

Supporting Information

Steric Inhibition of π -Stacking: 1,3,6,8-Tetraarylpyrenes as Efficient Blue Emitters in Organic Light Emitting Diodes (OLEDs)

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Experimental Section

General Aspects: All the palladium-mediated cross-coupling reactions were performed under a nitrogen gas atmosphere in oven-dried pressure tubes. ^1H and ^{13}C NMR spectra were recorded on a JOEL (400 MHz) spectrometer in CDCl_3 as a solvent. Chemical shifts are reported in δ -scale downfield from tetramethylsilane. The TGA and DSC measurements (DSC-7) were carried out using a Perkin-Elmer instrument at $10\text{ }^\circ\text{C}/\text{min}$ under a nitrogen gas atmosphere. UV-vis absorption spectra were recorded using a Jasco-550 spectrophotometer. Photoluminescence spectra and PL quantum yields were obtained from a Hitachi F-4500 and Spex Fluolog-2 spectrofluorimeters, respectively. The photoluminescence spectra of solutions were measured in spectral grade solvents using 90° angle of detection, and those of the thin solid films were measured by front-face detection. The ionization potentials were determined by photoelectron spectroscopy (Riken Keiki, AC2) with UV intensity of 5-30 nW. The current voltage (I - V) characteristics were recorded by Keithley model 2400 electrometer. The EL spectra were recorded using Hitachi F-4500 spectrofluorimeter by blocking the incident radiation. The Commission Internationale de l'Éclairage (CIE) coordinates of the devices were measured by a PR650 spectroscan spectrometer. All the measurements were carried out at ambient conditions.

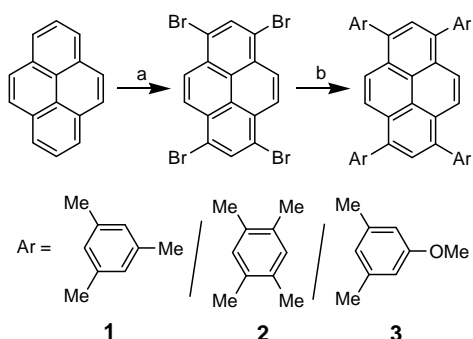
Dry tetrahydrofuran (THF) and anhydrous toluene were freshly distilled over sodium prior to use. All the reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminum sheets pre-coated with silica gel. Chromatography was conducted on

silica gel (60-120 mesh). All the commercial chemicals were used as received.

The starting materials, viz., 1,3,6,8-tetrabromopyrene,¹ dureneboronic acid,² and 2,6-dimethyl-4-methoxyphenylboronic acid³ were synthesized according to the earlier reported procedures. The mesityleneboronic acid was commercially available. The detailed general procedure for the preparation of sterically congested tetraarylpyrenes **1-3** is given below.

General Procedure for the Preparation of Tetraarylpyrenes **1-3** via Suzuki Coupling:

Scheme S1



Reagents and conditions: a) Br₂, nitrobenzene, 120 °C, 2h, 99%;
b) Ar-B(OH)₂, Pd(PPh₃)₄, 20% NaOH, toluene, 100 °C, 75-80%.

A 100 mL two-necked round bottom flask, removed hot from oven, was cooled under a N₂ atmosphere and charged with tetrabromopyrene (1.0 g, 1.93 mmol), 2,4,6-trimethylphenylboronic acid (2.8 g, 15.4 mmol), Pd(PPh₃)₄ (0.25 g, 10 mol%), 40 mL of toluene and 10 mL of 20% NaOH solution. The reaction mixture was heated at 110 °C. The pale-green turbid solution turned clear yellow color in 6h. Subsequently, the heating was continued for 16 h, after which time the color of the reaction mixture turned dark brown. At this stage, the reaction

mixture was cooled and extracted with CHCl_3 . The combined extracts were washed with water, dried over Na_2SO_4 and concentrated. The pure product was isolated by Silica-gel column chromatography using pet. ether as an eluent.

A similar procedure using dureneboronic acid and 2,6-dimethyl-4-methoxyphenylboronic acid was followed for the synthesis of **2** and **3**.

1,3,6,8-Tetrakis(2,4,6-trimethylphenyl)pyrene 1. Yield 78%; mp 242 °C; IR (KBr) cm^{-1} 3041, 1593, 1179; ^1H NMR (CDCl_3 , 400 MHz) δ 1.93 (s, 24H), 2.37 (s, 12H), 6.99 (s, 8H), 7.51 (s, 4H), 7.59 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 20.70, 21.14, 26.91, 124.77, 125.86, 128.04, 128.43, 129.01, 136.20, 136.75, 137.15.

1,3,6,8-Tetrakis(2,3,5,6-tetramethylphenyl)pyrene 2. Yield 75%; mp 291 °C; IR (KBr) cm^{-1} 3042, 1592, 1180; ^1H NMR (CDCl_3 , 400 MHz) δ 1.77 (s, 24H), 2.21 (s, 24H), 6.97 (s, 4H), 7.40 (s, 4H), 7.48 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 17.18, 20.16, 124.89, 125.80, 128.52, 129.17, 130.61, 132.73, 133.32, 137.43, 140.25.

1,3,6,8-Tetrakis(2,6-dimethyl-4-methoxyphenyl)pyrene 3. Yield 80%; mp 249 °C; IR (KBr) cm^{-1} 3042, 1592, 1179; ^1H NMR (CDCl_3 , 400 MHz) δ 1.91 (s, 24H), 3.78 (s, 12H), 6.73 (s, 8H), 7.50 (s, 4H), 7.52 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 20.07, 55.25, 112.71, 124.81, 125.89, 128.79, 129.71, 132.67, 136.00, 138.28, 158.66.

PL Quantum Yield Measurements

Solution State. For determination of fluorescence quantum yields, the solutions of tetraarylpyrenes **1-3** were prepared in cyclohexane (spectral grade) such that their absorbance at $\lambda = 330$ nm was ca. 0.042. These solutions were used for detecting fluorescence at 298 K. The excitation wavelength was chosen as 330 nm for all the samples and the emission in each case was recorded in a right angle mode between 355–630 nm. The quantum yield was calculated from the following relation:

$$\phi_u = \phi_s (A_s/A_u) (I_u/I_s) (\eta_u/\eta_s)^2$$

where the subscripts 's' and 'u' refer to standard and unknown samples, A_u and A_s to absorbances of the sample and the standard at the excitation wavelength, I_u and I_s to the integrated emission intensities (i.e., areas under the emission curves) of the sample and the standard, and η_u and η_s to the refractive indexes of the corresponding solutions (pure solvents are assumed). 9,10-Diphenylanthracene was chosen as a reference for quantum yield determination, for which the reported quantum yield in cyclohexane is 0.90.⁴

Solid State Photoluminescence. The films of pyrenes **1-3** were prepared on quartz plates by vacuum deposition (ca. 10^{-6} torr). The thickness of the films was uniformly maintained at 1000 Å during evaporation. The solid-state quantum efficiencies of these films were measured using an integrating sphere method.⁵ The excitation source was 325 nm laser beam for all the samples.

Electrochemical Measurements

The cyclic voltammetry experiments were performed on a BAS-100 B electrochemical analyzer. Data were collected and analyzed using the Electrochemical Analysis Software. All experiments were carried out in a three electrode compartment cell with a Pt wire counter electrode, a glassy carbon working electrode and Ag/AgNO₃ (0.1 M) reference electrode at varying scan rates. The supporting electrolyte used was 0.1 M tetrabutylammoniumhexafluorophosphate solution in dry dichloromethane and the cell containing the solution of the sample (1mM) and the supporting electrolyte was purged with a nitrogen gas thoroughly before scanning for its oxidation and reduction properties. The oxidation and reduction potentials were calculated by taking the average of the anodic and cathodic peak potentials. The HOMO and LUMO values were calculated by using the following general equation: $E_{\text{HOMO}} = E_{\text{ox}} + 4.8 \text{ eV}$;
 $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{g}}^{\text{opt}}$.

Fabrication and Characterization of OLEDs

The multilayer OLEDs were fabricated by employing the arylpyrenes **1-3** as emitting materials. The ITO coated glass substrates with a sheet resistance of $< 50 \text{ } \Omega/\text{sq}$ were cleaned sequentially in an ultrasonicator using acetone, detergent solution, deionized water, ethanol, 2-propanol, and then subjected to oxygen plasma and UV treatments.

Vacuum Deposition. Vacuum deposition of the organic materials such as NPB, **1** or **2** or

3, TPBI, LiF and Al was carried out under a pressure of 10^{-6} torr on top of the etched ITO glass substrates sequentially. The rate of deposition for organic materials was maintained in the range 0.1-0.5 Å/s. The evaporation rate and thickness of the organic layers were monitored by a quartz oscillator. After the vacuum deposition, the devices were sealed in an inert atmosphere glove box. EL spectra of the devices were obtained using a diode-array rapid analyzer system.

Electroluminescence Measurements. Current voltage and light intensity measurements were done on a Keithley 2400 Source meter and a Newport 1835C Optical meter equipped with a Newport 818-ST silicon photodiode, respectively.

X-Ray Crystal Structure Determinations. The single crystals of **1** suitable for the X-ray determination were grown by slow evaporation of their solutions. The crystal was mounted along its longest dimension and the intensity data were collected on a Bruker SMART/CCD diffractometer using MoK α ($\lambda = 0.71073$ Å) radiation at 100 K. The structure was solved by direct methods and refined on F^2 by a full-matrix least-squares technique using SHLEXL-97.⁶ All atoms with the exception of hydrogens were refined anisotropically. The details of structure and refinement are provided below. The solvent ethyl acetate was found to be highly disordered, and the minor positions were subjected to constrained refinement.

Table S1. X-Ray Crystallographic Details for the Tetramesitylpyrene 1.

Substrate	1
<i>M_f</i>	C ₁₆₁ H ₁₅₉ Cl ₃ O ₂
<i>M_w</i>	2232.23
solvent of crystallization	EtOAc/CHCl ₃
crystal system	triclinic
<i>a</i> (Å)	15.9641(2)
<i>b</i> (Å)	19.592(2)
<i>c</i> (Å)	21.963(2)
<i>α</i>	79.721°(3)
<i>β</i>	70.064°(3)
<i>γ</i>	88.050°(2)
<i>V</i> (Å ³)	6351.5(1)
space group	<i>P</i> -1
<i>ρ_{calc}</i> (g/cm ³)	1.167
<i>T</i> (K)	100
<i>R</i> ₁ [<i>I</i> >2σ(<i>I</i>)]	0.0945
<i>wR</i> ₂	0.1938

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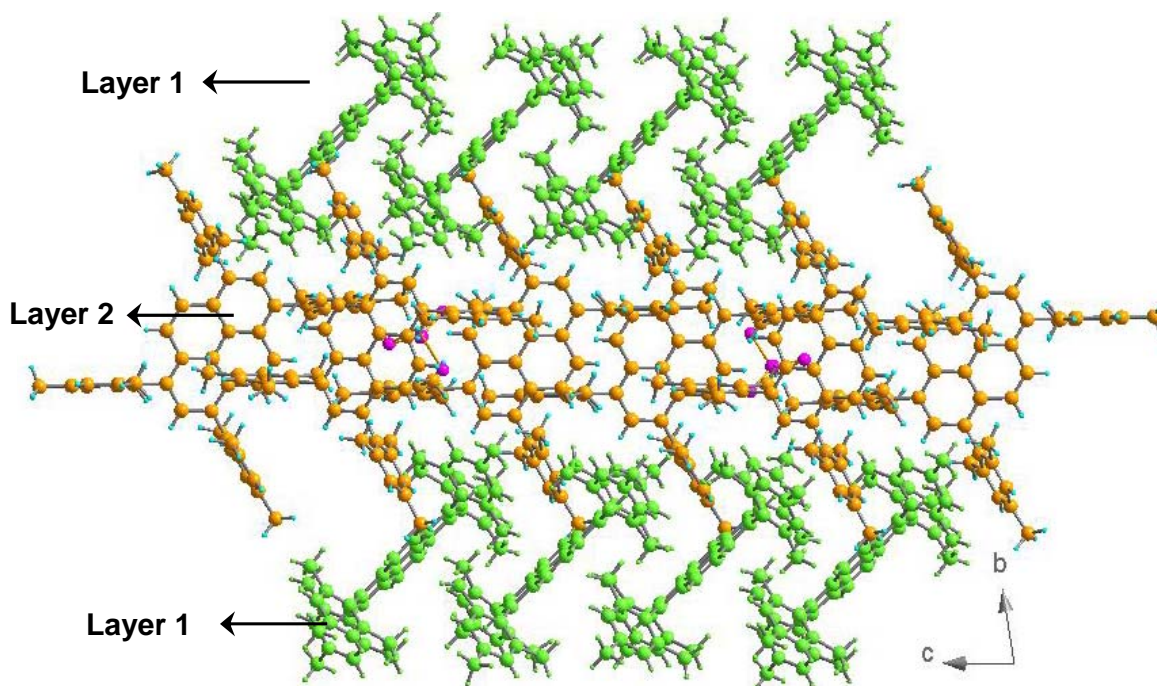


Figure S1. The crystal packing diagram of tetramesitylpyrene **1**. The orthogonal arrangement of the molecules in the unit cell may be readily observed down '*a*' axis. Two molecules of chloroform are included in the unit cell (shown magenta). The disordered ethyl acetate molecules have been removed for clarity.

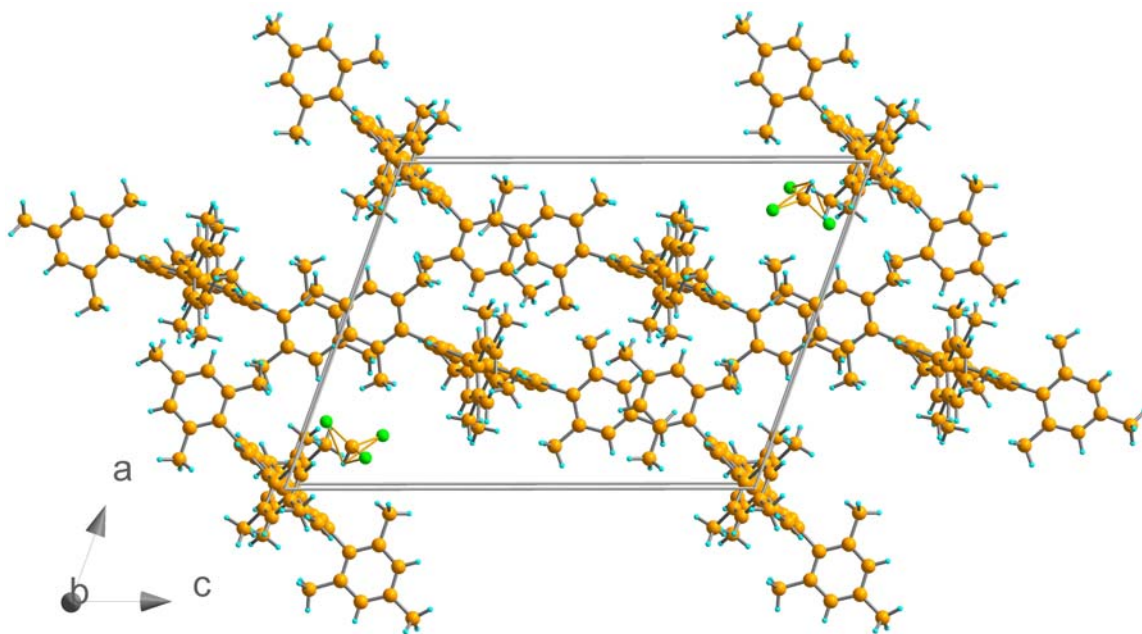


Figure S2. The arrangement of molecules in the central layer (Layer 2, Figure S1) of the unit cell of tetramesitylpyrene **1**. Two guest molecules of chloroform are included in the lattice (shown green). The disordered ethyl acetate molecules have been removed for clarity.

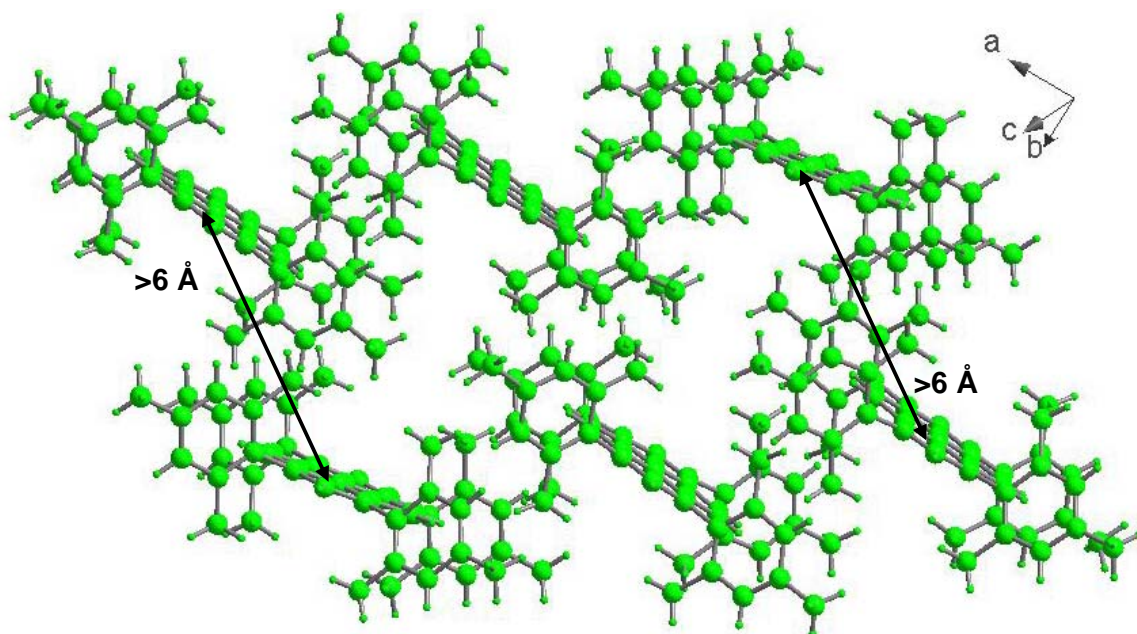


Figure S3. The arrangement of molecules in the layer 1 (Figure S1) of the unit cell of tetramesitylpyrene **1**. The distance between the centers of the pyrene rings is greater than the distance for efficient π -stacking, i.e., $< \text{ca. } 4 \text{ \AA}$.

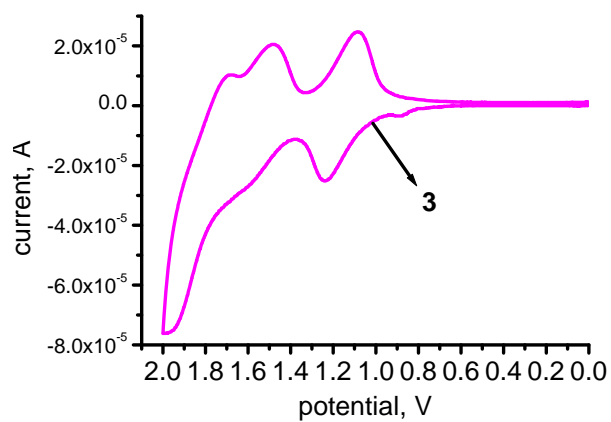
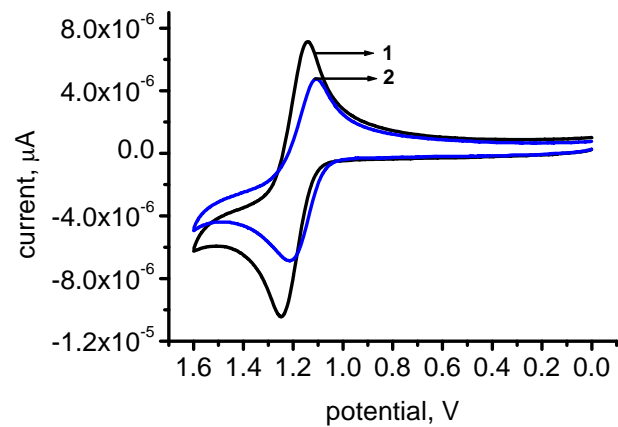


Figure S4. Typical cyclic voltammograms of **1-3** (1mM) in dichloromethane. Tetrabutylammonium hexafluorophosphate (0.1 M) was the supporting electrolyte.

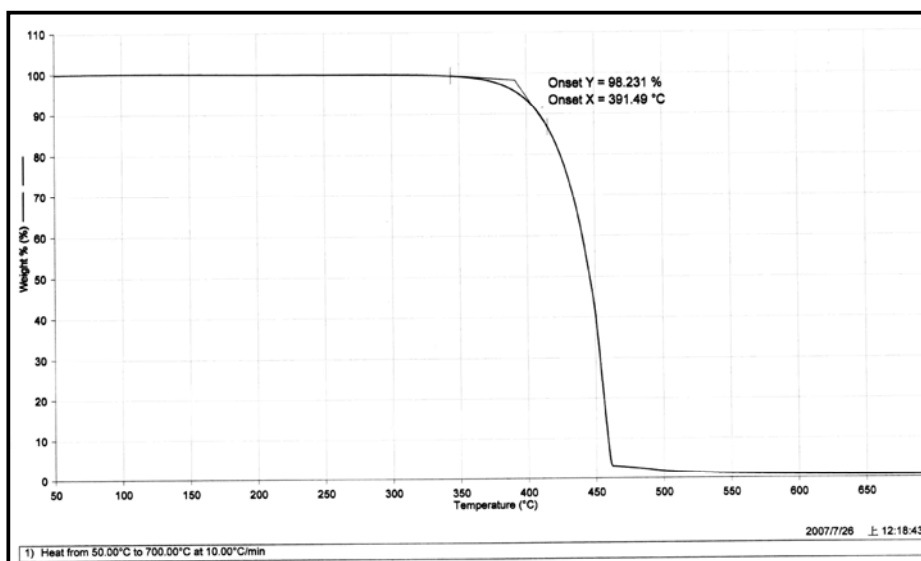
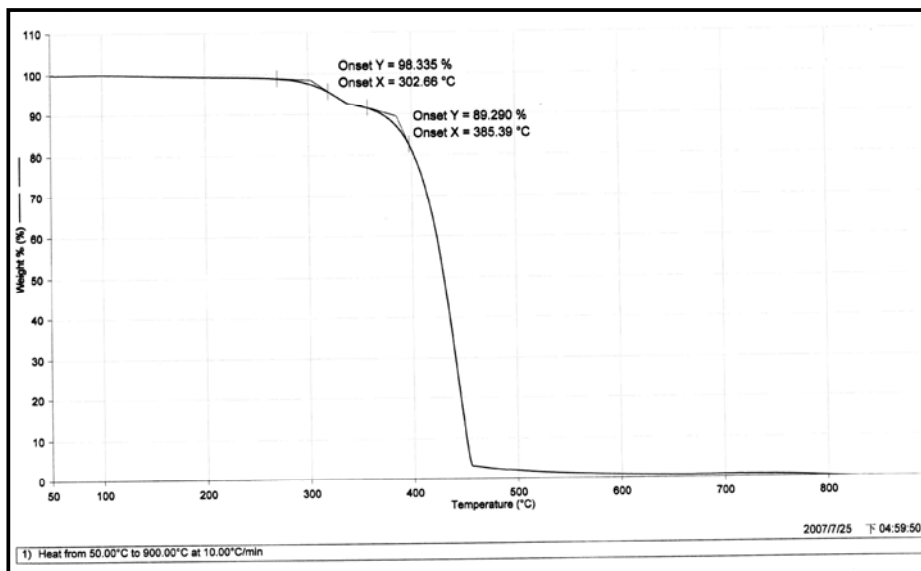


Figure S5. The TGA curves of **1** (top) and **3** (bottom).

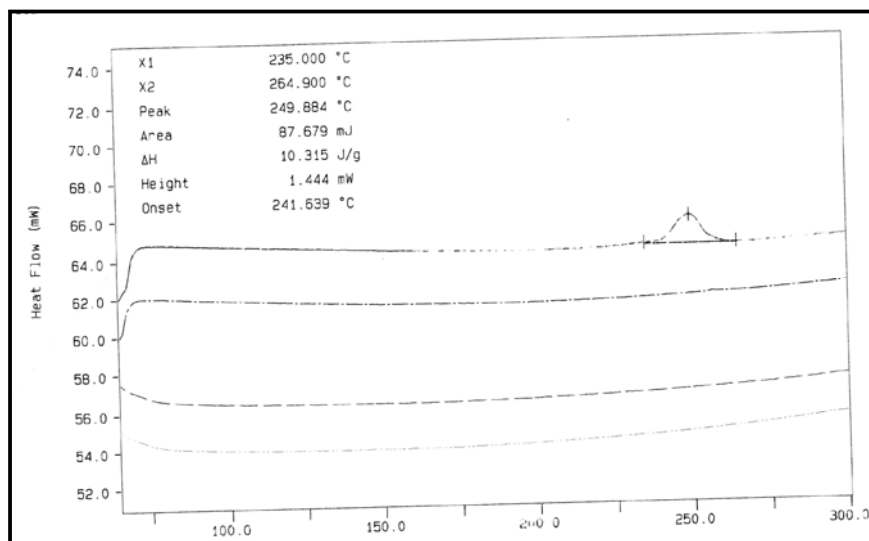
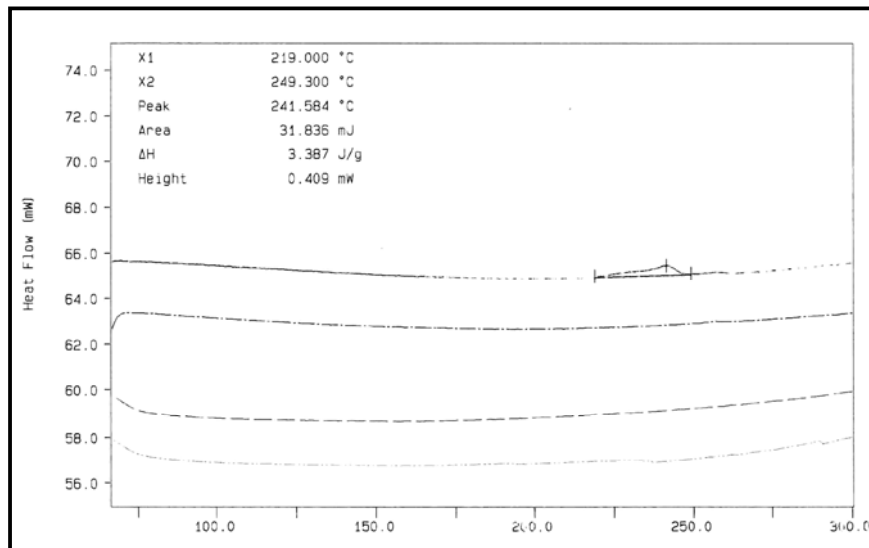


Figure S6. The DSC profiles of **1** (top) and **3** (bottom).

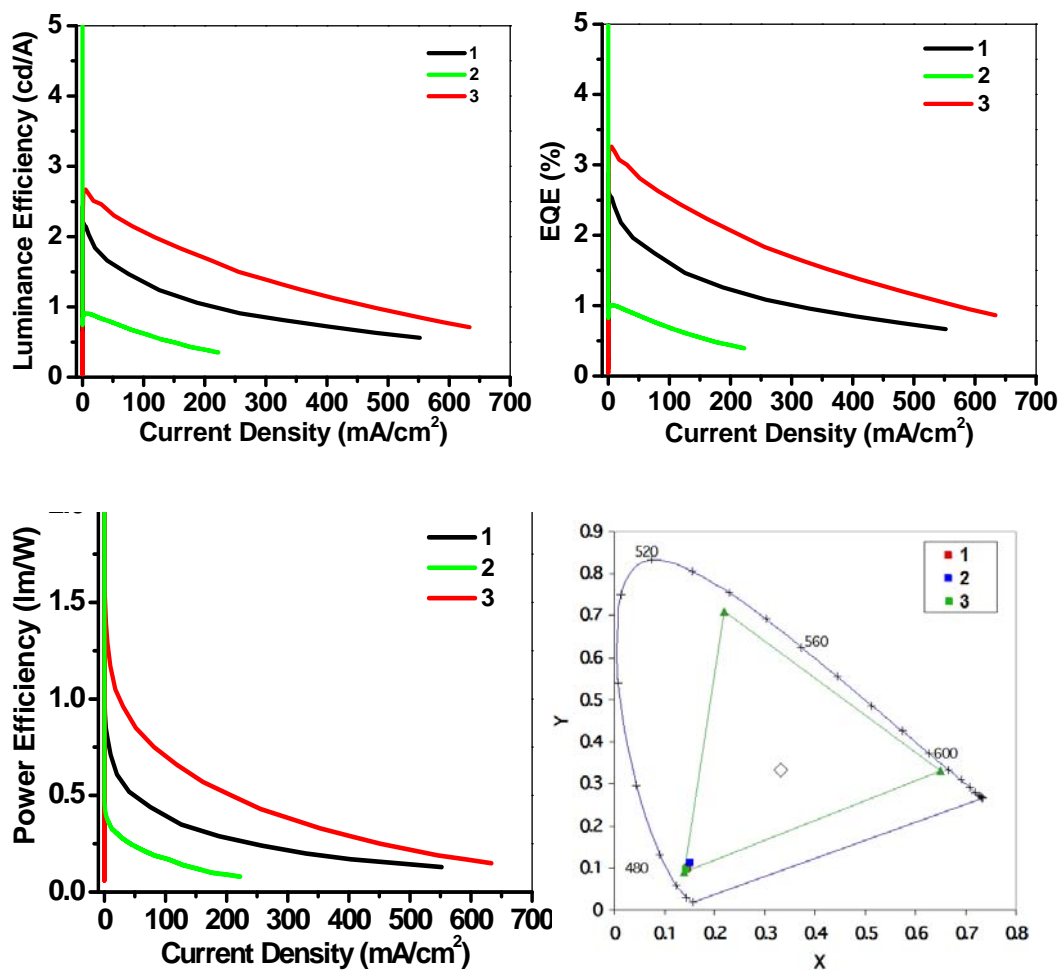


Figure S7. Top: The curves of luminescence (left) and external quantum efficiencies (right) of the devices made from **1-3**. Bottom: The power efficiencies (left) and CIE coordinates (right) for the devices of **1-3**. The common device configuration was: ITO/ NPB (400 Å)/**1-3** (100 Å)/TPBI (400 Å)/LiF (10 Å)/Al (1500 Å).

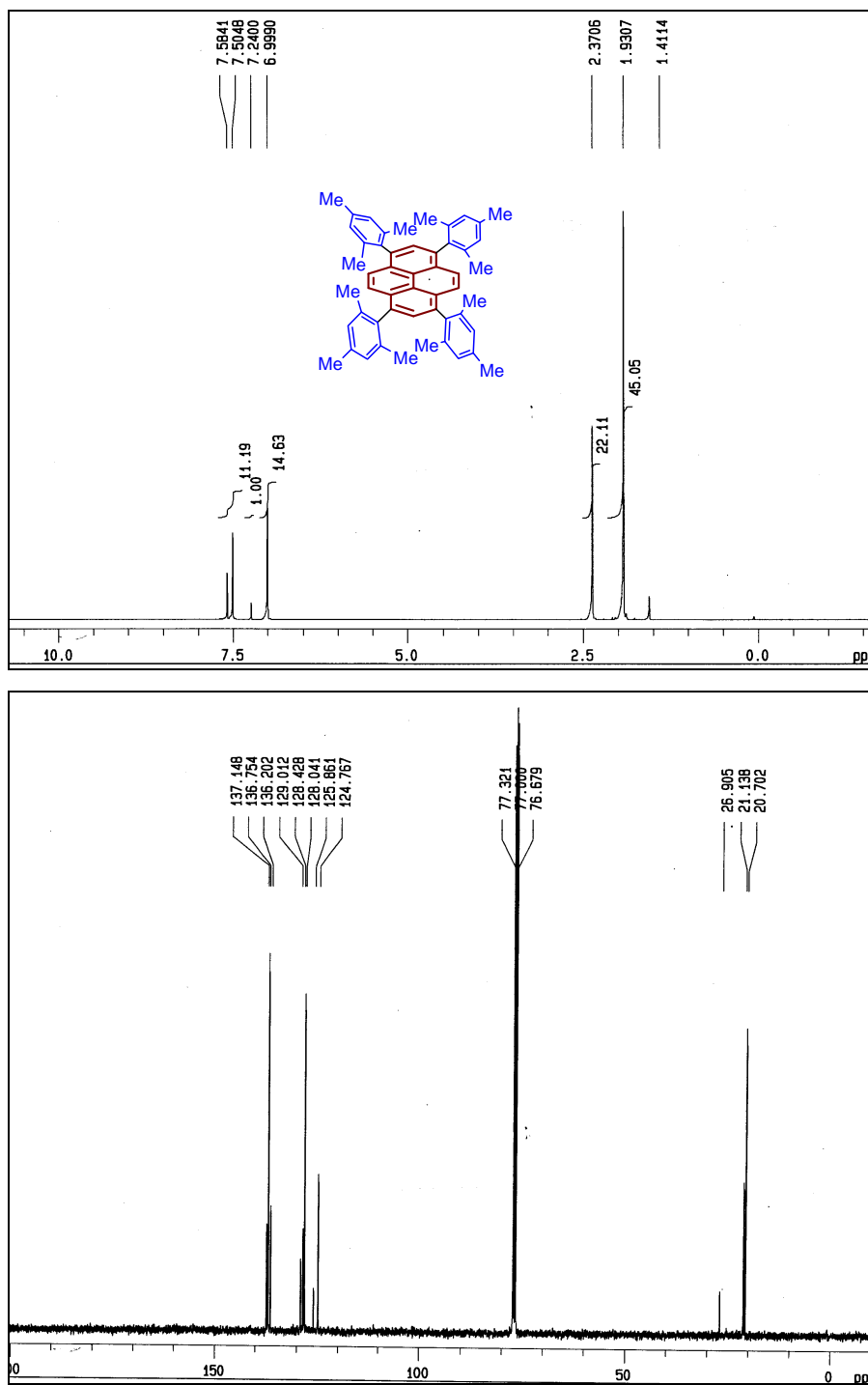


Figure S8. ^1H and ^{13}C NMR spectra of **1**.

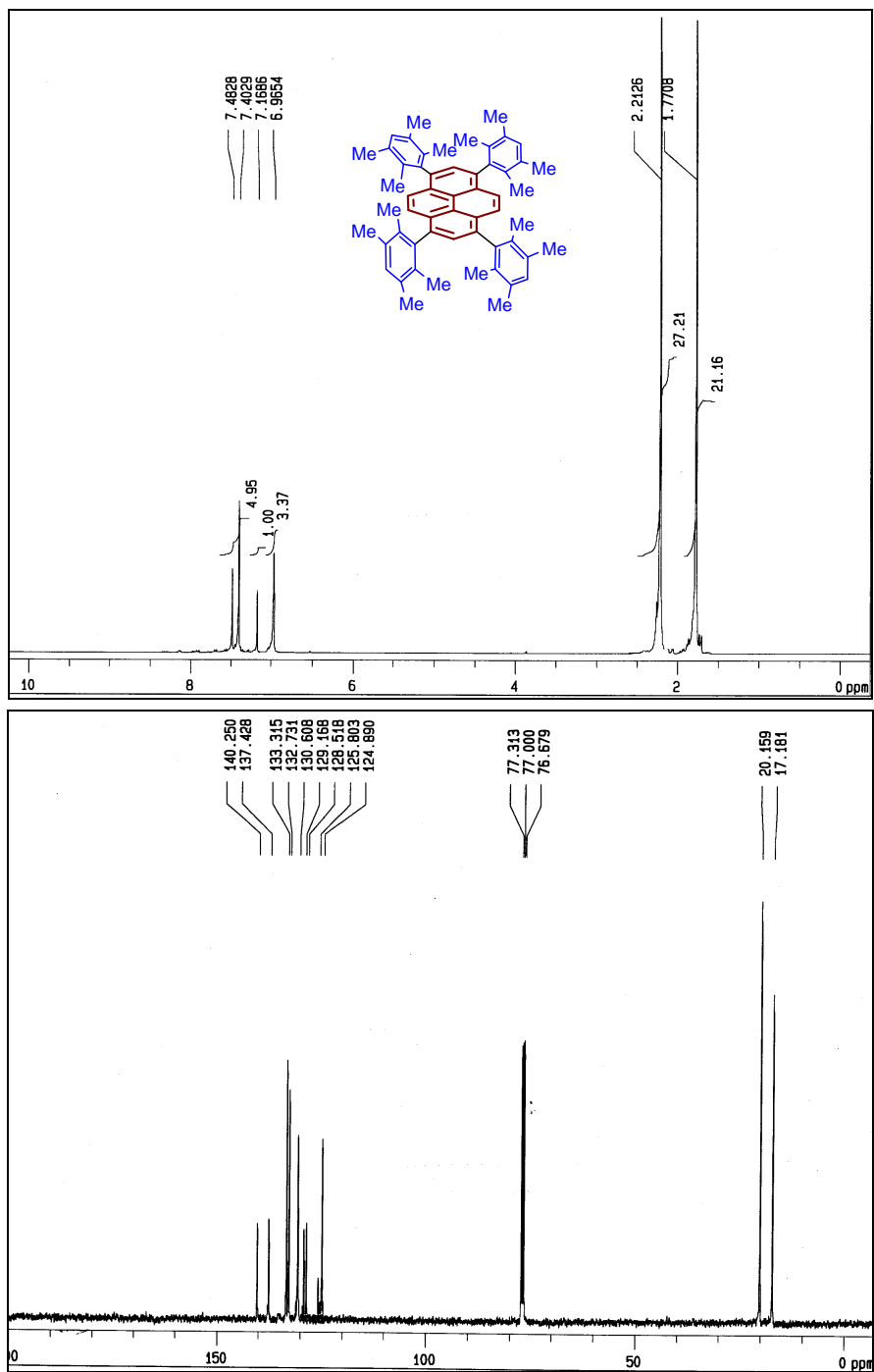


Figure S9. ^1H and ^{13}C NMR spectra of **2**.

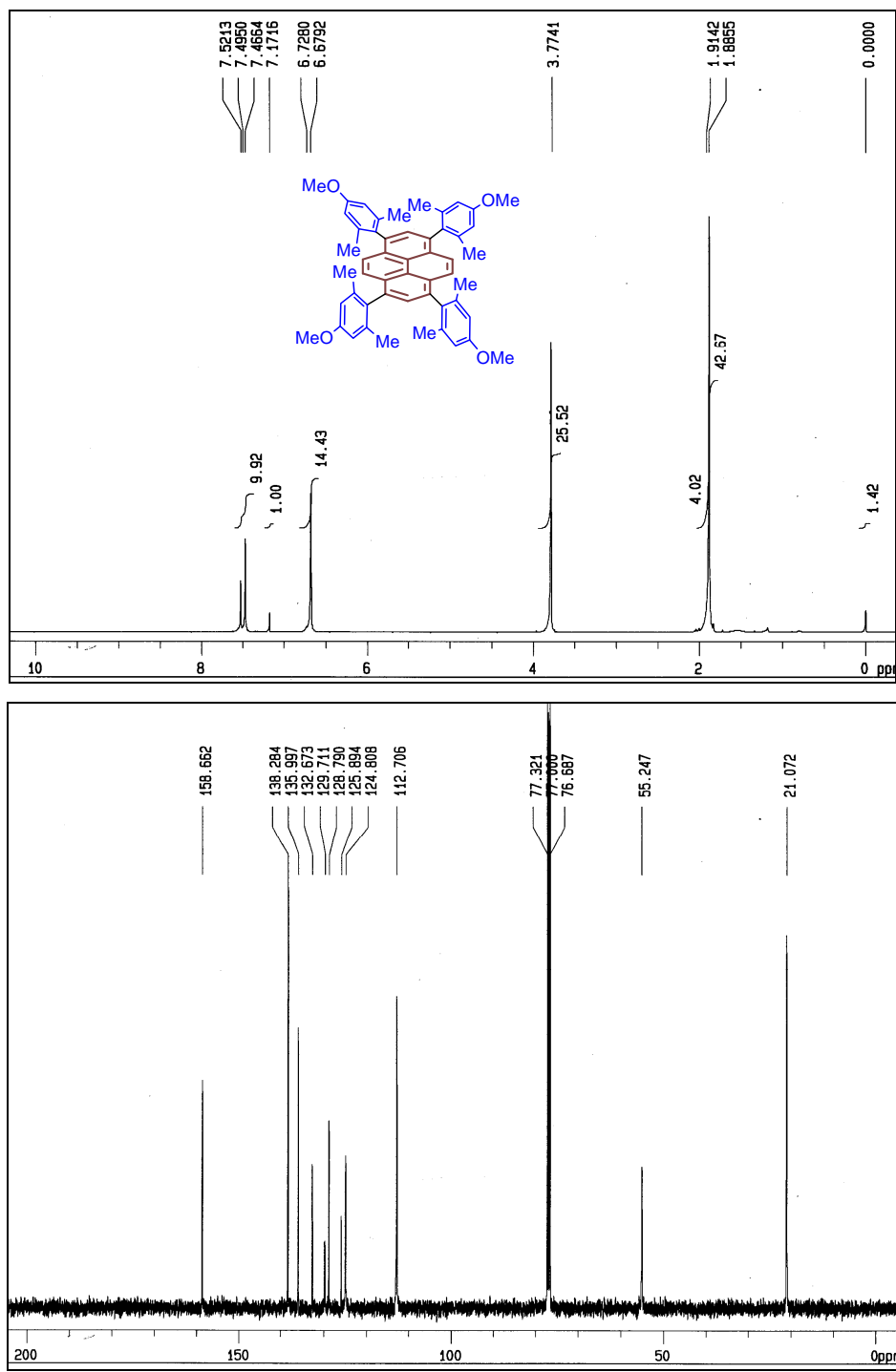


Figure S10. ¹H and ¹³C NMR spectra of 3.