Exploiting asymmetric anthracene-based multifunctional materials based on "bulky peripheral modification" strategy for constructing simplified efficient deep-blue fluorescent OLEDs

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Materials

All purchased reagents and raw materials used in the synthesis process were used without further purification unless other stated. All reaction processes were carried out under a protection of nitrogen atmosphere. The final compounds were further synthesized through Suzuki cross-coupling reaction, as shown in the experimental section. The final compounds with little impurity were preliminarily purified by means of silica gel column chromatography, then repeatedly using recrystallization, finally sublimation by gradient heating under vacuum condition. For devices fabrication, the used ITO coated glass substrates (20 Ω square⁻¹), MoO₃, LiF, TAPC, TPBi and *m*CP were commercially available.

Characterization

The intermediates and final compounds were confirmed by ¹H NMR or ¹³C NMR spectra on a Bruker-AF301 AT 400 MHz spectrometer. Mass spectra were recorded on an Agilent (1100 LC/MSD Trap) using APCI ionization. Differential scanning calorimetry (DSC) was measured under nitrogen on a PE Instruments DSC2920 unit at a heating rate of 10 °C min⁻¹ from 30 to 300 °C. The glass transition temperature (T_g) was determined from the second heating scan. Thermogravimetric analysis (TGA) was undertaken using a PerkinElmer Instruments Pyris1 TGA at a heating rate of 10 °C min⁻¹ from 30 to 600 °C under a nitrogen atmosphere. The thermal decomposition

temperatures (T_d) were corresponded to 5% weight loss temperatures. The UV-vis absorption spectra were measured on a Shimadzu UV-VIS-NIR Spectrophotometer (UV-3600) in the wavelength range of 190-1100 nm and the PL spectra were recorded on an Edinburgh Instruments (FLS 920 spectrometer). The absolute PLQYs were estimated on a Quantaurus-QY measurement system (C11347-11, Hamamatsu Photonics). Cyclic voltammetry was recorded on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature with a conventional threeelectrode system, which consisted of a platinum wire counter electrode, a Ag/AgNO₃ (0.1 M) reference electrode, and a glassy carbon working electrode of 2 mm diameter. A 0.10 M tetrabutylammonium hexafluorophosphate (n-Bu₄NPF₆) solutions in dry dichloromethane and N,N-dimethylformamide were employed as the supporting electrolyte, and ferrocene was added as a calibrant in the whole measurement. Atomic force microscopy (AFM) measurement equipment was Veeco NanoScope MultiMode.

Device fabrication and measurements

The ITO substrates were dipped into acetone, isopropyl alcohol and deionized water orderly, and clean with ultrasonic washer for 30 minutes. Before preparing devices, the ITO substrates were pretreated with oxygen plasma for 5 minutes. The devices were fabricated by evaporating organic materials, which deposited in the vacuum of 2×10^{-4} Pa and monitoring *via* crystal oscillator system. The *J-V-L* property and EL spectra of the devices were measured by a Keithley 2400 source meter equipped with a PR655 spectrometer, and the emitting areas were 0.09 cm² which determined by the overlaps of two electrodes. The transient EL spectra were measured by PAIOS: Platform for All-In-One Characterization of Solar Cells and OLED, Fluxim AG. All measurements were carried out at room temperature under ambient conditions.

The time-of-flight (TOF) transient photocurrent technique.

In the time-of-flight (TOF) transient-photocurrent technique, those samples were illuminated at 355 nm through the ITO electrode from an UV-FQ q-switched DPSS laser (pulse: 4 ns). The transient currents were measured using a digital phosphor

oscilloscope (DPO 3034; bandwidth: 300 MHz). The carrier mobility (μ) was calculated from the values of the transient time (T_t), the material thickness (D), and the applied voltage (V) using the following equation: $\mu = D/(T_t E) = D^2/(V T_t)$.

Additional data



Fig. S1 ¹H NMR spectrum of intermediate 1.



Fig. S2 ¹H NMR spectrum of intermediate 2.



Fig. S3 ¹H NMR spectrum of intermediate 3.



Fig. S4 ¹H NMR spectrum of intermediate 4.

8.81 8.79 8.79 8.78 8.74 8.73 8.73

 \sim 8.12 \sim 8.09 \sim 7.99 \sim 7.97 \sim 7.97 \sim 7.97 \sim 7.65 \sim 7.46 \sim 7.46







Fig. S5 ¹H NMR spectrum of *p*-15NCz3PhDPA.



Fig. S6 ¹³C NMR spectrum of *p*-15NCz3PhDPA.



Fig. S8 ¹H NMR spectrum of *p*-15NCz3PyDPA.



Fig. S9 ¹³C NMR spectrum of *p*-15NCz3PyDPA.



Fig. S10 HRMS of *p*-15NCz3PyDPA.



Fig. S11 PL spectra of *p*-15NCz3PhDPA and *p*-15NCz3PyDPA measured in different solvents with increasing polarity.



Fig. S12 Typical TOF transient photocurrent for (a and b) *p*-15NCz3PhDPA and (c and d) *p*-15NCz3PyDPA, respectively, under a specific applied field.



Fig. S13 PL spectra at 77 K for *p*-15NCz3PhDPA and *p*-15NCz3PyDPA in neat films.



Fig. S14 AFM images of (a) *p***-15NCz3PhDPA** and (b) *p***-15NCz3PyDPA** films before annealing; (c) *p***-15NCz3PhDPA** and (d) *p***-15NCz3PyDPA** films after annealing at 120 °C for 10 min. The thickness of the film is 100 nm.



Fig. S15 Transient EL decay of (a) *p*-15NCz3PhDPA and (b) *p*-15NCz3PyDPA based non-doped devices at different voltages.

Table S1 Natural transition orbital (NTO) analysis for the S_1 and T_1 states based on excited state optimized structures of *p*-15NCz3PhDPA and *p*-15NCz3PyDPA. The percentage indicates the possibility of the transition.

Compounds	Hole	Particle	Hole	Particle
p-15NCz3PhDPA	98.1 So		98.62	
p-15NCz3PyDPA		S ₁	98.55 So	