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Electronic Supplementary Information for:

A sky blue thermally activated delayed fluorescent emitter to achieve efficient white light emission through in situ metal complex formation

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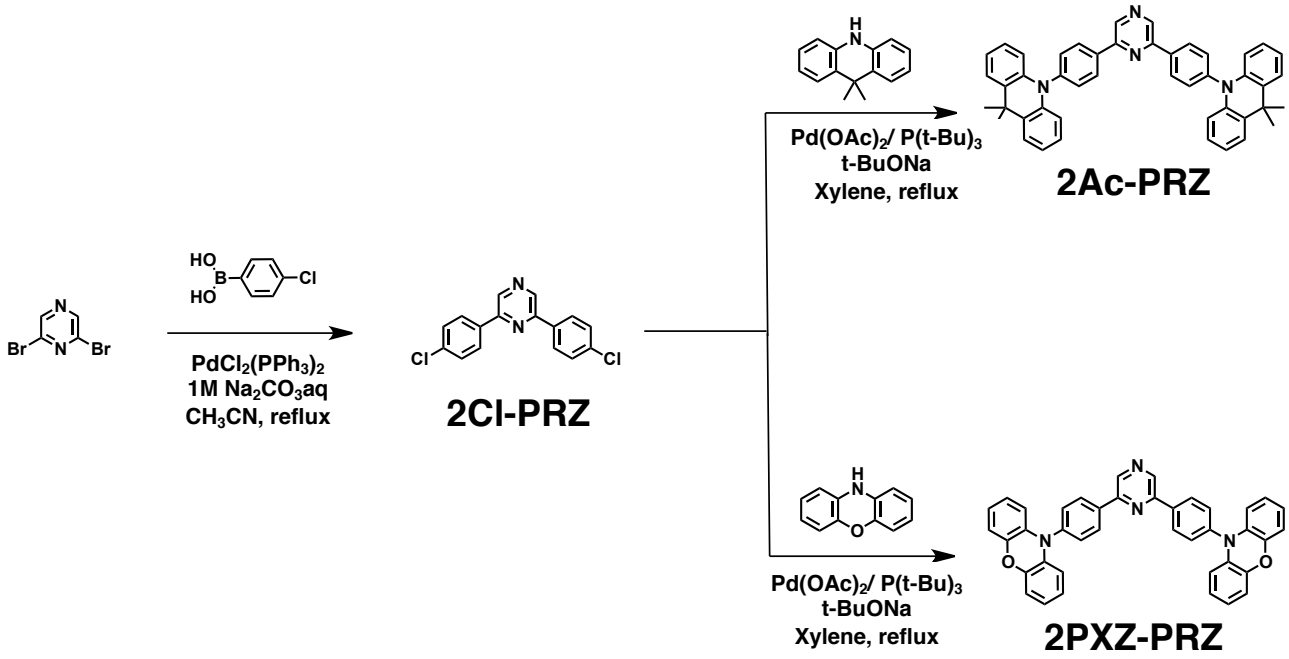
General Considerations:

Quantum chemical calculations were performed using the hybrid DFT functional Becke and Hartree-Fock exchange and Lee Yang and Parr correlation (B3LYP) as implemented by the Gaussian 09 program packages. Electrons were described by the Pople's 6-31G(d) and 6-311+G(d,p) basis sets for molecular structure optimization and single-point energy calculations, respectively. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL 400 (400 MHz) spectrometer. Mass spectrum was obtained using a JEOL JMS-K9 mass spectrometer. DSC was performed using a Perkin-Elmer Diamond DSC Pyris instrument under nitrogen atmosphere at a heating rate of 10 ˚C min^{-1}. TGA was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 ˚C min^{-1}. UV–vis spectra was measured using a Shimadzu UV-3150 UV–vis–NIR spectrophotometer. Photoluminescence spectra were measured using a FluoroMax-2 (Jobin-Yvon-Spex) luminescence spectrometer. The I_p was determined by a PYS under the vacuum (=10^{-3} Pa). Transient PL decay curves and time resolved photoluminescence spectra were measured by using a streak camera (C4334 from Hamamatsu Photonics) at 5 K and 300 K.

Device Fabrication and Characterization:

The substrates were cleaned with ultrapurified water and organic solvents, and then dry-cleaned for 30 minutes by exposure to UV–ozone. The organic layers were deposited onto the ITO substrates under the vacuum (=10^{-5} Pa), successively. LiF and Al was patterned using a shadow mask with an array of 2 mm × 2mm openings without breaking the vacuum (=10^{-5} Pa). The electroluminescent (EL) were taken using an optical multichannel analyzer Hamamatsu Photonics PMA-11. The current density–voltage and luminance–voltage characteristics were measured by using a Keithley source measure unit 2400 and a Minolta CS200 luminance meter, respectively.

Synthesis



Scheme S1. Synthetic routes of **2Ac-PRZ** and **2PXZ-PRZ**.

Synthesis of 2Cl-PRZ

2,6-Dibromopyrazine (0.95 g, 4.0 mmol), 4-chlorophenylboronic acid (1.25 g, 8.0 mmol), and aqueous Na_2CO_3 (1 M, 20 ml) were added to a round bottom flask. CH_3CN (80 ml) was added and nitrogen was bubbled through the mixture for 1.5 hour. Then, $PdCl_2(PPh_3)_2$ (0.14 g, 0.20 mmol) was added and the resultant mixture was stirred for 3 hours at reflux temperature under N_2 flow. After cooling to room temperature, the precipitate was filtered. The resulting solid was purified by chromatography on silica gel (eluent: toluene) to afford **2Cl-PRZ** (1.02 g, 85 %) as a white solid:^{1}H-NMR (400 MHz, DMSO-d6): δ 9.26 (s, 2H), 8.30 (d, 4H, J=8.8 Hz), 7.64 (d, 4H, J=8.8 Hz) ppm; MS: m/z = 301$[M + H]^+$(ASAP).

Synthesis of 2Ac-PRZ

9,10-Dihydro-9,9-dimethylacridine (0.63 g, 3.0 mmol), **2Cl-PRZ** (0.45 g, 1.5 mmol), and t-BuONa (0.43 g, 4.5 mmol) were added to a round bottom flask and nitrogen flow for 15 minutes. Xylene (20 ml) was added and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd(OAc)_2$ (17 mg, 0.075 mmol) and $[(^tBu)_3PH]BF_4$ (65 mg, 0.45 mmol) were added and the resultant mixture was stirred for 12 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The resulting solid was purified by column chromatography on silica gel to afford **2Ac-PRZ** (0.76 g, 78 %) as a pale yellow solid: ^{1}H-NMR (400 MHz, DMSO-d6): δ 9.42 (s, 2H), 8.63 (d, 4H, *J*=8.0 Hz), 7.56 (dd, 8H, *J*=8.4, 7.6 Hz),

7.02-6.91 (m, 8H), 6.26 (d, 4H, *J*=8.0 Hz), 1.65 (s, 12H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 151.02, 143.06, 140.66, 140.41, 136.23, 132.09, 130.12, 129.64, 126.42, 125.35, 120.78, 114.04, 36.00, 31.29 ppm; MS: m/z = 647 $[M + H]^+$(ASAP). ; Anal calcd for $C_{46}H_{38}N_4$: C, 85.42; H, 5.92; N, 8.66 %. Found: C, 85.46; H, 5.97; N, 8.64 %.

Synthesis of 2PXZ-PRZ

Phenoxazine (0.39 g, 2.1 mmol), **2Cl-PRZ** (0.30 g, 1.0 mmol), and t-BuONa (0.29 g, 3.0 mmol) were added to a round bottom flask and nitrogen flow for 15 minutes. Xylene (15 ml) was added and nitrogen was bubbled through the mixture for an hour. Then, $Pd(OAc)_2$ (11 mg, 0.05 mmol) and $[(^tBu)_3PH]BF_4$ (44 mg, 0.15 mmol) were added and the resultant mixture was stirred for 24 hours at reflux temperature under N_2 flow. The precipitate was filtered, and washed with brine, dried over anhydrous Na_2SO_4, filtered, and evaporated to dryness. The resulting solid was purified by column chromatography on silica gel to afford **2PXZ-PRZ** (0.35 g, 60 %) as a pale yellow solid: ^{1}H-NMR (400 MHz, DMSO-d6)：δ 9.40 (s, 2H), 8.59 (d, 4H, *J*=8.4 Hz), 7.65 (d, 4H, *J*=8.4 Hz), 6.79-6.67 (m, 12H), 5.99-5.97 (m, 4H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 150.85, 143.95, 140.77, 140.43, 136.44, 134.05, 131.61, 129.79, 123.29, 121.60, 115.61, 113.26 ppm; MS: m/z = 594 $[M]^+$(ASAP); Anal calcd for $C_{40}H_{26}N_4O_2$: C, 80.79; H, 4.41; N, 9.42 %. Found: C, 80.63; H, 4.52; N, 9.37 %.

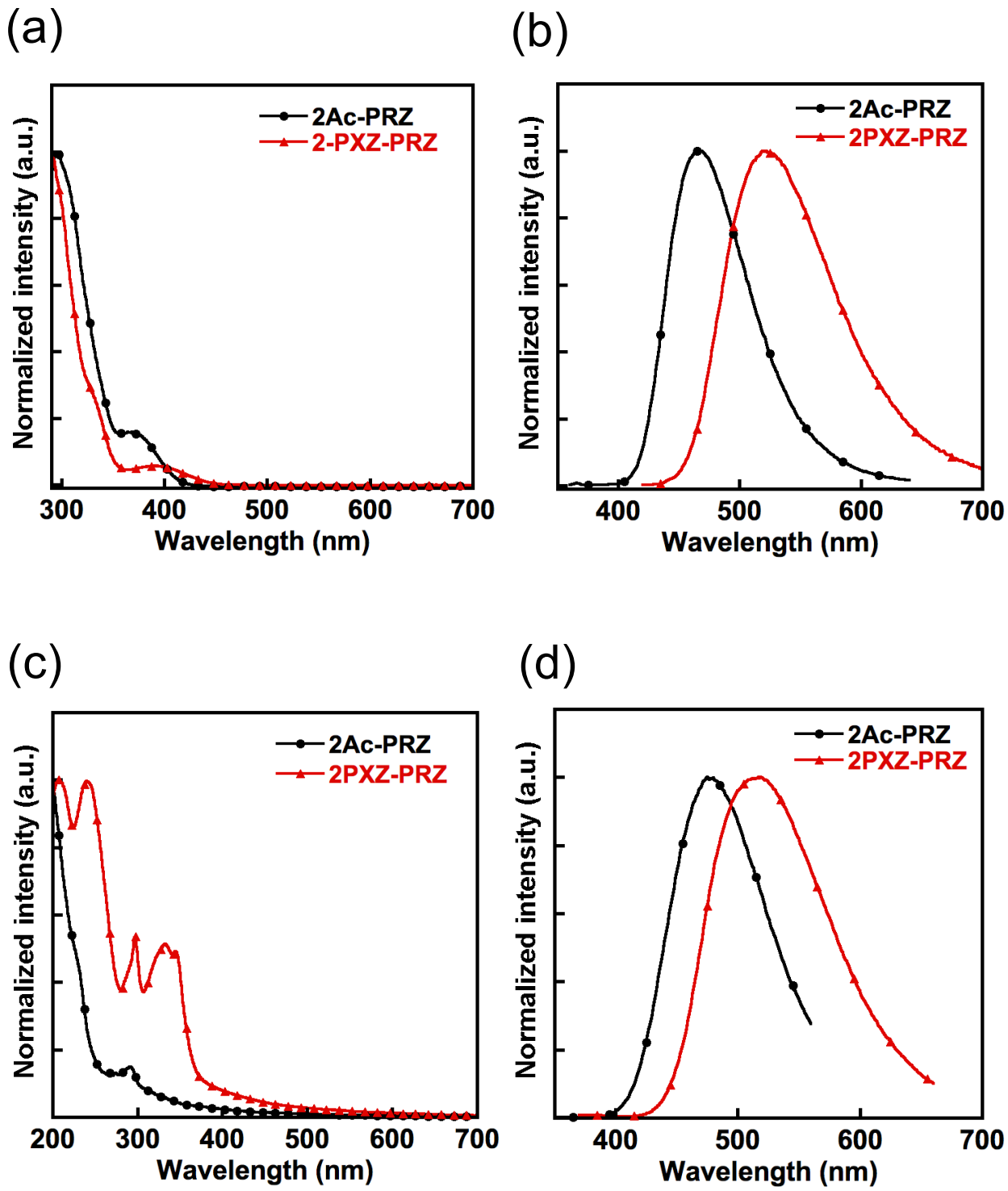


Figure S1. (a) UV–vis absorption, and (b) PL spectra of **PRZ** derivatives in toluene (1.0×10^{-5} M). (c) UV–vis absorption, and (d) PL spectra of 10 wt% **2Ac-PRZ**-doped DPEPO film, (d) 10 wt% **2PXZ-PRZ**-doped CBP film.

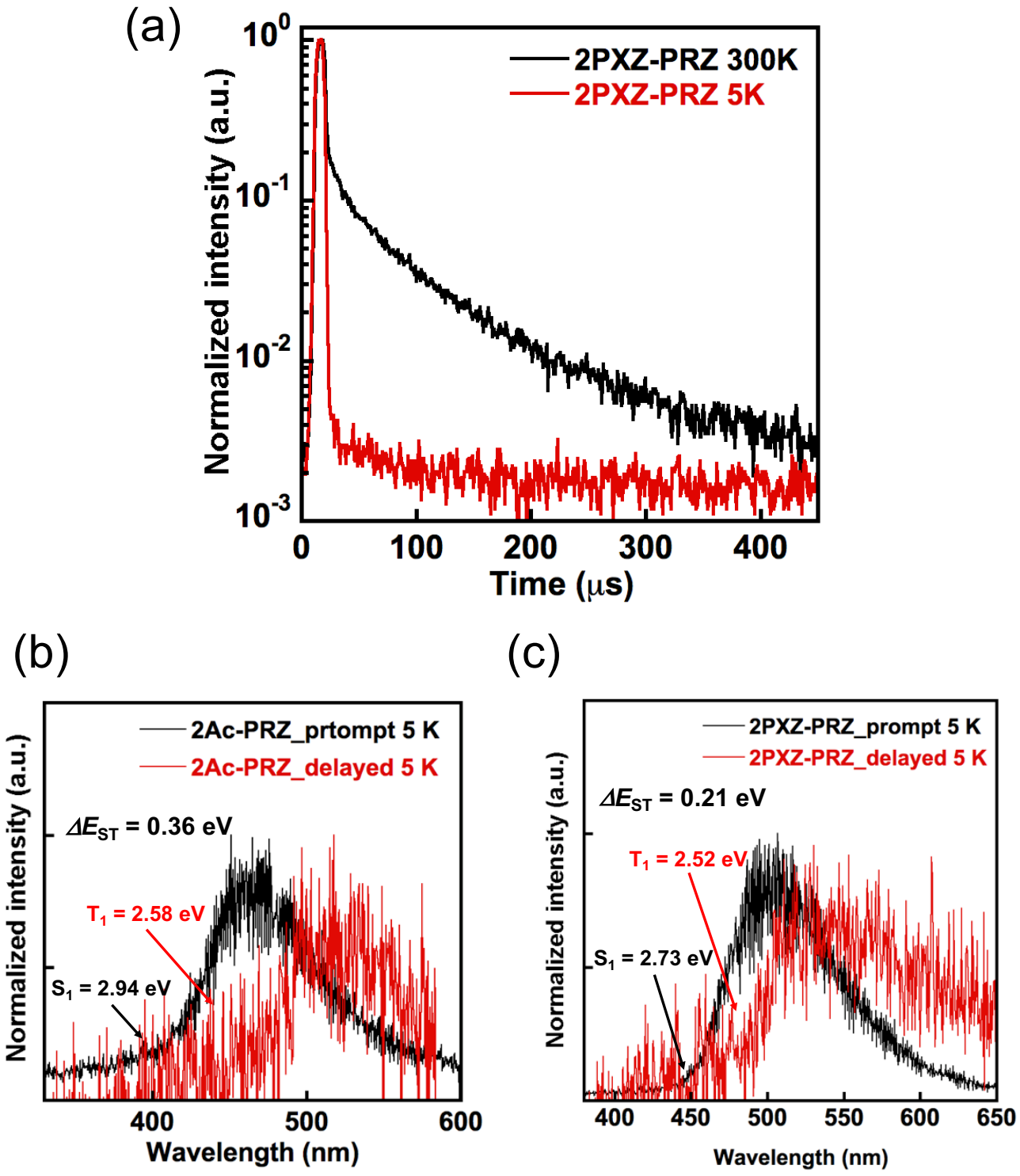


Figure S2. (a) Transient PL decay curves of **2PXZ–PRZ**-doped CBP film at 5 K and 300 K, and time resolved photoluminescence spectra of the (b) **2Ac–PRZ**-doped DPEPO and (c) **2PXZ–PRZ**-doped CBP film.

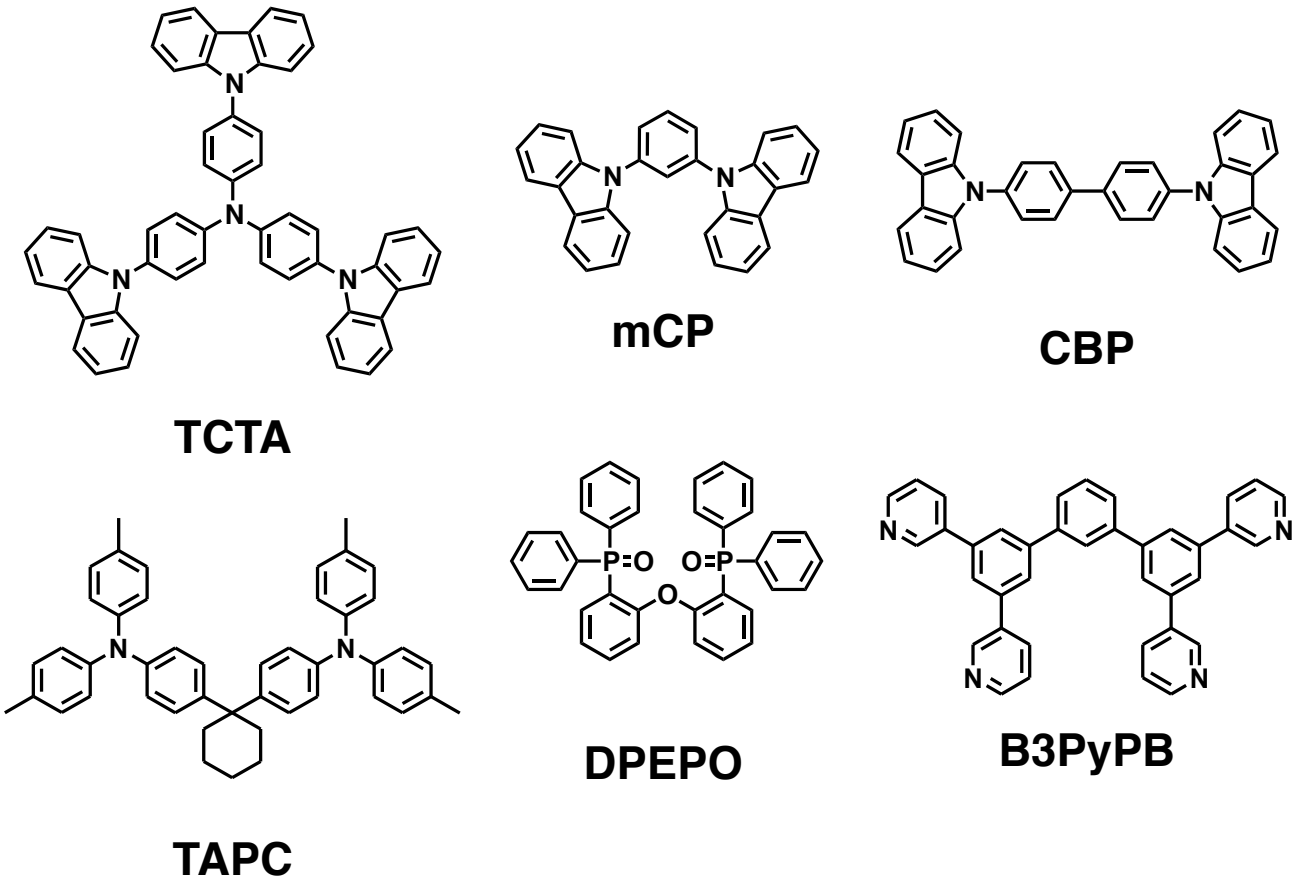


Figure S3. Chemical structures of materials used in this work.

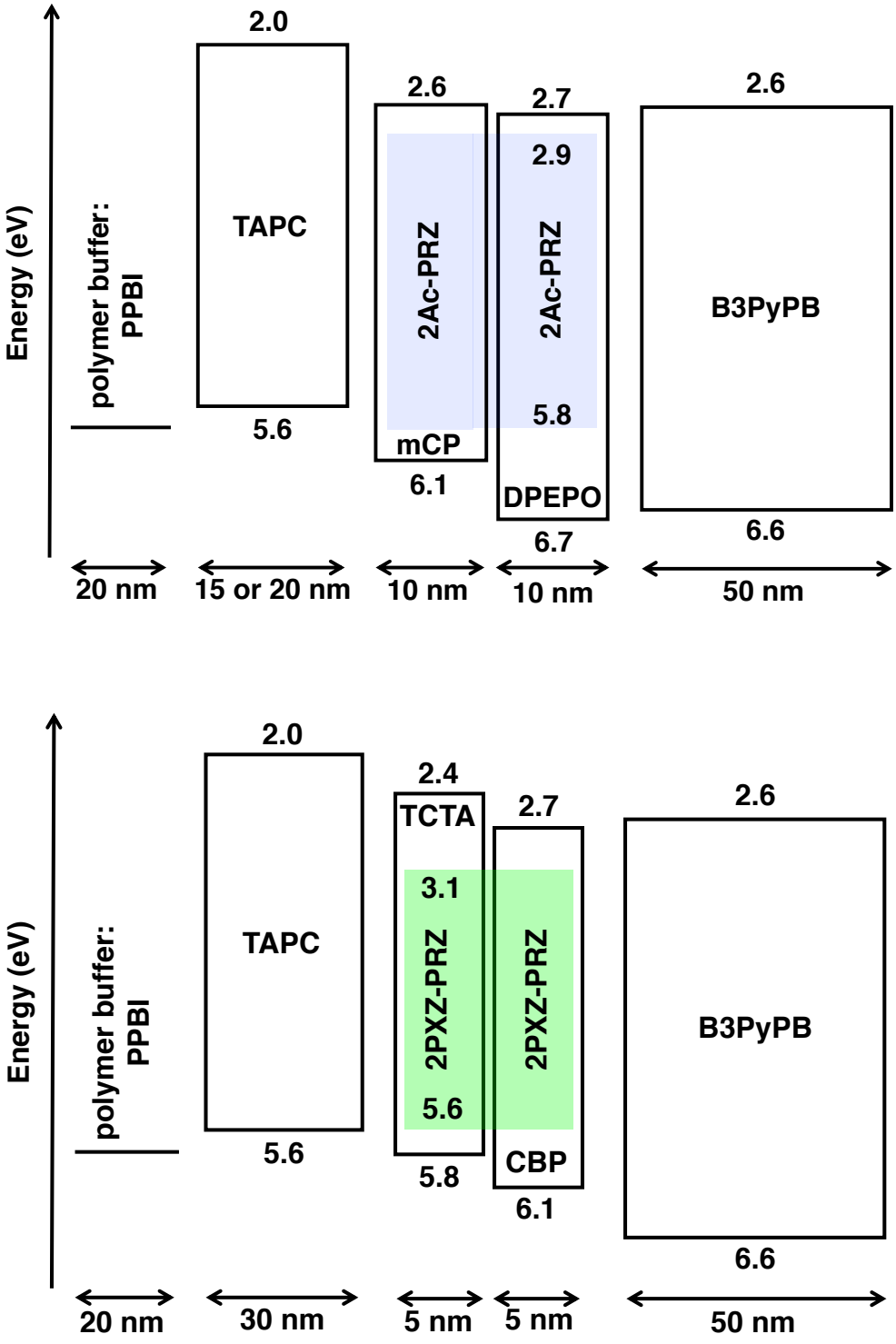


Figure S4. Energy diagram

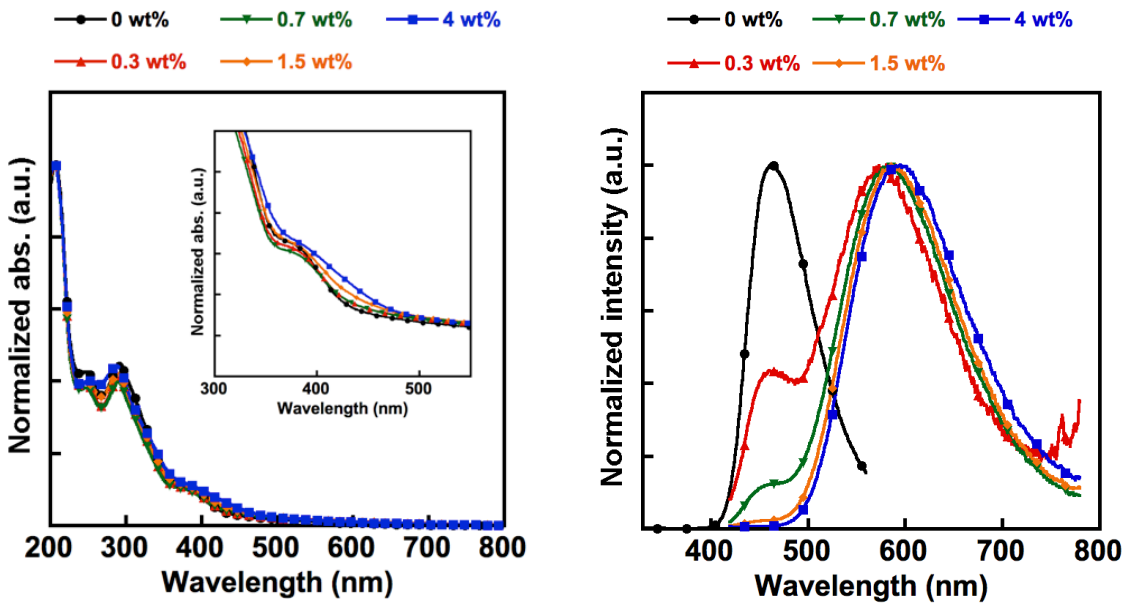


Figure S5 UV/vis absorption and PL spectra of neat film of **2Ac-PRZ** and co-deposited films with difference doping ratio.

Table 1. Photophysical properties

Compound	λ_{PL} (nm)	η_{PL} (%)
2Ac-PRZ	463	17.6
0.3wt% CuI: 2Ac-PRZ	463, 581	35.9
0.7wt% CuI: 2Ac-PRZ	463, 589	36.4
1.5wt% CuI: 2Ac-PRZ	586	26.9
4wt% CuI: 2Ac-PRZ	595	13.8

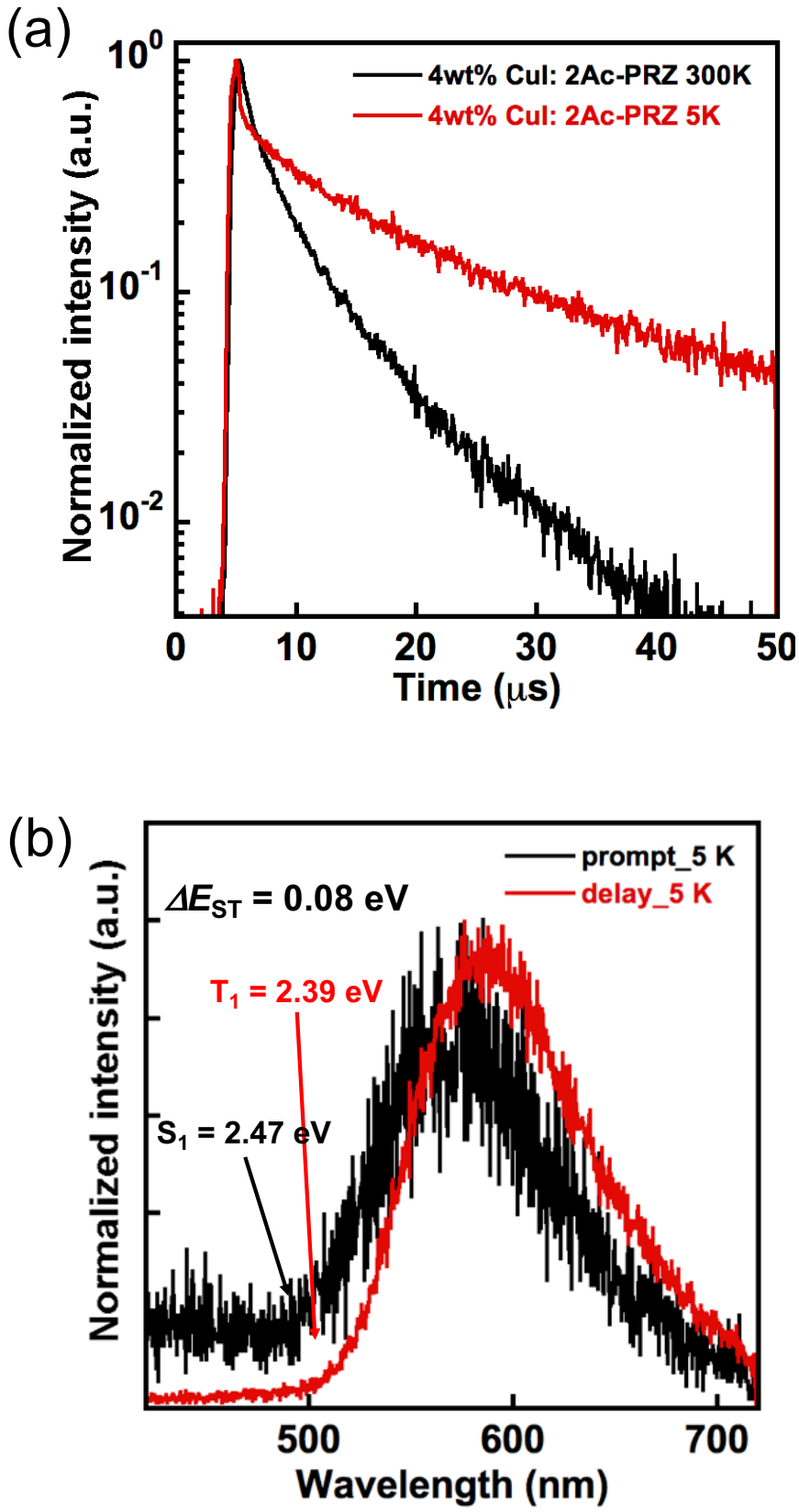


Figure S6. (a) Transient PL decay curves at 5 K and 300 K, and (b) time resolved photoluminescence spectra of 4wt% CuI-doped **2Ac-PRZ** film.

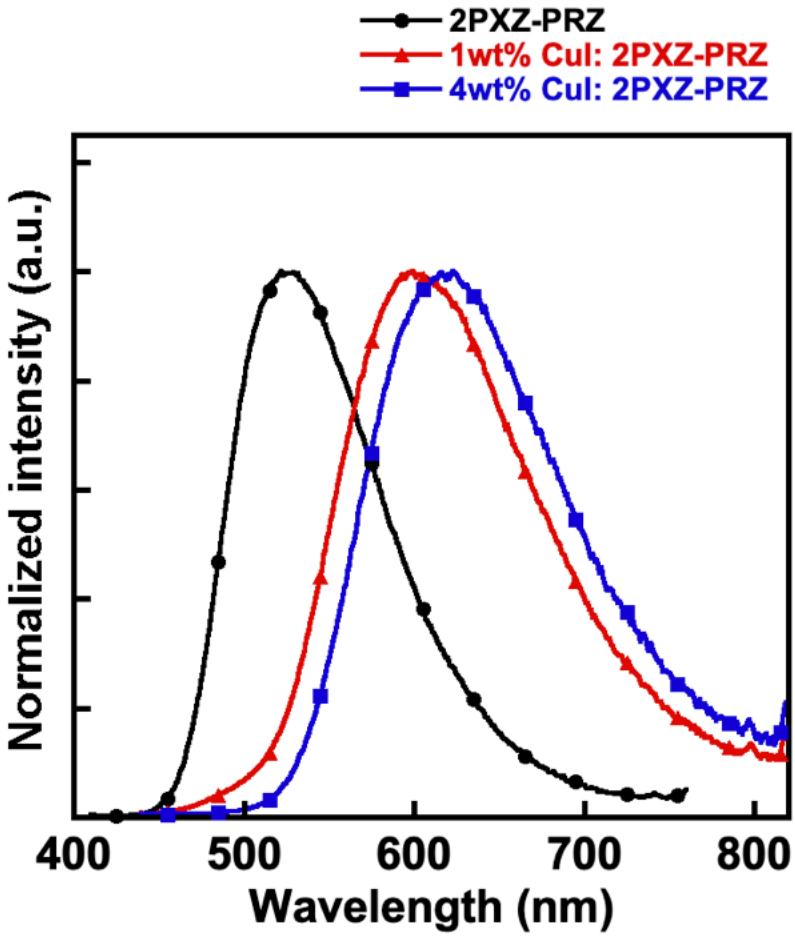


Figure S7 PL spectra of neat film of **2Ac-PRZ** and co-deposited films with difference doping ratio.

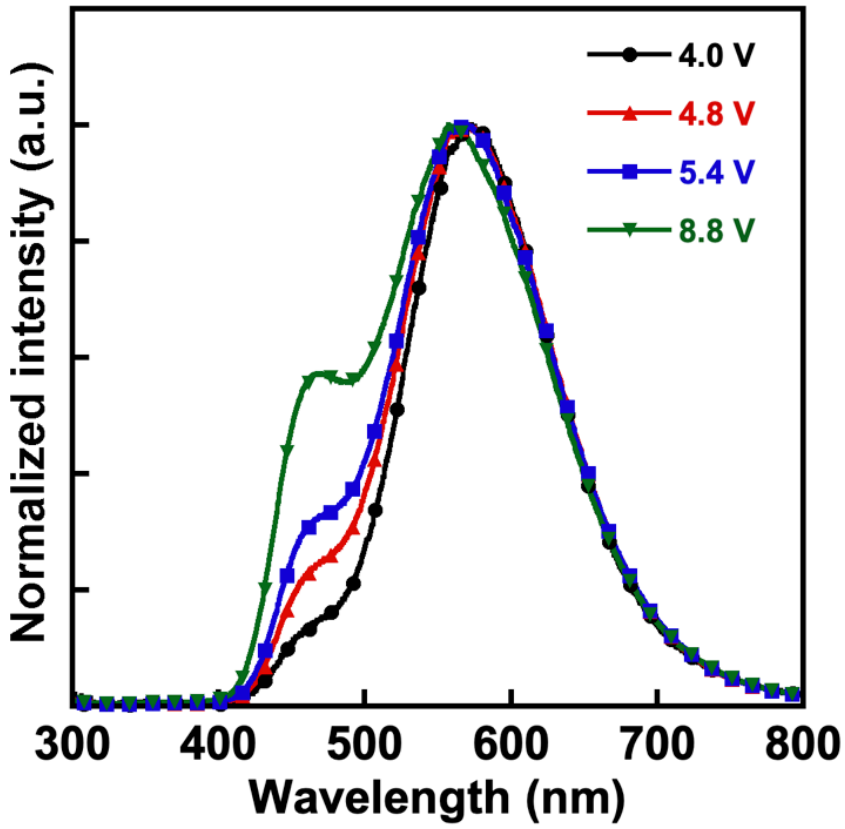


Figure S8 EL spectra of WOLED recorded at different voltages.