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Electronic Supplementary Information

Superior Upconversion Fluorescence Dopants for Highly Efficient Deep-Blue Electroluminescent Devices

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1. Experimental Section

Chemicals and Syntheses: All starting chemicals were obtained from commercial sources without further purification. 9-Phenyl-9*H*-carbazole-3-carbaldehyde, 4-(bis(4-fluorophenyl)amino)benzaldehyde, and diethyl (4-bromobenzyl)phosphonate were synthesized according to the literature methods.[S1–S3]

Preparation of (E)-3-(4-bromostyryl)-9-phenyl-9H-carbazole: 9-Phenyl-9*H*-carbazole-3-carbaldehyde (5.95 g, 22.0 mmol), diethyl 4-bromobenzylphosphonate (7.70 g, 25.0 mmol), and dry THF (30 mL) were added into a two-necked round bottom flask and cooled in an ice bath. A solution of potassium *tert*-butoxide (5.60 g, 50.0 mmol) in THF (20 mL) was added dropwise to the reaction mixture. After stirring for 15 min at 0 °C, the solution was returned to room temperature and was further stirred for 2 h. The mixture was extracted with ethyl acetate and washed with water. The combined organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (hexane/CH_2Cl_2 = 4:1) to afford white product in 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.25 (s, 1H), 8.15 (d, J = 7.6 Hz, 1H), 7.62−7.35 (m, 13H), 7.31−7.27 (m, 2H), 7.07 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 141.26 (C), 140.64 (C), 137.41 (C), 136.76 (C), 131.68 (2 CH), 130.11 (CH), 129.88 (2 CH), 129.18 (C), 127.68 (2 CH), 127.53 (CH), 126.96 (2 CH), 126.18 (CH), 125.04 (CH), 124.68 (CH), 123.72 (C), 123.24 (C), 120.61 (C), 120.33 (CH), 120.17 (CH), 118.64 (CH), 110.00 (CH), 109.95 (CH); HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{26}H_{18}BrN$, 423.0623; found, 423.0621.

Preparation of (E)-4-(4-bromostyryl)-N,N-bis(4-fluorophenyl)aniline: (*E*)-4-(4-bromostyryl)-*N*,*N*-bis(4-fluorophenyl)aniline was prepared according to a procedure similar to that of (*E*)-3-(4-bromostyryl)-9-phenyl-*9H*-carbazole by using 4-(bis(4-fluorophenyl)amino)benzaldehyde to replace the 9-phenyl-9*H*-carbazole-3-carbaldehyde. The desired product was obtained as a yellow solid (yield 89%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.44 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.8 Hz, 2H), 7.32 (d, J = 8.8 Hz, 2H), 7.06−6.92 (m, 11H), 6.88 (d, J = 16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ):

158.99 (d, $J_{C\text{-}F}$ = 242 Hz, 2 C), 147.63 (C), 143.42 (d, $J_{C\text{-}F}$ = 3 Hz, 2 C), 136.47 (C), 131.69 (2 CH), 130.69 (C), 128.70 (CH), 127.71 (2 CH), 127.47 (2 CH), 126.23 (d, $J_{C\text{-}F}$ = 7.6 Hz, 4 CH), 125.62 (CH), 122.10 (2 CH), 120.86 (C), 116.15 (d, $J_{C\text{-}F}$ = 22.8 Hz, 4 CH); HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{26}H_{18}BrF_2N$, 461.0591; found, 461.0594.

Preparation of (E)-4-(4-bromostyryl)-N,N-diphenylaniline: (*E*)-4-(4-bromostyryl)-*N*,*N*-diphenylaniline was prepared according to a similar procedure to (*E*)-3-(4-bromostyryl)-9-phenyl-*9H*-carbazole by using 4-(diphenylamino)benzaldehyde to replace the 9-phenyl-9*H*-carbazole-3-carbaldehyde. The desired product was obtained as a yellow solid (yield 89%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.45 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.34 (d, *J* = 8.8 Hz, 2H), 7.28−7.24 (m, 4H), 7.11 (d, *J* = 7.6 Hz, 4H), 7.05−7.01 (m, 5H), 6.90 (d, *J* = 16 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.56 (C), 147.40 (2 C), 136.52 (C), 131.68 (2 CH), 130.90 (C), 129.28 (4 CH), 128.84 (CH), 127.71 (2 CH), 127.38 (2 CH), 125.56 (CH), 124.54 (4 CH), 123.33 (2 CH), 123.11 (2 CH), 120.81 (C); HRMS (*m/z*): $[M]^+$ calcd for $C_{26}H_{20}BrN$, 425.0779; found, 425.0772.

Synthesis of (E)-9-phenyl-3-(4-(pyren-1-yl)styryl)-9H-carbazole (PCzSP): (*E*)-3-(4-bromostyryl)-9-phenyl-*9H*-carbazole (0.826 g, 2.00 mmol), 1-pyreneboronic acid (0.541 g, 2.20 mmol), K_2CO_3 (0.930 g, 2.00 M), and the catalyst $Pd(PPh_3)_4$ (113 mg) were added into a flask containing a mixture of toluene, ethanol, and water (3:1:1, v/v, 18 mL). The reaction mixture was allowed to reflux at 90 °C for 12 h. After cooling to room temperature, the solution was extracted twice with ethyl acetate (100 mL × 2). The combined organic layers were washed with H_2O (100 mL × 2) and dried with anhydrous $MgSO_4$, and the solvent was evaporated on a rotary evaporator. The crude product was purified through a silica gel column (CH_2Cl_2/*n*-hexane, 1:4) to afford PCzSP as a yellow powder (yield 79%). ^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 8.33−7.99 (m, 11H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.68−7.57 (m, 7H), 7.50−7.40 (m, 5H), 7.36−7.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, *δ*): 141.27 (C), 140.58 (C), 139.87 (C), 137.47 (C), 137.41 (C), 136.81 (C), 131.43 (C), 130.91 (2 CH), 130.49 (C), 129.84 (2 CH), 129.71 (C, CH), 129.62 (C), 128.40 (C), 127.49 (2 CH), 127.46 (2

CH), 127.42 (CH), 127.37 (CH), 127.33 (CH), 126.94 (2 CH), 126.22 (CH), 126.12 (CH), 125.94 (CH), 125.25 (CH), 125.03 (CH), 124.97 (C), 124.89 (C), 124.75 (CH), 124.66 (2 CH), 123.76 (C), 123.33 (C), 120.38 (CH), 120.14 (CH), 118.61 (CH), 109.98 (CH), 109.92 (CH); HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{42}H_{27}N$, 545.2143; found, 545.2138. Anal. calcd for $C_{42}H_{27}N$: C 92.45, H 4.99, N 2.57; found: C 92.31, H 5.04, N 2.53.

Synthesis of (E)-4-fluoro-N-(4-fluorophenyl)-N-(4-(4-(pyren-1-yl)styryl)phenyl)aniline (DFASP): By the same procedure as that described for PCzSP, DFASP was prepared from (*E*)-4-(4-bromostyryl)-*N*,*N*-bis(4-fluorophenyl)aniline, 1-pyreneboronic acid, K_2CO_3, and $Pd(PPh_3)_4$ to give 87% yield. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.23−7.98 (m, 9H), 7.67 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.8 Hz, 2H), 7.17 (d, J = 16 Hz, 1H), 7.12−7.04 (m, 5H), 7.00−6.90 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 158.95 (d, $J_{C\text{-}F}$ = 242 Hz, 2 C), 147.44 (C), 143.50 (d, $J_{C\text{-}F}$ = 2.3 Hz, 2 C), 140.12 (C), 137.30 (C), 136.51 (C), 131.43 (C), 131.18 (C), 130.91 (2 CH), 130.53 (C), 128.39 (C), 128.28 (CH), 127.46 (2 CH), 127.38 (1C, 2CH), 126.56 (2 CH), 126.23 (d, $J_{C\text{-}F}$ = 7.6 Hz, 4 CH), 126.11 (2 CH), 125.97 (CH), 125.19 (CH), 125.08 (CH), 124.97 (C), 124.87 (C), 124.79 (2 CH), 124.67 (CH), 122.27 (2 CH), 116.18 (d, $J_{C\text{-}F}$ = 22.7 Hz, 4 CH); HRMS (EI) *m/z*: $[M]^+$ calcd for $C_{42}H_{27}F_2N$, 583.2112; found, 583.2109. Anal. calcd for $C_{42}H_{27}F_2N$: C 86.43, H 4.66, N 2.40; found: C 86.31, H 4.70, N 2.37.

Synthesis of (E)-N,N-diphenyl-4-(4-(pyren-1-yl)styryl)aniline (DPASP): By the same procedure as that described for PCzSP, DPASP was prepared from (*E*)-4-(4-bromostyryl)-*N*,*N*-diphenylaniline, 1-pyreneboronic acid, K_2CO_3, and $Pd(PPh_3)_4$ with the yield of 85%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.25−7.98 (m, 9H), 7.68 (d, J = 8 Hz, 2H), 7.62 (d, J = 8 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.29−7.25 (m, 4H), 7.19 (d, J = 16.4 Hz, 1H), 7.15−7.03 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 147.54 (2 C), 147.46 (C), 140.14 (C), 137.41 (C), 136.66 (C), 131.50 (C, CH), 130.93 (2 CH), 130.59 (C), 129.30 (4 CH), 128.50 (2 CH), 127.43 (4 CH), 126.59 (2 CH), 126.30 (C, CH), 126.01 (CH), 125.28 (CH), 125.10 (CH), 125.02 (C), 124.93 (C), 124.8 (CH), 124.68 (CH), 124.53

(4 CH), 123.57 (C, 2 CH), 123.07 (C, 2 CH); HRMS *m/z*: $[M]^+$ calcd for $C_{42}H_{29}N$, 547.2300; found, 547.2305. Anal. calcd for $C_{42}H_{29}N$: C 92.11, H 5.34, N 2.56; found: C 91.89, H 5.32, N 2.47.

Methods: ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 MHz NMR or Mercury-400 MHz NMR spectrometer. Mass spectra were undertaken with a JMS-700 HRMS instrument. Elemental analysis was operated with an Elementar vario EL cube instrument. The UV/Vis and PL spectra were, respectively, measured on a Hitachi U-3300 model and a Hitachi F-4500 fluorescence spectrophotometer. The quantum yields of blue emitters in solid state were determined by using a calibrated integrating sphere. The fluorescence decay curves were performed on an Edinburgh FLS 980 spectrometer using the time correlated single photon counting (TCSPC) technique with a hydrogen-filled lamp as the excitation source. The pulse width of the nanosecond flash lamp is typically ~1 ns with repetition rate of 40 kHz. The instrument response function was determined by scattering light at the excitation wavelength using a Ludox solution. Time-resolved fluorescence decay curves were analyzed by deconvoluting the observed decay with the instrument response function to obtain the intensity decay function represented as a sum of discrete exponentials.

The TGA and DSC measurements were carried out using TA Instruments Q500 and Q10 at a speed of 20 and 10 °C/min under a nitrogen gas atmosphere, respectively. Electrochemical measurements were conducted with a CH Instrument equipment (Model 600A) using a three electrode configuration system. A Pt disc was used as the working electrode, and a silver wire and an $Ag/AgNO_3$ electrode were employed as the counter and the reference electrodes, respectively. All experiments were measured using CH_2Cl_2 solutions containing 0.1 M tetra-*n*-butylammonium fluoride (TBAF). The reported potentials were referenced to the ferrocene/ferrocenium redox couple. The molecular geometry optimizations and molecular orbitals were simulated *via* the method of density functional theory (DFT) implemented in the Gaussian 09 package. 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 employed to described all atoms. The molecular orbitals were generated with the Gaussview 5.0 software.

OLED device fabrication and Characterization: All chemicals used for device fabrication were purified by temperature gradient vacuum sublimation. OLEDs were fabricated on the indium-tin oxide (ITO)-coated glass substrates (thickness: 100 nm and sheet resistance: 30 Ω/sq). Prior to fabricating device, the ITO glasses were sequentially cleaned in ultrasonic bath using neutral detergent, distilled water and acetone, and treated by UV-ozone. All organic and cathode layers were deposited onto ITO glass at a base pressure of 5×10^{-7} Torr without breaking vacuum. Organic materials and lithium fluoride (LiF) were evaporated with the deposition rates of 1 and 0.1 Å/s, respectively. The deposition rate of blue emitter was adjusted according to the volume concentration in the host material. Finally, Al cathode was deposited on the top of the organic layers, and the resulting emission area was 9 mm^2. The electroluminescence (EL) performance of all devices were acquired using a Keithley 2400 source meter and a optical meter (Newport 1835-C) equipped with a calibrated silicon photodiode (Newport 818-ST). The EL spectra were measured with a Konica Minolta CS-2000 spectrometer.

The transient EL experiments were carried out on a function generator (Agilent 8114A) and an indigenously developed time-resolved emission spectrometer. The OLEDs were driven by a voltage pulse 6 V with repetition rate of 20 kHz and pulse width of 10 μs. To prevent the recombination of trapped charges, a reverse pulse voltage was applied during measurement after the excitation. The emission decay curves at specific wavelengths were collected using a cooled photomultiplier tube (PMT) detector (Becker & Hickl GmbH PMC-100) integrated with a 300 nm focal length monochromator (Princeton Instruments Acton SP2300). The time-resolved photon counting was performed *via* a multi-channel scaling (MCS) card (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).

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[S2] J. Ostrauskaite, V. Voska, J. Antulis, V. Gaidelis, V. Jankauskas and J. V. Grazulevicius, *J. Mater. Chem.*, **2002**, *12*, 3469.

[S3] Z. He, C.-W. Kan, C.-L. Ho, W.-Y. Wong, C.-H. Chui, K.-L. Tong, S.-K. So, T.-H. Lee, L. M. Leung and Z. Lin, *Dyes Pigments*, **2011**, *88*, 333.

2. Thermal behaviors of styrylpyrene-based materials

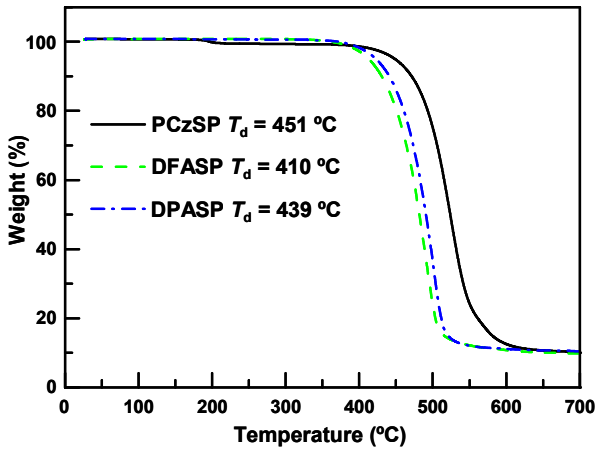


Figure S1. TGA profiles of PCzSP, DFASP, and DPASP.

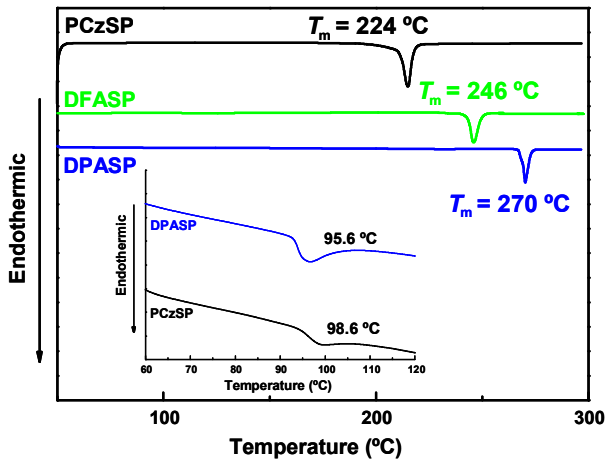


Figure S2. DSC curves of styrylpyrene-based materials measured at 10 °C/min under N_2.

3. Solvatochromic experiments and Lippert–Mataga analysis

Table S1. Spectroscopic data of PCzSP, DFASP, and DPASP in various solvents

Solvent	$\Delta f(\varepsilon,n)$[a]	PCzSP			DFASP			DPASP		
		λ_{abs} (nm)	λ_f (nm)	$\Delta\nu$ (cm^{-1})	λ_{abs} (nm)	λ_f (nm)	$\Delta\nu$ (cm^{-1})	λ_{abs} (nm)	λ_f (nm)	$\Delta\nu$ (cm^{-1})
n-Hexane	0.0012	356	421	4336	374	427	3318	376	431	3393
n-Butyl ether	0.0976	356	433	4995	374	443	4164	376	448	4274
Ethyl ether	0.1659	356	440	5362	374	455	4760	374	460	4999
Ethyl acetate	0.1994	356	349	5818	374	470	5461	376	475	5543
THF	0.2099	358	455	5954	378	482	5708	378	489	6005
DCM	0.2169	360	460	6038	378	486	5878	380	496	6154
Acetonitrile	0.3055	360	483	7030	376	515	7178	378	520	7224

[a] The ε and n values are obtained from http://www.stenutz.eu/chem/solv23.php.

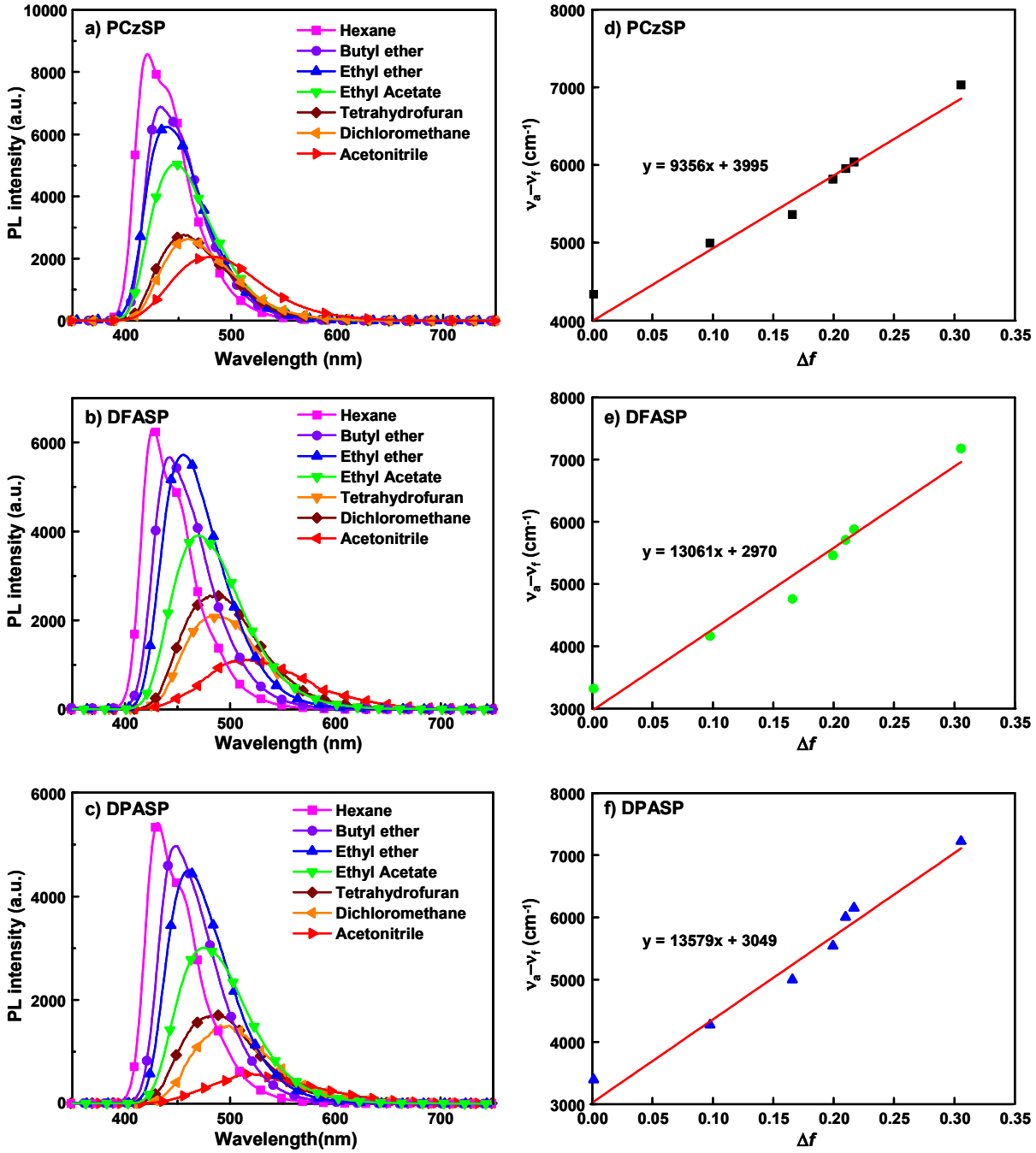


Figure S3. (a)-(c) Solvatochromic PL spectra and (d)-(f) Lippert–Mataga plots of styrylpyrene-based materials with increasing polarity of solvents.

4. DFT simulation, electrochemistry, and photophysical property

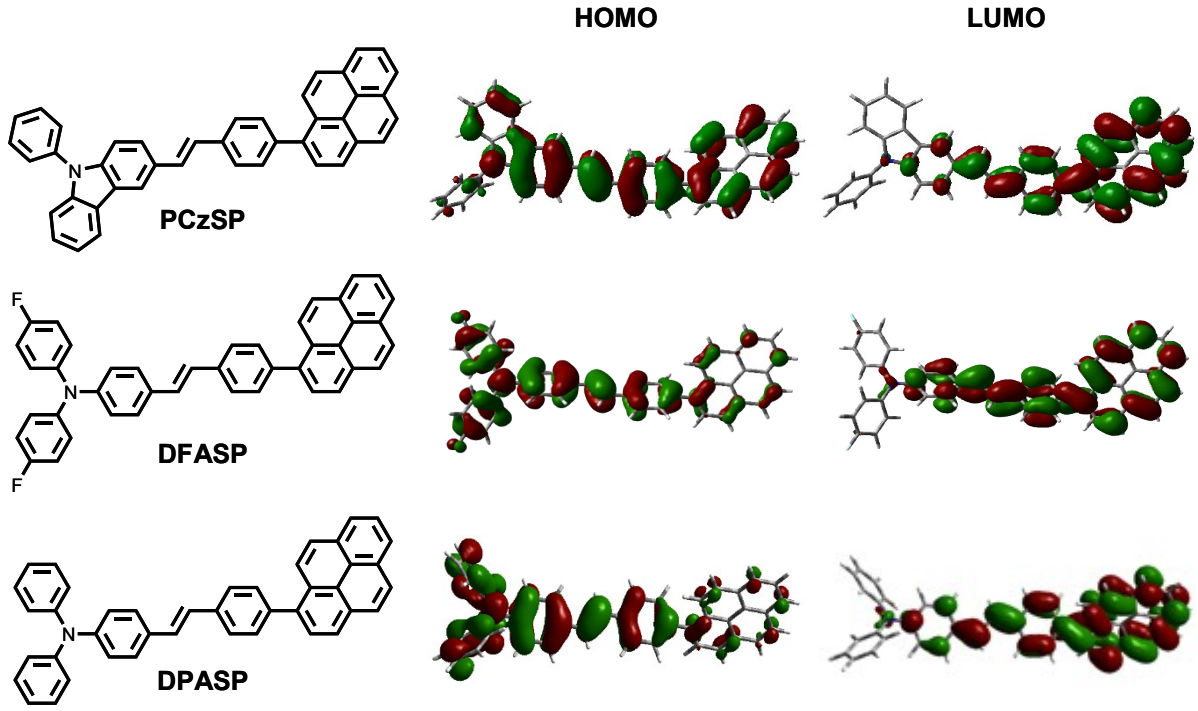


Figure S4. Frontier molecular orbitals of PCzSP, DFASP, and DPASP simulated at B3LYP/6-31G* level.

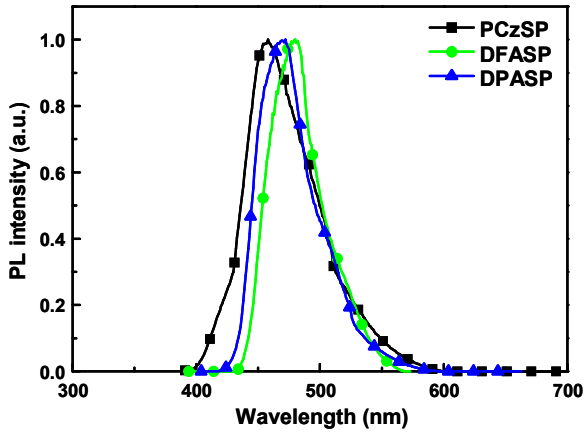


Figure S5. Emission spectra of styrylpyrene-based materials in thin films.

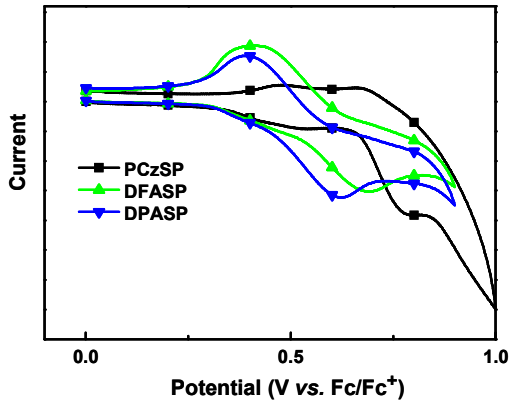


Figure S6. Cyclic voltammograms of PCzSP, DFASP, and DPASP in $CH_2Cl_2$for oxidation.

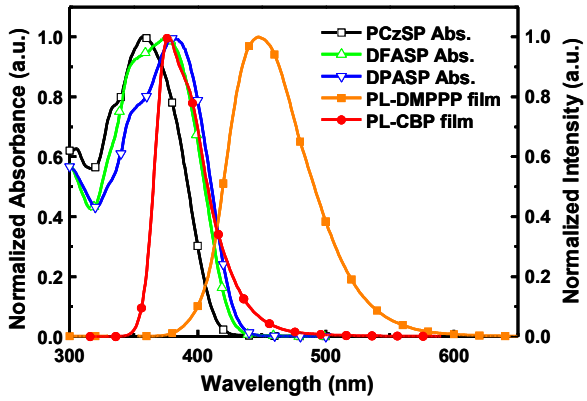


Figure S7. Absorption spectra of PCzSP, DFASP, and DPASP in comparison with emission spectrum of CBP and DMPPP.

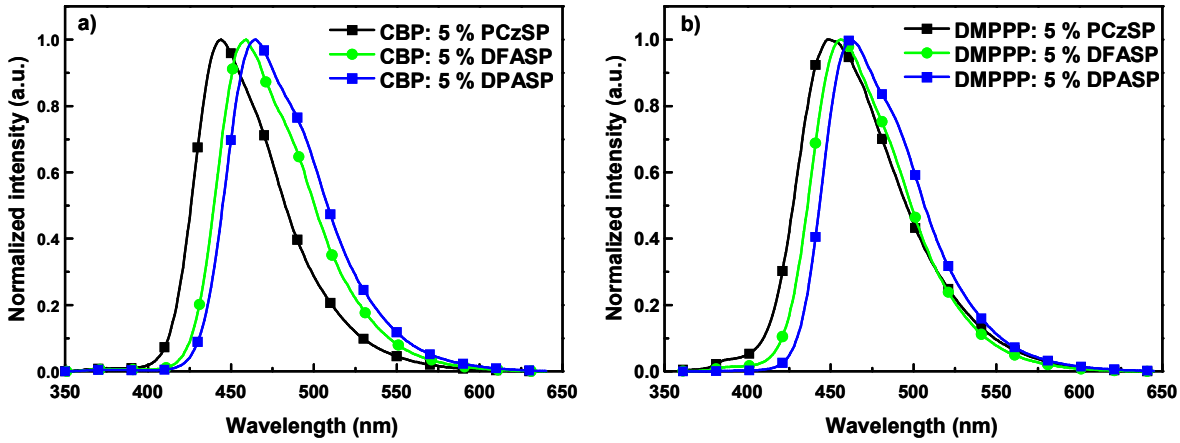


Figure S8. PL spectra of PCzSP-, DFASP-, and DPASP-doped CBP and DMPPP films at a dopant concentration of 5%.

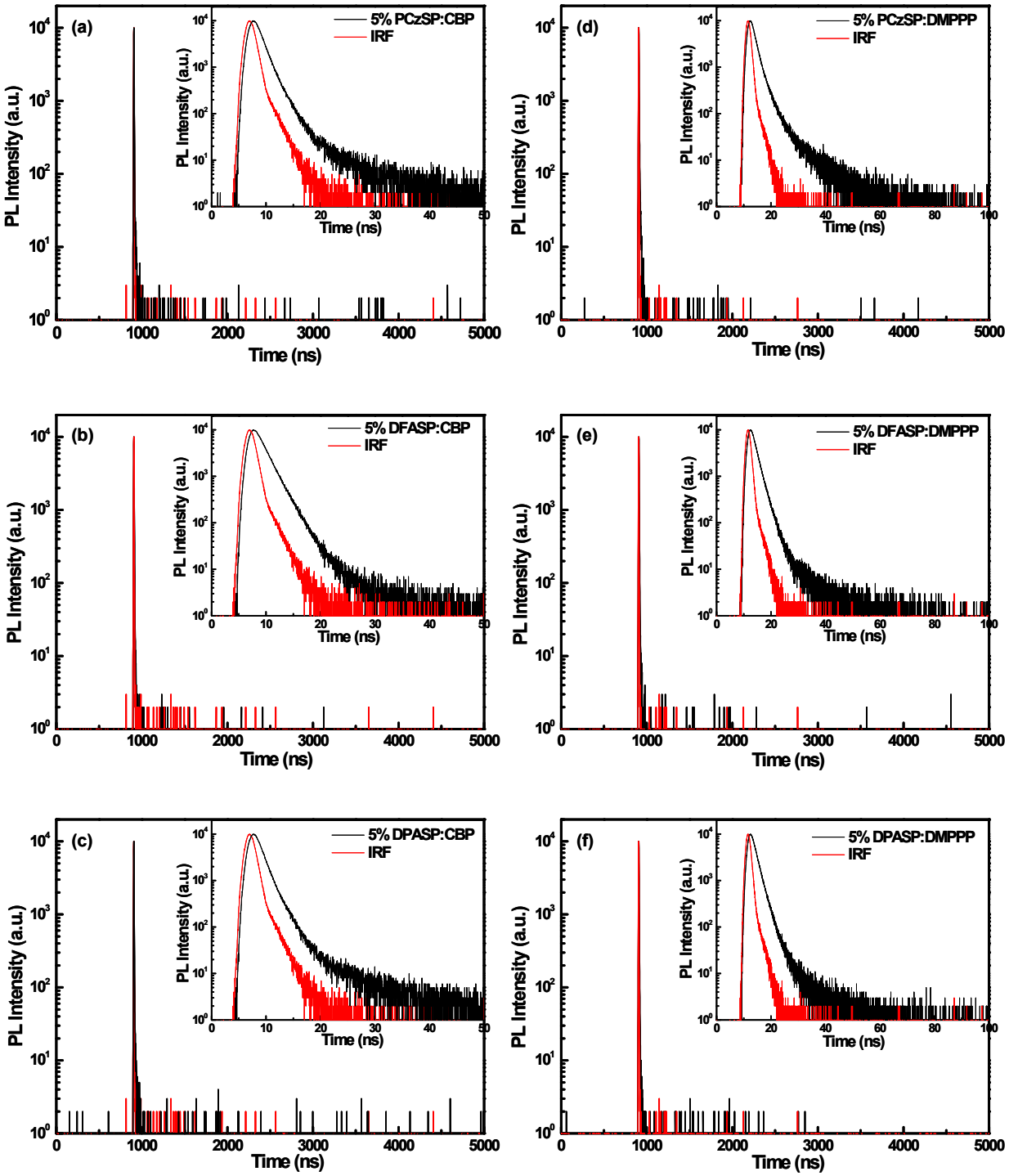


Figure S9. Transient PL curves of PCzSP-, DFASP-, and DPASP-doped (a-c) CBP and (d-f) DMPPP films in an oxygen-free environment. The lifetimes are 1.1, 1.5, and 1.2 ns for PCzSP-, DFASP-, and DPASP-doped CBP films, respectively, while the lifetimes of DMPPP films doped with PCzSP, DFASP, and DPASP are 1.4, 1.5, and 1.5 ns, respectively.

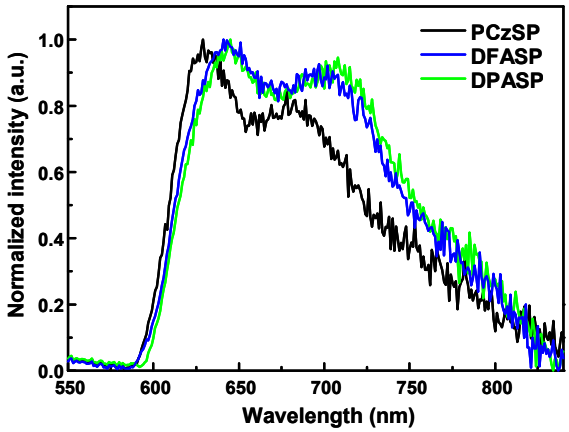


Figure S10. The 1 ms-delayed phosphorescence spectra (measured at 77 K) of PCzSP-, DFASP-, and DPASP-doped PMMA films using FIrpic as the triplet sensitizer.

5. OLED performance of styrylpyrene-based materials

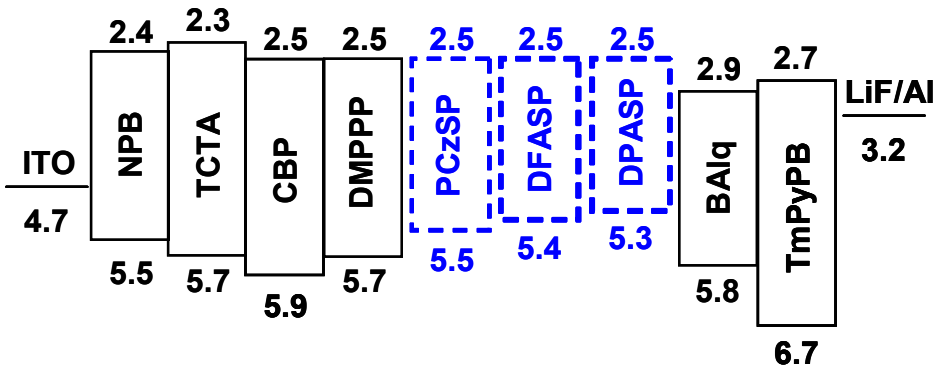


Figure S11. Energy level diagram of deep-blue EL devices.

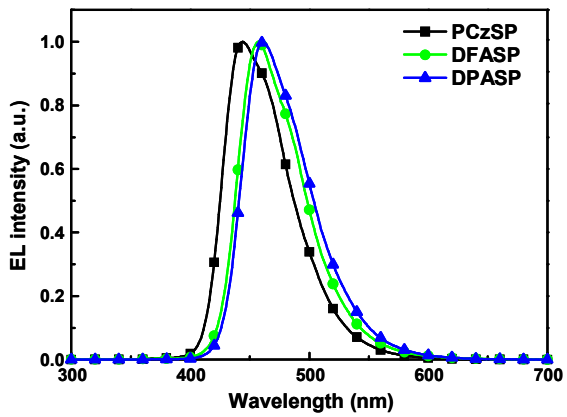


Figure S12. EL Spectra of PCzSP, DFASP, and DPASP doped in the CBP host (Devices A-C).

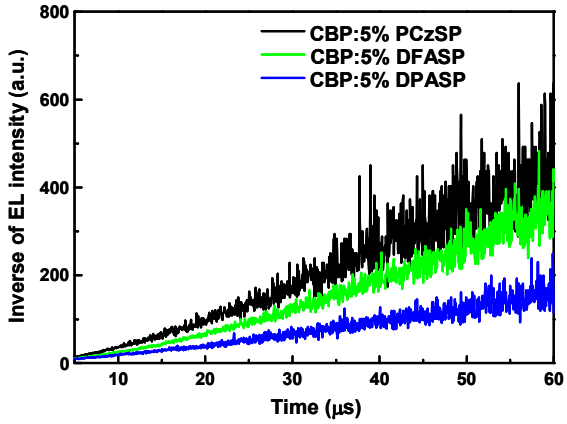


Figure S13. Plots of the inverse of relative transit EL intensity *versus* time for devices A-C.

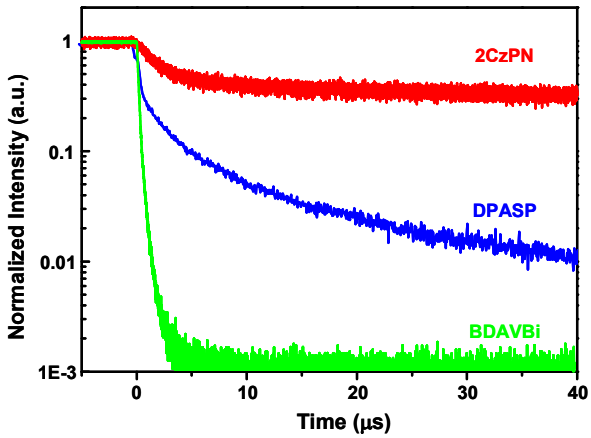


Figure S14. Transient EL decay curves of devices containing BDAVBi, DPASP, and 2CzPN as the dopant. The device structures is NPNPB (20 nm)/NPB (40 nm)/DPVBi: 3% BDAVBi (40 nm)/Alq_3 (30 nm)/LiF (1 nm)/Al (100 nm) for BDAVBi-based device, ITO/NPB (30 nm)/TCTA (20 nm)/CBP: 5% DPASP (30 nm)/TmPyPB (30 nm)/LiF (1 nm)/Al(100 nm) for DPASP-based device (the same as device C), and NPB (35nm)/mCP (10 nm)/mCP: 5% 2CzPN (15 nm)/PPT (10 nm)/TPBi (40 nm)/LiF (1nm)/Al (100 nm) for 2CzPN-based device.

Table S2. EL data of DPASP-based devices hosted by CBP.

Device[a]	EML	V_{on} (V)	EQE_{max} (%)	CE_{max} (cd/A)	PE_{max} (lm/W)	λ_{max} (nm)	CIE (x, y)
S1	CBP	3.9	1.7	1.0	0.6	400	(0.17, 0.11)
S2	1% DPASP	3.1	10.1	14.2	12.7	457	(0.14, 0.14)
S3	3% DPASP	3.0	10.8	14.7	13.2	461	(0.14, 0.16)
S4	5% DPASP	3.0	12.0	18.5	16.5	462	(0.14, 0.17)

[a]ITO/NPB (30 nm)/TCTA (20 nm)/CBP: x% dopant (30 nm)/TmPyPB (30 nm)/LiF (1 nm)/Al (100 nm)

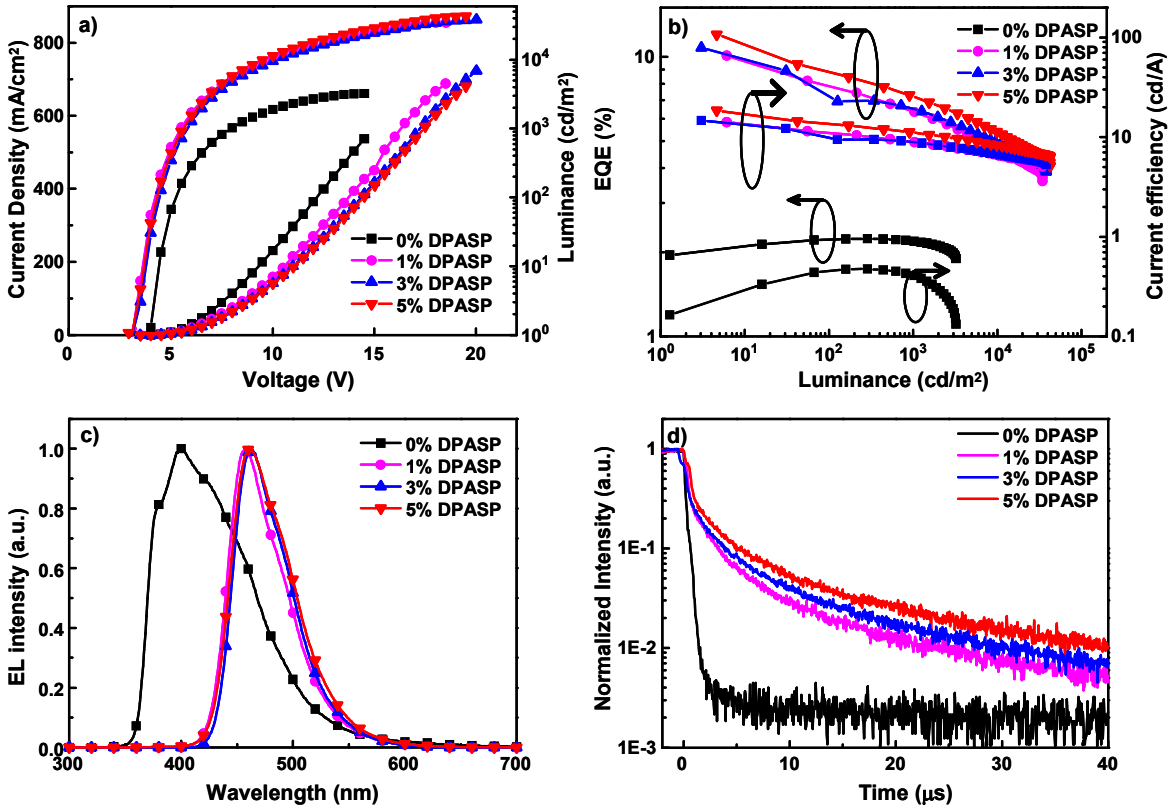


Figure S15. EL characteristics of blue devices doped with DPASP at different concentrations. (a) Current density-voltage-luminance (*J-V-L*) characteristics. (b) Plot of external quantum efficiency and current efficiency as a function of luminance. (c-d) EL spectra and transient EL of devices doped with different concentrations of DPASP.

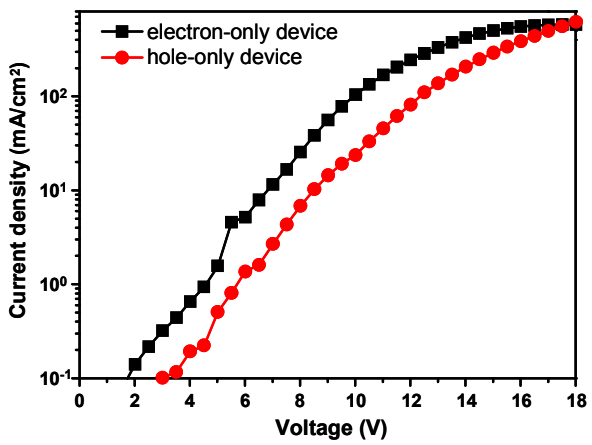


Figure S16. *J-V* curves of the hole-only and electron-only devices for DMPPP with the respective structures of ITO/NPB (20 nm)/DMPPP (30 nm)/NPB (20 nm)/Al (100 nm) and ITO/BCP (20 nm)/DMPPP (30 nm)/BCP (20 nm)/LiF (1 nm)/Al (100nm).

6. Discussion on delayed fluorescence for DMPPP device

Considering the PL quantum yield of 0.75, theoretical maximum EQE of DMPPP device is 3.75%, assuming the electron/hole recombination ratio of 100%, exciton formation ratio of 25%, and light outcoupling efficiency of 20%. However, the EQE of DMPPP device is 5.4% (Figure S17a), much higher than its theoretical maximum value. This manifests that DMPPP device can harvest triplet excitons *via* the up-conversion of triplet to singlet state. Moreover, DMPPP device also exhibit delayed fluorescence in its transient EL. To understand the origin of the delayed fluorescence in DMPPP device, the photophyiscal measurements of DMPPP were performed. The PL spectra of DMPPP in solution do not change with the solvent used. This result suggests that the singlet excited state of DMPPP is not charge-transfer feature, which is different from the TADF and HLCT materials. Moreover, The S_1 and T_1 energies of DMPPP are found to be 3.15 and 2.05 eV, showing a large ΔE_{ST} value of 1.1 eV for DMPPP. The transient PL decay of the DMPPP film exhibits two short lifetimes of 1.5 and 8.1 ns. Thus, we could rule out that the delayed fluorescence comes from the TADF of DMPPP and attribute the delayed fluorescence in DMPPP device to the extra radiative singlet excitons generated from the efficient TTA of DMPPP. Notably, the energy of $2T_1$ is larger than that of S_1, suggesting the TTA process of DMPPP is possible to produce additional singlet excitons.

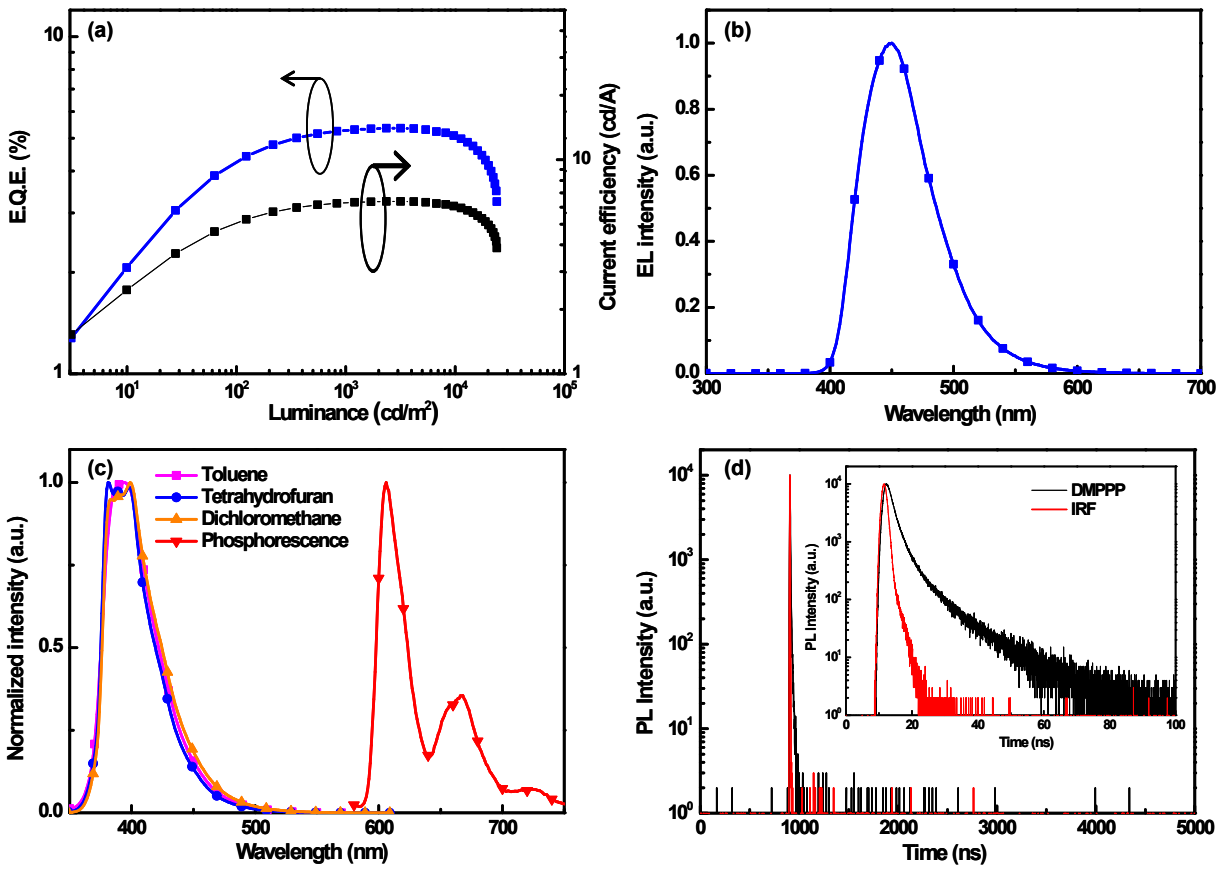


Figure S17. Device performance and photophisical property for DMPPP. (a) *J-V-L* curve and (b) EL spectra of DMPPP-based device with ITO/NPB (60 nm)/DMPPP (25 nm)/BAlq (20 nm)/LiF (1 nm)/Al (100 nm). (c) Fluorescence and phosphorescence spectra of DMPPP. (d) Transient PL curve for DMPPP film. The phosphorescence spectra of DMPPP was measured in toluene at 77 K.

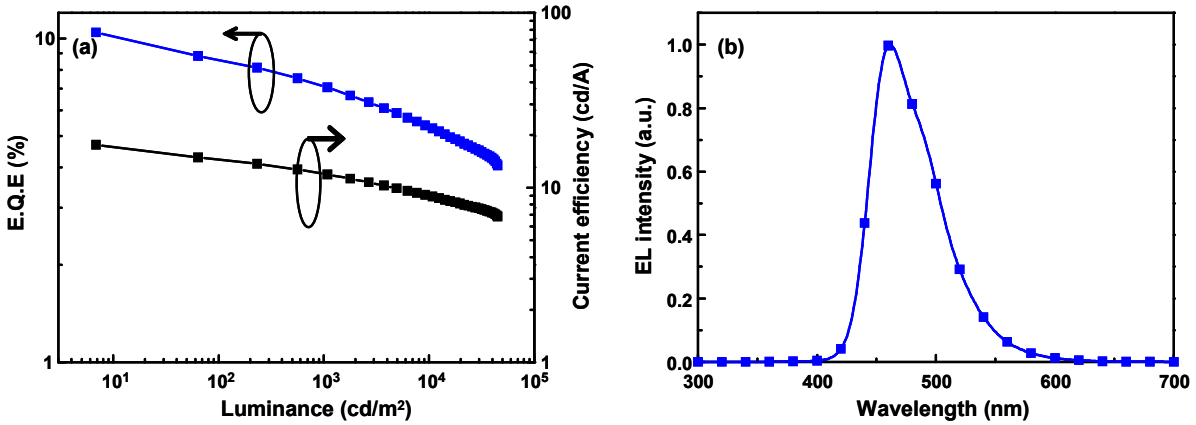
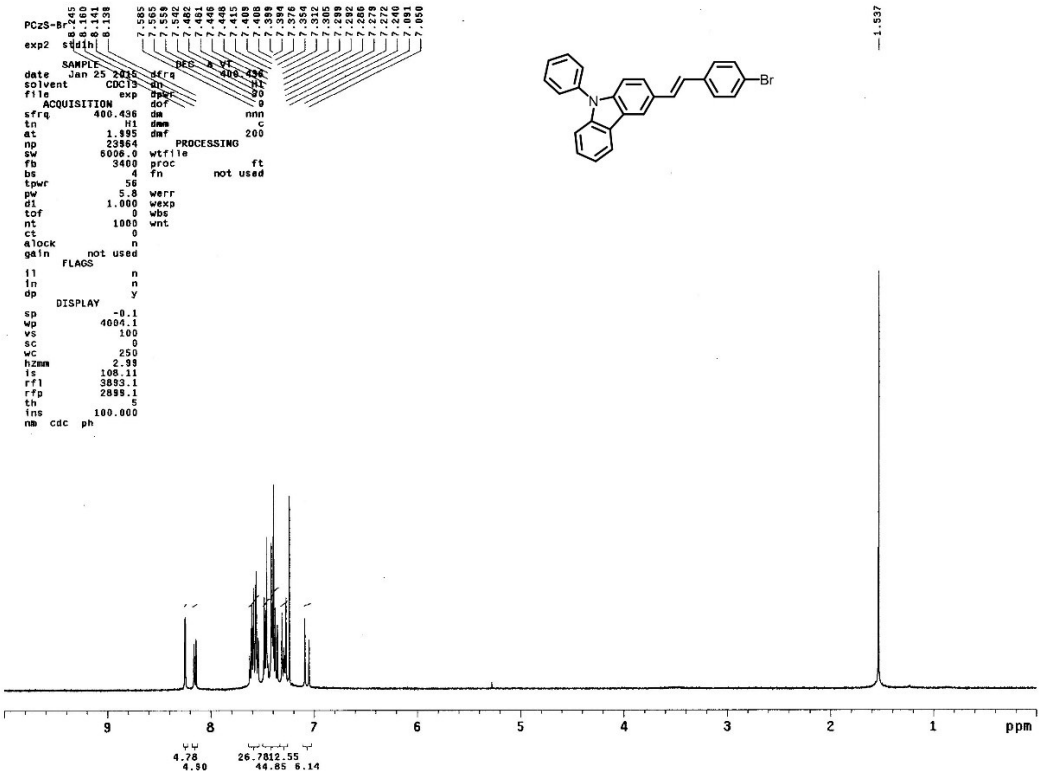
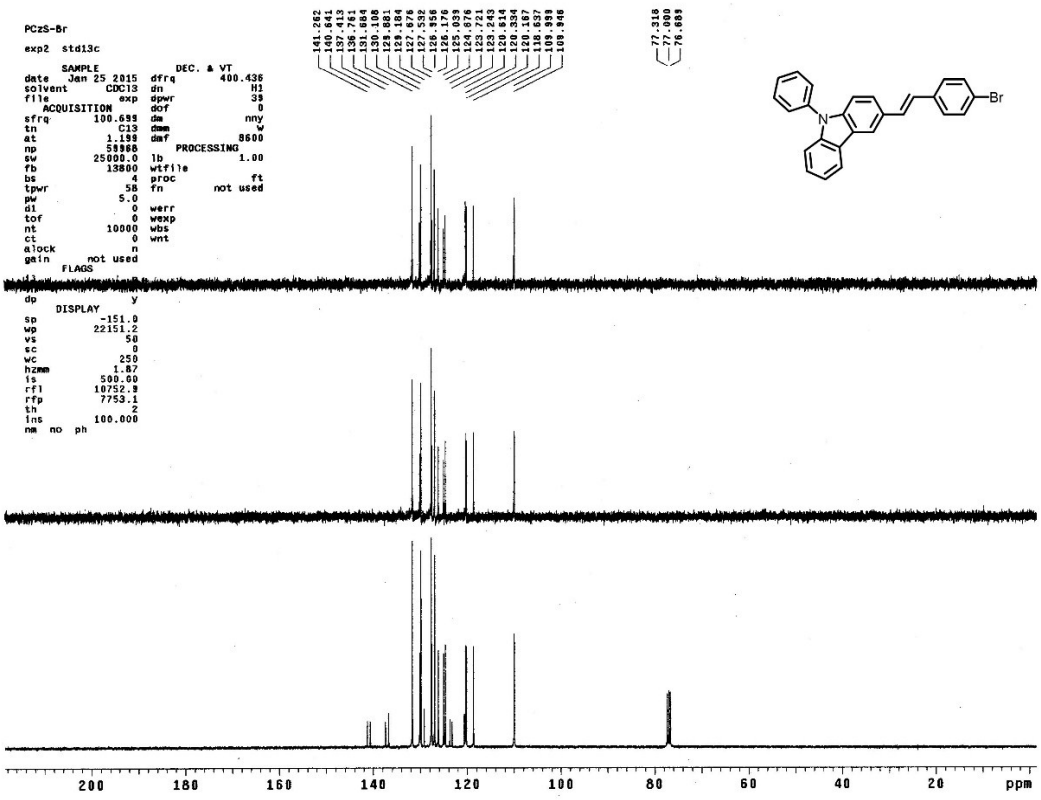
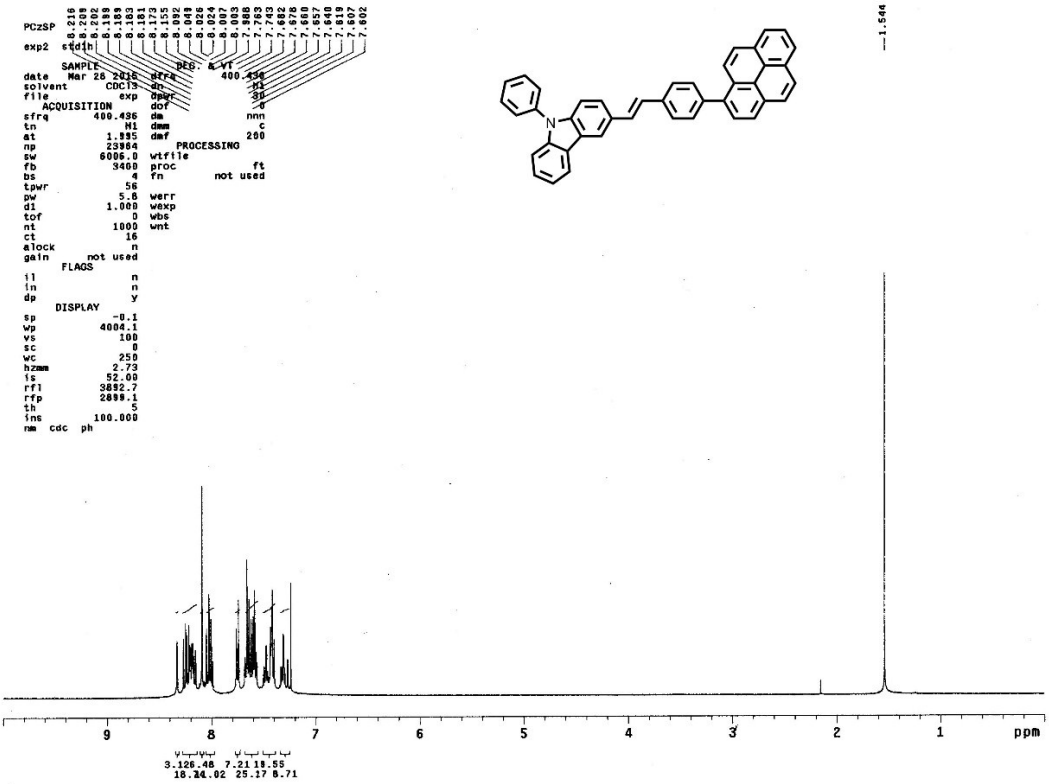


Figure S18. (a) Plot of external quantum efficiency as a function of luminance and (b) EL spectrum for device G, a DPASP-doped CBP-hosted device with the structure of ITO/NPB (60 nm)/NPB: DPASP (3 wt%, 10 nm)/CBP: DPASP (5 wt%, 15 nm)/BAlq (20 nm)/LiF (1 nm)/Al (100 nm). The structure is similar to that of device F except the host is CBP.

6. ^{1}H and ^{13}C NMR spectra



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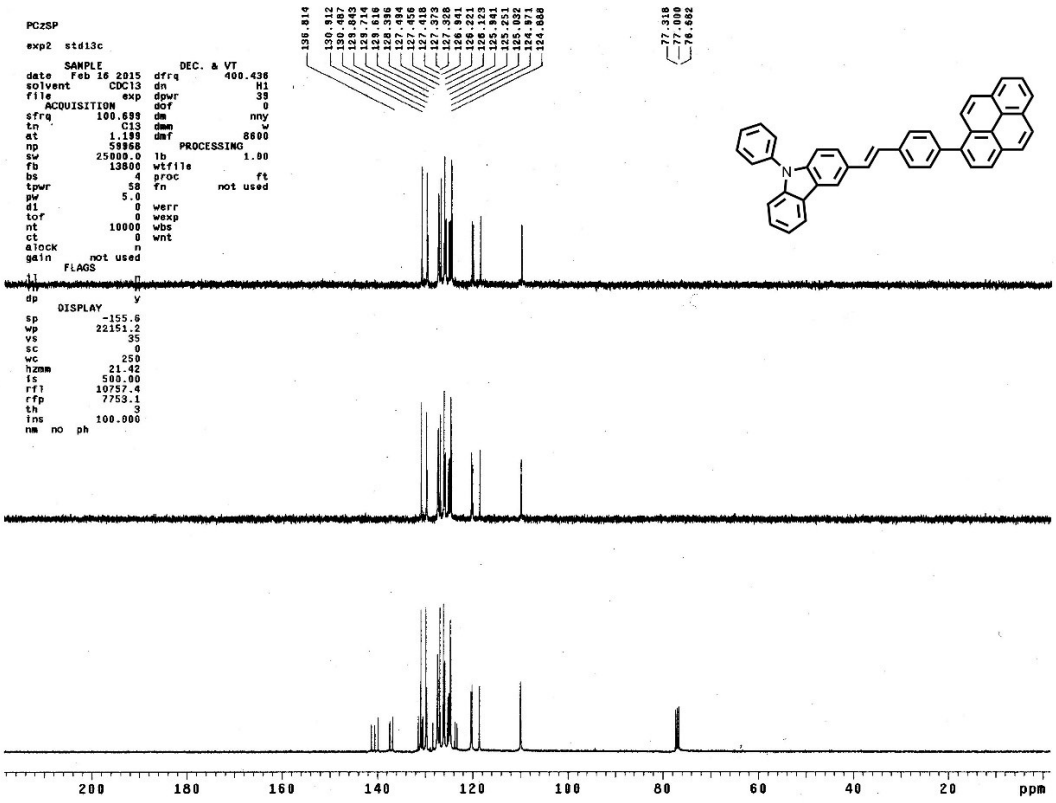
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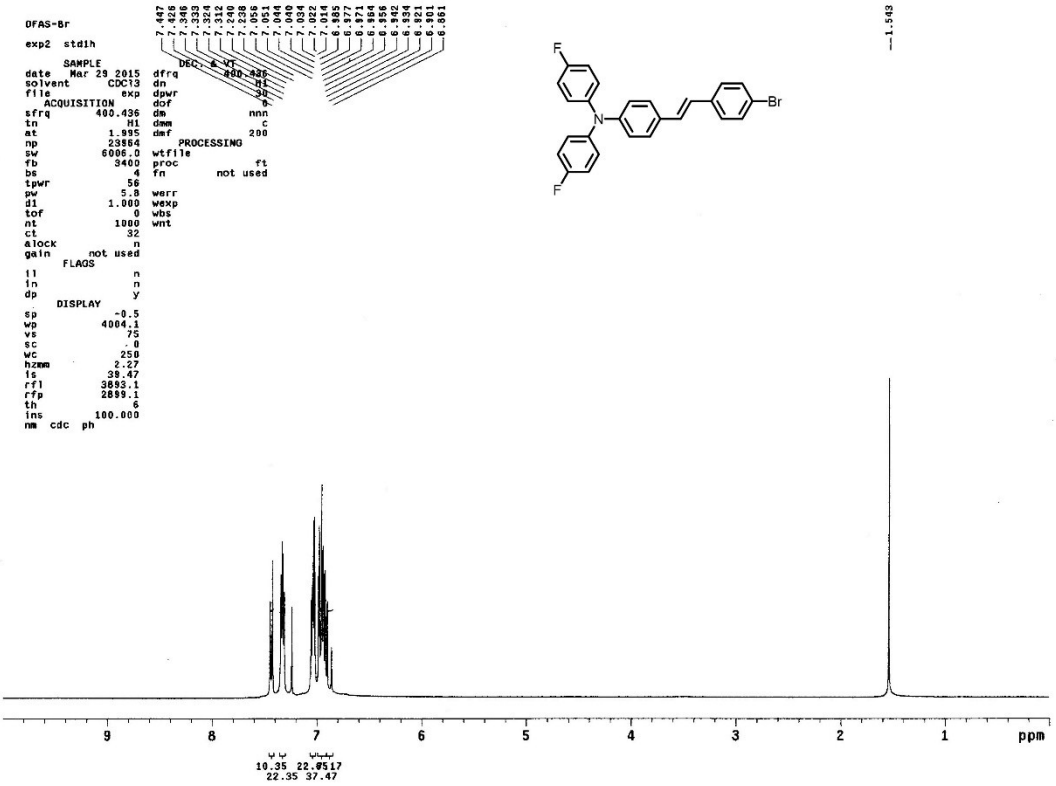
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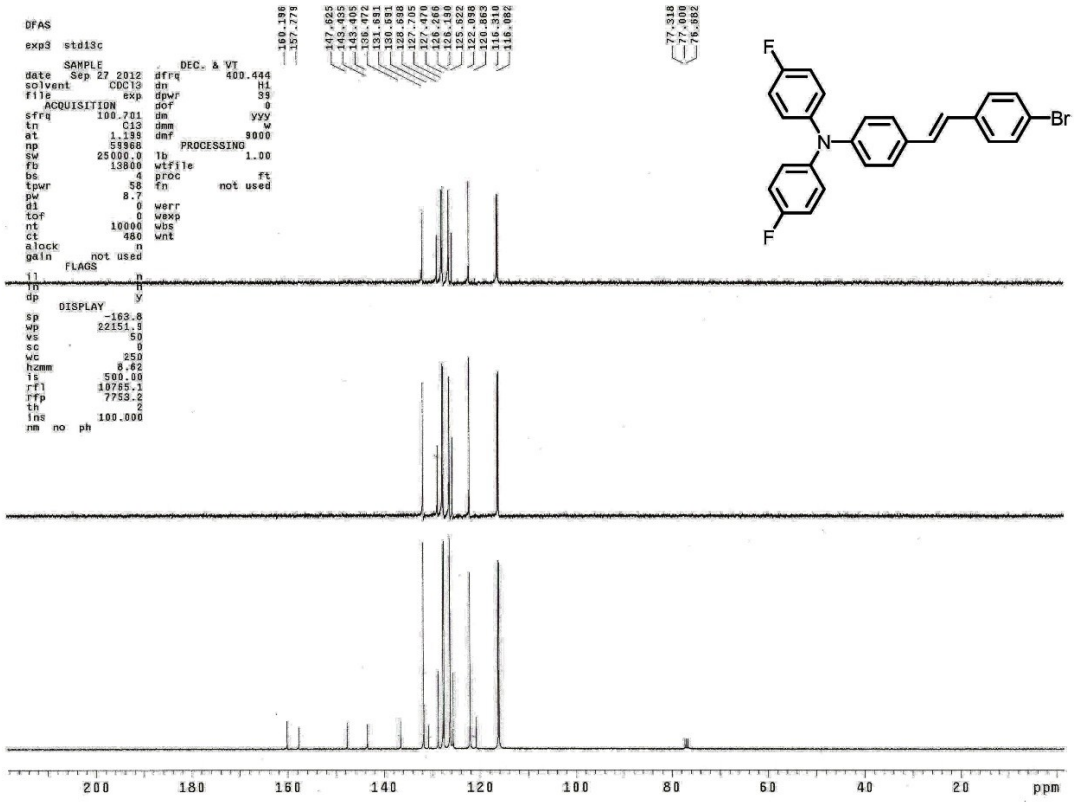
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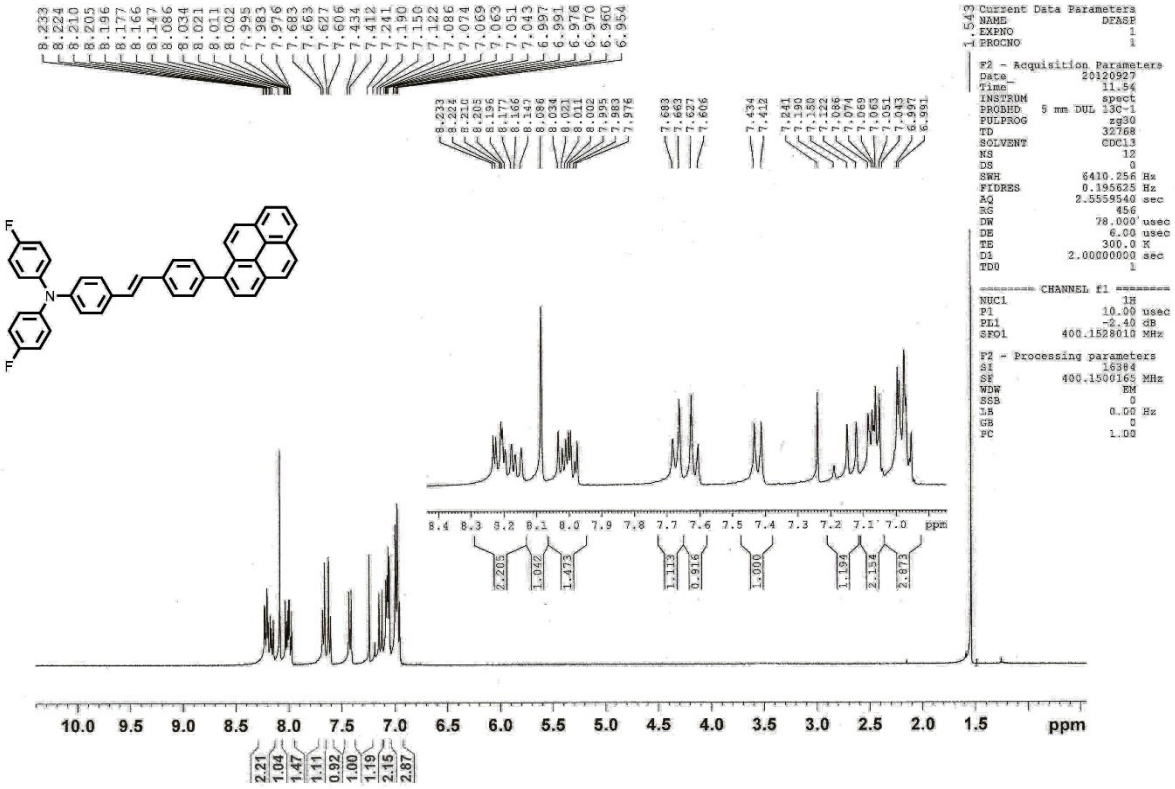
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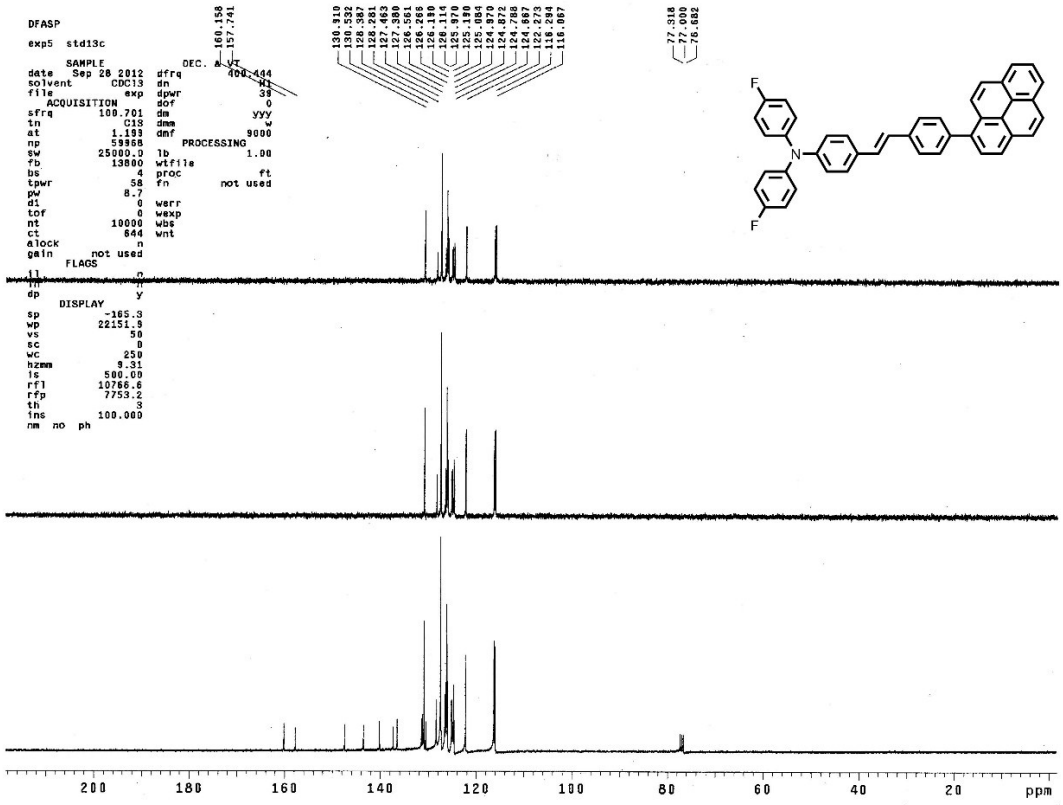
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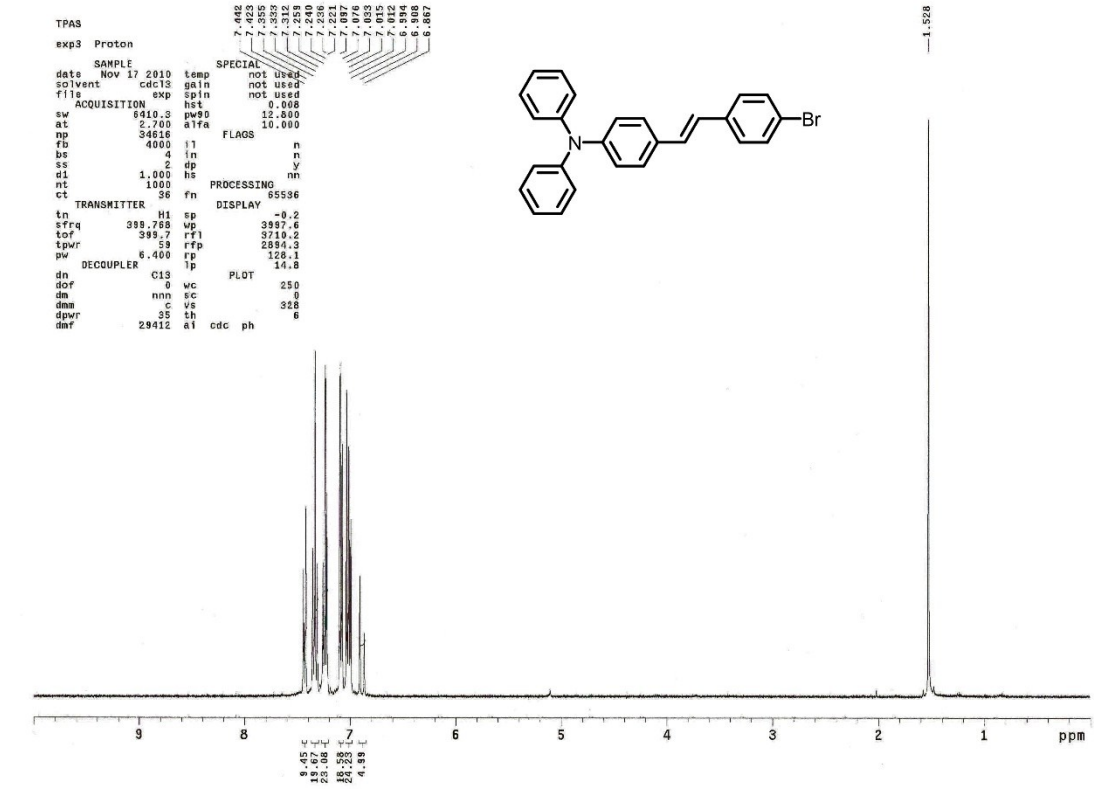
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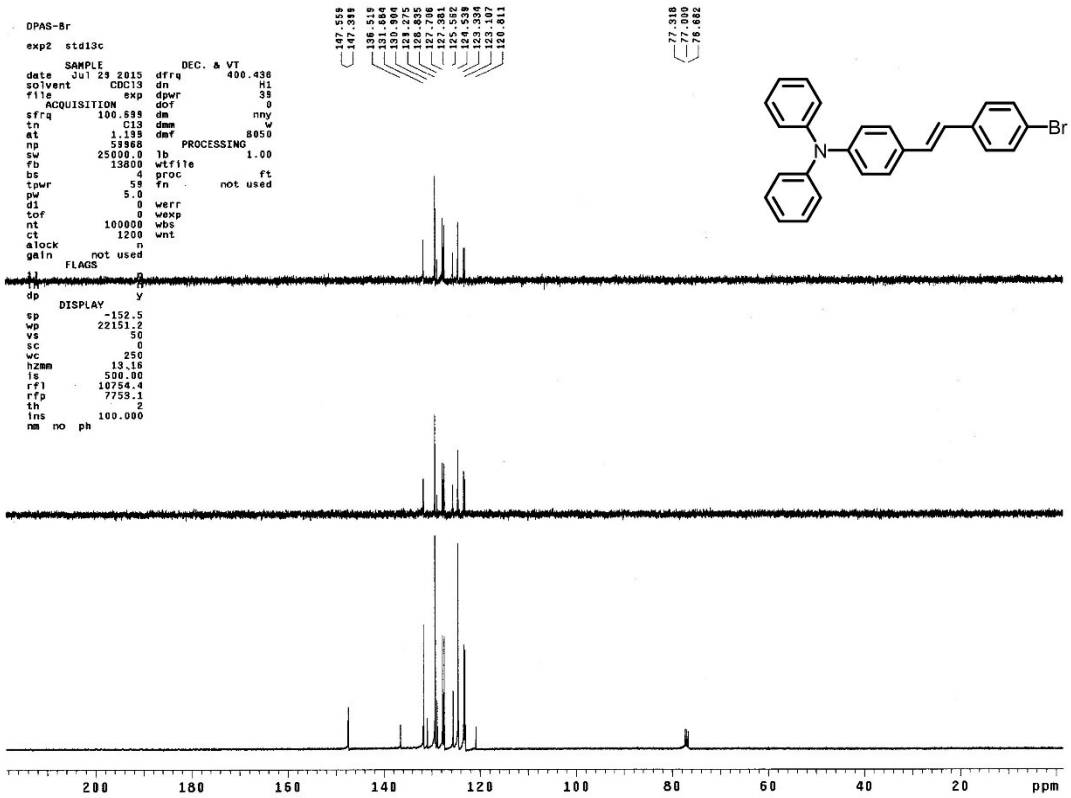
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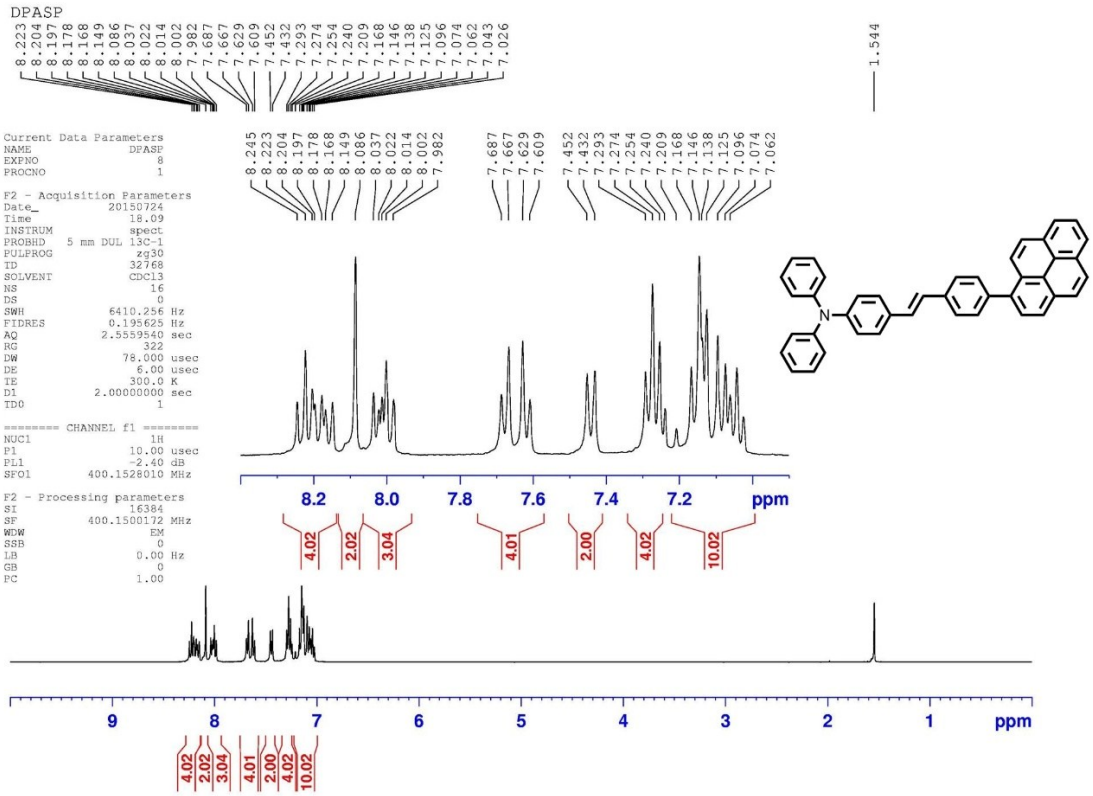
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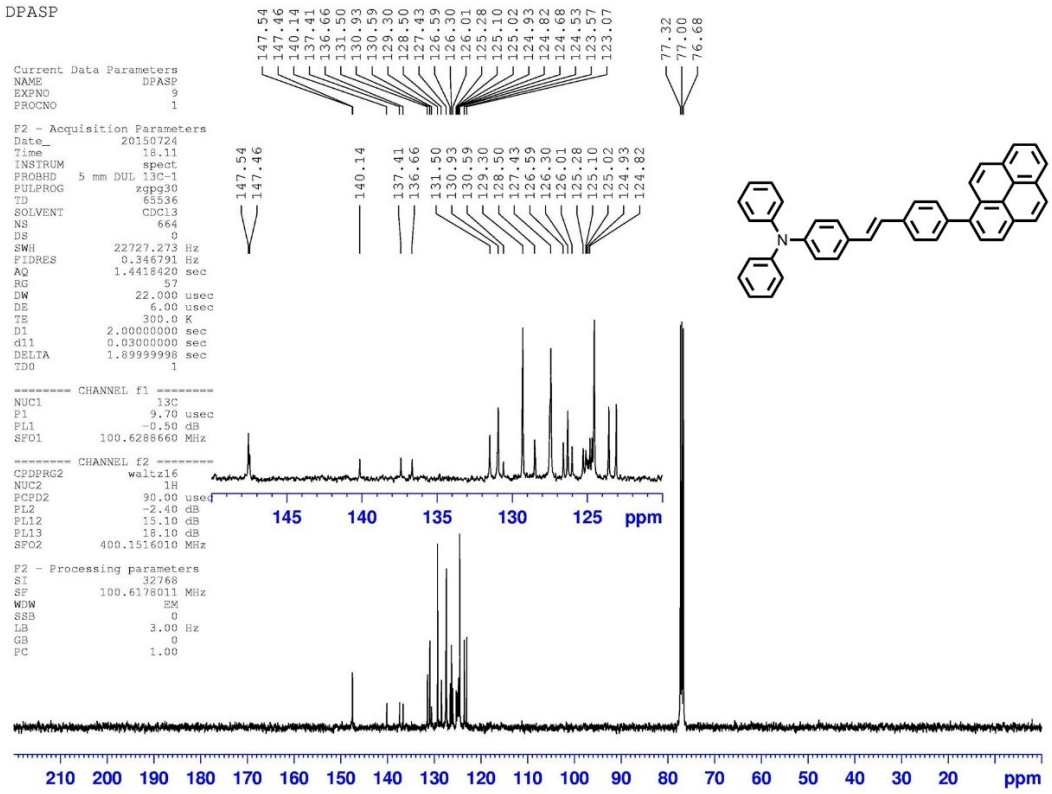
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