Supplementary information

Efficient Delayed Fluorescence from Triplet-triplet Annihilation for Deep-blue Electroluminescence

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General Information

^{1}H and ^{13}C NMR spectra were carried out on a Bruker AV-400 MHz NMR spectrometer. Mass spectra were determined using a JMS-700 HRMS instrument. The absorption spectra were recorded on a Hitachi U-3300 model, while PL spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer. The TGA measurements were carried out using Perkin-Elmer TGA 7 under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The HOMO energy levels were determined from each neat thin film with the Riken Keiki Co. AC-II photoelectron spectrometer.

The molecular geometry optimizations and electronic properties were computed by carrying out the Gaussian 03 program with density functional theory (DFT) and time-dependent DFT (TDDFT) calculations, in which the Becke's three-parameter functional combined with Lee, Yang, and Parr's correlation functional (B3LYP) hybrid exchange-correlation functional with the 6-31G* basic set were used. The molecular orbitals were visualized on the Gaussview 4.1 software.

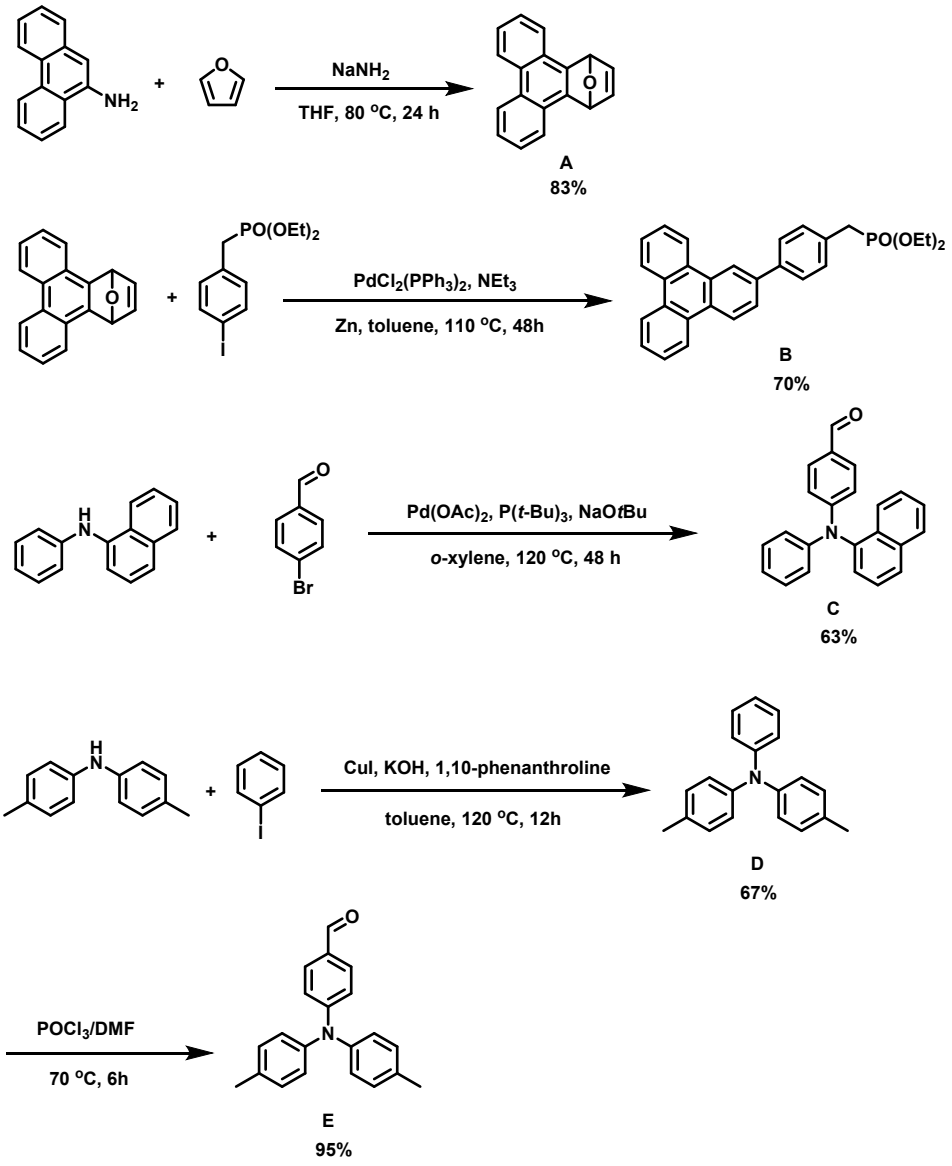
OLEDs were fabricated on indium-tin oxide (ITO)-coated glass substrates of thickness 100 nm and sheet resistance 30 Ω/sq. The ITO glasses were sequentially cleaned in ultrasonic bath using neutral detergent, distilled water and acetone and treated by UV-ozone

immediately prior to device fabrication. All organic and cathode layers were deposited using high-vacuum thermal evaporation (~5 × 10^{-7} Torr) without breaking vacuum. The deposition rates were ~0.1 nm/s for the organic materials and 0.01 nm/s for lithium fluoride (LiF), which were evaluated using calibrated thickness monitor. The deposition rate of dopant was adjusted according to the volume concentration in the host material. The Al cathode formed on the top of the organic layers, and the emission area was 3×3 mm^2. The electroluminescence (EL) characteristics of all devices were measured with a Keithley 2400 sourcemeter and luminance colorimeter (BM-7, Topcon). The EL spectra were recorded on a spectrometer (Hitachi F-4500).

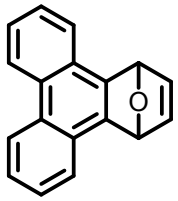
The time evolution of the electroluminescence properties of OLEDs was measured by an indigenously developed time-resolved emission spectrometer. In the typical experiment, OLEDs were driven by a pulse generator (Agilent 8114A) with voltage amplitude of 6 V, repetition rate of 20 kHz and pulse duration time of 10 μs. The light emitted from the samples was collected by a fiber-bundle and dispersed through a spectrometer (Princeton Instruments Acton SP2300). Subsequently, the selected signal (λ ~ 450 nm) was detected by using a cooled photomultiplier tube (PMT) detector (Becker & Hickl GmbH PMC-100) operated in photon-counting mode. The PMT pulses were recorded by using a fast multiscaler (Becker & Hickl GmbH MSA-300) with time resolution of 5 ns. The entire system was synchronized with a digital delay generator (Stanford Research Systems DG645).

Synthesis

Synthesis of 1,4-dihydro-1,4-epoxytriphenylene (A), diethyl 4-(triphenylen-2-yl) benzylphosphonate (B), 4-(naphthalen-1-yl(phenyl)amino)benzaldehyde (C), 4-methyl-*N*-phenyl-*N*-*p*-tolylaniline (D) and 4-(di-*p*-tolylamino)benzaldehyde (E):



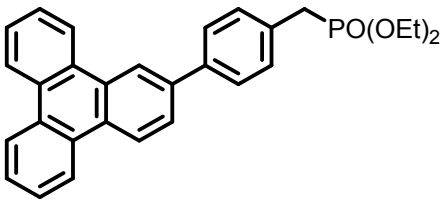
Procedures for the synthesis of 1,4-dihydro-1,4-epoxytriphenylene (A):



9-Bromophenanthrene (18.6 g, 72.3 mmol), sodium amide (8.47 g, 217.0 mmol) were charged in a two-necked bottle. The bottle was then vacuumed and purged with nitrogen, and dried THF (120 mL) and furan (78.1 mL, 1.07 mmol) were added to the bottle. The mixture in the bottle was heated to 70 °C for reaction for 24 hours, and the resulting was filtered to remove the salts. The filtrate was condensed to remove the solvent, and then purified by chromatography with hexanes to yield **A** (14.7 g, 83%) as white solid powder.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.73-8.71 (m, 2H), 7.95-7.92 (m, 2H), 7.65-7.60 (m, 4H), 7.27 (s, 2H), 6.38 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.0, 144.1, 128.8, 127.2, 126.7, 126.0, 123.6, 123.2, 82.1. HRMS *m*/*z*: $[M]^+$ calcd for $C_{18}H_{12}O$, 244.0888; found, 244.0885.

Procedures for the synthesis of diethyl 4-(triphenylen-2-yl)benzylphosphonate (B):

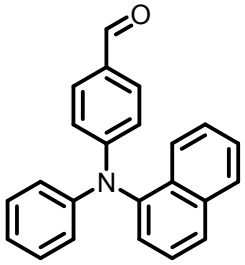


Compound **A** (760 mg, 3.11 mmol), zinc (1.85 g, 28.2 mmol), and $PdCl_2(PPh_3)_2$ (198 mg, 0.28 mmol) were charged in a two-necked bottle. The bottle was then vacuumed and purged with nitrogen, and dried toluene (30 mL), diethyl 4-iodobenzylphosphonate (0.65 mL, 2.82 mmol) and triethyl amine (3.91 mL, 28.2 mmol) were added to the bottle. The mixture in the bottle was heated to 110 °C for reaction for 48 hours, and the resulting was filtered to remove metal. The filtrate was condensed to remove the solvent, and then purified by

column chromatography (ethyl acetate/hexanes = 1/2) to obtain **B** (0.90 g, yield= 70%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.85 (s, 1H), 8.76-8.67 (m, 5H), 7.89 (dd, J = 8.6, J = 1.6 Hz, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.71-7.66 (m, 4H), 7.47 (d, J = 8.2 Hz, 2H), 4.12-4.05 (m, 4H), 3.26 (d, J = 20.0 Hz, 2H), 1.30 (t, J = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 139.4, 139.4, 139.0, 130.8, 130.7, 130.2, 130.1, 129.8, 129.8, 129.5, 129.3, 128.7, 127.2, 127.2, 127.1, 127.0, 127.0, 125.9, 123.6, 123.1, 123.1, 121.3, 62.1. 62.0, 34.0, 32.6, 16.3, 16.3. HRMS m/z: $[M]^+$ calcd for $C_{29}H_{27}O_3P$, 454.1698; found, 454.1703.

Procedures for the synthesis of 4-(naphthalen-1-yl(phenyl)amino)benzaldehyde (C):

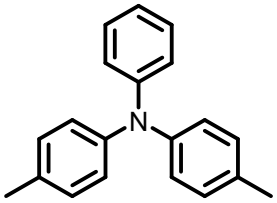


4-Bromobenzaldehyde (1.00 g, 5.40 mmol), 1-anilinonaphthalene (1.42 g, 6.48 mmol) and $Pd(OAc)_2$ (25 mg, 0.11 mmol) and NaO*t*Bu (623 mg, 6.48 mmol) were charged in a sealed tube. The sealed tube was deoxygenated and purged with nitrogen, and added dried *o*-xylene (30 mL) and tri-*tert*-butylphosphine (0.23 ml, 0.11 mmol). The reaction was heated to 120 °C, and stirred for 48 hours. The resulting was filtered to remove metal and then concentrated under reduced pressure and the residue was purified by column chromatography (hexanes/CH_2Cl_2 = 1/1) to afford **C** (1.10 g, 63%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.76 (s, 1H), 7.91 (d, J = 8.4 Hz, 1H), 7.85 (t, J = 7.4 Hz, 2H), 7.63 (d, J = 8.8 Hz, 2H), 7.52-7.22 (m, 8H), 7.11 (t, J = 7.4 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 190.4, 153.8, 146.2, 141.8, 135.3, 131.5, 130.8, 129.6,

128.6, 128.5, 127.7, 127.6, 127.0, 126.5, 126.4, 124.8, 124.7, 123.6, 117.7. HRMS *m*/*z*: $[M]^+$ calcd for $C_{23}H_{17}NO$, 323.1310; found, 323.1304.

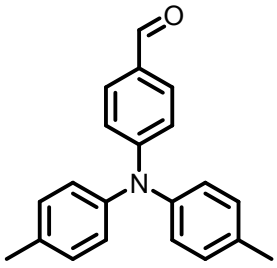
Procedures for the synthesis of 4-methyl-*N*-phenyl-*N*-*p*-tolylaniline (D):



4, 4'-Dimethyldiphenylamine (0.99 g, 5.0 mmol), KOH (2.52 g, 45.0 mmol), CuCl (99 mg, 1.0 mmol) and 1,10-phenanthroline (180 mg, 1.0 mmol) were charged in a two-necked bottle. The bottle was deoxygenated and purged with nitrogen, and added dried toluene (12 mL) and iodobenzene (0.67 ml, 6.0 mmol). The reaction was heated to 120 °C, and stirred for 12 hours. The resulting was filtered to remove metal and then concentrated under reduced pressure and the residue was purified by column chromatography (hexanes/CH_2Cl_2 = 1/1) to afford **D** (916 mg, 67%) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.22-7.18 (m, 2H), 7.07-6.91 (m, 11H), 2.31 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.3, 145.4, 132.3, 129.8, 129.0, 124.4, 122.9, 121.7, 20.8. HRMS *m*/*z*: $[M]^+$ calcd for $C_{20}H_{19}N$, 273.1517; found, 273.1516.

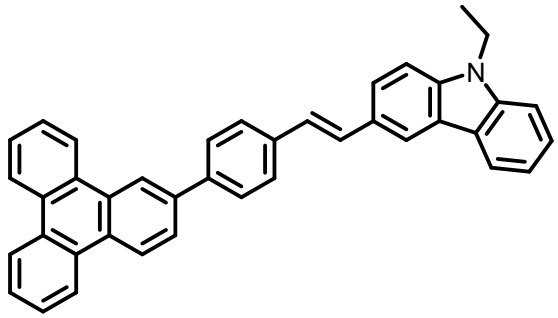
Procedures for the synthesis of 4-(di-*p*-tolylamino)benzaldehyde (E):



N,*N*-Dimethylformamide (6.0 ml) was charged in a two-necked bottle. The bottle was deoxygenated and purged with nitrogen, and added $POCl_3$ (0.86 mL, 5.27 mmol) in an ice bath, and then stirred for 30 mins. Compound **D** (1.2 g, 4.39 mmol) soluted in DMF (6.0 ml)

was added stepwise. The reaction was heated to 70 °C, and stirred for 6 hours. The resulting was distilled to remove solvent under reduced pressure and the residue was purified by column chromatography (hexanes/CH_2Cl_2 = 6/1) to afford **E** (1.26 g, 95%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.75 (s, 1H), 7.62 (d, J = 8.8 Hz, 2H), 7.13 (d, J = 8.0 Hz, 4H), 7.05 (d, J = 8.0 Hz, 4H), 6.92 (d, J = 8.8 Hz, 2H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 190.4, 153.7, 143.5, 135.0, 131.3, 130.3, 128.3, 126.4, 118.2, 21.0. HRMS m/z: $[M]^+$ calcd for $C_{21}H_{19}NO$, 301.1467; found, 301.1471.

Procedures for the synthesis of (*E*)-9-ethyl-3-(4-(triphenylen-2-yl)styryl)-9H-carbazole (TSCz)

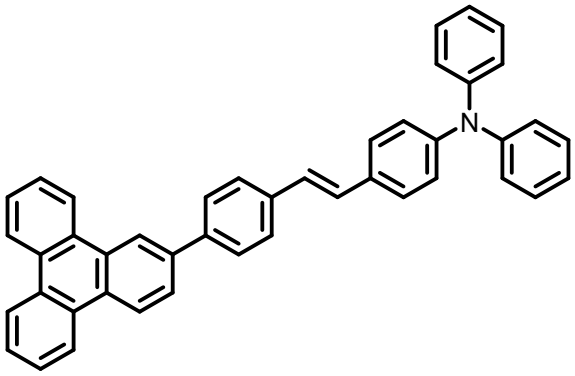


Compound **B** (100 mg, 0.22 mmol) and *N*-ethylcarbazole-3-carboxaldehyde) (59 mg, 0.26 mmol) and dry THF (10 ml) were charged in two-necked bottle in an ice bath, and potassium *tert*-butoxide (49 mg, 0.44 mmol) in dry THF (10 ml) was added under nitrogen. The reaction mixture was stirred for 15 min at 0 °C, followed by 1 h at room temperature. The solution mixture was extracted with ethyl acetate and washed with water. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a crude product that was purified by sublimating at a temperature of 260 °C to obtain **TSCz** (90 mg, yield = 78%) as yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.89 (d, J = 1.6 Hz, 1H), 8.78-8.65 (m, 5H), 8.28 (d, J = 1.2 Hz, 1H), 8.14 (d, J = 7.6 Hz, 1H), 7.94 (dd, J = 8.4, J = 2.0 Hz, 1H), 7.83 (d, J = 8.0 Hz, 2H), 7.73-7.65 (m, 7H), 7.50-7.39 (m, 4H), 7.27-7.23 (m, 2H), 4.38 (q, J = 7.2 Hz, 2H), 1.45 (t, J

= 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3/CS_2$, δ): 140.2, 139.6, 139.4, 137.2, 130.0, 130.0, 129.8, 129.7, 129.7, 129.6, 128.7, 128.5, 127.5, 127.2, 127.1, 127.0, 126.7, 126.0, 125.8, 125.4, 124.5, 123.8, 123.3. 122.9, 121.3, 120.5, 119.1, 118.8, 108.5, 37.6, 13.9. HRMS *m*/*z*: $[M]^+$ calcd for $C_{40}H_{29}N$, 523.2300; found, 523.2299. Anal. calcd for $C_{40}H_{29}N$: C 91.74, H 5.58, N 2.67; found: C 91.37, H 5.80, N 2.43.

Procedures for the synthesis of (*E*)-*N*,*N*-diphenyl-4-(4-(triphenylen-2-yl)styryl)aniline (TSTA)

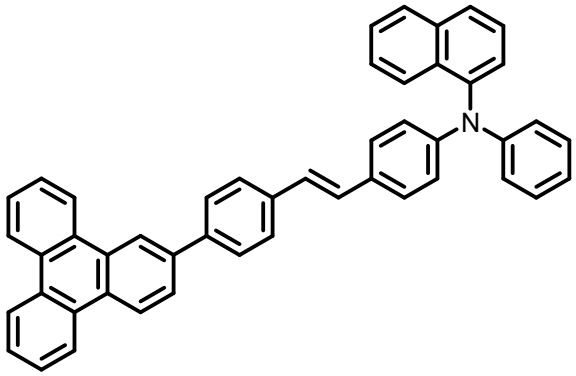


Compound **B** (1.0 g, 2.20 mmol) and 4-(*N*,*N*-diphenylamino)benzaldehyde (0.72 g, 2.64 mmol) and dry THF (20 ml) were charged in two necked-bottle in an ice bath, potassium *tert*-butoxide (0.49 g, 4.4 mmol) in dry THF (20 ml) was added under nitrogen. The reaction mixture was stirred for 15 min at 0 °C, followed by 1 h at room temperature. The solution mixture was extracted with ethyl acetate and washed with water. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a crude product that was purified by sublimating at a temperature of 260 °C to obtain **TSTA** (1.04 g, yield = 82%) as yellow solid.

^{1}H NMR (400 MHz, CD_2Cl_2 , δ): 8.93 (d, J = 1.6 Hz, 1H), 8.81-8.69 (m, 5H), 7.98 (dd, J = 8.4, J = 1.6 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.73-7.68 (m, 6H), 7.46 (d, J = 8.4 Hz, 2H), 7.31-7.27 (m, 4H), 7.22-7.04 (m, 10H). ^{13}C NMR (100 MHz, CD_2Cl_2, δ): 147.9, 140.0,

139.7, 137.5, 131.8, 130.5, 130.4, 130.1, 130.0, 129.7, 129.3, 128.8, 127.9, 127.8, 127.3, 126.7, 126.5, 125.0, 124.4, 123.8, 123.5, 121.7. HRMS *m*/*z*: $[M]^+$ calcd for $C_{44}H_{31}N$, 573.2457; found, 573.2460. Anal. calcd for $C_{44}H_{31}N$: C 92.11, H 5.45, N 2.44; found: C 91.94, H 5.46, N 2.45.

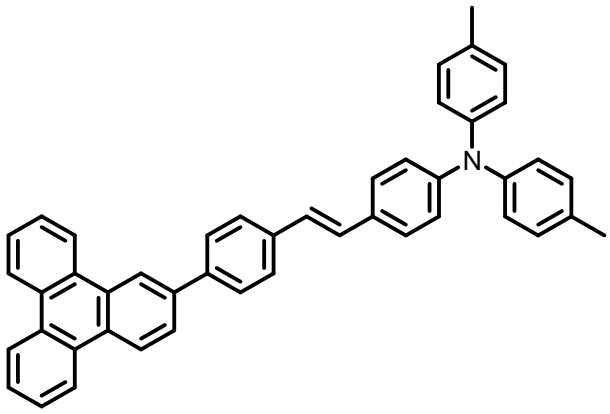
Procedures for the synthesis of (*E*)-*N*-phenyl-*N*-(4-(4-(triphenylen-2-yl)styryl) phenyl)naphthalen-1-amine (TSNA)



Compound **B** (1.06 g, 2.23 mmol) and **C** (0.91 g, 2.8 mmol) and dry THF (20 ml) were charged in two-necked bottle in an ice bath; potassium *tert*-butoxide (523 mg, 4.66 mmol) in dry THF (20 ml) was added under nitrogen. The reaction mixture was stirred for 15 min at 0 °C, followed by 1 h at room temperature. The solution mixture was extracted with ethyl acetate and washed with water. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a crude product that was purified by sublimating at a temperature of 320 °C to obtain TSNA (1.15 g, yield = 79%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.90 (s, 1H), 8.79-8.66 (m, 5H), 7.98-7.91 (m, 3H), 7.85-7.80 (m, 3H), 7.71-7.63 (m, 6H), 7.55-7.48 (m, 2H), 7.42-7.37 (m, 4H), 7.27-6.99 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.5, 148.4, 143.6, 139.8, 139.6, 137.5, 135.8, 131.6, 130.8, 130.4, 130.4, 130.1, 129.9, 129.5, 129.2, 128.8, 128.7, 127.8, 127.7, 127.2, 127.1, 126.8, 126.6, 126.4, 126.2, 124.4, 124.3, 123.7, 122.8, 122.6, 121.6, 121.5. HRMS *m*/*z*: $[M]^+$

calcd for $C_{48}H_{33}N$, 623.2613; found, 623.2616. Anal. calcd for $C_{48}H_{33}N$: C 92.42, H 5.33, N 2.25; found: C 92.38, H 5.08, N 2.33.

Procedures for the synthesis of (*E*)-4-methyl-*N*-*p*-tolyl-*N*-(4-(4-(triphenylen-2-yl) styryl)phenyl)aniline (TSMA)



Compound **B** (1.20 g, 2.64 mmol) and **E** (0.96 g, 3.17 mmol) and dry THF (20 ml) were charged in two-necked bottle in an ice bath, potassium *tert*-butoxide (593 mg, 5.28 mmol) in dry THF (20 ml) was added under nitrogen. The reaction mixture was stirred for 15 min at 0 °C, followed by 1 h at room temperature. The solution mixture was extracted with ethyl acetate and washed with water. The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to afford a crude product that was purified by sublimating at a temperature of 290 °C to obtain TSMA (1.15 g, yield = 82%) as yellow solid. ^{1}H NMR (400 MHz, CD_2Cl_2 , δ): 8.92 (d, J = 1.2 Hz, 1H), 8.81-8.69 (m, 5H), 7.97 (d, J = 8.4, J = 1.6 Hz, 1H), 7.85 (d, J = 8.4 Hz, 2H), 7.73-7.66 (m, 6H), 7.41 (d, J = 8.8 Hz, 2H), 7.20-6.97 (m, 12H), 2.33 (s, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2 , δ): 148.4, 145.4, 139.8, 139.7, 137.5, 133.4, 130.7, 130.4, 130.4, 130.3, 130.1, 129.9, 129.2, 128.9, 127.8, 127.8, 127.7, 127.6, 127.2, 126.4, 126.1, 125.2, 124.3, 123.7, 122.4, 121.7, 20.9. HRMS *m*/*z*: $[M]^+$ calcd for $C_{46}H_{35}N$, 601.2770; found, 601.2767. Anal. calcd for $C_{46}H_{35}N$: C 91.81, H 5.86, N 2.33; found: C 91.67, H 5.92, N 2.32.

Photophysical and thermal properties of TSs

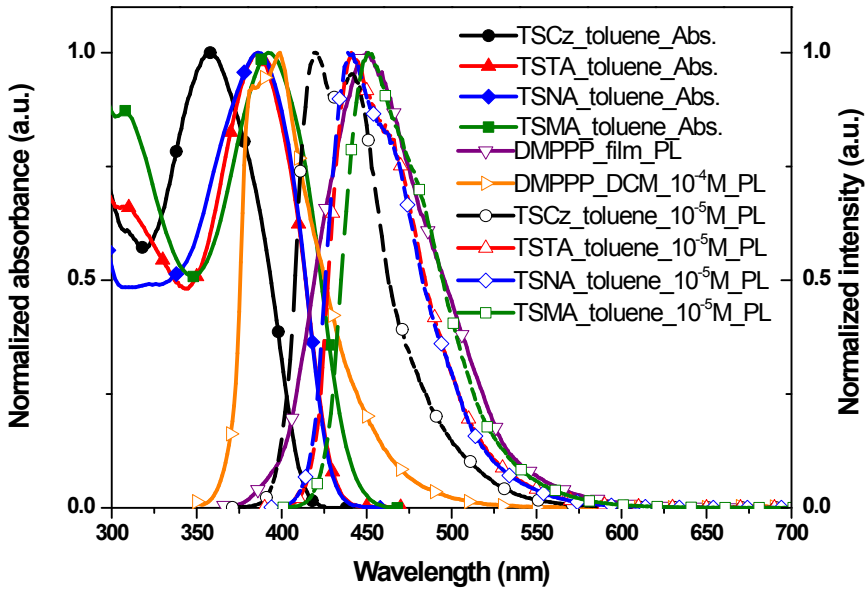


Figure S1. Ultraviolet–visible absorptions and photoluminescence spectra of TSs in toluene (10^{-5} mol l^{-1}) and of DMPPP.

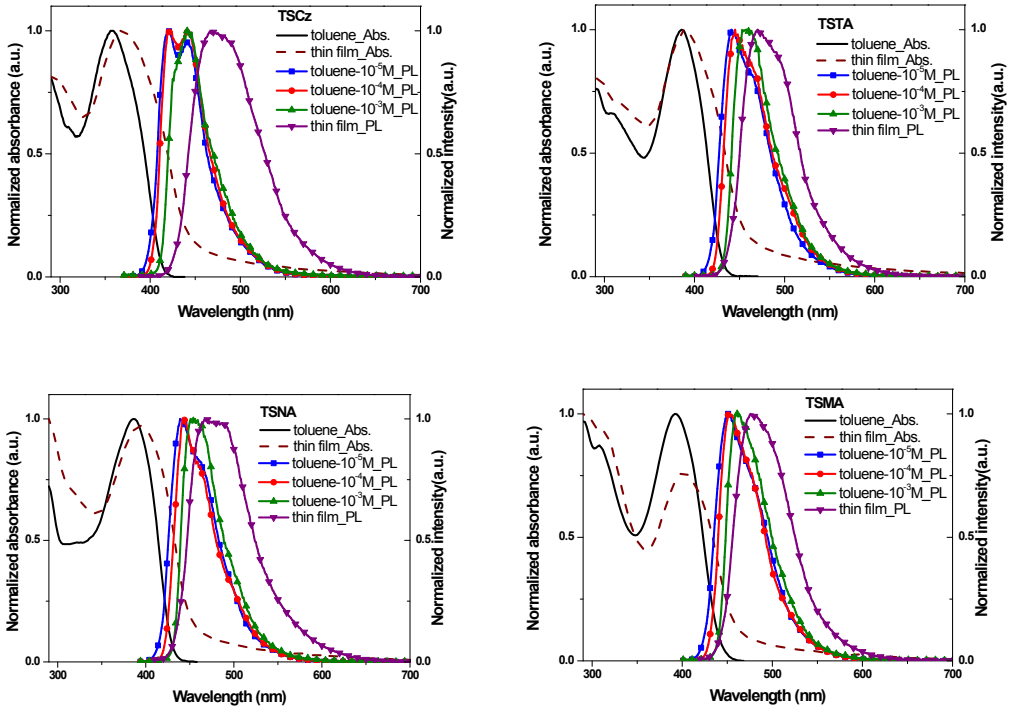


Figure S2. UV absorption and PL spectra of TSs in thin film state and in toluene solution (10^{-5} ~ 10^{-3} M).

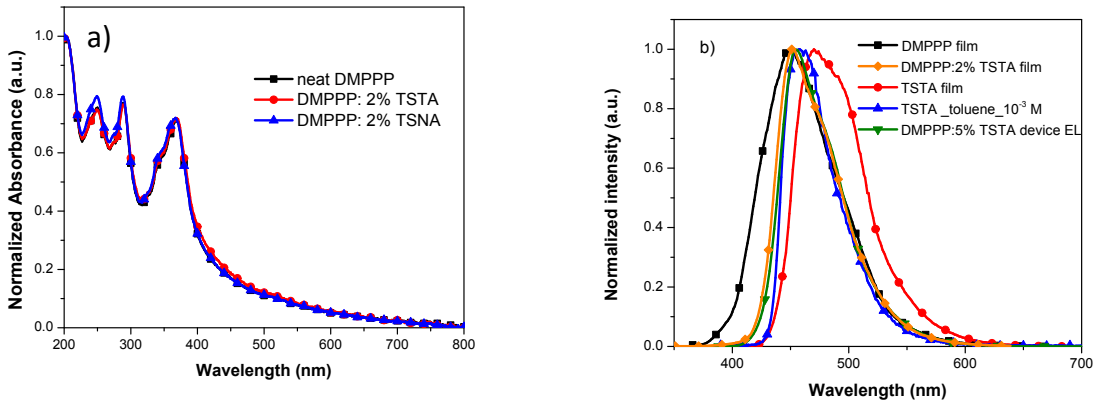


Figure S3. (a) UV absorption DMPPP and doped DMPPP films. (b) PL spectra of DMPPP, DMPPP:2% TSTA and TSTA films and of TSTA in toluene; EL spectrum of device B.

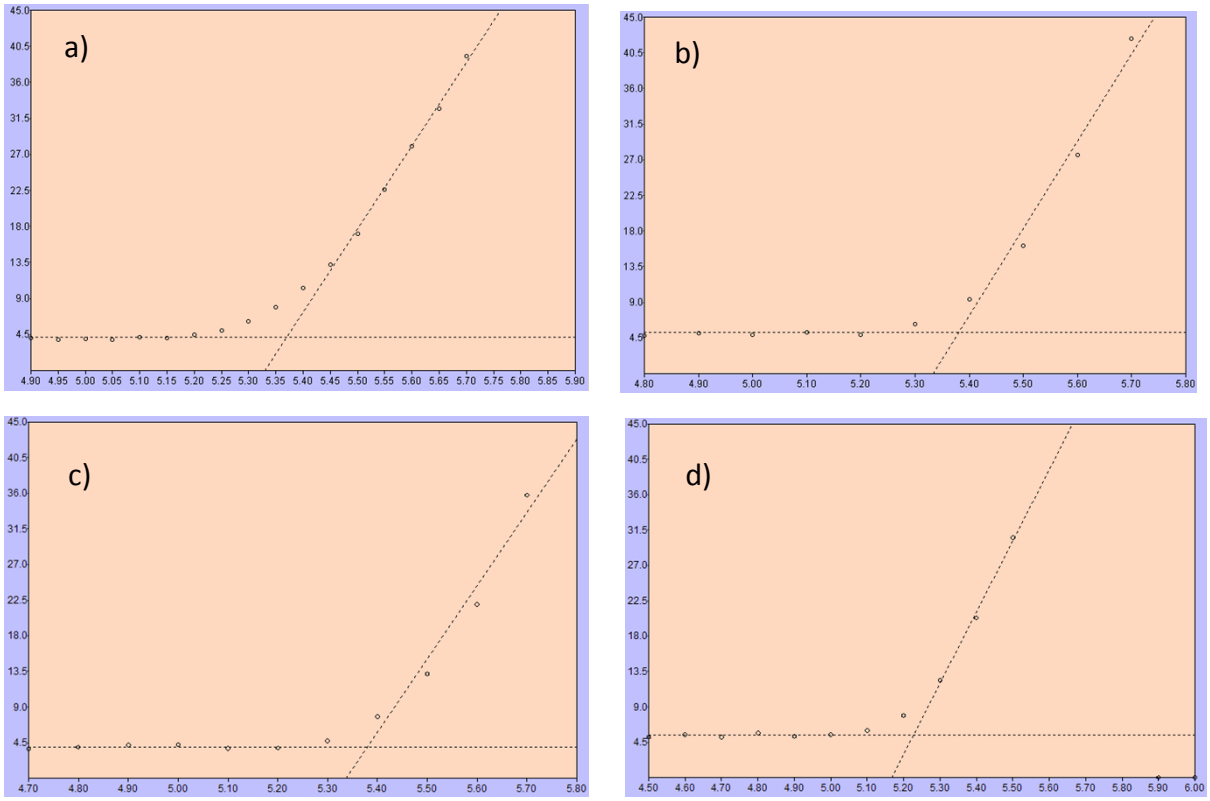


Figure S4. HOMO energy levels of a) TSCz, b) TSTA, c) TSNA, and d) TSMA meaused by photoelectron spectrometer (AC-II).

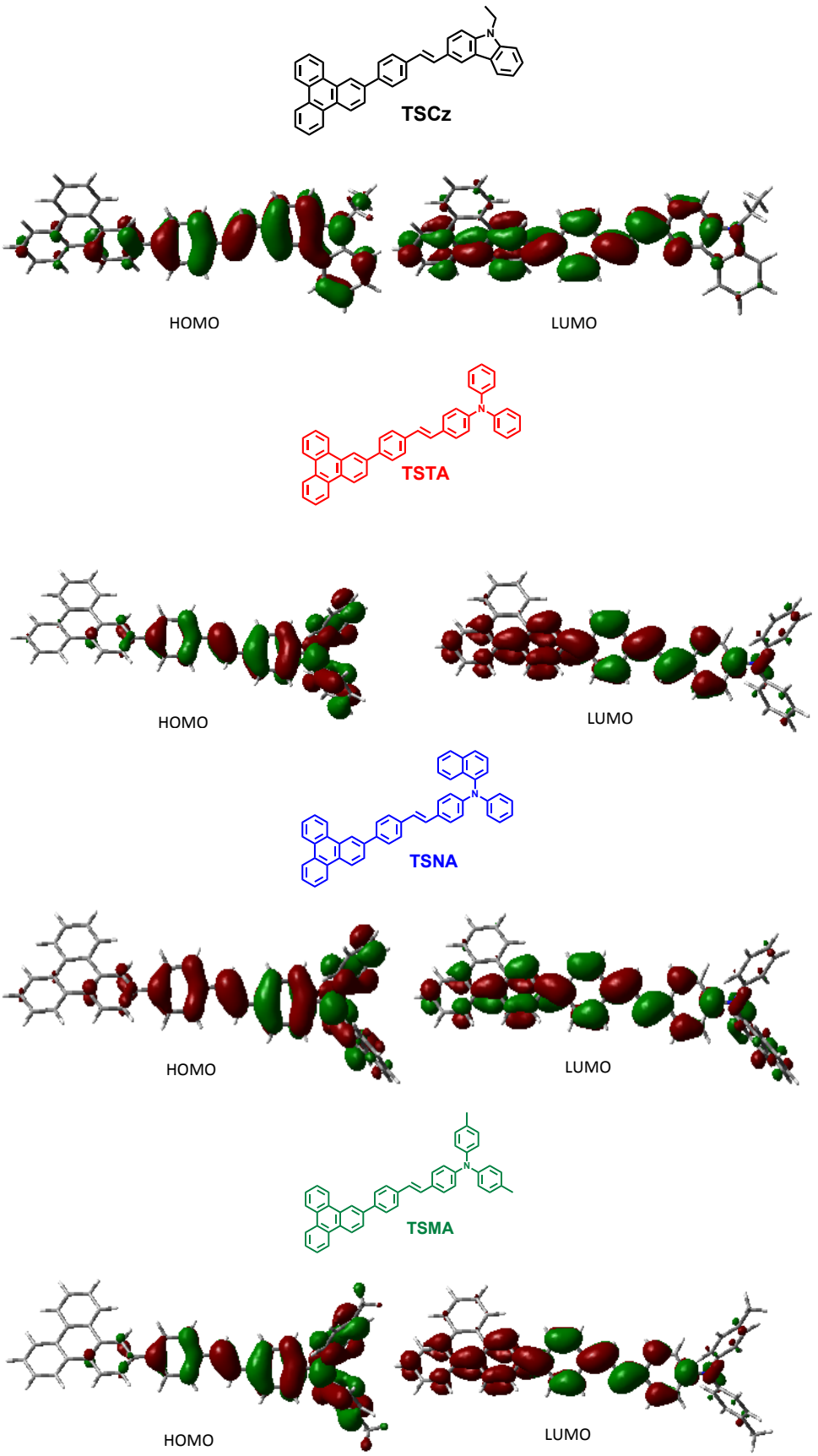


Figure S5. Calculated HOMO and LUMO density maps of TSs.

Electroluminescence performance of devices A-E

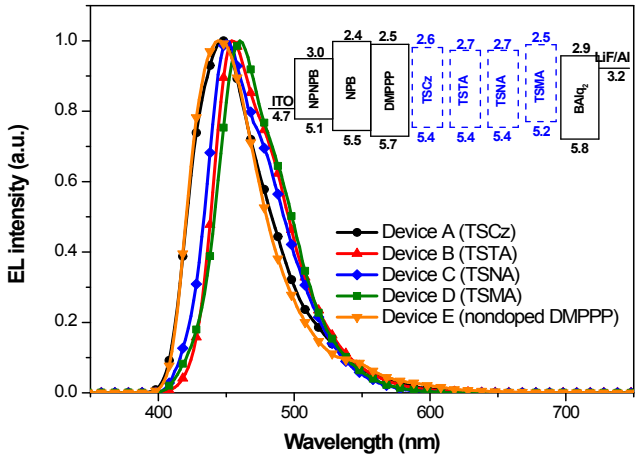


Figure S6. EL spectra of devices A-E at 8V. Inset, HOMO and LUMO energy levels used in the devices.

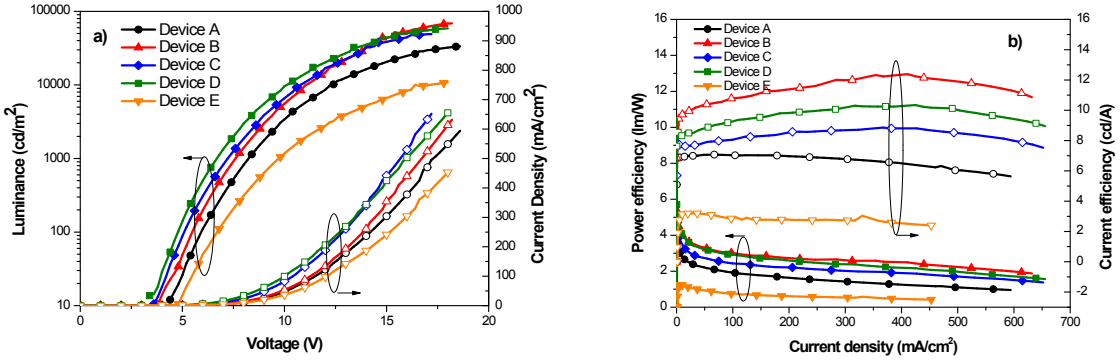


Figure S7. Electroluminescence performance of devices A-E. (a) Luminance and current density versus voltage. (b) Power efficiency and current efficiency versus current density.

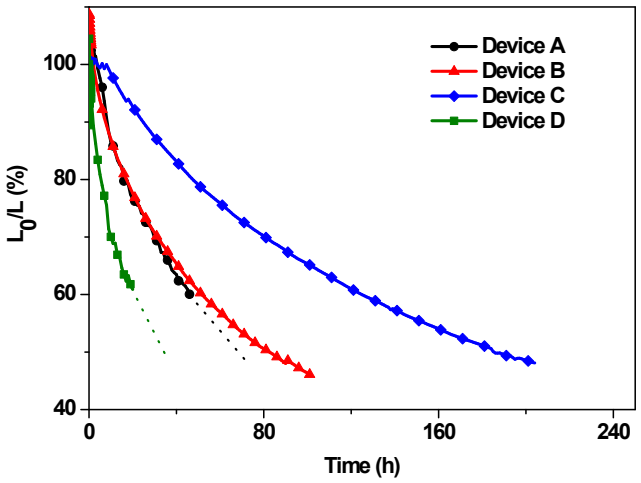


Figure S8. Operation lifetime of devices A-D measured at initial luminance of 2,000 cd m^{-2} under constant current for each device.

Transient EL

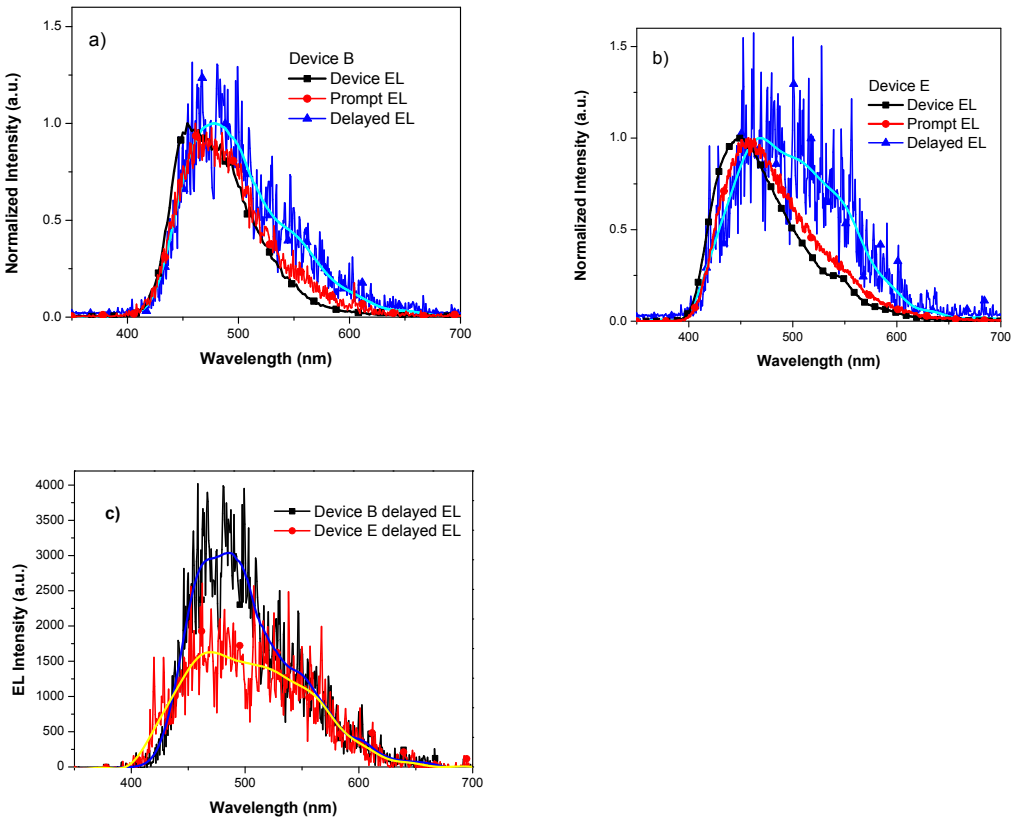


Figure S9. EL spectra (a) The device EL and prompt and delayed (5 μs) EL spectra of device B and (b) device E at 4 V. (c) The delayed EL spectra of devices B and E measured at 4V at the delayed time of 5 μs.

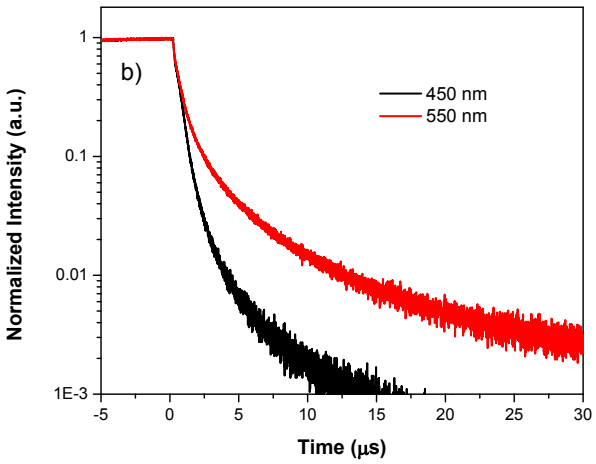


Figure S10. Transient EL of device E measured at 450 and 550 nm.

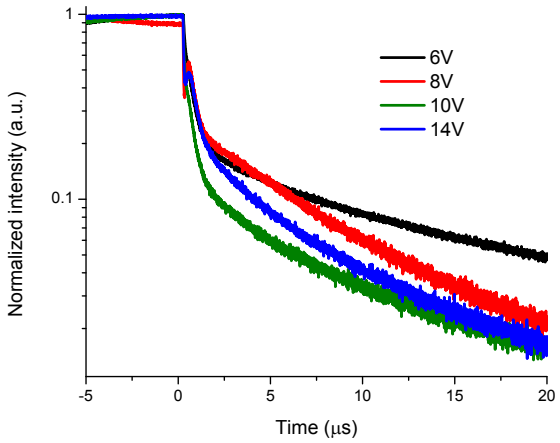


Figure S11. Transient EL of device B measured at 450 nm at different voltage.

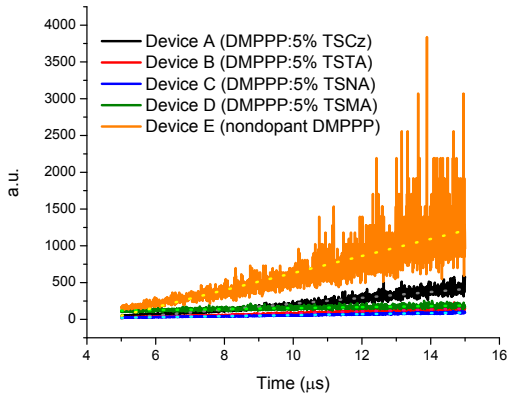


Figure S12. Plots of the inverse of relative transit EL intnesity versus time of Fig. 3(a) between 5~15μs. The slopes obtained from linear fit for devices A-E are 39.9±0.3, 12.55±0.07, 6.93±0.03, 6.9±0.1 and 116.0±1.7 μs^{-1}, respectively.

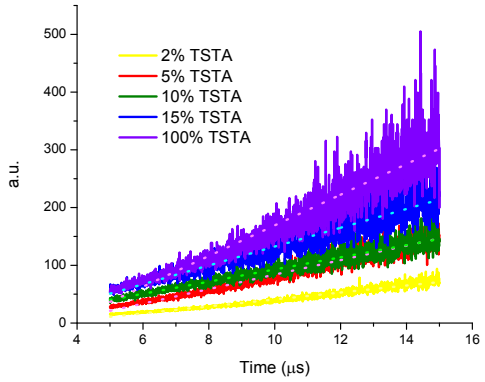


Figure S13. Plots of the inverse of relative transit EL intnesity versus time of Fig. 3(b) between 5~15 μs. The slopes obtained from linear fit with increasing TSTA from 2% to 100% are 6.03±0.03, 12.55±0.07, 10.54±0.07, 16.3±0.1 and 26.5±0.2 μs^{-1}, respectively.

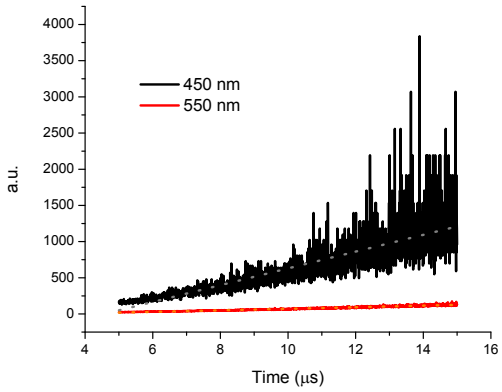


Figure S14. Plots of the inverse of relative transit EL intnesity versus time of Fig. S10 between 5~15 μs. The slopes obtained from linear fit for the device E measured at 450 and 550 nm are 116.0±1.7 and 10.74±0.05 μs^{-1}, respectively.

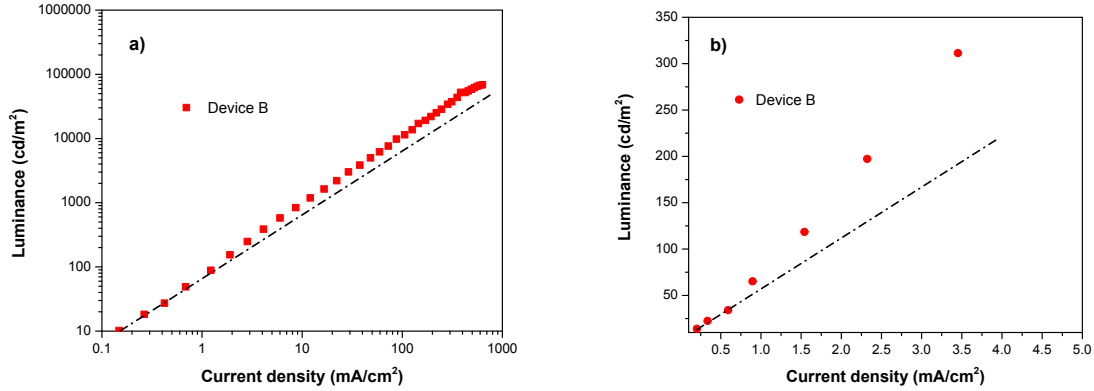


Figure S15. Dependence of the luminance of device B on the current density. (a) High injection current. (b) Low injection current.

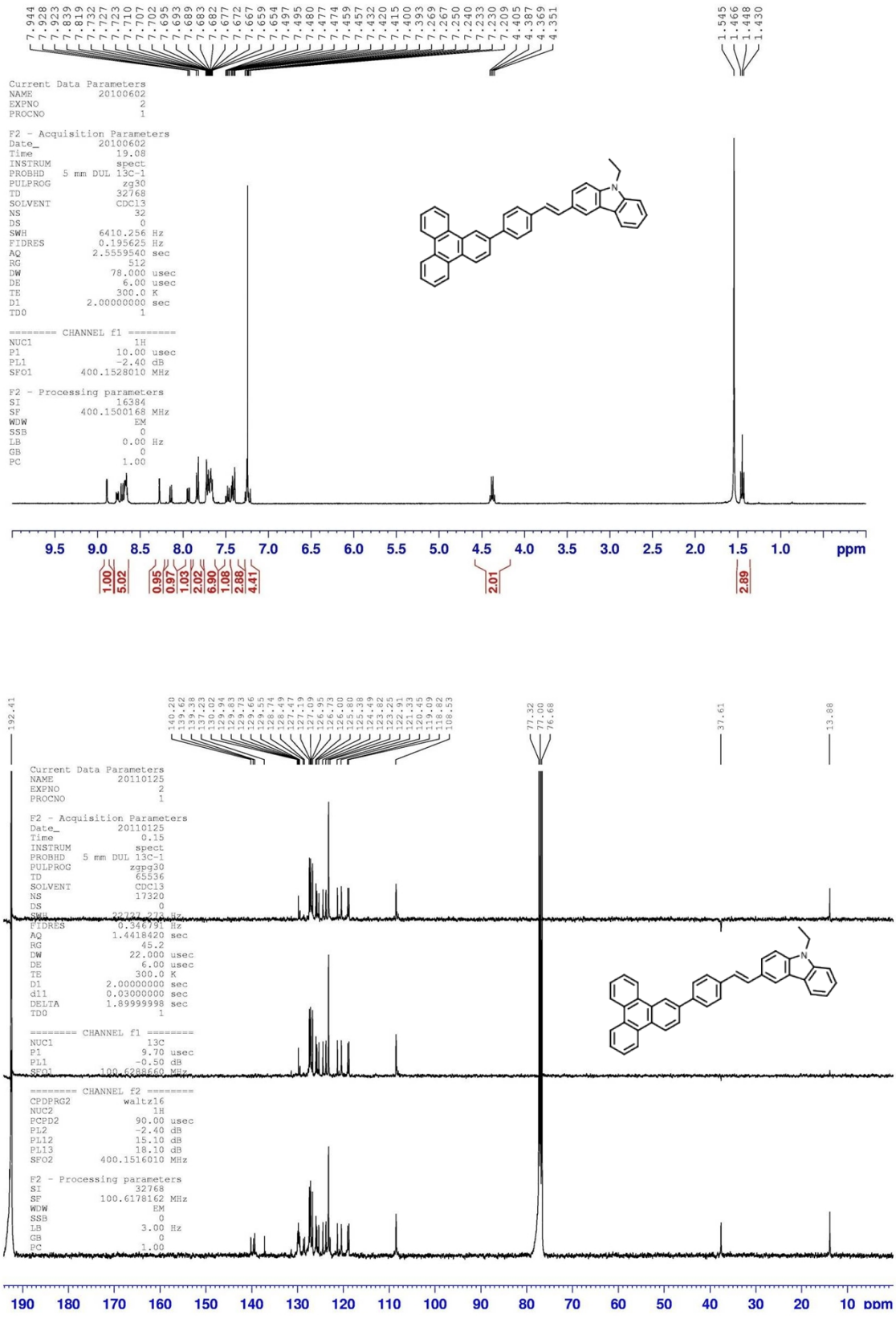


Figure S16. ^{1}H and ^{13}C NMR spectra of TSCz.

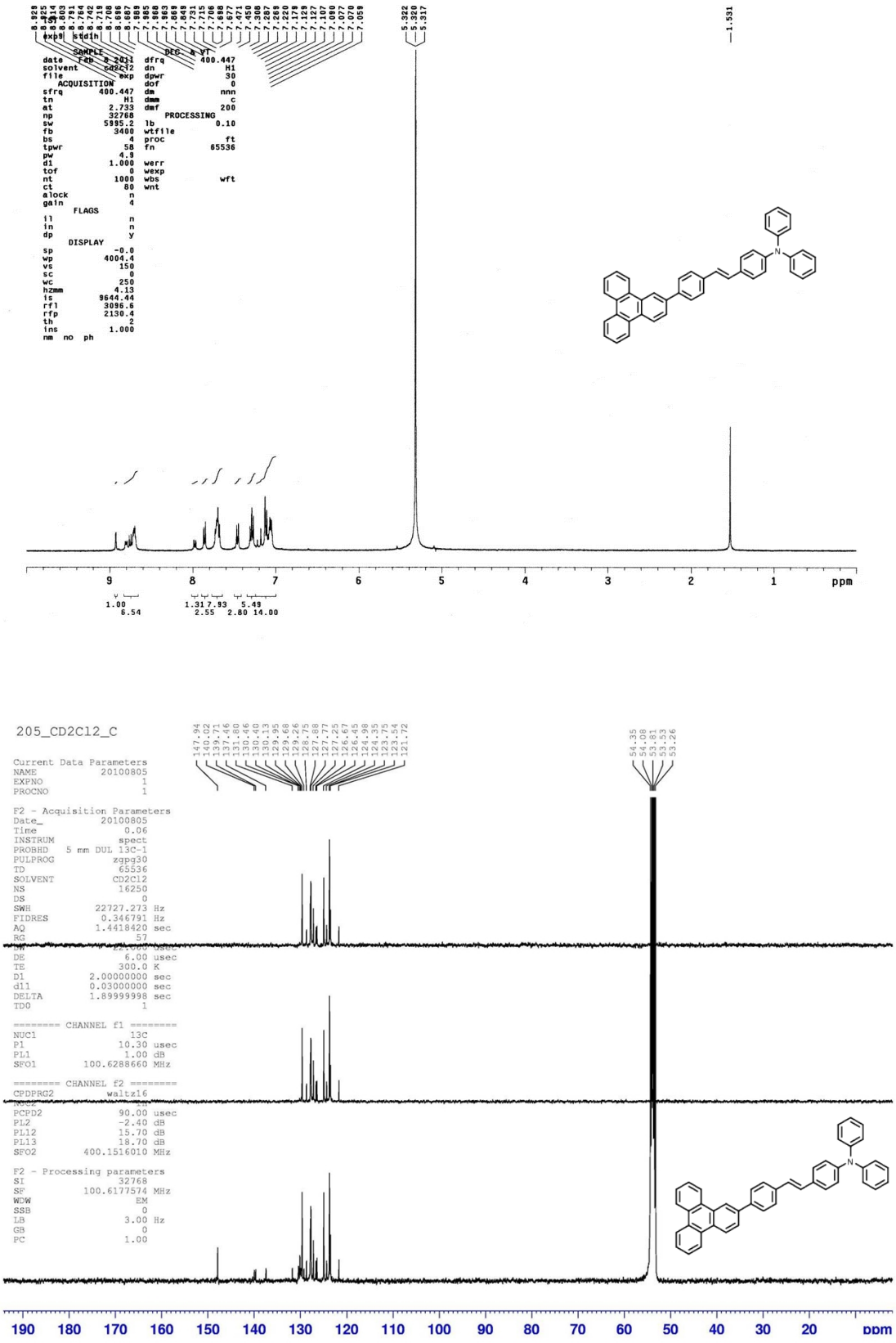


Figure S17. ^{1}H and ^{13}C NMR spectra of TSTA.

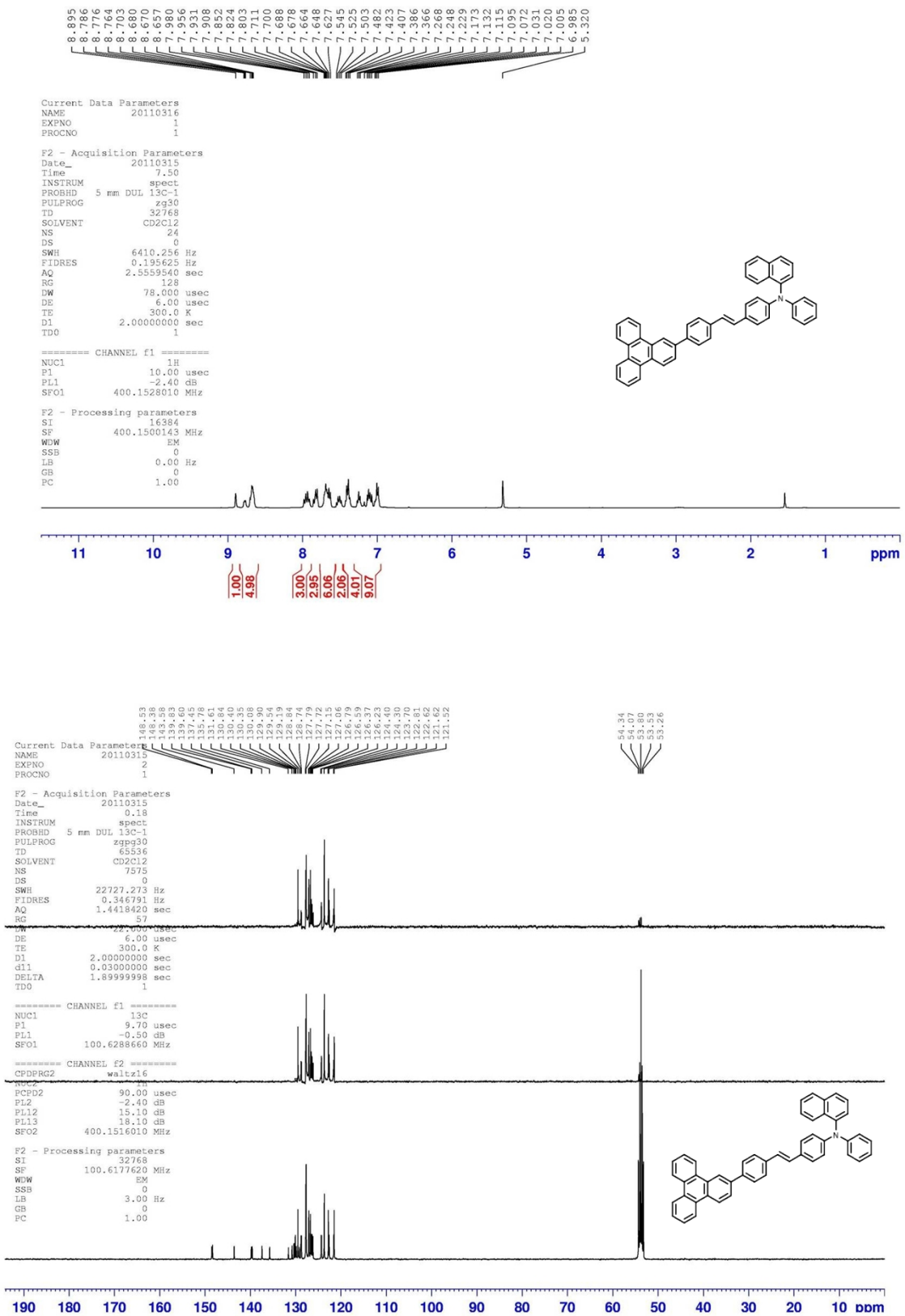


Figure S18. ^{1}H and ^{13}C NMR spectra of TSNA.

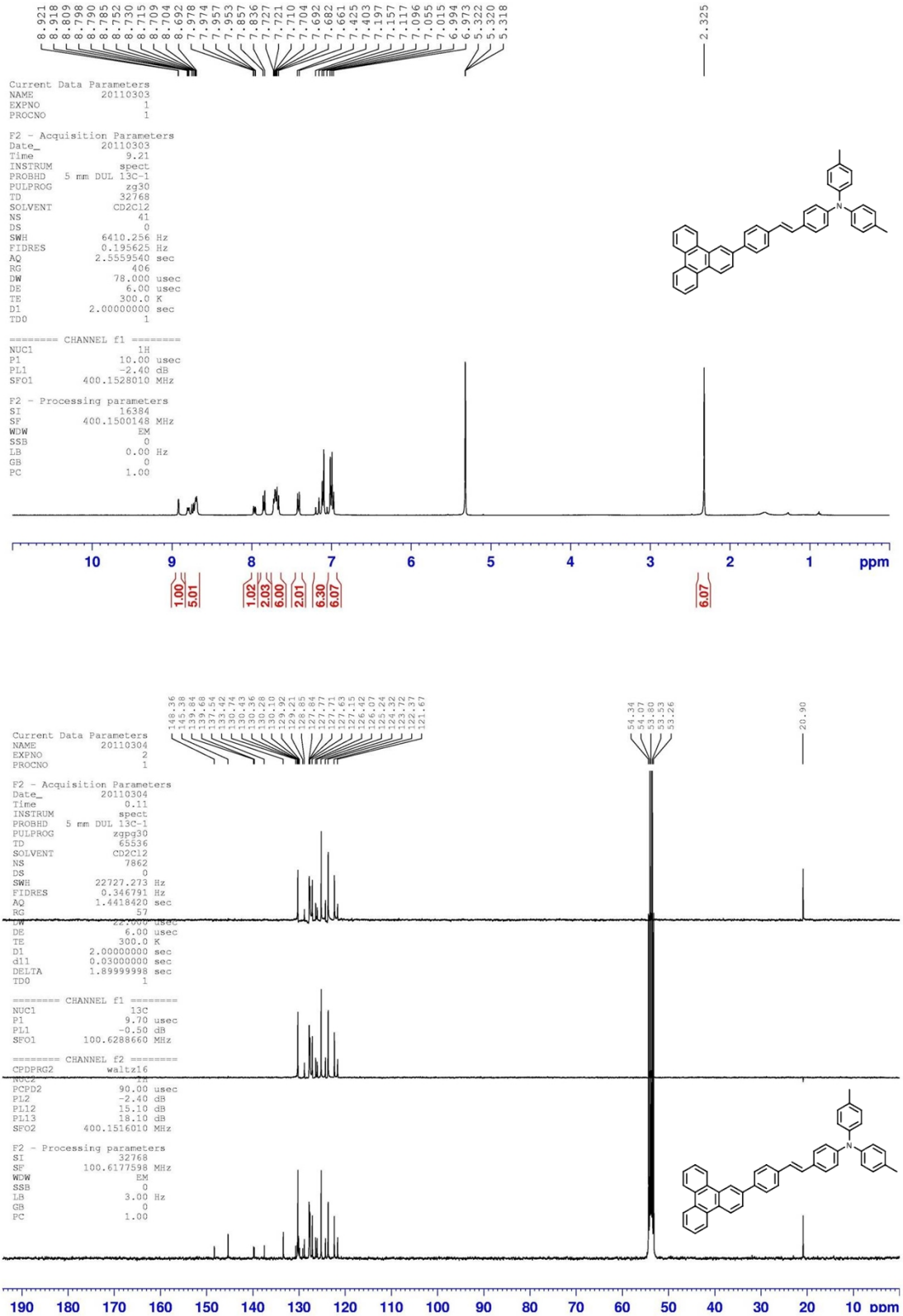


Figure S19. ^{1}H and ^{13}C NMR spectra of TSMA