# Novel Hyperbranched Phthalocyanine as a Hole Injection Nanolayer in Organic Light-Emitting Diodes[a]

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A novel organic hyperbranched copper phthalocyanine was synthesized for use as a hole injection nanolayer on ITO in organic light-emitting diodes (OLEDs). This material is soluble in organic solvents which allows for processing under anhydrous conditions, unlike water based conventional polymer hole injection layer materials such as poly(3,4-ethylenedioxythiophene)(PEDOT)/polystyrene sulfonate (PSS). The hyperbranched layer increased the luminous efficiency and brightness of single layer OLED devices, in addition to reducing current leakage which causes crosstalk in panel devices, compared to devices prepared from PEDOT/PSS. Therefore, this material is more suitable for OLED applications due to its processing and performance advantages over conventional commercial conducting polymer compositions.
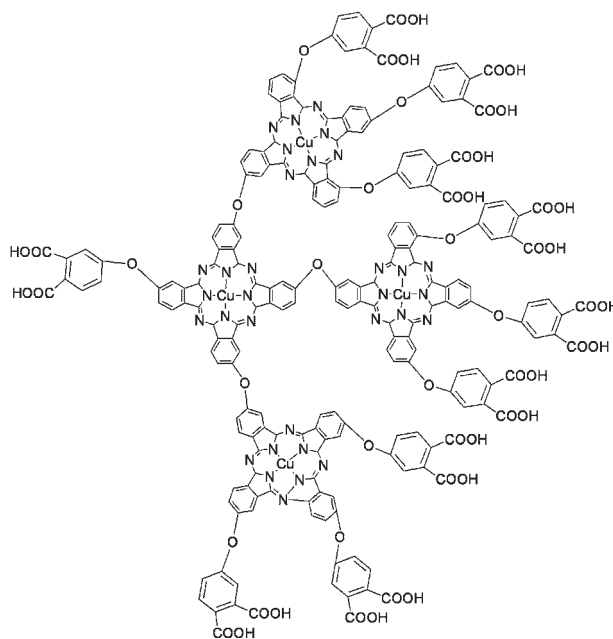
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[a] 🖥 Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at http://www.mrc-journal.de, or from the author.

Introduction

Interfacial engineering of electrical devices between the anode surface and an overlying organic layer is an important method for tuning electronic properties. In particular, interfacial engineering at the anode surface in organic light-emitting diodes (OLEDs) has been used to improve device performance. Several different interfacial engineering techniques have been effectively employed to modify the electronic characteristics of the anode, such as anode modification by plasma treatment,[1,2] chemical

modification,[3–5] introducing a hole injection layer (HIL)[6–10] or p-type doped HILs[11,12] and a hole transporting interlayer between HIL and the emitting layer.[12,13] A layer of commercially available poly(3,4 - ethylenedioxythiophene) (PEDOT) / polystyrene sulfonate (PSS) on indium tin oxide (ITO) is known to improve the device efficiency, due to improvements in the hole injection from ITO.[10,15] However, PEDOT/PSS composi- tions are prepared from an aque- ous medium, so the film forming process, such as spin-coating, can- not be conducted in inert glove box. Since the resultant film is very hygroscopic, it is necessary to minimize exposure to moisture in air after baking the film. In addi- tion, since PEDOT/PSS is a disper- sion in water with a large particle size distribution (average ca. 60 nm),[15] control of film quality due to particle size is another issue. A hole injection material which is soluble in an organic solvent can avoid these issues.

Herein we introduce a novel hole injection material based on hyperbranched copper phthalo- cyanine (HBCuPc), which is soluble in polar organic solvents and gives significantly enhanced luminous efficiency (ca. 50 times) for single layer OLEDs.[16,17] Copper phthalacyanine (CuPc) was first introduced into OLEDs by Van Slyke et al. as an intermediate layer between ITO and a hole transport diamine (N,N'-diphenyl-N,N'-(2-naphthyl)- (1,1′-phenyl)-4, 4′-diamine (NPB)) layer to stabilize the hole injection contact, which resulted in an improvement in device efficiency and operational lifetime.[18] However, since the effective hole injection efficiency from ITO into the hole transport diamine (NPB) layer tended to decrease as the CuPc interlayer thickness increased,[19] the incor- poration of this layer had only a modest effect on the device efficiency as long as the CuPc layer was sufficiently thin.[18,19] We propose using a thin HBCuPc layer (5 nm), as shown in Scheme 1, as a hole injection interfacial layer between ITO and an emitting layer (tris(8-hydroxyquinoline) aluminum (Alq$_3$)) for single layer OLED devices. The chemical structure of the hyper- branched Pc investigated as a good hole injection material is shown in Scheme 1. The hyperbranched Pc with a cyano
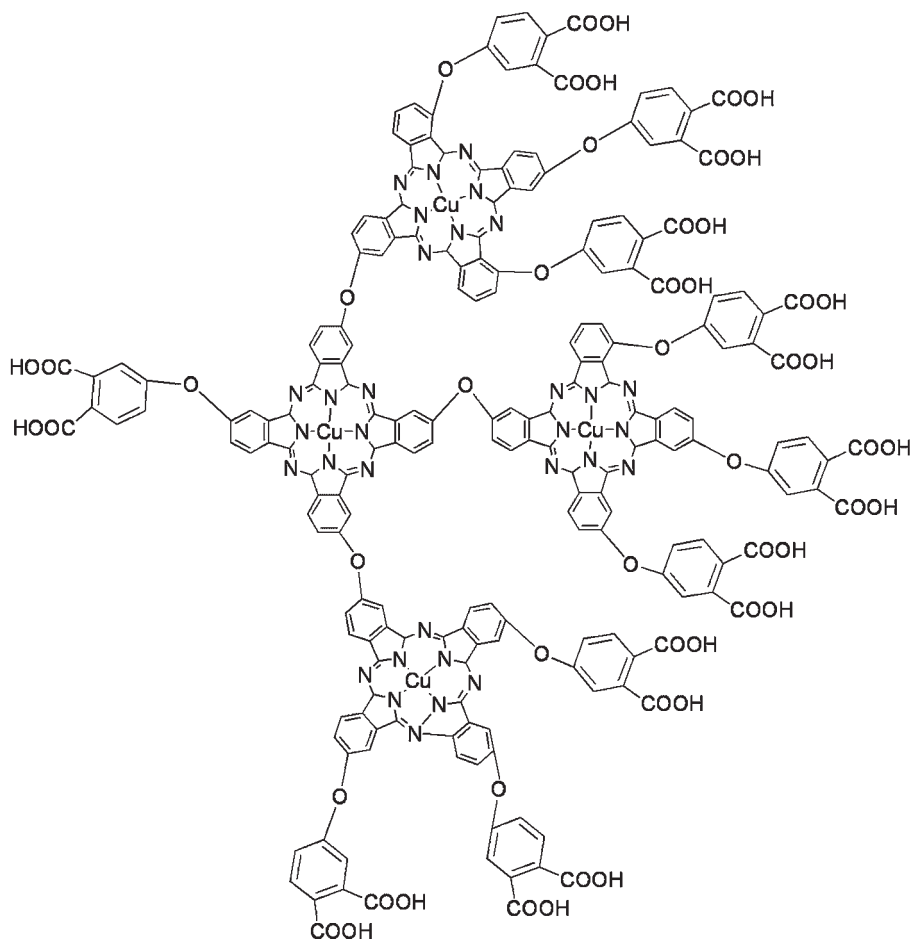
Scheme 1. The chemical structure of the hyperbranched copper phthalocyanine (HBCuPc-COOH) used as an anode interfacial layer for organic light-emitting diodes.

group at the terminal position was synthesized by a copper fusion technique consisting of 4,4′-oxybis(phthalonitrile) and CuCl in dimethylacetamide (DMAc). The extent of the cyclotetramerization reaction was monitored in real time by the increase in the absorption extinction coefficient of the products in comparison to the absorption of the copper phthalocyanine complex.[15,16] Hyper- branched CuPc with a −COOH end group (HBCuPc−COOH) was obtained by hydrolysis of the cyano group using potassium hydroxide.[20] The structure of the hyper- branched Pc was determined by ^{1}H NMR, IR and UV-vis spectra (see Supporting Information). We achieved a luminous efficiency of 1.92 cd·A^{-1} and a maxi- mum brightness of 13 000 cd·m^{-2} from the Alq$_3$ single layer device, which is indeed better than the device efficiency (1.70 cd·A^{-1}) and maximum brightness (7 500 cd·m^{-2}) of the Alq$_3$ device when using a conven- tional PEDOT/PSS layer (ca. 50 nm) as a hole injection layer.

Experimental Part

Preparation of Monomer, 4,4′-Oxybis(phthalonitrile)

Dimethyl sulfoxide (DMSO) and *N,N*-dimethylacetamide (DMAc) were dried with calcium hydride and then distilled under reduced pressure. All other chemicals were reagent grade and were used as received unless otherwise stated.

In a flask, 7.27 g (40 mmol) of 4-nitrophthalonitrile were dissolved in 60 mL of DMSO. Then 11.04 g (80 mmol) of cesium fluoride were added into the flask and the mixture was stirred at room temperature for 6 h. The reaction mixture was poured into 1 000 mL of water. The crude product was collected by filtration, washed with water, and dried under a vacuum. The pure product was obtained by recrystallization from methanol (Scheme 2). The white powdery product was dried in vacuum, affording 4.21 g of 4,4′-oxybis(phthalonitrile). The yield was 72%, and the product had a melting point of 254 °C (as measured by DSC, the literature value is 254–256 °C).

^{1}H NMR: $\delta = 8.24$–8.21 (d, 2H), 8.04 (d, 2H), 7.72–7.68 (t, 2H) (see Figure S1a, Supporting Information).

^{13}C NMR: $\delta = 158.4$, 136.6, 124.7, 124.7, 117.1, 115.7, 115.2, 110.6 (Figure S1b).

IR (KBr): 3 433, 3 102, 3 073, 3 039, 2 924, 2 233, 1 727, 1 588, 1 568, 1 483, 1 418, 1 309, 1 278, 1 251, 1 203, 1 093, 968, 906, 852, 528 cm^{-1} (Figure S2).
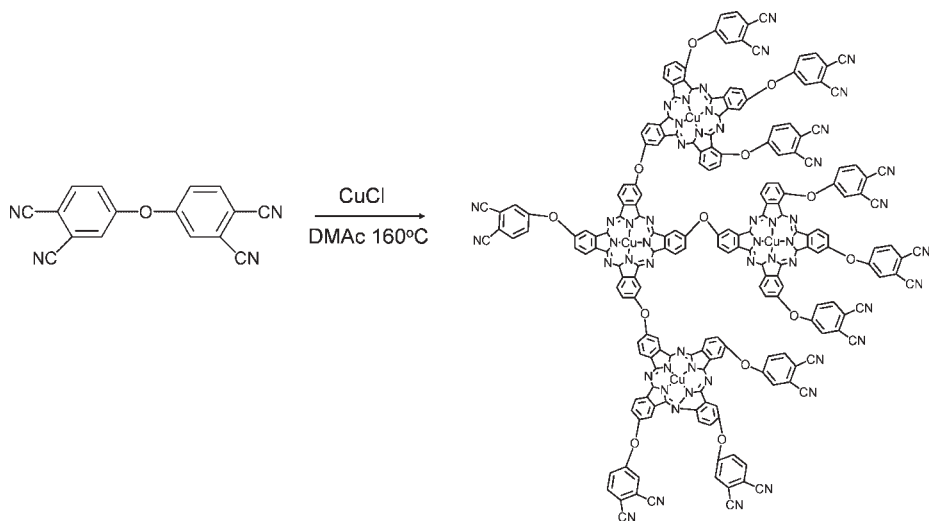
Preparation of −CN Ended Hyperbranched CuPc

To a flask, 1.21 g (4.5 mmol) of 4,4′-oxybis(phthalonitrile) and 0.14 g (1.5 mmol) of CuCl were dissolved in 40 mL of DMAc, and then the mixture was stirred at 160 °C for 4 h. The reaction mixture was poured into 800 mL of water. The crude product was collected by filtration, washed with water and dried in vacuum. After refluxing in methanol twice, the product was filtered and rinsed with cold methanol three times. The dark blue powdery product was dried in vacuum, affording 0.88 g of −CN ended hyperbranched CuPc (Scheme 3).

^{1}H NMR: $\delta = 8.24$–8.21 (d), 8.04 (d), 7.71–7.69 (t), 7.57–7.54 (m), 7.53–7.42 (m).

IR (KBr): 3 324, 3 103, 3 074, 3 040, 2 358, 2 337, 2 234, 1 956, 1 774, 1 723, 1 589, 1 568, 1 484, 1 418, 1 358, 1 310, 1 280, 1 251, 1 202, 1 168, 1 093, 968, 926, 905, 851, 755, 724, 701 cm^{-1} (Figure S3).
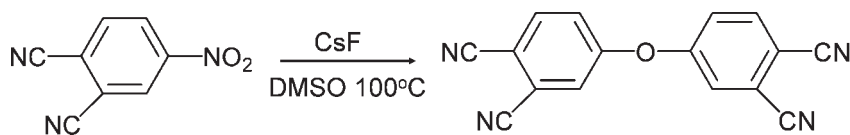
Scheme 3. Preparation of −CN ended hyperbranched CuPc.

Preparation of −COOH Ended Hyperbranched CuPc

In a 200 mL flask, 1 g of −CN ended hyperbranched CuPc. and 0.1 g (10 wt.-%) of potassium hydroxide were dissolved in 120 mL of water/ethanol (1:1 volume) mixed solvent. The mixture was refluxed for 24 h until the evolution of ammonia ceased. The dark blue clear solution was poured into 300 mL of water and the pH of the solution was adjusted to 3–4. The dark blue precipitate was collected by filtration and rinsed with dilute hydrochloric acid and then water (Scheme 4). 0.65 g of −COOH ended hyperbranched CuPc was obtained.

^{1}H NMR: $\delta = 8.24$–8.21 (d), 8.04 (d), 7.71–7.69 (t), 7.57–7.54 (m), 7.53–7.42 (m) (Figure S4).

IR (KBr): 3 377, 2 914, 2 647, 1 723 1 646, 1 534, 1 470, 1 224, 1 105, 1 043, 999, 834, 755, 702, 625, 574, 544 cm^{-1} (Figure S3).

GPC: $\overline{M}_w = 11\,462$, $\overline{M}_n = 7\,692$, $\overline{M}_w/\overline{M}_n = 1.49$ (refractive index detector against PS standard).

UV-vis: λ_{max} (ε): $= 676$ nm (Figure S5).

TGA: 382 °C (10% weight loss) (Figure S6).

OLED Fabrication and Characterization

The HBCuPc-COOH was dissolved in dimethylformamide and spin coated in an inert atmosphere (glove box) to give 5 nm films on ITO (work function of ITO = 4.85 eV). PEDOT/PSS dispersed in water was spin coated in air to give 60 nm films on ITO. The HBCuPc-COOH and PEDOT/PSS films were baked on the hotplate in N$_2$ glove box at 130 °C for 30 min and 200 °C for 10 min, respectively. A green emitting Alq$_3$ (LumTec Corp.) was deposited by vacuum evaporation below 3×10^{-7} Torr. A 1 nm thick layer of LiF and 150 nm of Al were then sequentially deposited on the emitting layer under a vacuum below 5×10^{-7} Torr. The OLED devices were encapsulated with a glass lid using an ultraviolet cured epoxy resin. The current-voltage-luminescence (*I-V-L*) characteristics were obtained with a Keithley

Scheme 2. Preparation of monomer, 4,4′-oxybis(phthalonitrile).
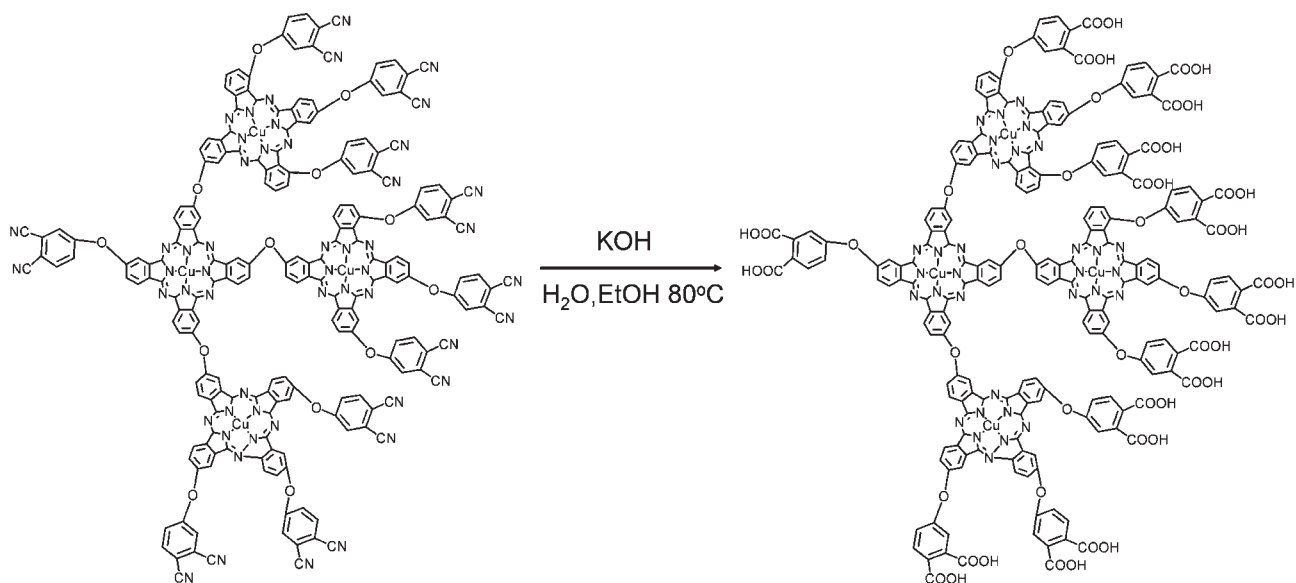
Scheme 4. Preparation of –COOH ended hyperbranched CuPc.

238 source-measure unit and a Photo Research PR650 spectrophotometer.

Results and Discussion

Single layer OLED devices were fabricated using Alq_3 (60 nm) as an emitting layer, and LiF (1 nm)/Al (150 nm) as a cathode. Single layer OLED devices were chosen for fabrication as the single layer structure is able to clearly show the effect of only the HBCuPc-COOH layer on charge injection and transport, as reported in previous literature.[10,11] A 5 nm thick HBCuPc-COOH layer was applied to the ITO anode by spin coating in a glove box prior to vapor deposition of the Alq_3 layer. The material possesses excellent adhesion and film forming capabilities on ITO due to the –COOH end group. An Alq_3 device using PEDOT/PSS on top of ITO as a hole injection layer was also fabricated for comparison. The current-voltage-luminance (*I-V-L*) characteristics of the devices were shown in Figure 1. The incorporation of HBCuPc-COOH does not change the *I-V* characteristics, as shown in Figure 1(a). The measured workfunction of ITO, HBCuPc-COOH, and PEDOT/PSS by ultraviolet photoelectron spectroscopy in air (Surface Analyzer, model AC2, Riken Keiki Co., Ltd) was 4.85, 5.28 and 5.20 eV, respectively. Since the energy barrier from ITO to Alq_3 (highest occupied molecular orbital: −5.8 eV) is 0.95 eV, we can enhance hole injection by forming a thin HBCuPc-COOH layer on top of the ITO. No meaningful change in *I-V* between the device using HBCuPc-COOH layer and the device without the layer indicates that electrons are the majority carriers in Alq_3 devices. The device using PEDOT/PSS showed a slightly
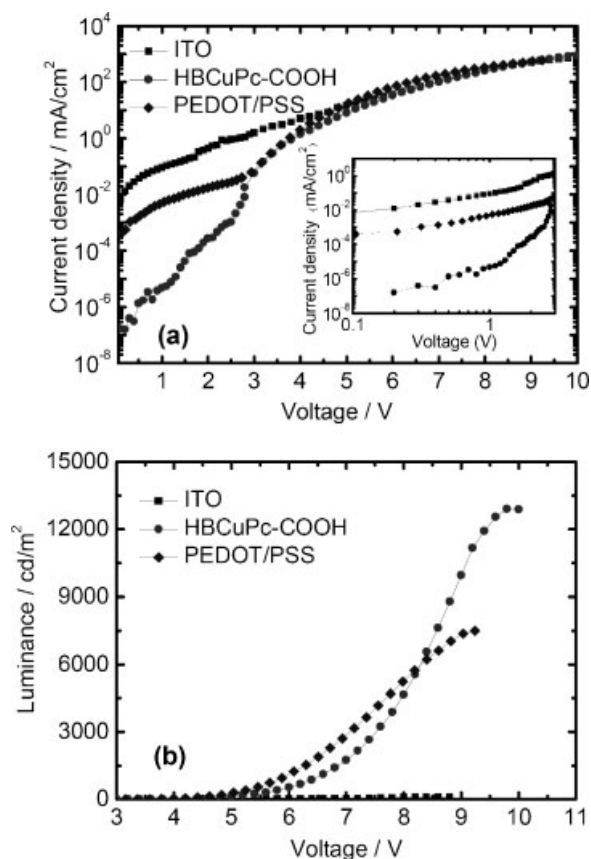

Figure 1. The current-voltage-luminance (*I-V-L*) characteristics of the Alq_3 (60 nm) devices with a LiF (1 nm)/Al (150 nm) cathode using HBCuPc-COOH (5 nm) or PEDOT/PSS (60 nm) spin cast on ITO. (a) Log-linear plot of current-voltage characteristics; inset: log-log plot of current-voltage characteristics below 3 V. (b) Linear plot of luminance-voltage characteristics.
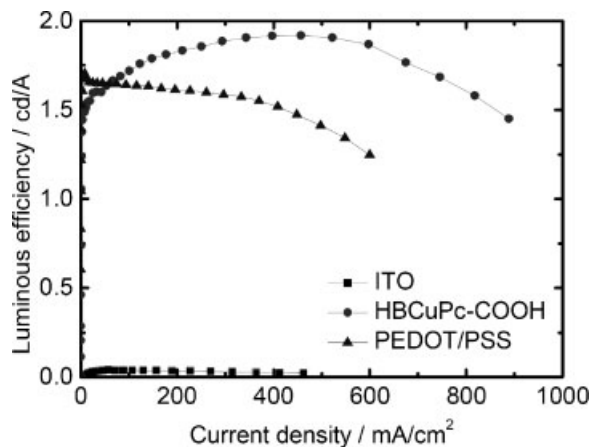
Figure 2. The luminous efficiencies of the Alq3 (60 nm) devices with a LiF (1 nm)/Al (150 nm) cathode using HBCuPc-COOH (5 nm) or PEDOT/PSS (60 nm) spin cast on ITO.

higher current density compared with the device using HBCuPc-COOH, in spite of the slightly lower workfunction by 0.08 eV. This could be due to better hole conducting properties of the conducting polymer layer.

However, the luminance of the device using HBCuPc-COOH was significantly enhanced compared with both the device without the HBCuPc-COOH layer (i.e., ITO/Alq$_3$/LiF/Al device) and the device using a PEDOT/PSS layer, as shown in Figure 1(b). The maximum luminance of the ITO/Alq$_3$/LiF/Al device was ≈ 100 cd $\cdot$ m^{-2}. However, the maximum luminance of the ITO/HBCuPc-COOH/Alq$_3$/LiF/Al was $\approx 13\,000$ cd $\cdot$ m^{-2}, and was almost twice that (7 500 cd $\cdot$ m^{-2}) of the device using PEDOT/PSS. We found that the HBCuPc-COOH layer greatly reduced the leakage current below the turn-on voltage (≈ 3 V) (see the inset of Figure 1(a)), which is an advantage of the HBCuPc-COOH layer compared with a conventional PEDOT/PSS layer. Although a PEDOT/PSS layer can suppress the leakage current, it possesses a relatively high lateral conductivity, which is disadvantageous for display applications that require patterning in order to avoid cross-talk. In addition, since the PEDOT/PSS layer needs to be thick enough (i.e., > 50 nm), it develops a strong, visible region light absorption. Since the HBCuPc-COOH layer is very thin (≈ 5 nm), these disadvantages are not observed. When we utilized the HBCuPc-COOH nanolayer in the Alq$_3$ single layer device, the device efficiency reached 1.92 cd $\cdot$ A^{-1} (Figure 2), which is a 50 fold enhancement compared to the device without any layer (0.0386 cd $\cdot$ A^{-1}) and even better than the luminous efficiency (1.70 cd $\cdot$ A^{-1}) of the same device using a conventional PEDOT/PSS layer (ca. 60 nm) for a hole injection layer. Since the device using a HBCuPc-COOH nanolayer shows better luminous efficiency despite no significant change in *I-V* characteristics, this implies that the layer is a more efficient electron

blocker at the HBCuPc-COOH/Alq$_3$ interface for improved electron-hole balance over the PEDOT/PSS layer.

The performance of the ITO/HBCuPc-COOH/Alq$_3$/LiF/Al device in terms of maximum brightness was comparable to multilayer devices of ITO/NPB/Alq$_3$/LiF/Al reported elsewhere (the maximum brightness was 13 500 cd $\cdot$ m^{-2} for the device in ref.[21]). The luminous efficiency of our device is comparable or lower than the reported data (ca. 2.0 cd $\cdot$ A^{-1} in ref.[21] or ca. 3.5 cd $\cdot$ A^{-1} in ref.[19]). The device stability was also investigated by measuring the device half-lifetime while operating the devices at initial brightness of 100 cd $\cdot$ m^{-2} as a function of time. The device half-lifetime of ITO/HBCuPc-COOH/Alq$_3$/LiF/Al was 18 h, while that of ITO/Alq$_3$/LiF/Al was 6 min. Although the device lifetime was greatly improved by utilizing the CuPcCOOH layer, the absolute lifetime is still short because we fabricated simplified single layer devices to study the hole injection characteristics of the HBCuPc-COOH layer. Therefore, we are currently trying to improve the device performance in terms of the device stability, as well as the device efficiency, by optimizing the device structure.

Conclusion

In conclusion, we have synthesized a novel organic hyperbranched CuPc soluble in organic solvent. When we introduced it as a hole injection nanolayer on ITO, the layer improved the luminous efficiency and brightness of the single layer OLED devices compared to conventional PEDOT/PSS from an aqueous medium. The improved luminous efficiency can be attributed to facilitation of hole injection from ITO into the emitting layer and efficient blocking of electrons for better charge carrier balance. The improved device characteristics (i.e, low current leakage) and performance (i.e, higher luminous efficiency and brightness), as well as the processability in an inert glove box, indicates that our approach of using a novel thin interfacial nanolayer on the ITO surface has advantages over the conventionally used thicker conducting polymer layer (PEODT/PSS). Moreover, the hyperbranched hole injection material provides the tailored solubility in polar organic solvents necessary to enable the fabrication of high quality multilayer polymer light-emitting diodes. As a result, this type of materials will be one of the promising candidates as a hole injection material for both solution and vacuum processed OLED devices.

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