

Electronic Supplementary Information

Enhanced Lifetime of Organic Light-emitting Diodes Using Soluble Tetraalkyl-substituted Copper Phthalocaynines as Anode Buffer Layer

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General Experimental

Materials Synthesis

All materials were purchased from Sigma-Aldrich and used directly without further purification. ¹H NMR spectra were obtained from CDCl₃ solutions on a Bruker Ascend 400 NMR spectrometer at 298 K. High-resolution mass spectrometry measurements were recorded on a Q-Exactive mass spectrometer. The CuEtPc was prepared in a five-step synthesis using 4-methylphthalonitrile (**1**) as starting material with the reported synthesis as tetra-*n*-butyl substituted copper (II) phthalocyanine (CuBuPc), as illustrated in **Scheme S1** and **S2**.

4-Bromomethylphthalonitrile (**2**)

A 1 L carbon tetrachloride was added to a mixture of 4-methylphthalonitrile (12 g, 82.2 mmol), *N*-bromosuccinimide (24 g, 134.8 mmol), and azobisisobutyronitrile (0.6 g, 3.65 mmol) in a two-necked round-bottom flask under an inert atmosphere of argon. The reaction mixture was stirred and heated at 80 °C for 12 h. The resulting mixture was cooled down to room temperature and filtered. The residue on the filter paper was washed with CH₂Cl₂ (200 ml). The filtrates were combined and the solvents were removed by rotary evaporation. The resulting crude product was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether (v/v, 1/1) as the eluent to afford **2** as a white solid (9.1 g, 50%). ¹H NMR (CDCl₃, 400 MHz) δ 7.85 (d, *J* = 1.8 Hz, 1H, phenyl's H), 7.81 (d, *J* = 8.1 Hz, 1H, phenyl's H), 7.76 (dd, *J* = 8.1, 1.8 Hz, 1H, phenyl's H), 4.49 (s, 2H, -CH₂).

(3,4-Dicyanobenzyl)triphenylphosphonium bromide (3)

A mixture of triphenylphosphine (5.4 g, 20.6 mmol), 4-bromomethylphthalonitrile (**2**) (3.0 g, 13.7 mmol) tetrahydrofuran (600 mL) was put in a 1 L one-necked round-bottom flask equipped with a condenser and a stirring bar. The mixture was stirred and refluxed for 24 h. The reaction mixture was allowed to cool down to room temperature and a 300 ml petroleum ether was introduced. The resulting suspension was stirred for 5 min and then filtered. The precipitate was collected, washed with CH₂Cl₂/petroleum (v/v, 1/2, 300 ml) and then dried under ambient condition to give **3** as a white solid (6.6 g, 40%). ¹H NMR (CDCl₃, 400 MHz) δ 8.07 (d, *J* = 8.2 Hz, 1H, phenyl's H), 7.87–7.79 (m, 9H, phenyl's H), 7.67–7.63 (m, 6H, phenyl's H), 7.55 (d, *J* = 8.2 Hz, 1H, phenyl's H), 7.48 (s, 1H, phenyl's H), 6.11 (d, *J* = 15.8 Hz, 2H, –CH₂).

4-Vinylphthalonitrile (4)

A mixture of potassium carbonate (0.49 g, 3.6 mmol), formalin (35~40%, 10 ml) and **3** (0.58 g, 1.2 mmol) was put in a 50 ml one-necked round-bottom flask equipped with a condenser and a stirring bar. The mixture was stirred at room temperature for 2 h. The product was extracted with CH₂Cl₂ (30 ml × 3), and the combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The crude produce was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether (v/v, 1/1) as the eluent to give **4** (0.14 g, 75%). ¹H NMR (CDCl₃, 400 MHz) δ 7.83 (d, *J* = 1.7 Hz, 1H, phenyl's H), 7.79 (d, *J* = 8.1 Hz, 1H, phenyl's H), 7.74 (dd, *J* = 8.2, 1.7 Hz, 1H, phenyl's H), 6.76 (dd, *J* = 17.5, 10.9 Hz, 1H, –CH), 6.00 (d, *J* = 17.5 Hz, 1H, –CH₂), 5.64 (d, *J* = 10.9 Hz, 1H, –CH₂).

4-Ethylphthalonitrile (5)

A mixture of **4** (1.0 g, 6.5 mmol), palladium on carbon (10%, 0.50 g) and 30 ml degassed ethanol was put in a 50 ml one-necked round-bottom flask equipped with a condenser and a stirring bar. The suspension was stirred at room temperature under an atmosphere of hydrogen for 8 h. The resulting mixture was filtered, and the residue on the filter paper was washed with CH₂Cl₂ (10 ml). The filtrate was collected and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether (v/v, 1/1) as the eluent to give **5** (0.96 g, 95%). ¹H NMR (CDCl₃, 400 MHz) δ 7.72 (d, *J* = 8.1 Hz, 1H, phenyl's H), 7.63 (d, *J* = 1.8 Hz, 1H, phenyl's H), 7.57 (dd, *J* = 8.1, 1.8 Hz, 1H, phenyl's H), 2.77 (q, *J* = 7.6 Hz, 2H, –CH₂), 1.28 (t, *J* = 7.6 Hz, 3H, –CH₃).

Tetra-*n*-ethyl-substituted copper(II) phthalocyanine (CuEtPc)

A mixture of **5** (1.0 g, 6.4 mmol), copper(II) chloride (0.24 g, 1.8 mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.2 mL) and 1-pentanol (2 ml) was put in a 50 ml two-necked round-bottom flask equipped with a condenser and a stirring bar. The mixture was stirred and refluxed under argon for 2 h. The reaction mixture was cooled down to room temperature. After that, a 50 ml petroleum ether was introduced to precipitate the product. The suspension was stirred for 5 min, and then filtered. The residue on the filter paper was washed with CH₂Cl₂ (30 ml). The filtrates were combined and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel with CH₂Cl₂/ethanol (v/v, 1/3) as the eluent to give a blue product. The product was further purified by repeated recrystallization from CH₂Cl₂/ethanol to give CuEtPc (0.44 g, 40%). To fulfill the requirements of

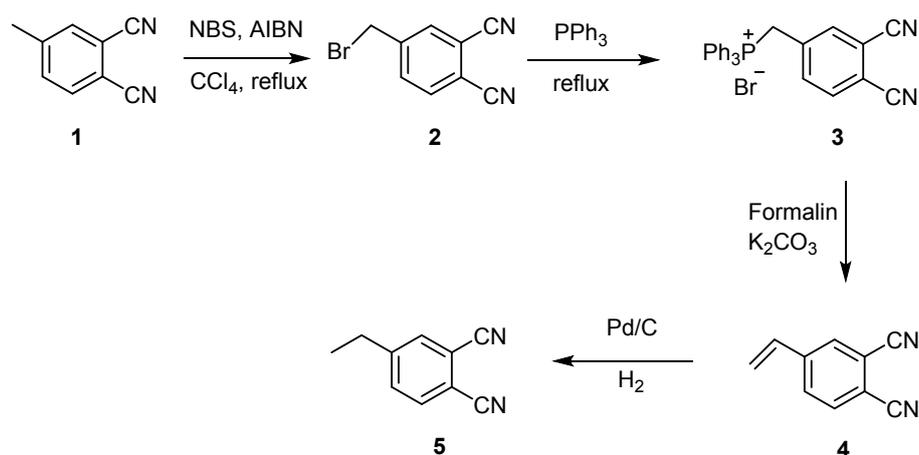
electronic applications, the product was further purified by vacuum sublimation in a sublimation machine (Technol VDS-80) operated at 400 °C and $\sim 3 \times 10^{-3}$ Pa. Elemental analysis calcd (%) for $C_{40}H_{32}CuN_8$: C, 69.80; H, 4.69; N, 16.28; found: C, 69.97; H, 4.41; N, 16.36. ESI-MS: m/z (M^+) 688.21. UV-Vis ($CHCl_3$): λ_{max} = 678 nm ($161254 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), 611 nm ($35774 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$). IR (KBr): ν = 2960, 2928, 2869, 1614, 1506, 1456, 1404, 1342, 1317, 1167, 1138, 1097, 1057, 827, 745, 721 cm^{-1} .

Device Fabrication and Characterization

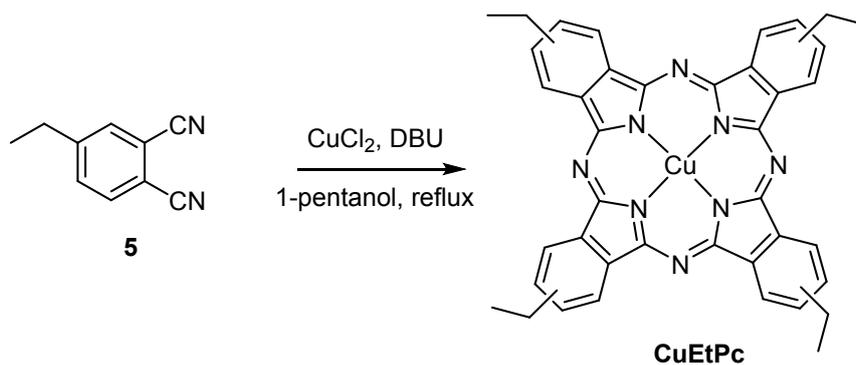
The OLEDs were fabricated on patterned ITO glass with a sheet resistance of $20 \text{ }\Omega/\square$. The PEDOT:PSS buffer layer (Nichem, Al4083) was prepared on the ITO surface at a spin-coating rate of 4000 rpm, while the CuEtPc and CuBuPc layers at a rate of 1000 rpm. The thicknesses of spin-coated layers was examined on KLA-TENCOR D-100 profiler. Other layers were grown by thermal evaporation under a vacuum of $\sim 1 \times 10^{-6}$ Torr (Mbraun MB200), and the layer thickness was monitored in-situ using quartz crystal monitors during deposition. After fabrication, all OLEDs were encapsulated using UV adhesive under a nitrogen atmosphere. The emissive area of the devices was 10 mm^2 . The current-voltage-luminance characteristics were recorded using an automatic system containing a source-measure unit (Keithley 2400) and a calibrated spectrometer (Photo Research PR680). The micrographs of the dark spots of the OLEDs during device operation were recorded by a CCD detector (JVC, TK-C9200EC).

Atomic Force Microscopy (AFM)

Morphologies of the surfaces of ITO and the spin-coated thin films were recorded by AFM using a MFP-3D-Stand Alone scanning probe in tapping mode. The thin film samples were prepared by the same method as the above device fabrication, that is, spin-coated on a ITO substrate from a PEDOT:PSS water suspension (Nichem, Al4083) at a rate of 4000 rpm and the solutions of CuEtPc and CuBuPc in 1,2-dichlorobenzene (10 mg/ml) at a rate of 1000 rpm.



Scheme S1. Synthetic route to 4-ethylphthyanitrile.



Scheme S2. Synthesis of unsymmetrical tetra-*n*-ethyl-substituted copper(II) phthalocyanine.

TGA Measurement

The TGA curves of CuEtPc and CuBuPc exhibit that the materials possess a decomposition onset at 492 °C for CuEtPc and 464 °C for CuBuPc, respectively.

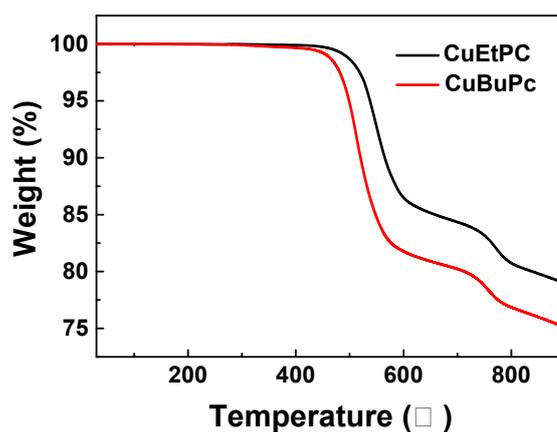


Fig. S1 TGA curves of CuEtPc and CuBuPc.

Hole-only Devices

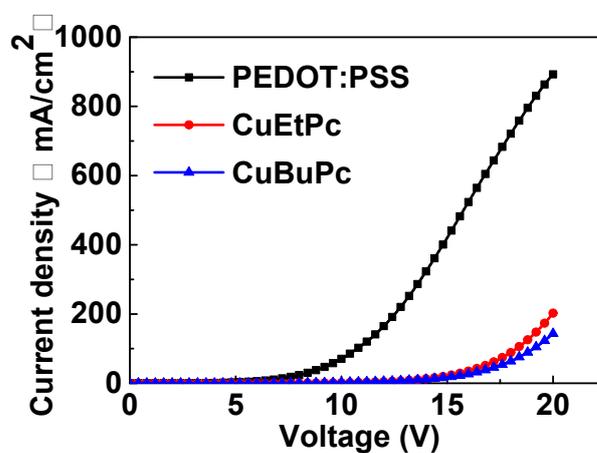


Fig. S2 L-V characteristics of the hole-only devices (in which the currents are dominated by holes) with various anode buffer layers.