

Supporting information

Synthesis, structure, physical properties and OLED application of pyrazine–triphenylamine fused conjugated compounds

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1. Experimental

1.1 Reagents and instruments

Most reagents were purchased from Alfa Aesar or Aldrich and used as supplied unless otherwise noted. All the solvents used in photophysical measurements and electrochemical measurements were of HPLC grade quality. All other solvents were obtained commercially and purified using standard procedures. Silica gel with 200-300 mesh were used in column chromatography, and precoated silica gel plates were utilized in thin-layer chromatography (TLC) and monitored by UV light. SHIMADZU GCMS-QP2010 puls spectrometer was employed in EI mass spectrometric measurements. Bruker Biflex III mass spectrometer was engaged in Matrix-assisted laser desorption/ionization reflectron time-of-flight (MALDI-TOF) mass spectrometry. Nuclear magnetic resonance (NMR) spectra were measured on Bruker Avance DPS-400 spectrometer at room temperature (298 K), and chemical shifts were referenced to the residual solvent peaks. Elemental analyses were recorded on a Carlo-Erba-1106 instrument. UV-Vis spectra were performed on a Hitachi U-3010 spectrometer, and Fluorescence emission spectra were monitored using a Hitachi F-4500.

Cyclic voltammetry measurements were monitored on a CHI660D electrochemical workstation (CH Instruments, Austin, TX). A dry weighing bottle was served as the container. The working electrode glassy carbon (3.0 mm in diameter) was polished on a felt pad with 0.05 μm alumina (Buehler, Ltd., Lake Bluff, IL), sonicated in deionized water for 2 min, and then dried before usage. The counter electrode platinum wire was rubbed with an abrasive paper, washed with deionized water and acetone, and dried. The reference electrode platinum wire was rubbed with an abrasive paper, washed with deionized water and acetone, and also dried. Ferrocene was added as external standard. The scan rate was 50 mV/s.

1.2 Synthesis procedures and characterization data for new compounds

Synthesis of compound 1

Diaminomaleonitrile (108 mg, 1.0 mmol) and 4,4'-bis(N,N-diphenylamino)benzil (540 mg, 1.0 mmol) were dissolved in anhydrous acetic acid (50 mL) with catalytic amount of 2-iodoxybenzoic acid (IBX). The solution was refluxed for 24 hours under Argon atmosphere. After that the crude product was concentrated in vacuo and purified by column chromatography (CH_2Cl_2 /petroleum ether=1/2), affording compounds **1** (542 mg, yield 88%). ^1H NMR (300 MHz, CDCl_3) δ 7.50 (d, 4 H), 7.34-7.29 (m, 8 H), 7.16-7.12 (m, 12 H), 6.96-6.93 (d, 4 H). ^{13}C NMR (75 MHz, CDCl_3) δ 154.09, 150.78, 146.55, 130.87, 129.76, 128.33, 127.54, 126.09, 124.80, 120.32, 113.77. HRMS ($M+1$) = 617.2440 (calc. 617.2454).

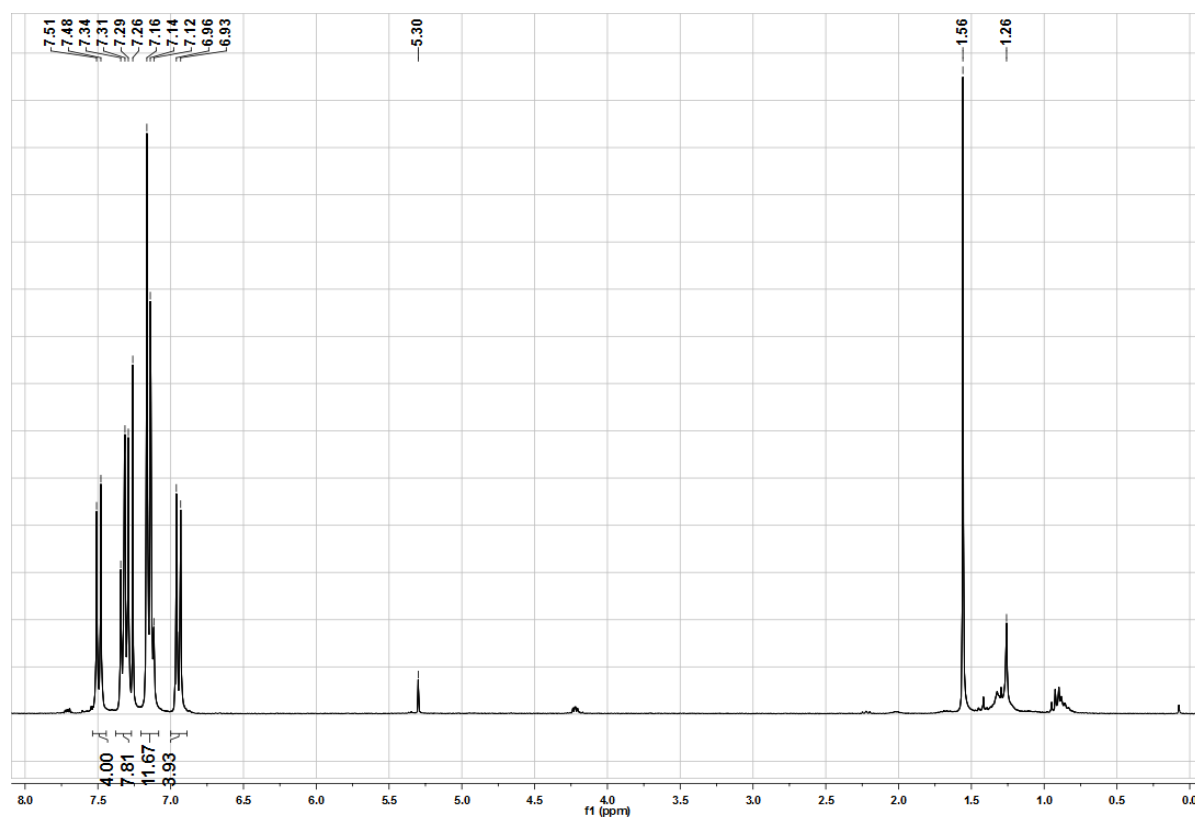
Synthesis of compound **2**

The procedure was the same with above except that diaminomaleonitrile was replaced by 2,3-Diaminopyridine (109 mg, 1.0 mmol). This reaction gave compounds **2** (549 mg, yield 89%). ^1H NMR (300 MHz, CDCl_3) δ 9.10-9.09 (m, 1 H), 8.47-8.44 (m, 1 H), 7.67-7.64 (m, 1 H), 7.59 (d, 2 H), 7.49 (d, 2 H), 7.31-7.27 (m, 7 H), 7.15-7.13 (m, 8 H), 7.10-7.08 (m, 3 H), 7.07-7.06 (m, 2 H), 7.04-7.00 (m, 3 H). ^{13}C NMR (75 MHz, CDCl_3) δ 156.15, 154.56, 153.25, 149.73, 149.39, 149.18, 147.27, 147.24, 138.16, 136.00, 131.85, 131.45, 131.24, 130.86, 129.56, 125.45, 125.32, 124.76, 123.91, 123.85, 121.99, 121.41. HRMS ($M+1$) = 618.2673 (calc. 618.2658).

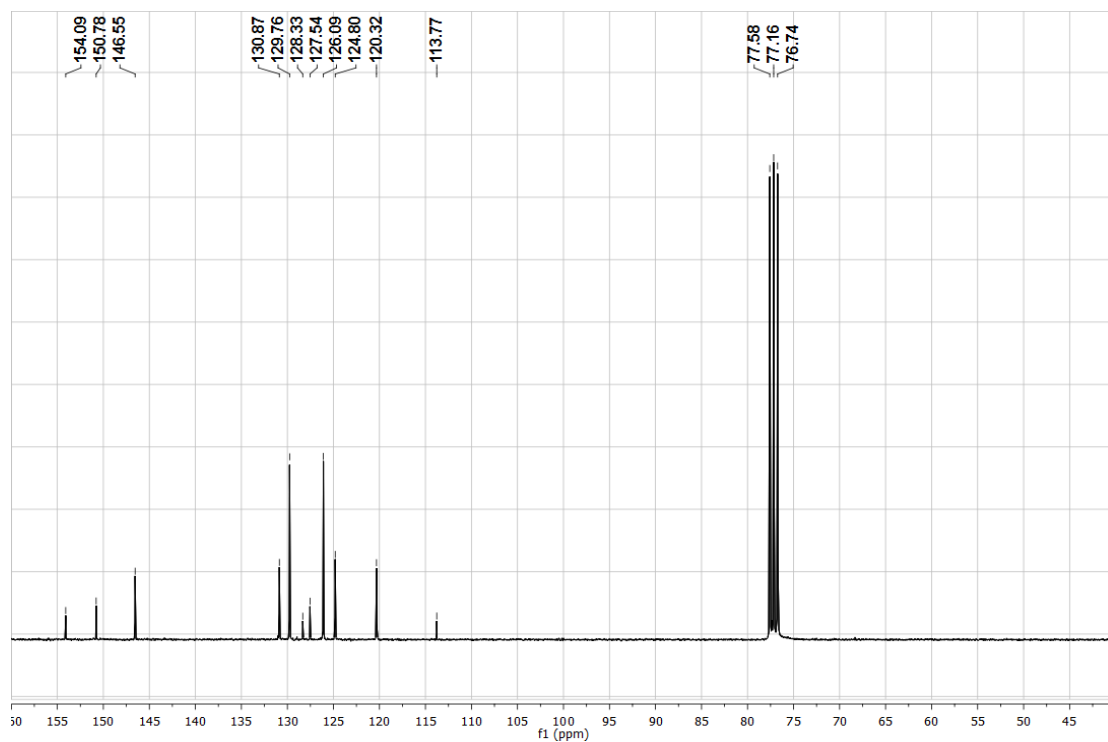
Synthesis of compound **3**

The procedure was the same with above except that 2,3-Diaminopyridine was replaced by 2,3,6,7-Tetraamino-9,9-bis(2-ethylhexyl) fluorene (596 mg, 1.0 mmol). This reaction gave compounds **3** (787 mg, yield 80%). ^1H NMR (300 MHz, CDCl_3) δ 8.45 (s, 1 H), 8.13 (s, 1 H), 8.09 (s, 1 H), 7.72-7.69 (m, 1 H), 7.54-7.52 (m, 1 H), 7.51-7.44 (m, 5 H), 7.29 (d, 6 H), 7.14 (d, 8 H), 7.09-7.04 (m, 8 H). ^{13}C NMR (75 MHz, CDCl_3) δ 167.90, 164.67, 152.15, 149.17, 148.58, 147.46, 143.96, 141.77, 136.57, 132.62, 131.02, 129.50, 128.95, 125.11, 123.59, 122.32, 117.76, 111.66, 106.33, 68.31, 54.93, 46.33, 38.89, 34.92, 34.87, 33.66, 33.32, 32.07, 30.52, 29.84, 29.59, 29.51, 29.40, 29.24, 29.08, 28.05, 26.95, 26.67, 26.62, 24.90, 23.91, 23.13, 22.84, 22.77, 14.87, 14.26, 14.19, 13.98, 13.95, 11.11, 10.26. HRMS ($M+1$) = 984.5613 (calc. 984.5508).

^1H NMR of compound 1



^{13}C NMR of compound 1



HRMS of compound 1

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

3 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

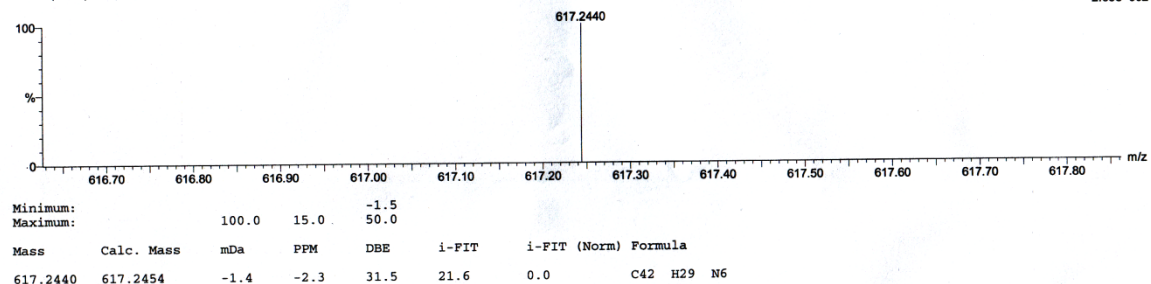
Elements Used:

C: 0-42 H: 0-29 N: 0-6

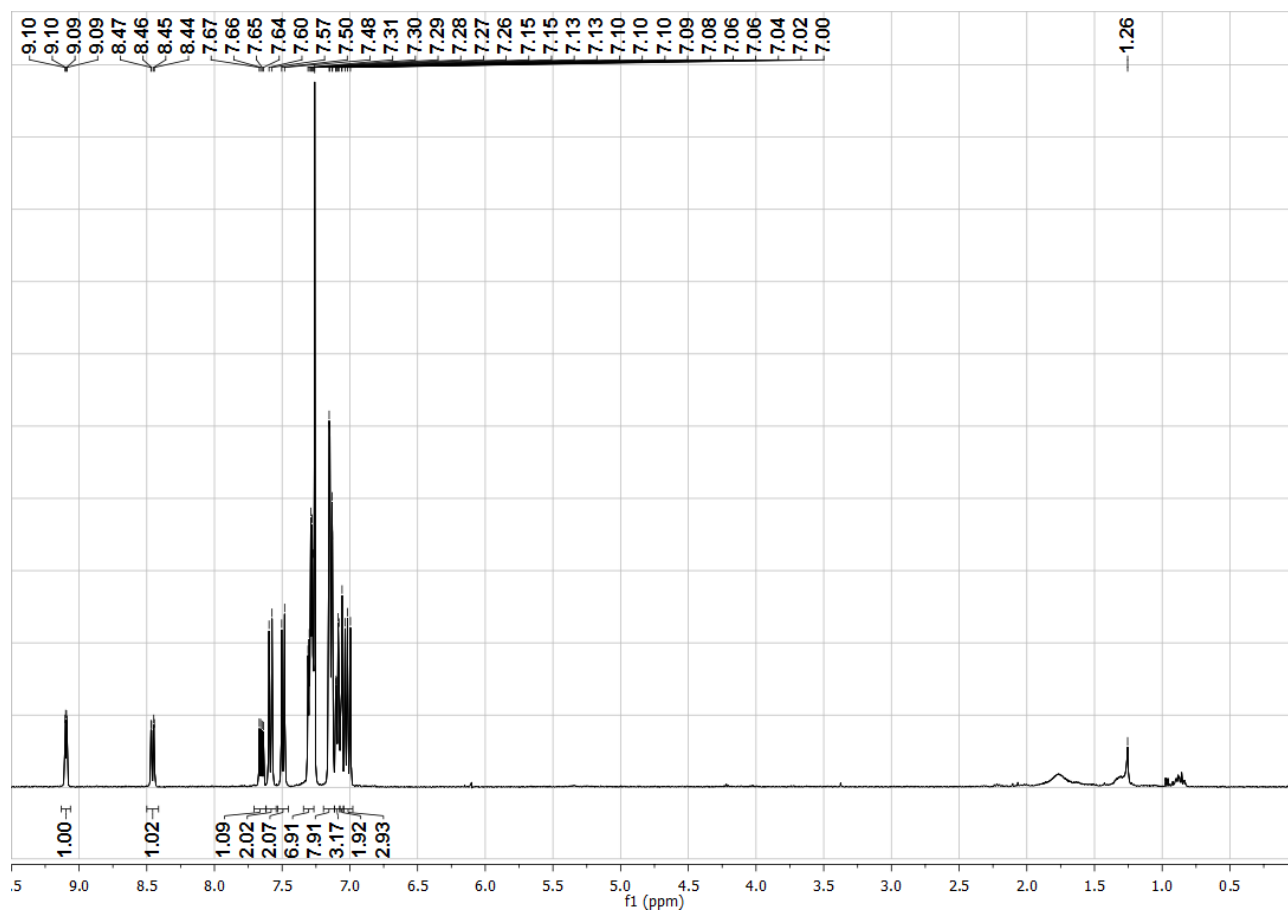
C42H28N6

XL-1 3 (0.082) Cm (1:6)

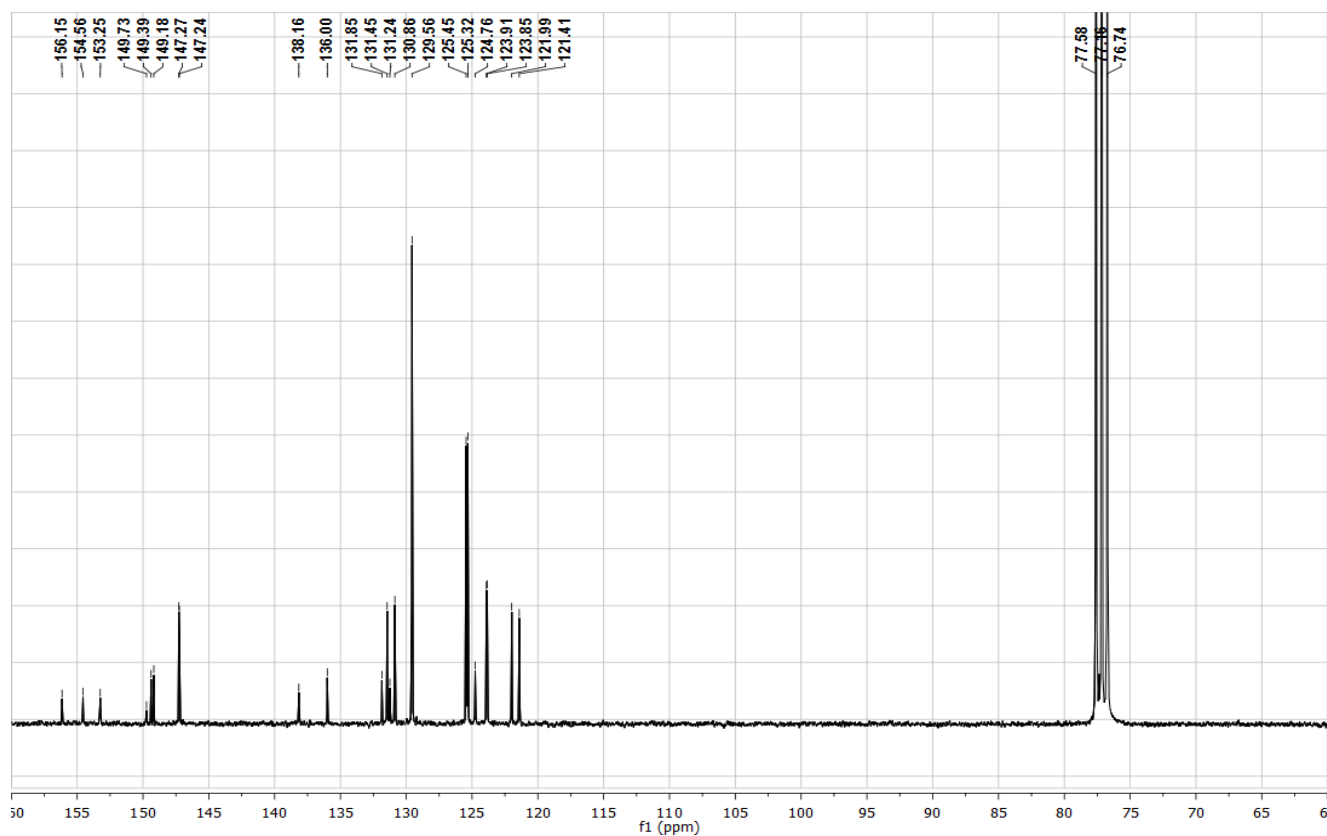
1: TOF MS ES+
2.65e+002



¹H NMR of compound 2



¹³C NMR of compound 2



HRMS of compound 2

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

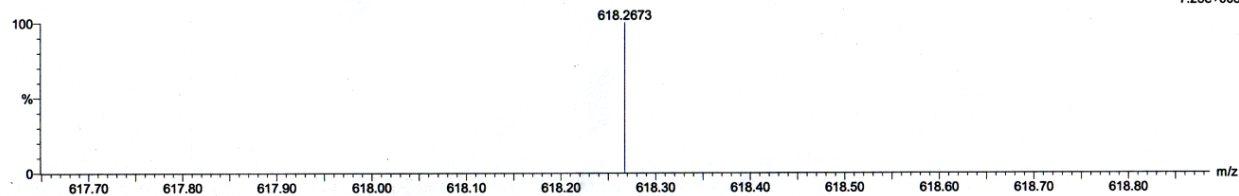
Elements Used:

C: 0-43 H: 0-32 N: 0-5

C₄₃H₃₁N₅

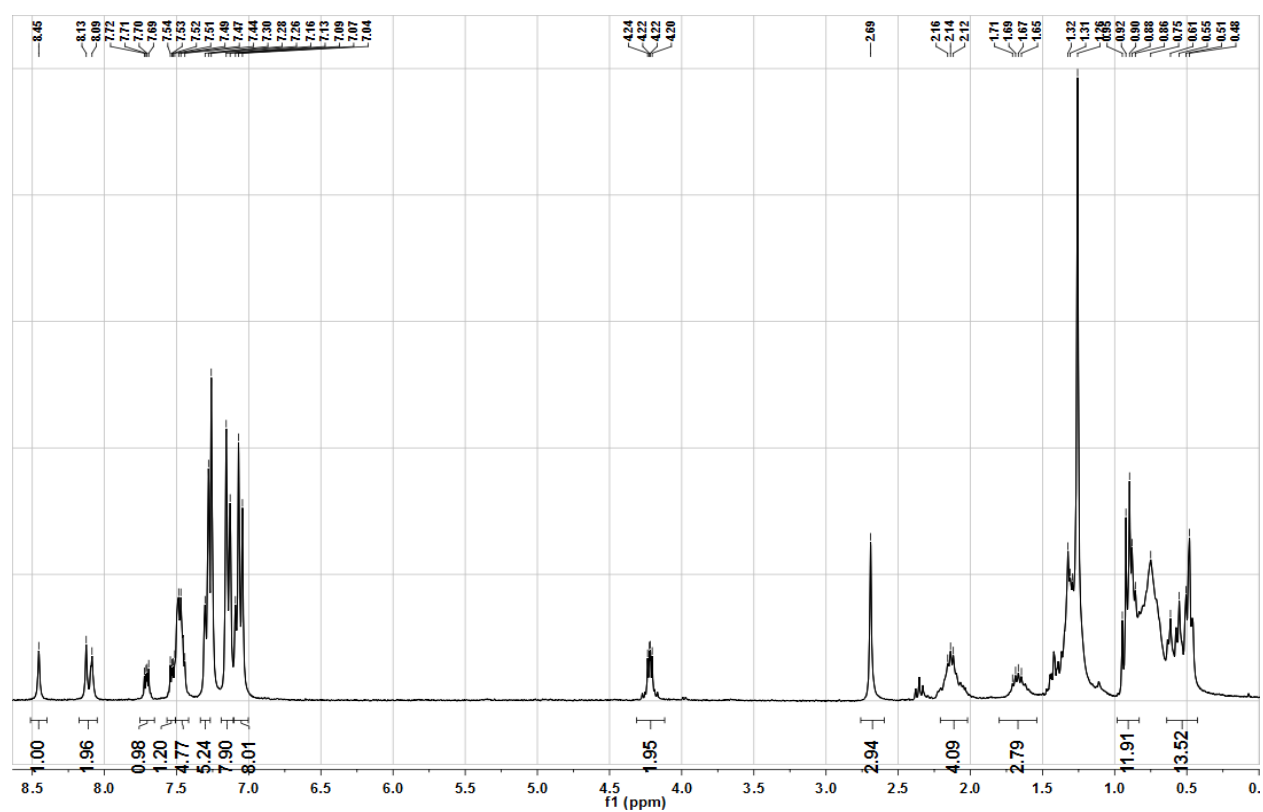
XL-4 3 (0.083) Cm (1:21)

1: TOF MS ES+
7.23e+003

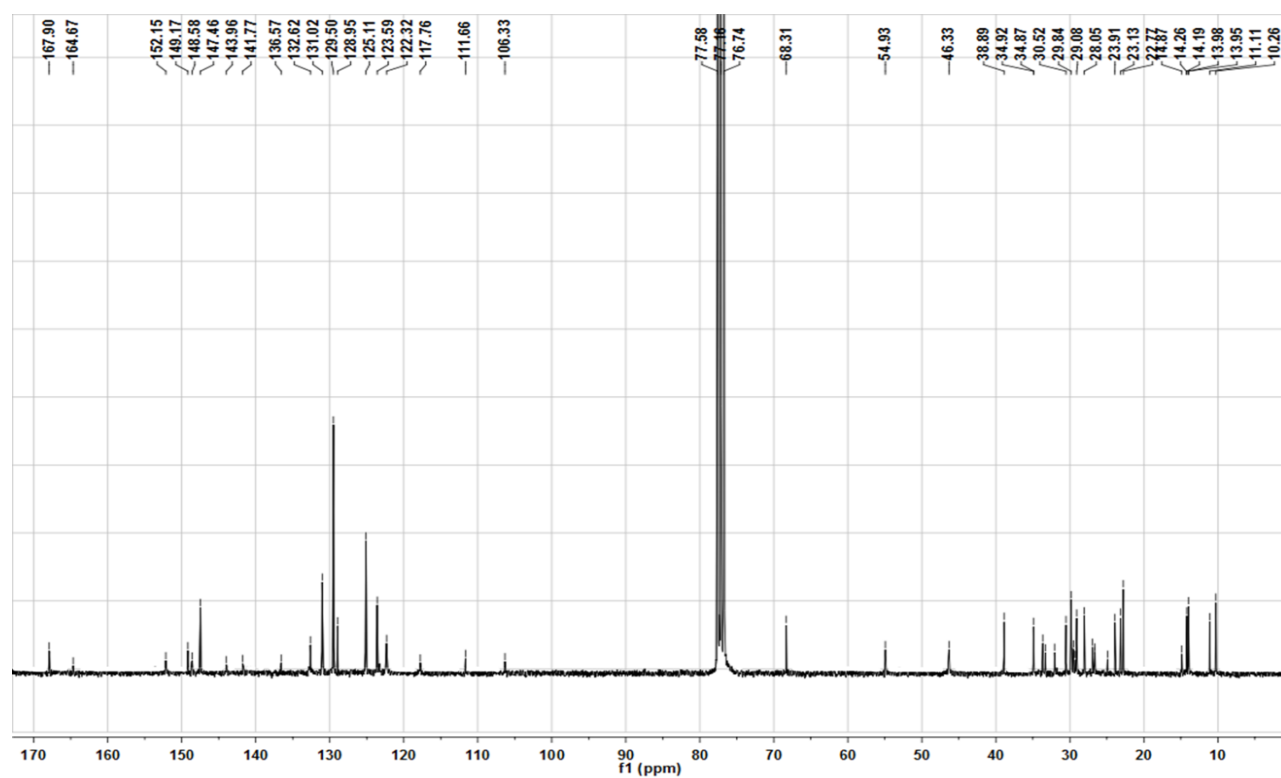


Minimum:				-1.5				
Maximum:	100.0	15.0		50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
618.2673	618.2658	1.5	2.4	30.5	29.9	0.0	C43	H32 N5

¹H NMR of compound 3



¹³C NMR of compound 3



HRMS of compound 3

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 15.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

2 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

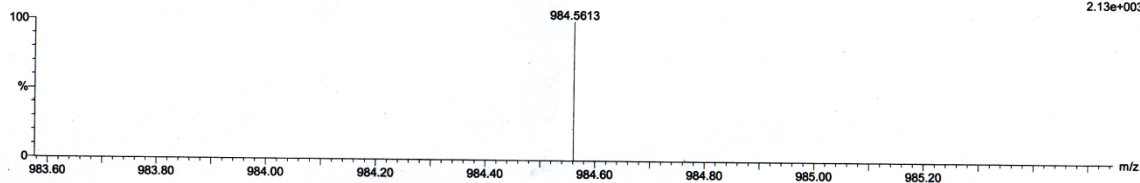
Elements Used:

C: 0-69 H: 0-70 N: 0-5 O: 0-1

C₆₉H₆₉N₅O₁

XL-6 3 (0.083) Cm (1:21)

1: TOF MS ES+
2.13e+003



Minimum:								
Maximum:	100.0	15.0		-1.5				
				50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula	
984.5613	984.5580	3.3	3.4	37.5	27.6	0.0	C ₆₉ H ₇₀ N ₅ O	

2.

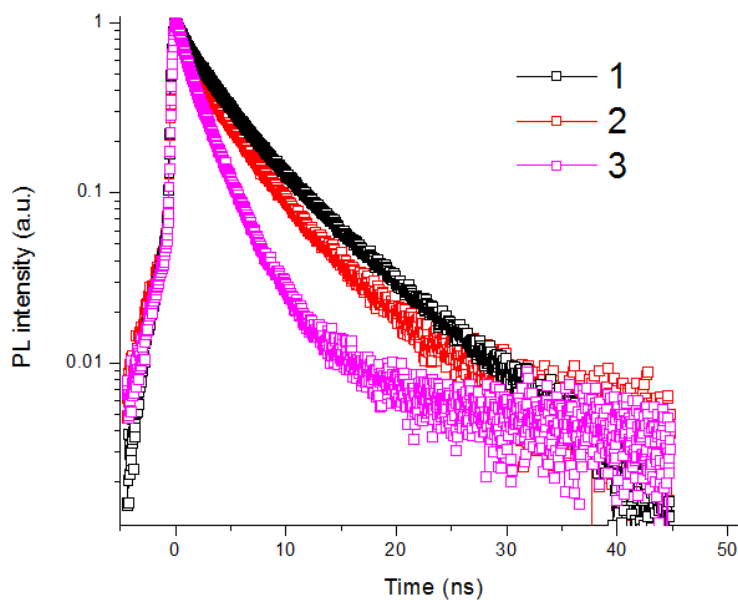


Figure S2 The lifetime of films of compound 1, 2 and 3

3.OLED devices

All devices were fabricated on commercial ITO-coated glass substrates. The ITO substrates were treated in order by ultrasonic bath sonication of detergent, de-ionized water, acetone and isopropanol, each with a 20 min interval. Then the ITO substrates were dried with nitrogen gas and baked in an oven at 80°C for 30 min. After that, oxygen plasma treatment was carried out in a plasma cleaner (FEMTO). Subsequently, the substrates were transferred into a thermal evaporator, where the organic, inorganic and metal functional layers were grown layer by layer at a base pressure better than 4×10^{-4} Pa. The evaporation rates were monitored with several quartz crystal microbalances located above the crucibles and thermal boats. For organic semiconductors and metal oxides, the typical evaporation rates were about 0.1 nm/s. For aluminium and LiF, the evaporation rates were about 1 to 5 nm/s and 0.01 nm/s, respectively. The intersection of Al and ITO forms a $1 \text{ mm} \times 1 \text{ mm}$ active device area. J-V and L-V data were collected with a source meter (Agilent B2902A) and a luminance meter (Konica Minolta, LS-110) with a customized Labview program. The electroluminescence spectra are measured with a spectrophotometer (Photo Research Inc., PR-705).

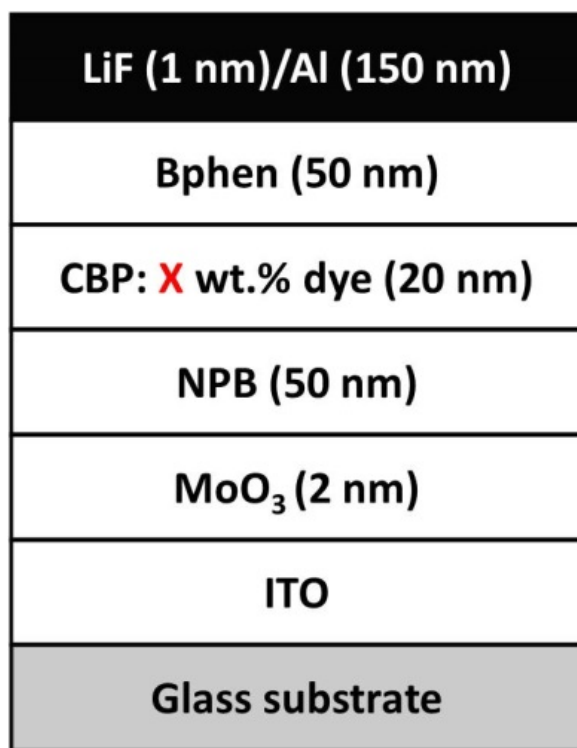


Figure S3-1 The OLED device structure

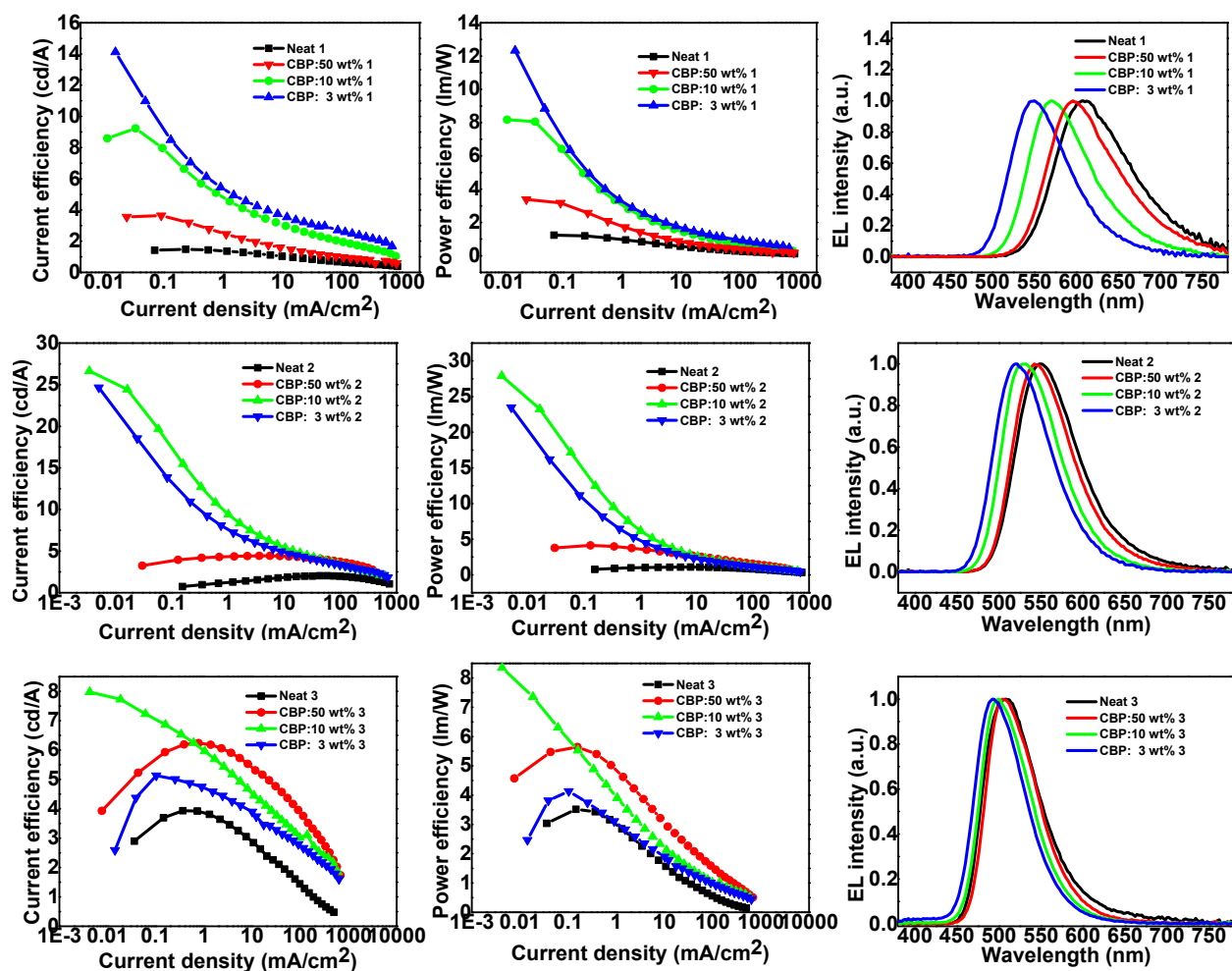


Figure S3-2 The current efficiency-current density, power efficiency-current density and electroluminescence spectra of compounds 1-3 (The EL spectra were collected at 6V)