Novel Green Small-molecule Host Materials for Solution-processed Organic Light-emitting Diodes

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The authors report novel small-molecule green-fluorescent hosts for solution processed OLEDs. 9,10-Diarylanthracene and fluorene moieties were introduced to the 9 and 10 positions of an anthracene core to give the strong amorphous characteristics. These novel hosts show sufficient optical, electrical, and thermal properties with very good solubility in organic solvents. Utilizing these solution-processed hosts, a maximum current efficiency of 7.8 cd/A is demonstrated with a general fluorescent dopant.

Organic light-emitting diodes (OLEDs) have apparent advantages for the ultimate display because of its good self-emitting nature and have been attracted intensive researches. Extremely high efficiency, low driving voltages, and long device lifetime have been reported in devices to date.[1] As far as device fabrication, there are some concerns even with such good device performance. The most common technology in the fabrication of OLEDs is a fine-shadow-mask method utilizing thermal evaporation of small molecular materials with which several manufactures currently produce real products. However, there are still issues regarding cost effectiveness, high resolution, and scalability to large mother-glass formats. In contrast, solution processed OLEDs have been considered to overcome these disadvantages owing to simple printing and no vacuum technologies. Nevertheless, this method has serious limitations due to lack of good soluble small molecules and polymer materials and relatively poor device performance in efficiency and lifetime. Many efforts have been carried out to improve device performance of solution-processed OLEDs. Efforts have been limited to polymeric materials[2] and soluble phosphorescent small molecular materials.[3]

In this letter, we report novel soluble small-molecular-host materials and their application to green fluorescent OLEDs. 9,10-Bis(aryl)anthracenes are known to be blue emission dyes with high fluorescent quantum yield and high chemical stability.[4] Their film-forming properties by solution process are very poor. On the other hand, fluorene chemical units have been studied as OLED host materials for solution-processed OLEDs.[5] They have excellent chemical and thermal stabilities, high fluorescence quantum yields, good morphological properties, and acceptable hole-transporting properties. Therefore, we designed and synthesized two anthracene derivatives having 9,10-diarylanthracene and fluorene moieties, namely, 10′-(9,9-dimethyl-9*H*-fluoren-2-yl)-9,10-diphenyl-2,9′-bianthracene (FADPA) and 10′-(9,9-dimethyl-9*H*-fluoren-2-yl)-9,10-di(naphthalen-2-yl)-2,9′-bianthracene (FADNA), as shown in Figure 1.

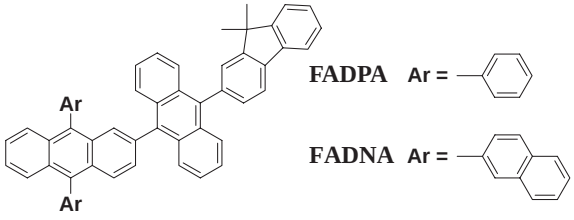

Figure 1. Chemical structures of FADPA and FADNA.

FADPA and FADNA were synthesized as follows. 2-Bromo-9,10-diarylanthracene was prepared from aryl bromide and 2-bromoanthraquinone via arylmagnesium bromide. The aryl–aryl bond formation was accomplished by the Suzuki coupling reaction using Pd catalyst. As a fluorene moiety with anthracene core, 9-bromo-10-(9,9-dimethyl-9*H*-fluoren-2-yl)anthracene was prepared from the Suzuki reaction of 9,10-dibromoanthracene and 9,9-dimethyl-9*H*-fluoren-2-yl boronic acid. The Suzuki coupling reaction of this 9-bromo-10-(9,9-dimethyl-9*H*-fluoren-2-yl)anthracene and corresponding 9,10-diarylanthracene-2-yl boronic acid which was prepared from 2-bromo-9,10-diarylanthracene produced FADPA and FADNA[6] in 20% overall yield.

Optical and electrical properties of FADPA and FADNA are summarized in Table 1. The UV–visible maximum absorption wavelengths of FADPA and FADNA in THF solution are in the range of 360–400 nm with structureless absorption bands arising from π–π^* transitions. And maximum wavelengths of photoluminescence (PL) spectra in solution are in the blue region near 450 nm with a full width at half emission maximum of 55 nm. In addition, the PL spectra of films on glass of these compounds show about 10 nm red-shifts compared to those of their solutions. This indicates that FADPA and FADNA do not have planar stacking due to steric hindrance,[7] and these small red-shifts can be explained by the suppression of the intermolecular π–π^* stacking of FADPA and FADNA. The highest occupied molecular orbital (HOMO) energy levels and the lowest unoccupied molecular orbital (LUMO) energy levels of synthesized materials were obtained according to our reported cyclic voltammetry method.[8a] The HOMO energy levels of FADPA and FADNA are 5.94 and 5.87 eV, respectively. The HOMO and LUMO energy levels of our compounds with anthracene core are consistent with previous results.[4b,5c]

Table 1. Optical and electrical properties of FADPA and FADNA

	Solution (THF)		Film		HOMO	LUMO
	λ_{ab} /nm	λ_{em} /nm	λ_{ab} /nm	λ_{em} /nm	/eV	/eV
FADPA	359	450	364	458	5.94	3.09
	378		386			
	397		402			
FADNA	361	453	384	466	5.87	3.03
	380		404			
	399					

The thermal instability or low glass-transition temperature (T_g) of the amorphous organic layer may result in the degradation of organic devices owing to morphological changes. To investigate the thermal stabilities of FADPA and FADNA, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were carried out. FADPA and FADNA show high T_g and melting temperature (T_m) at 204, 237, and 304, 350 °C, respectively. The 5% weight loss temperature (T_{5d}) corresponding to the endothermic evaporation is observed at 389 and 439 °C for FADPA and FADNA, respectively. These results indicate that FADPA and FADNA are amorphous materials with having a good thin-film-formation characteristics.

Both materials, FADPA and FADNA, show a very good solubility in general organic solvents such as toluene and xylene. These two materials were investigated as the host materials in OLEDs. The 10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1*H*,5*H*,11*H*-benzo[*l*]pyrano[6,7,8-*ij*]quinolizin-11-one (C545T) was chosen as a dopant material to give green fluorescent OLEDs. The emission spectra (λ_{em} 458 nm for FADPA, λ_{em} 466 nm for FADNA) of our novel host materials and the absorption band of C545T (λ_{ab} 480 nm) are spectrally overlapped. As the result, good energy transfer from these hosts to the C545T dopant is expected. The devices of ITO/PEDOT:PSS (40 nm)/TCTA (20 nm)/FADPA (or FADNA): C545T (40 nm)/TPBI (30 nm)/LiF/Al were fabricated and investigated. The layers of PEDOT:PSS (Baytron P® Al 4084), 4,4′,4″-tris(*N*-carbazolyl)triphenylamine (TCTA) and FADPA (or FADNA):C545T were prepared by spin coating. Toluene solutions for TCTA and emissive layers were used for this process. The 20-nm thickness of TCTA interlayer was controlled by our reporting method.[8b] The successive layers of 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene (TPBI) and cathode were deposited by thermal evaporation at a base pressure of 10^{-6} mbar.

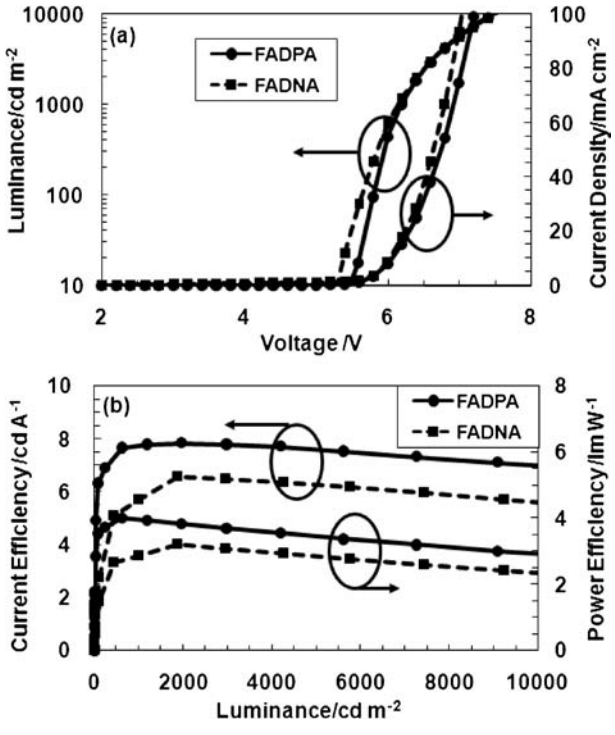

Figure 2. (a) *I–V* and *L–V*, and (b) efficiency–brightness characteristics of OLEDs with FADPA and FADNA host materials.

The doping concentration effects were investigated with 0.5, 1.0, and 2.0% doped devices. As doping concentration increases, poor electroluminescence (EL) performance, having lower current and power efficiencies and higher driving voltage, is observed. This dependency can be explained by the self-quenching effect of dopants at high doping concentration.[9] Figure 2 shows EL performance of the devices with C545T 0.5% doping concentration. The brightness and current density characteristics of FADPA and FADNA were quite similar and operation driving voltage for 1000 cd/m^2 is only 6.2 V. With solution-based spin-coating process, the maximum current efficiencies of 7.8 and 6.5 cd/A were achieved with FADPA and FADNA host materials, respectively.

In summary, we have presented novel soluble host materials for fluorescence OLEDs based on small molecular material. The novel host materials, FADPA and FADNA, showed sufficient optical and electrical properties to apply to fluorescence green OLEDs. Also, thermal stability of these materials proved to be stable. It was demonstrated that FADPA and FADNA can be easily solution processed and yield highly efficient OLEDs with a conventional fluorescent green dopant, C545T.

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6 Spectral data: FADPA: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.94 (m, 32H), 1.54 (s, 3H), 1.53 (s, 3H); MS (HFAB) *m/z*: 698.2969 [M$^+$]. FADNA: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26–8.16 (m, 36H), 1.52 (s, 3H), 1.49 (s, 3H); MS (HFAB) *m/z*: 798.3283 [M$^+$].

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