. calcd. for C₁₈H₁₃NO₂: C, 78.53; H, 4.76; N, 5.09; O, 11.62. Found: C, 78.53; H, 4.72; N, 5.07.

2-Phenyl-5-(1-naphthyl)aniline (3e). ¹H NMR (CDCl₃) δ 8.08 (d, 1H), 7.91 (d, 1H), 7.86 (d, 1H), 7.59–7.45 (m, 7H), 7.44–7.36 (m, 2H), 7.25 (d, 1H), 6.97 (d, 1H), 6.91 (s, 1H), 3.62 (s, -NH₂-). Anal. calcd. for C₂₂H₁₅NO₂: C, 81.21; H, 4.65; N, 4.30; O, 9.83. Found: C, 81.19; H, 4.63; N, 4.27.

2,5-Di(1-naphthyl)aniline (3f). ¹H NMR (CDCl₃) δ 8.12 (d, 1H), 7.93–7.79 (m, 5H), 7.60–7.47 (m, 8H), 7.23 (d, 1H), 6.99 (d, 1H), 6.95 (s, 1H), 3.55 (s, -N*H*₂-). Anal. calcd. for C₂₆H₁₇NO₂: C, 83.18; H, 4.56; N, 3.73; O, 8.52. Found: C, 83.19; H, 4.56; N, 3.72.

Iodobenzenes derivatives (4a–4f). 8.00 mmol of the anilines (**3a–3f**) was added to a solution of *p*-TsOH·H₂O (3.44 g, 18.08 mmol) in MeCN (24 mL). The resulting suspension of amine salt was cooled to 0 °C and a solution of NaNO₂ (0.83 g, 12.03 mmol) and KI (2.49 g, 15.00 mmol) in H₂O (4 mL) was gradually added to it. The reaction mixture was stirred for 30 min then allowed to cool to room temperature and stirred for 12 h. Then H₂O (50 mL), NaHCO₃ (1 M; until pH = 9–10) and Na₂S₂O₃ (2 M, 20 mL) was added to the reaction mixture. The precipitated aromatic iodide was extracted with Et₂O (3 × 30 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue purified by silica gel column chromatography using hexane as the eluent, obtaining **4a–4f** as a white powder in moderate yield.

3-(1-Naphthyl)iodobenzene (4a). Yield: 62% (1.63 g). ¹H NMR (CDCl₃) δ 7.93–7.84 (m, 3H), 7.66 (s, 1H), 7.59–7.49 (m, 3H), 7.46–7.34 (m, 4H). Anal. calcd. for C₁₆H₁₁I: C, 58.20; H, 3.36; I, 38.44. Found: C, 58.19; H, 3.33.

2-Methyl-5-(1-naphthyl)iodobenzene (4b). Yield: 54% (1.48 g). ¹H NMR (CDCl₃) δ 7.97 (s, 1H), 7.91–7.85 (m, 3H), 7.54–7.45 (m, 3H), 7.40–7.34 (m, 3H), 2.54 (s, 3H). Anal. calcd. for C₁₇H₁₃I: C, 59.32; H, 3.81; I, 36.87. Found: C, 59.31; H, 3.78.

2-Methyl-3-(1-naphthyl)iodobenzene (4c). Yield: 58% (1.60 g). ¹H NMR (CDCl₃) δ 7.95–7.87 (m, 3H), 7.55–7.48 (m, 2H), 7.41 (d, 2H), 7.31–7.22 (m, 2H), 6.98 (t, 1H), 2.14 (s, 3H). Anal. calcd. for C₁₇H₁₃I: C, 59.32; H, 3.81; I, 36.87. Found: C, 59.29; H, 3.80.

2,5-Diphenyliodobenzene (4d). Yield: 51% (1.45 g). ¹H NMR (CDCl₃) δ 8.20 (s, 1H), 7.61 (d, 2H), 7.49~7.36 (m, 10H). Anal. calcd. for C₁₈H₁₃I: C, 60.69; H, 3.68; I, 35.63. Found: C, 60.68; H, 3.67.

2-Phenyl-5-(1-naphthyl)iodobenzene (4e). Yield: 68% (2.21 g). ¹H NMR (CDCl₃) δ 8.12 (s, 1H), 7.98–7.88 (m, 4H), 7.57–7.41 (m, 10H). Anal. calcd. for C₂₂H₁₅I: C, 65.04; H, 3.72; I, 31.24. Found: C, 65.01; H, 3.72.

2,5-Di(1-naphthyl)iodobenzene (4f). Yield: 50% (1.83 g). ¹H NMR (CDCl₃) δ 8.19 (s, 1H), 8.05 (t, 1H), 7.98–7.92 (m, 5H), 7.63–7.44 (m, 10H). Anal. calcd. for C₂₆H₁₇I: C, 68.43; H, 3.76; I, 27.81. Found: C, 68.42; H, 3.75.

Asymmetric bulky aryl-substituted anthracenes (5a–5f). 4.0 mmol of iodobenzene (4a–4f), 10-(2-naphthyl)anthracene-9boronic acid (1.74 g, 5.00 mmol), Pd(PPh_3)₄ (0.14 g, 3 mol%), and K₂CO₃ (1.66 g, 12.01 mmol) were added to a mixture of toluene (80 mL). After adding deionized water (20 mL), the resulting mixture was refluxed for 12 h under an inert atmosphere. The mixture was cooled to room temperature and quenched with H₂O. The organic layer was extracted with CH₂Cl₂ (3 × 30 mL) and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue purified by silica gel column chromatography using dichloromethane/hexane (1 : 7) as eluent, and further purified by train sublimation under 5.4 × 10⁻⁵ Torr.

9-(2-Naphthyl)-10-(3-(1-naphthyl)phenyl)anthracene (5a). Yield: 76% (1.54 g, white powder). ¹H NMR (C₆D₆) δ 8.31 (d, 1H), 8.08 (d, 2H), 7.88–7.85 (m, 3H), 7.76 (d, 2H), 7.71–7.70 (m, 1H), 7.67–7.60 (m, 4H), 7.52–7.49 (d, 2H), 7.46–7.43 (m, 2H), 7.36–7.27 (m, 5H), 7.20–7.19 (m, 2H), 7.13–7.11 (m, 2H). ¹³C NMR (C₆D₆) 141.4, 140.1, 139.8, 139.7, 137.5, 137.4, 137.0, 134.4, 133.9, 133.3, 133.2, 133.1, 132.1, 130.6, 130.5, 130.46, 130.45, 130.42, 129.7, 129.5, 129.4, 128.6, 128.5, 128.4, 128.3, 128.2, 128.0, 127.5, 127.4, 127.3, 126.5, 126.4, 126.3, 126.2, 125.9, 125.6, 125.5, 125.4. HRMS(FAB) calcd for C₄₀H₂₆: 506.2035. Found: 506.2030 [M]⁺. Anal. calcd for C₄₀H₂₆: C, 94.83; H, 5.17. Found: C, 94.82; H, 5.16.

9-(2-Naphthyl)-10-(2-methyl-5-(1-naphthyl)phenyl)anthracene (5b). Yield: 63% (1.31 g, white powder). ¹H NMR (C₆D₆): δ 8.36 (t, 1H), 7.95–7.92 (m, 2H), 7.89–7.85 (m, 2H), 7.79–7.71 (m, 4H), 7.66 (d, 1H), 7.60 (d, 1H), 7.54–7.47 (m, 3H), 7.39–7.26 (m, 7H), 7.19–7.16 (m, 2H), 7.11–7.10 (m, 2H), 2.05 (d, 3H). 13 C NMR (C₆D₆) 140.1, 139.1, 138.9, 137.4, 137.3, 137.0, 136.98, 136.91, 134.4, 133.9, 133.3, 133.2, 133.1, 132.1, 130.7, 130.5, 130.4, 130.2, 129.89, 129.87, 129.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.6, 127.4, 126.8, 126.53, 126.50, 126.3, 126.2, 125.8, 125.7, 125.6, 125.58, 125.54, 125.53, 19.55, 19.54. HRMS(FAB) calcd for C₄₁H₂₈: 520.2191. Found: 520.2185 [M]⁺. Anal. calcd for C₄₁H₂₈: C, 94.58; H, 5.42. Found: C, 94.56; H, 5.42.

9-(2-Naphthyl)-10-(2-methyl-3-(1-naphthyl)phenyl)anthracene (**5c**). Yield: 41% (0.85 g, white powder). ¹H NMR (C_6D_6) δ 8.09–8.07 (m, 1H), 8.01–7.97 (m, 2H), 7.89–7.82 (m, 2H), 7.77–7.75 (m, 2H), 7.72–7.67 (m, 3H), 7.63 (t, 1H), 7.50 (d, 1H), 7.47–7.42 (m, 3H), 7.36–7.25 (m, 7H), 7.20 (t, 1H), 7.14–7.10 (m, 2H), 1.87 (d, 3H). ¹³C NMR (C_6D_6) 141.5, 140.3, 139.5, 137.4, 137.18, 137.16, 137.09, 137.05, 136.9, 136.8, 134.1, 133.9, 133.1, 132.62, 132.61, 131.1, 130.7, 130.53, 130.50, 130.49, 130.47, 130.3, 130.28, 130.22, 130.21, 129.74, 129.70, 128.6, 128.4, 128.3, 128.22, 128.20, 128.1, 127.6, 127.1, 126.9, 126.7, 126.5, 126.3, 126.2, 126.1, 126.0, 125.9, 125.7, 125.6, 125.5, 17.5, 17.4. HRMS(FAB) calcd for C₄₁H₂₈: 520.2191. Found: 520.2177 [M]⁺. Anal. calcd for C₄₁H₂₈: C, 94.58; H, 5.42. Found: C, 94.54; H, 5.39.

9-(2-Naphthyl)-10-(2,5-diphenyl)phenyl)anthracene (5d). Yield: 49% (1.04 g, white powder). ¹H NMR (C₆D₆) δ 8.00 (d, 2H), 7.83 (s, 1H), 7.78–7.63 (m, 8H), 7.54–7.46 (m, 3H), 7.34–7.26 (m, 5H), 7.20 (t, 2H), 7.13 (t, 2H), 7.04–7.01 (m, 2H), 6.79–6.73 (m, 2H), 6.70–6.67 (m, 1H). ¹³C NMR (C₆D₆) 142.7, 142.6, 141.4, 141.3, 140.55, 140.53, 140.44, 140.40, 138.4, 137.6, 136.9, 136.8, 136.7, 133.85, 133.81, 133.1, 131.4, 131.2, 130.7, 130.5, 130.48, 130.42, 129.8, 129.7, 129.01, 129.02, 128.7, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.57, 127.50, 127.35, 127.33, 127.30, 127.0, 126.98, 126.95, 126.46, 126.43, 126.2, 125.6, 125.3. HRMS(FAB) calcd for C₄₂H₂₈: 532.2191. Found: 532.2179 [M]⁺. Anal. calcd for C₄₂H₂₈: C, 94.70; H, 5.30. Found: C, 94.65; H, 5.28.

9-(2-Naphthyl)-10-(2-phenyl-5-(1-naphthyl)phenyl)anthracene (5e). Yield: 69% (1.60 g, white powder). ¹H NMR (C_6D_6) δ 8.37 (t, 1H), 8.07 (d, 2H), 7.77–7.56 (m, 10H), 7.56–7.50 (m, 1H), 7.48 (t, 2H), 7.42–7.26 (m, 10H), 7.04–6.99 (m, 2H), 6.80–6.68 (m, 2H). ¹³C NMR (C_6D_6) 142.6, 141.8, 141.7, 141.5, 141.2, 140.3, 139.7, 138.5, 137.9, 137.8, 137.5, 137.4, 136.7, 136.4, 136.3, 134.6, 134.4, 133.8, 133.7, 133.1, 132.1, 130.7, 130.6, 130.5, 130.4, 130.1, 129.7, 128.7, 128.6, 128.2, 127.54, 127.52, 127.26, 127.23, 127.0, 126.4, 126.2, 125.9, 125.6, 125.3. HRMS(FAB) calcd for C₄₆H₃₀: 582.2348. Found: 582.2328 [M]⁺. Anal. calcd for C₄₆H₃₀: C, 94.81; H, 5.19. Found: C, 94.78; H, 5.18.

9-(2-Naphthyl)-10-(2,5-di(1-naphthyl)phenyl)anthracene (5f). Yield: 71% (1.79 g, white powder).¹H NMR (C₆D₆) δ 8.50 (t, 1H), 8.37 (d, 1H), 8.29 (d, 1H), 8.11 (d, 1H), 7.79–7.68 (m, 8H), 7.64 (t, 1H), 7.60–7.57 (m, 1H), 7.51–7.44 (m, 2H), 7.41–7.28 (m, 10H), 7.24 (t, 1H), 7.17–7.08 (m, 2H), 6.93 (m, 1H), 6.79–6.68 (m, 2H). ¹³C NMR (C₆D₆) 140.7(5), 140.6(8), 140.4, 139.8, 139.4, 138.4, 138.3, 137.2, 136.8, 136.6, 136.5, 134.9, 134.4, 134.1, 133.7, 133.0, 132.5, 132.4, 132.27, 132.24, 132.1, 131.37, 131.34, 130.4, 130.3, 130.2, 130.1, 129.7, 129.6, 129.33, 129.31, 128.6, 128.5, 128.33, 128.30, 128.17, 128.14, 128.0, 127.8, 127.6, 127.4, 127.3, 127.12, 127.08, 126.64, 126.61, 126.5, 126.3, 126.2, 126.1, 126.0, 125.67, 125.64, 125.51, 125.49, 125.44, 125.40, 125.16, 125.14, 125.0, 124.7, 124.6. HRMS(FAB) calcd for $C_{50}H_{32}$: 632.2504. Found: 632.2498 [M]⁺. Anal. calcd for $C_{50}H_{32}$: C, 94.90; H, 5.10. Found: C, 94.89; H, 5.08.

Device fabrication and characterization

The OLED devices were fabricated on glass substrates precoated with a 150 nm thick indium tin oxide (ITO) layer with a sheet resistance of $\sim 10 \Omega$ per square. The ITO glass was precleaned using a conventional solvent cleaning method. The ITO surface was cleaned again with a UV ozone treatment immediately before depositing the HIL layer. 2-Methyl-9,10-di(2-naphthyl)anthracene (MADN) was used as a reference material because it is used widely as a blue EML host material. The organic, LiF, and Al layers were deposited sequentially onto the substrate without breaking the vacuum. The other commercially available organic materials were used as received. The current-voltage characteristics of the OLEDs were measured using a source measure unit (Keithley 236). The electroluminescence spectra, luminance, and CIE color coordinates were measured using a spectroradiometer (Photo Research PR650). Assuming Lambertian emission, the external quantum efficiency (EQE) was calculated from the luminance, current density, and electroluminescence spectrum.

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