Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Towards high efficiency solid emitters with aggregation-induced emission and electron-transport characteristics

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Content

Experimental

General information. 1-(4-bromophenyl)-1,2,2-triphenylethene (**1**) was prepared

following our previously published procedures.[1] Dimesitylboron fluoride (**2**) was perchased from Aldrich and used as received. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer. HRMS spectra were measured on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. Element analysis was performed on an Elementar Vario EL equipment (Germany). The $\Phi_{F,s}$ value in THF solution was estimated using quinine sulfate (Φ_F = 54% in 0.1 M H_2SO_4) as standard, while the $\Phi_{F,f}$ value of the solid film was determined using an integrating sphere. Single-crystal X-ray diffraction intensity data were collected on an Oxford Diffraction Xcalibur, Sapphire3, Gemini ultra was used along with the attendant suite of programs. The structure and refinement were conducted using the SHELXL suite of X-ray programs (version 6.10). TGA measurement was carried on a TA TGA Q5000 under nitrogen at a heating rate of 20 ^{o}C min^{-1}. Thermal transitions were investigated by a TA DSC Q1000 under nitrogen at a heating rate of 10 ^{o}C min^{-1}. The ground-state geometries were optimized using the density functional with B3LYP hybrid functional at the basis set level of 6-31G (d). All the calculations were performed using the Gaussian 03 package. Cyclic voltammograms (CV) were recorded on a Zahner IM6e Electrochemical Workstation with Pt, glassy carbon, and Ag/AgCl electrodes as counter, working, and reference electrodes, respectively at a scan rate of 100 mV s^{-1}, with 0.1 M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as the supporting electrolyte in anhydrous dichloromethane (DCM) purged with nitrogen. The HOMO energy levels were derived from the onset oxidation potentials ($E_{onset\text{-}ox}$) according to the equation: HOMO = $-(E_{onset\text{-}ox} + 4.8 - E_{ferrocene})$ eV. And the $E_{onset\text{-}ox}$ for TPEDMes is determined to be 1.454 eV by CV measurement.

EL device fabrication. The devices were fabricated on 80 nm-ITO coated glass with a sheet resistance of 25Ω □$^{-1}$. Prior to loading into the pretreatment chamber, the ITO-coated glass was soaked in ultrasonic detergent for 30 min, followed by spraying with deionized water for 10 min, soaking in ultrasonic de-ionized water for 30 min, and oven-baking for 1 h. The cleaned samples were treated by perfluoromethane plasma with a power of 100 W, gas flow of 50 sccm, and pressure of 0.2 Torr for 10 s in the pretreatment chamber. The samples were transferred to the organic chamber with a base pressure of 7×10^{-7} Torr for the deposition of NPB, emitter, and TPBi, which served as hole-transport, light-emitting, and eelectrontransport layers, respectively. The samples were then transferred to the metal chamber for cathode deposition to lithium fluoride (LiF) capped with aluminium (Al). The light-emitting area was 4 mm^2. The current density–voltage characteristics of the devices were measured by a HP4145B semiconductor parameter analyzer. The forward direction photons emitted from the devices were detected by a calibrated UDT PIN-25D silicon photodiode. The luminance and external quantum efficiencies of the devices were inferred from the photocurrent of the photodiode. The electroluminescence spectra were obtained by a PR650 spectrophotometer. All measurements were carried out under air at room temperature without device encapsulation.

Synthesis of TPEDMesB. Into a 100 mL one-necked round bottom flask was placed 617.0 mg (1.5 mmol) of 1-(4-bromophenyl)-1,2,2-triphenylethene (**1**). The flask was evacuated under vacuum and flushed with dry nitrogen for three times. Then 40 mL of THF was added. The mixture was cooled to −78 °C, and 0.72 mL (2.5 M in hexane, 1.8 mmol) of *n*-BuLi was slowly added. The mixture was stirred for more than 1 h at −78 °C.

Then 482.2 mg (1.8 mmol) of dimesitylboron fluoride (**2**) in 5 mL of THF was slowly injected to the reaction solution. 3 h later, the mixture was warmed slowly to room temperature. The crude product was purified on a silica-gel column using chloroform/hexane (1/5 by volume) as eluent. A white-green solid was obtained in 82.5% yield. ^{1}H NMR (400 MHz, $CDCl_3$-*d*), δ (TMS, ppm): 7.24, 7.22, 7.11, 7.10, 7.09, 7.04, 7.03, 7.01, 7.00, 6.98 (aromatic protons of tetraphenylethene moiety), 6.78 (s, 4H, aromatic protons in phenyl rings connected to B atom), 2.28 (s, 6H, methyl protons para to B atom), 1.96 (s, 12 H, methyl protons ortho to B atom). ^{13}C NMR (100 MHz, $CDCl_3$-*d*), δ (TMS, ppm): 147.67, 143.52, 143.41, 143.17, 141.79, 140.99, 140.78, 138.45, 135.72, 131.35, 131.31, 131.25, 130.85, 128.06, 127.67, 127.64, 127.50, 126.58, 126.54, 126.49, 23.36, 21.18. HRMS (MALDI-TOF, m/z): [M^+] calcd. for $C_{44}H_{41}B$: 580.3301; Found, 580.3254.

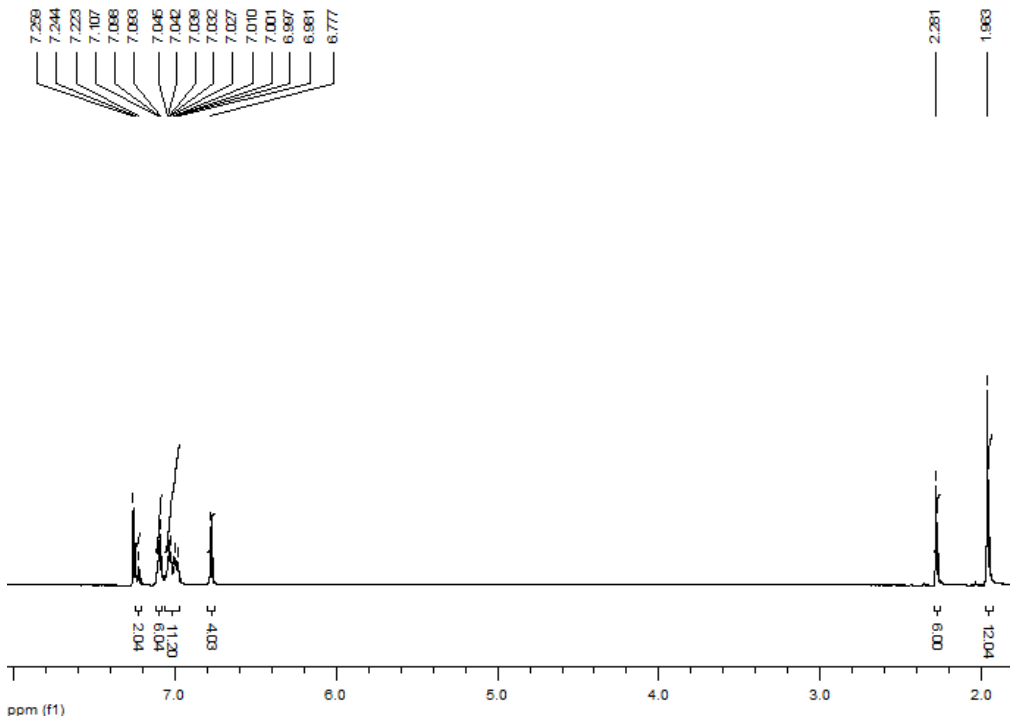

Fig. S1 ^{1}H NMR spectrum of TPEDMesB in $CDCl_3$-*d*.

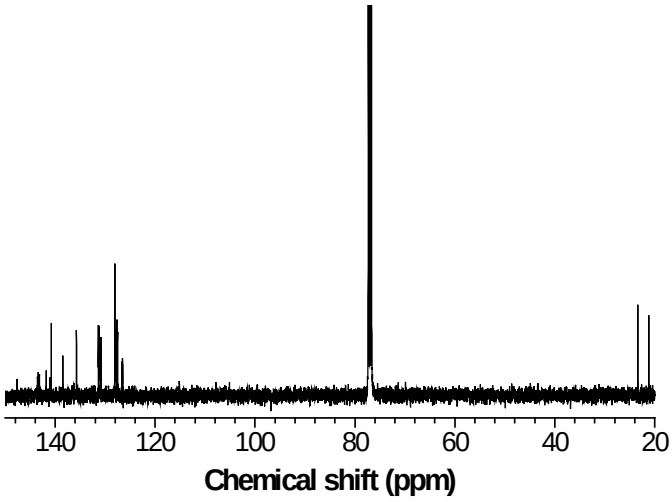

Fig. S2 ^{13}C NMR spectrum of TPEDMesB in $CDCl_3$-*d*.

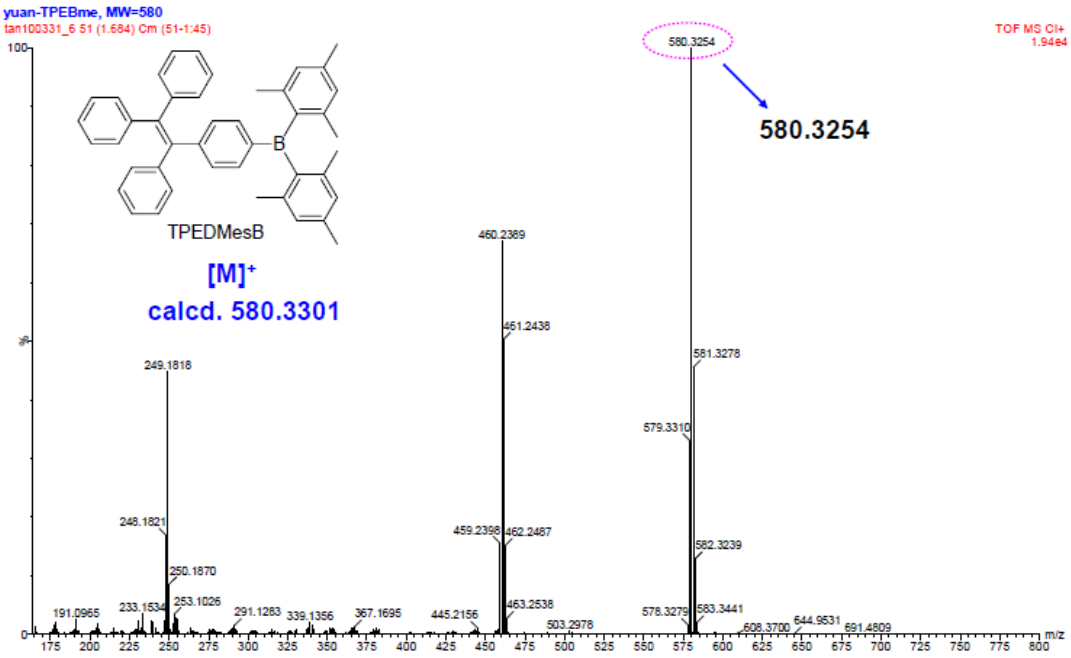

Fig. S3 MALDI-TOF mass spectrum of TPEDMesB.

Table S1 Element analysis result of TPEDMesB

content	*first run*	*second run*	*average value*	*theoretical value*
C (%)	90.73	90.73	90.73	91.02
H (%)	7.12	7.05	7.09	7.12

Table S2 Crystal data and structure refinement for TPEDMesB

Compound reference	TPEDMesB
Chemical formula	$C_{44}H_{41}B$
Formula Mass	580.58
Crystal system	Triclinic
a/Å	10.7027(2)
b/Å	17.7028(3)
c/Å	19.3060(6)
α/°	106.086(2)
β/°	103.506(2)
γ/°	97.0900(10)
Unit cell volume/Å^3	3347.44(13)
Temperature/K	143.0
Space group	*P*-1
No. of formula units per unit cell, *Z*	4
No. of reflections measured	23031
No. of independent reflections	12719
R_{int}	0.0204
Final R_1 values ($I > 2\sigma(I)$)	0.0796
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2109
Final R_1 values (all data)	0.0924
Final $wR(F^2)$ values (all data)	0.2245

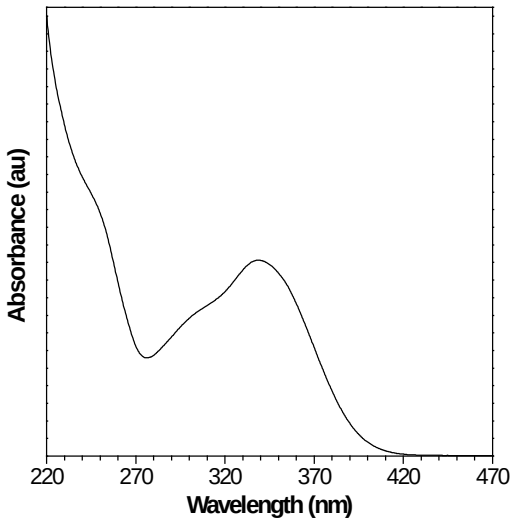

Fig. S4 Absorption spectra of TPEDMesB in THF.

		Diam. (nm)	% Number	Width (nm)
Z-Average (d.nm): 143.1	Peak 1:	84.00	100.0	27.86
PdI: 0.163	Peak 2:	0.000	0.0	0.000
Intercept: 0.963	Peak 3:	0.000	0.0	0.000
Result quality : Good				

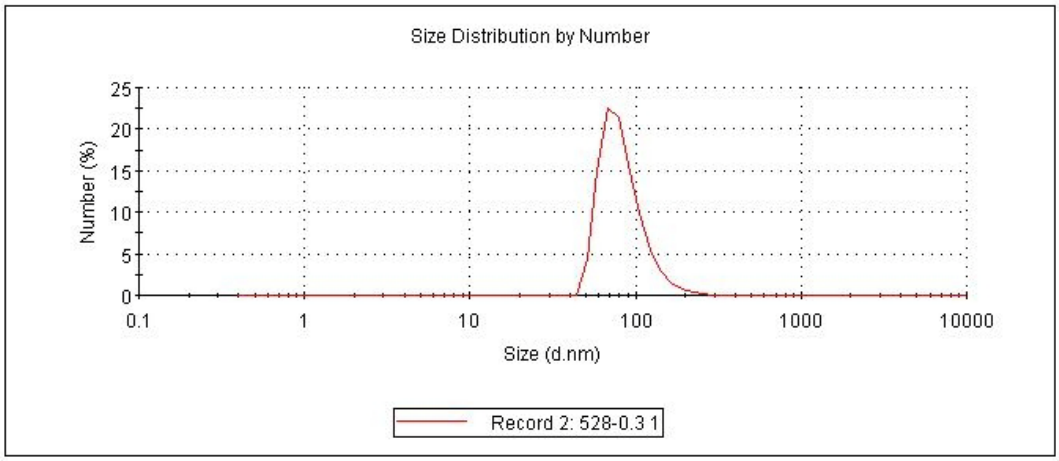

Fig. S5 Dynamic light scattering result of the nano-aggregates in 20/80 THF/water aqueous mixture.

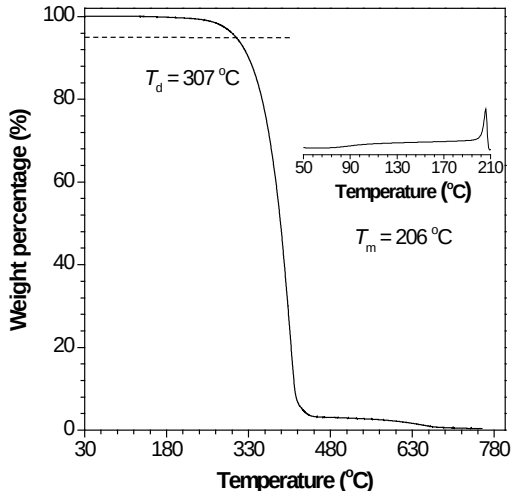

Fig. S6 TGA thermogram of TPEDMesB recorded under nitrogen at a heating rate of 20 ^{o}C min^{-1}. Inset: DSC thermogram of TPEDMesB recorded under nitrogen during the first heating cycle at a scan rate of 10 ^{o}C min^{-1}.

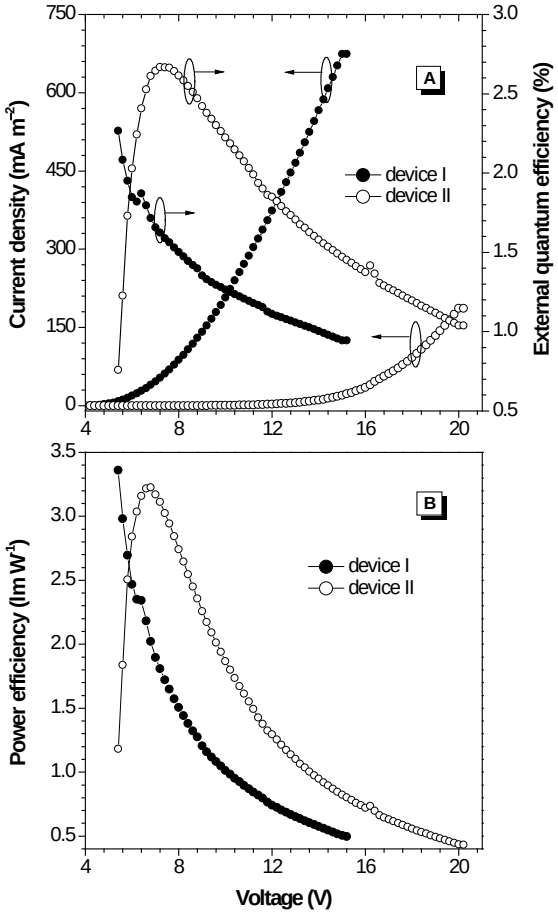

Fig. S7 (A) Current density–external quantum efficiency–voltage plots and (B) power efficiency–voltage plots for multilayer light-emitting diodes of TPEDMesB with a general device configuration of ITO/NPB/X /LiF/Al [X = TPEDMesB/TPBi (device I), X = TPEDMesB (device II)].

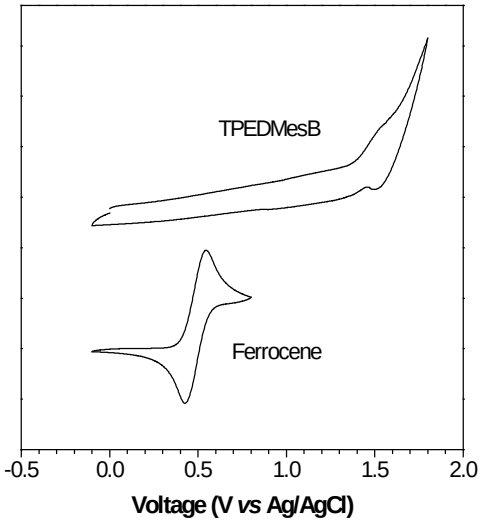

Fig. S8 Cyclic voltammogram of TPEDMesB in CH_2Cl_2 with 0.1 M Bu_4NPF_6 as a supporting electrolyte.

References

[1] W. Z. Yuan, P. Lu, S. Chen, J. W. Y. Lam, Z. Wang, Y. Liu, H. S. Kwok, Y. Ma, B. Z. Tang, *Adv. Mater.*, 2010, **22**, 2159.