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Supporting information

Highly Efficient, Deep-Red Organic Light-Emitting Devices Using Energy Transfer from Exciplexes

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General Considerations:

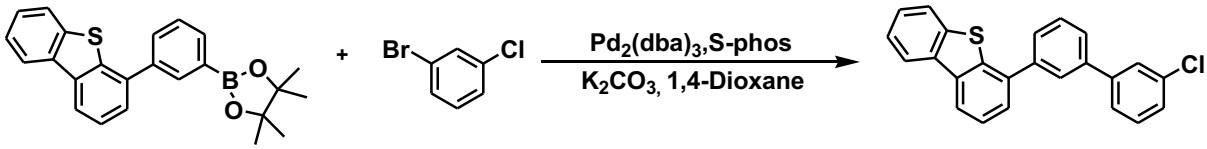
Quantum chemical calculations were performed using the hybrid DFT functional Becke and Hartree-Fock exchange and Lee Yang and Parr correlation (B3LYP) as implemented by the Gaussian 09 program packages. Electrons were described by the Pople's 6-31G(d) and 6-311+G(d,p) basis sets for molecular structure optimization and single-point energy calculations, respectively. ^{1}H NMR spectrum was 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 × 2 mm 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.

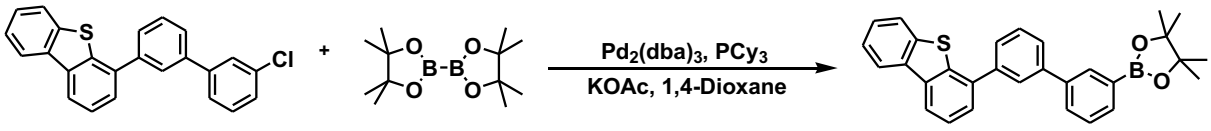
Synthetic Procedure:



Scheme S1

4-(3′-chloro-[1,1′-biphenyl]-3-yl)dibenzo[*b*,*d*]thiophene:

(3-(dibenzo[b,d]thiophen-4-yl)phenyl)boronic acid (0.82 g, 2.7 mmol), 1-bromo-3-chlorobenzene (0.34 g, 3.0 mmol), and K_2CO_3 aq (0.74 g, 5.4 mmol) were added to a round bottom flask. 1,4-dioxane (20 mL) was added, and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (40 mg, 0.05 mmol) and S-phos (40 mg, 0.10 mmol) were added and the resultant mixture was stirred for 1 hours at reflux temperature under N_2 flow. The mixture was extracted $CHCl_3$ (4 × 10 mL), and washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexanes→hexanes/$CHCl_3$ = 8/1) to afford **4-(3′-chloro-[1,1′-biphenyl]-3-yl)dibenzo[*b*,*d*]thiphene** (0.99 g, 93%) as a colorless viscous oil: ^{1}H-NMR (400MHz, DMSO-d_6) : δ = 8.44–8.35 (m, 2H), 8.08-7.91 (m, 2H), 7.84–7.70 (m, 4H), 7.69–7.58 (m, 3H), 7.54–7.39 (m, 4H) ppm.

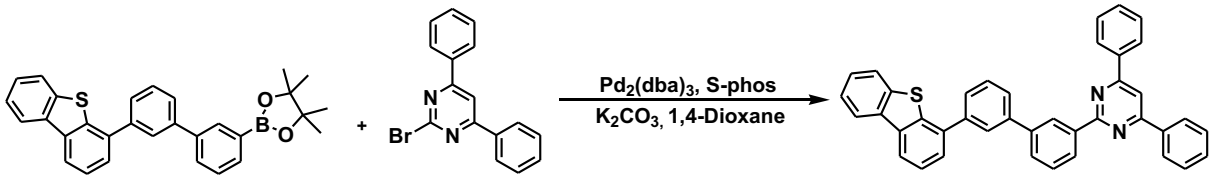


Scheme S2

2-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane:

4-(3′-chloro-[1,1′-biphenyl]-3-yl)dibenzo[*b*,*d*]thiophene (3.70 g, 9.97 mmol), 4,4,4′,4′,5,5,5′,5′-octamethyl-2,2′-bi(1,3,2-dioxaborolane) (3.79 g, 14.9 mmol), and KOAc (2.93 g, 29.9 mmol) were added to a round bottom flask. 1,4-dioxane (40 mL) was added, and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (180 mg, 0.20 mmol) and PCy_3 (110 mg, 0.40 mmol) were added and the resultant mixture was stirred for 12 hours at reflux temperature under N_2 flow. The mixture was extracted $CHCl_3$ (4 × 20

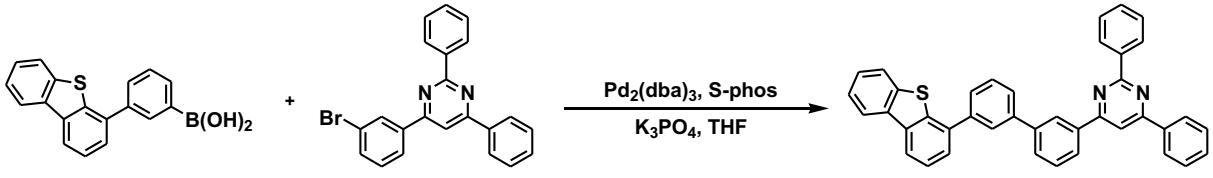
mL), and washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: hexanes→hexanes/$CHCl_3$ = 10/1) to afford **2-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (3.20 g, 69%) as a white solid: ^{1}H-NMR (400MHz, $CDCl_3$) : δ = 8.24–8.14 (m, 2H), 8.12 (s, 1H), 7.99 (s, 1H), 7.87–7.75 (m, 3H), 7.72 (dd, *J* = 5.7, 1.6 Hz, 2H), 7.63–7.40 (m, 6H), 1.39–1.29 (m, 12H) ppm.



Scheme S3

2-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-4,6-diphenylpyrimidine (4DBT46PM):

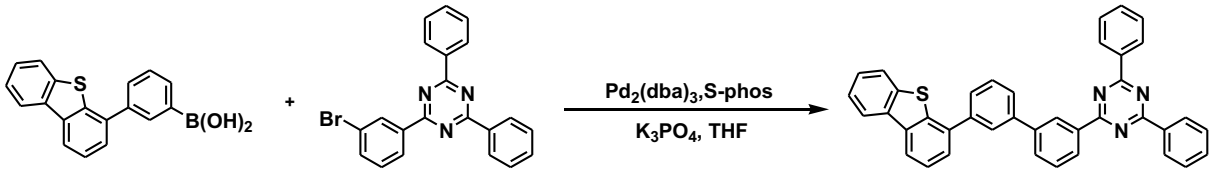
2-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborol ane (1.00 g, 2.16 mmol), 2-bromo-4,6-diphenylpyrimidine (0.74 g, 2.37 mmol), and K_2CO_3 aq (0.59 g, 4.32 mmol) were added to a round bottom flask. 1,4-dioxane (15 mL) was added, and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (30 mg, 0.04 mmol) and S-phos (20 mg, 0.08 mmol) were added and the resultant mixture was stirred for 1 hours at reflux temperature under N_2 flow. The mixture was extracted EtOAc (4 × 20 mL), and washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: $CHCl_3$) to afford **2-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-4,6-diphenylpyrimidine** (0.89 g, 72%) as a white solid: ^{1}H-NMR (400MHz, $CDCl_3$) : δ = 9.07 (t, J = 1.6 Hz, 1H), 8.75 (dd, J = 7.7, 1.4 Hz, 1H), 8.36-8.29 (m, 4H), 8.25-8.16 (m, 3H), 8.07 (s, 1H), 7.88–7.74 (m, 4H), 7.72–7.41 (m, 12H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 164.82, 164.46, 141.83, 141.18, 141.09, 139.80, 138.81, 138.70, 137.48, 136.92, 136.31, 135.79, 130.79, 129.54, 129.37, 129.00, 128.95, 127.69, 127.39, 127.30, 127.25, 127.02, 126.97, 126.78, 125.16, 124.38, 122.72, 121.72, 120.57, 110.47ppm; MS: m/z = 567 $[M]^+$; Anal calcd for $C_{40}H_{26}N_2S$: C, 84.77; H, 4.62; N, 4.94; S, 5.66%. Found: C, 84.79; H, 4.62; N, 4.72; S, 5.35%; HPLC analysis for 99.6% (eluent: THF/H_2O = 6.5/3.5).



Scheme S4

4-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-2,6-diphenylpyrimidine (4DBT26PM):

3-(dibenzo[b,d]thiophen-4-yl)phenylboronic acid (1.74 g, 4.5 mmol), 4-(3-bromophenyl)-2,6-diphenylpyrimidine (1.64 g, 5.4 mmol), and K_3PO_4aq (2.86 g, 13.5 mmol) were added to a round bottom flask. THF (20 mL) was added, and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (84 mg, 0.092 mmol) and S-phos (77 mg, 0.188 mmol) were added and the resultant mixture was stirred for 1 hours at reflux temperature under N_2 flow. The mixture was extracted $CHCl_3$ (4 × 10 mL), and washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The resulting solid was purified through silica gel pad (eluent: toluene) to afford **4-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-2,6-diphenylpyrimidine** (1.5 g, 62%) as a colorless solid: 1H-NMR (400 MHz, $CDCl_3$) δ = 8.78-8.71 (m, 2H), 8.58 (s, 1H), 8.34-8.27 (m, 3H), 8.23-8.17 (m, 2H), 8.14 (d, J = 1.8 Hz, 1H), 8.09 (s, 1H), 7.87 (d, J = 7.8 Hz, 1H), 7.82-7.75 (m, 3H), 7.71-7.64 (2H), 7.63-7.42 (m, 10H); ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 164.79, 164.66, 164.51, 141.70, 141.35, 141.21, 139.47, 138.62, 138.21, 138.06, 137.49, 136.74, 136.34, 136.76, 130.77, 130.64, 129.63, 129.48, 129.45, 128.90, 128.46, 127.52, 127.28, 127.20, 126.91, 126.84, 126.43, 126.25, 125.19, 124.43, 122. 68, 121.74, 120.64, 110.44 ppm; MS: m/z = 567 $[M]^+$; Anal calcd for $C_{40}H_{26}N_2S$: C, 84.77; H, 4.62; N, 4.94; S, 5.66%. Found: C, 84.99; H, 4.56; N, 4.91; S, 5.55%; HPLC analysis for 99.2% (eluent: THF/H_2O = 6.5/3.5).



Scheme S5

2-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-4,6-diphenyl-1,3,5-triazine (4DBT46TRZ):

3-(dibenzo[b,d]thiophen-4-yl)phenylboronic acid (1.60 g, 5.26 mmol), 2-(3-bromophenyl)-4,6-diphenyl-1,3,5-triazine (1.70 g, 4.38 mmol), and K_3PO_4 aq (2.78 g, 13.1 mmol) were added to a round bottom flask. THF (30 mL) was added, and nitrogen was bubbled through the mixture for 1 hour. Then, $Pd_2(dba)_3$ (81 mg, 0.089 mmol) and S-phos (75 mg, 0.18 mmol) were added and the resultant mixture was stirred for 1 hours at reflux temperature under N_2 flow. The mixture was extracted $CHCl_3$ (4 × 10 mL), and washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to dryness. The resulting solid was purified through silica gel pad (eluent: toluene) to afford **2-(3′-dibenzo[*b*,*d*]thiophen-4-yl)-[1,1′-biphenyl]-3-yl)-4,6-diphenyl-1,3,5-triazine** (0.99

g, 93%) as a colorless solid: ^{1}H-NMR (400 MHz, $CDCl_3$) δ = 9.10 (s, 1H), 8.84-8.75 (m, 5H), 8.25-8.13 (m, 3H), 7.94 (d, J = 7.8 Hz, 1H), 7.87-7.76 (m, 3H), 7.69 (t, J = 7.8 Hz, 2H), 7.64-7.40 (10H); ^{13}C-NMR (100 MHz, $CDCl_3$) : δ = 171.70, 171.61, 141.44, 141.38, 141.22, 139.54, 138.69, 136.91, 136.83, 136.35, 136.18, 135.80, 132.52, 131.37, 129.49, 129.21, 128.99, 128.67, 128.11, 127.76, 127.51, 127.23, 126.96, 126.83, 125.19, 124.44, 122.72, 121.75, 120.64 ppm; MS: m/z = 568 $[M]^+$; Anal calcd for $C_{39}H_{25}N_3S$: C, 82.51; H, 4.44; N, 7.40; S, 5.65%. Found: C, 82.50; H, 4.36; N, 7.31; S, 5.43%; HPLC analysis for 99.9% (eluent: THF/H_2O = 6.5/3.5).

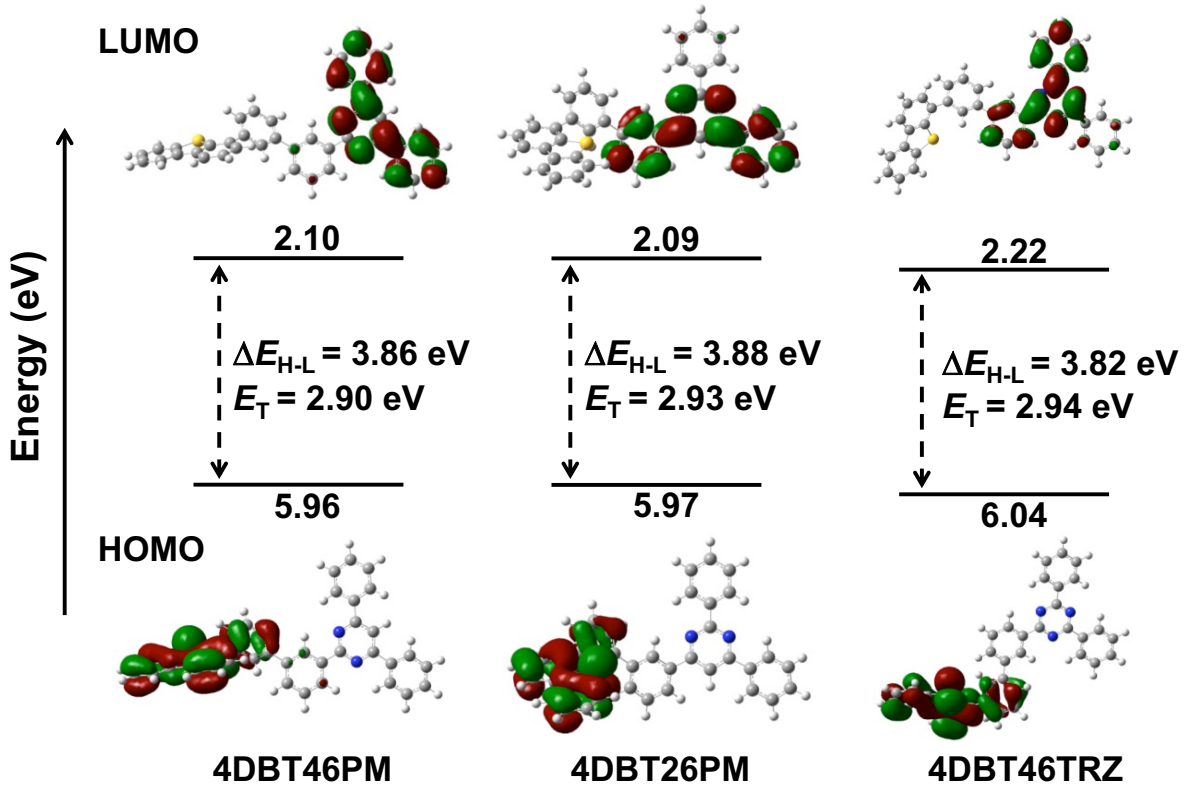


Fig. S1 The optimized structures and the spatial distributions of the HOMOs and LUMOs for the DBT-azine derivatives calculated at the B3LYP/6-31+G(d,p)//B3LYP/6-31G(d,p) level.

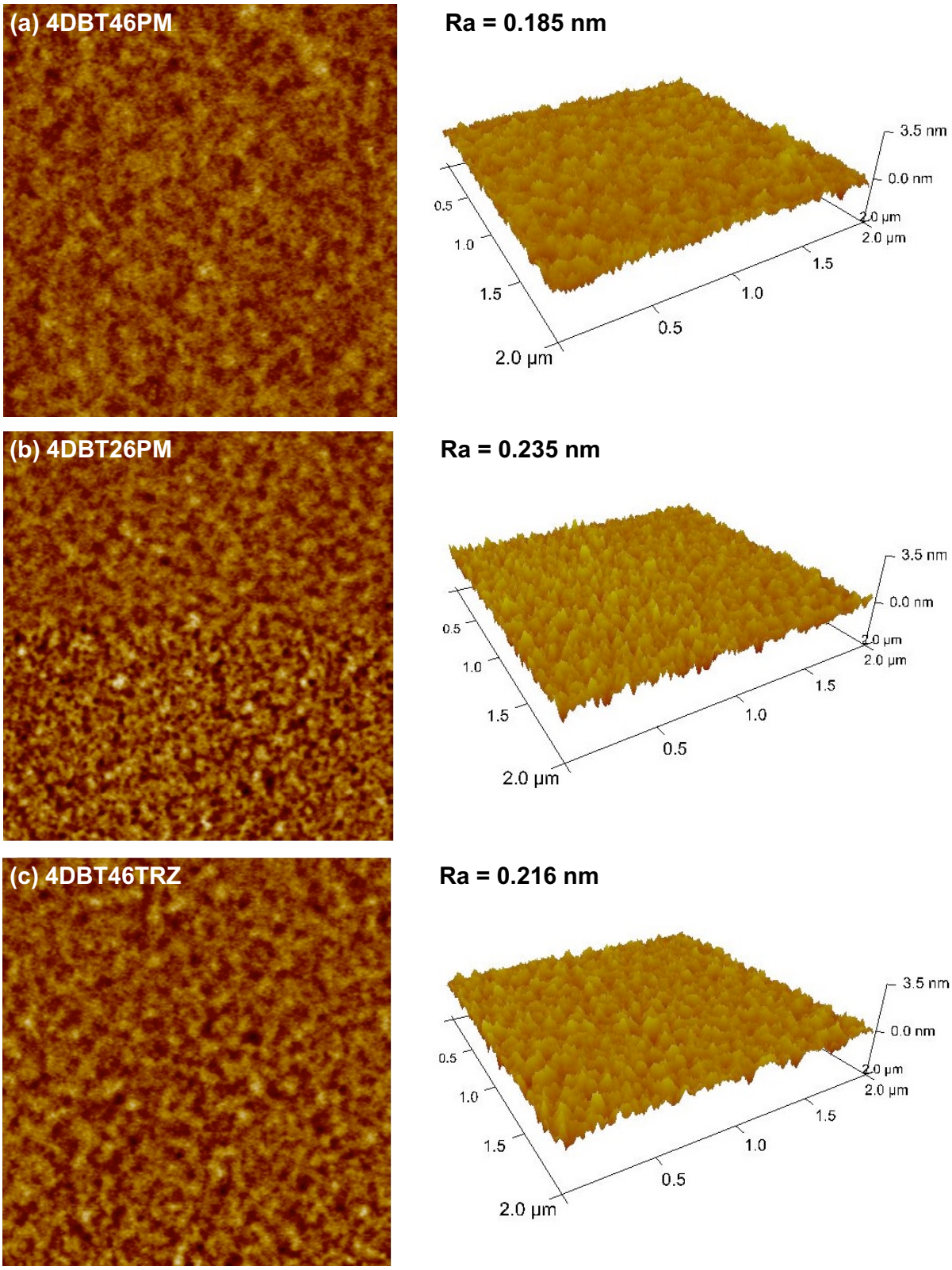
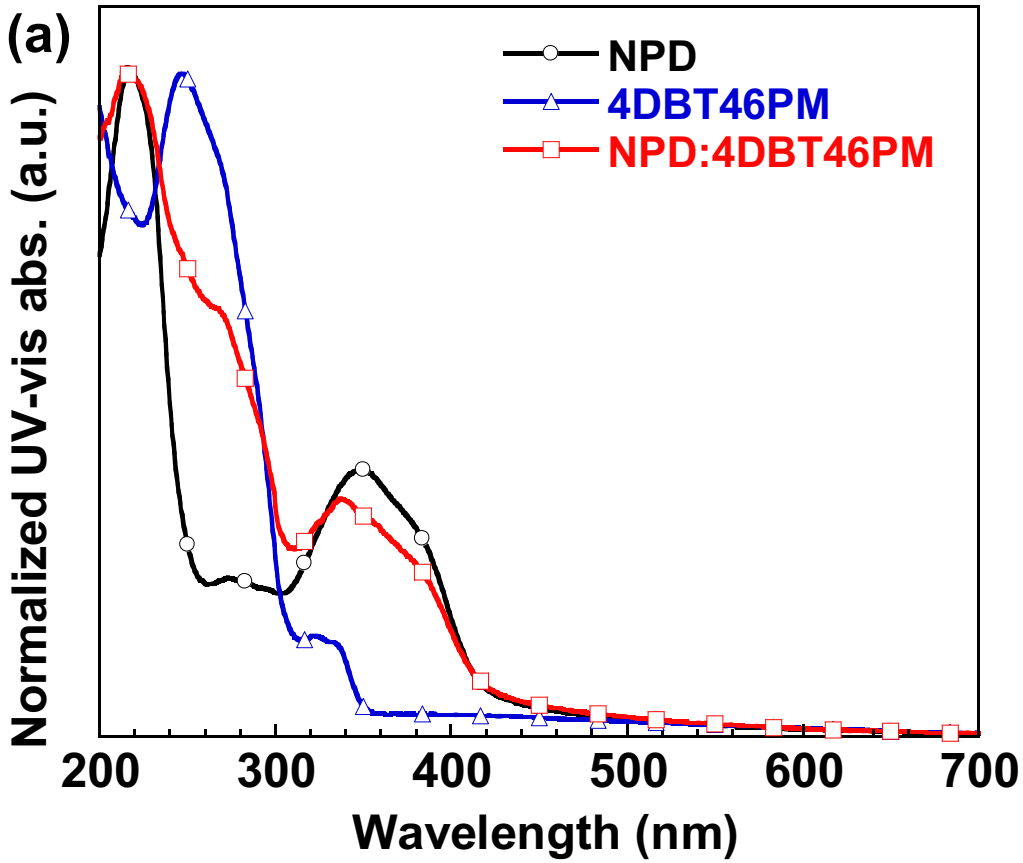
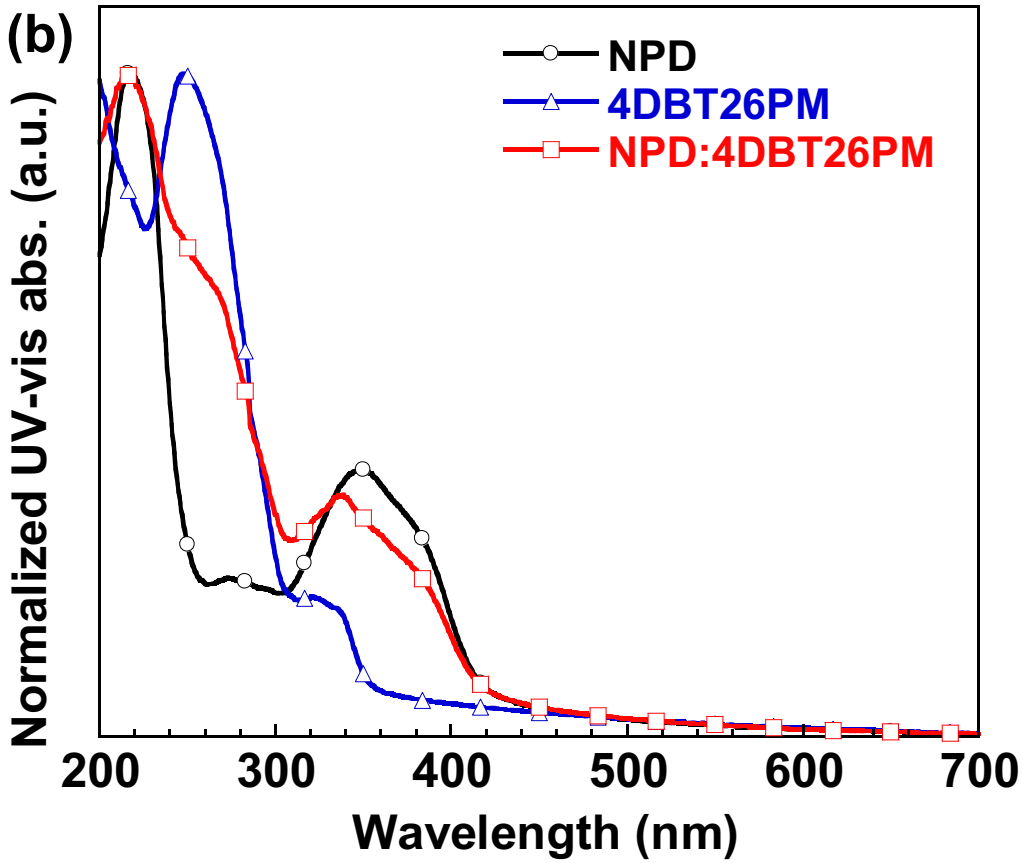


Fig. S2 AFM 2D and 3D image; (a) 4DBT46PM, (b)4DBT26PM, and (c) 4DBT46TRZ.


(a)
Normalized UV-vis abs. (a.u.)
NPD
4DBT46PM
NPD:4DBT46PM
200
300
400
500
600
700
Wavelength (nm)


(b)
NPD
4DBT26PM
NPD:4DBT26PM
Normalized UV-vis abs. (a.u.)
200
300
400
500
600
700
Wavelength (nm)

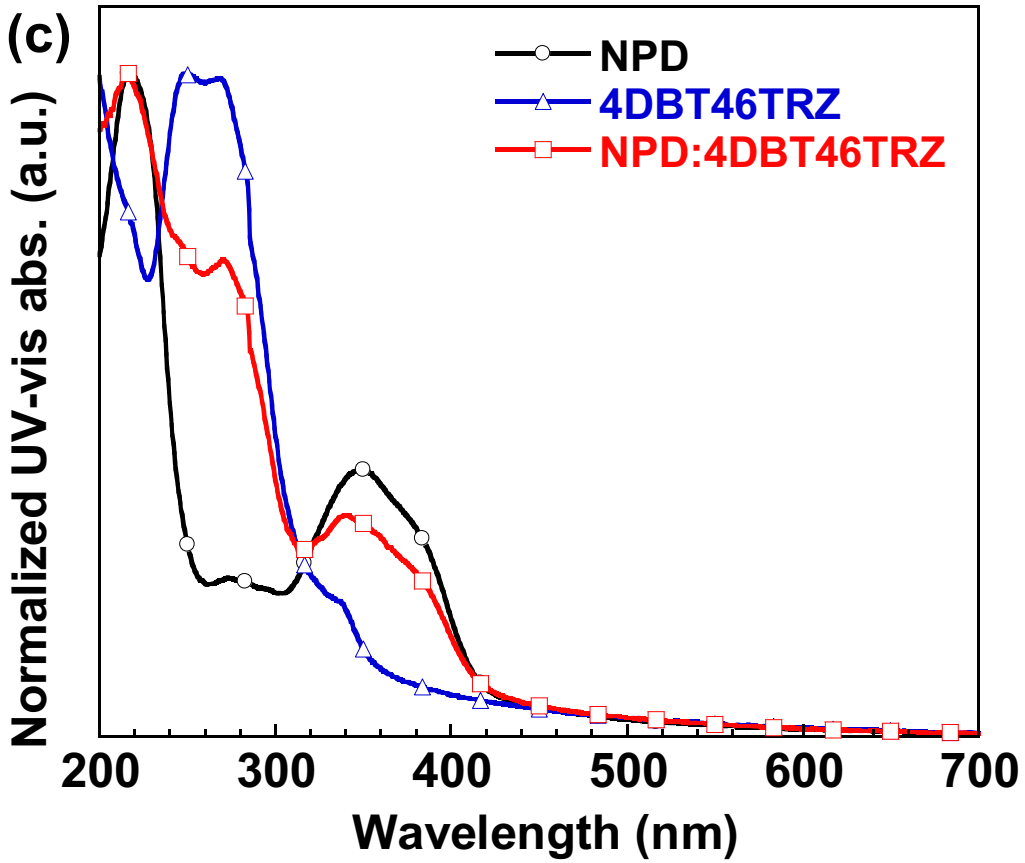


Fig. S3 UV-vis absorption spectra of (a) 4DBT46PM, (b) 4DBT26PM, and (c) 4DBT46TRZ.

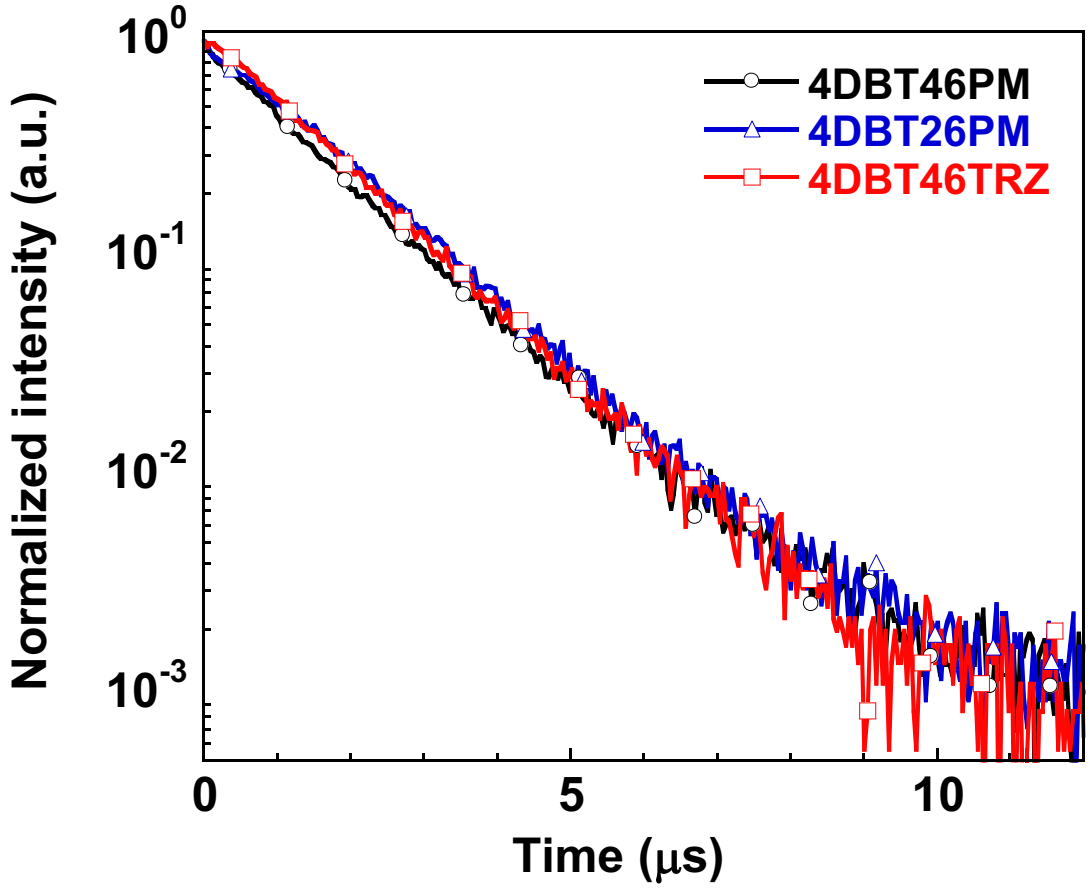


Fig. S4 Photoluminescence decay curves of the 1 wt% $(DPQ)_2Ir(dpm)$ doped NPD:DBT-azine derivative film at room temperature.

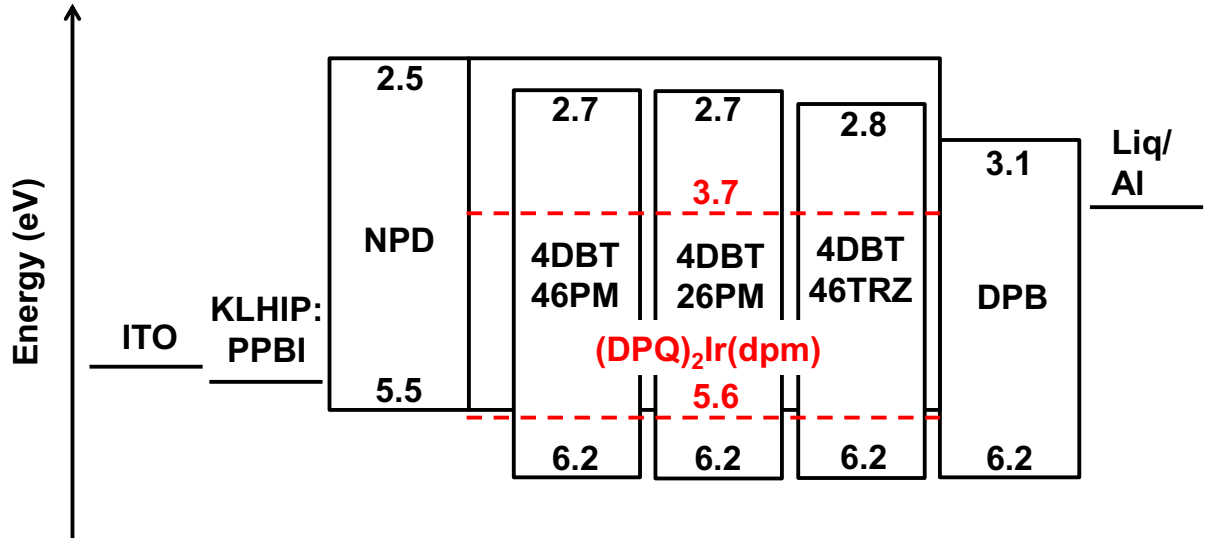
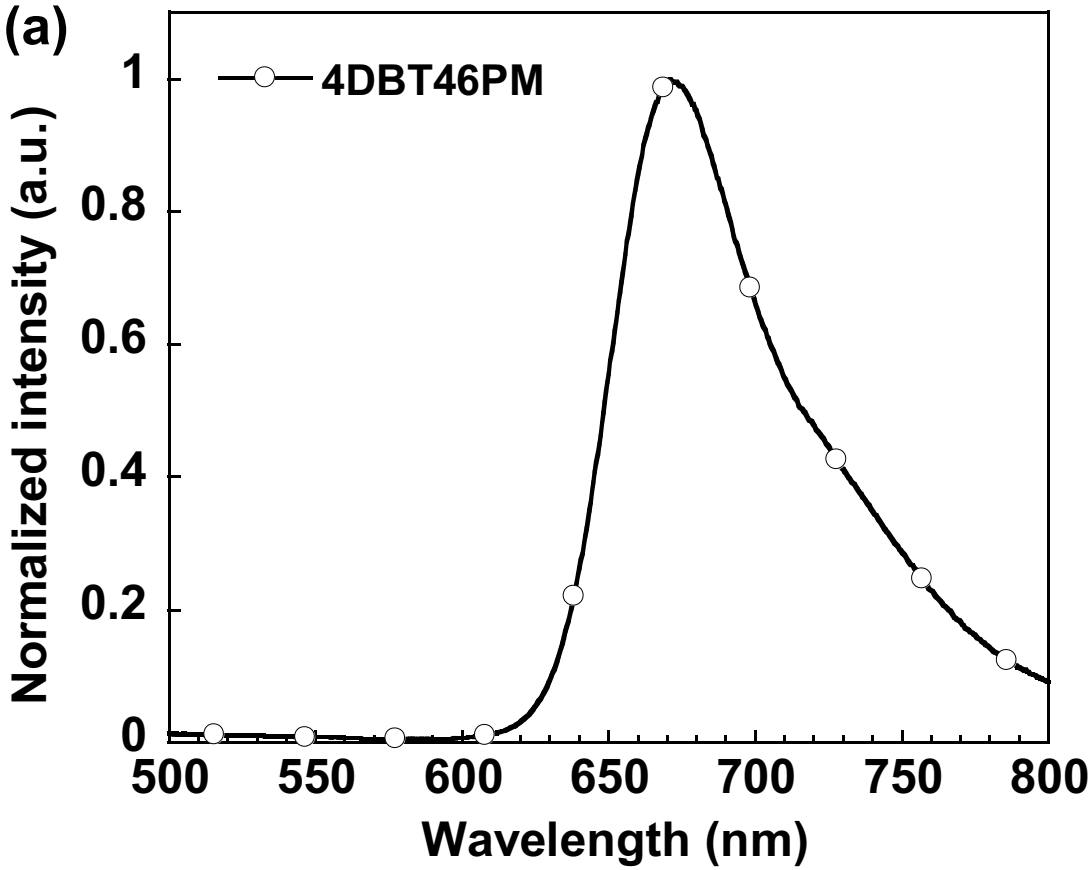
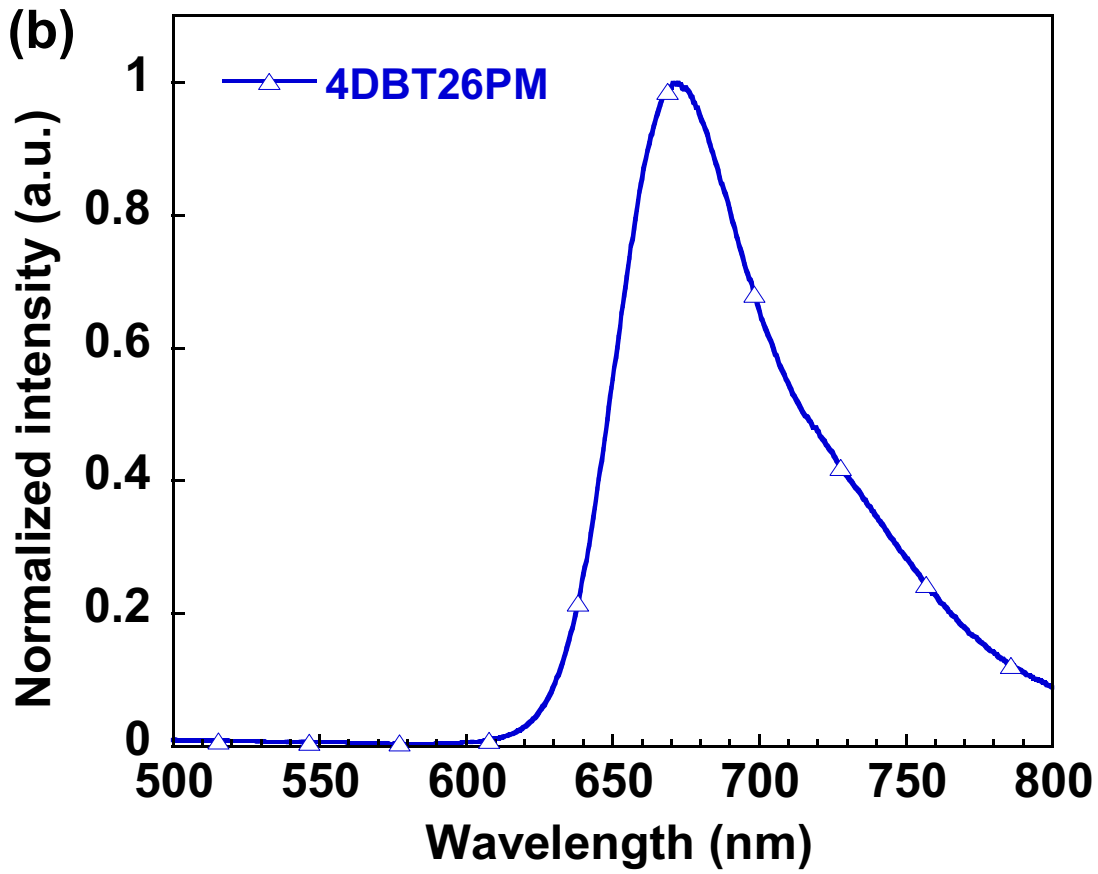


Fig. S5. Energy diagram of deep-red phosphorescent OLEDs.


(a)
4DBT46PM
Normalized intensity (a.u.)
1
0.8
0.6
0.4
0.2
0
500
550
600
650
700
750
800
Wavelength (nm)


(b)
4DBT26PM
Normalized intensity (a.u.)
1
0.8
0.6
0.4
0.2
0
500
550
600
650
700
750
800
Wavelength (nm)

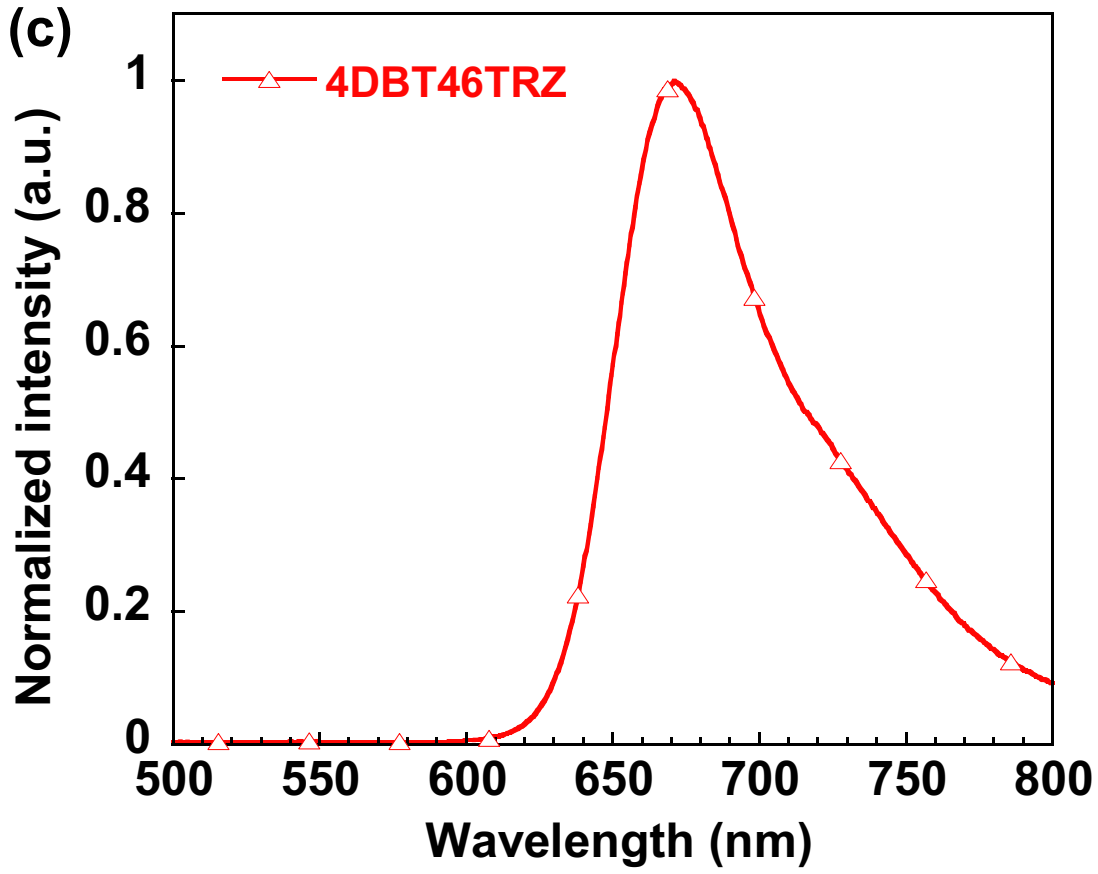


Fig. S6. EL spectra of deep-red phosphorescent OLEDs; (a) 4DBT46PM, (b)4DBT26PM and (c) 4DBT46TRZ.

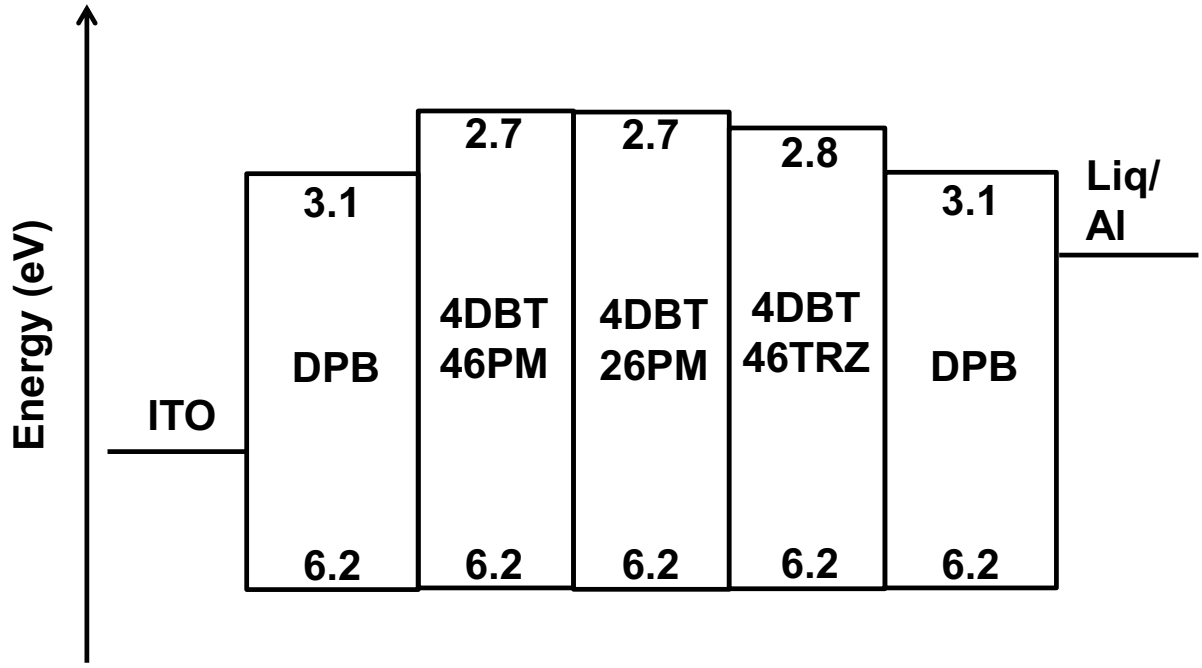


Fig. S7. Energy diagram of electron only device.

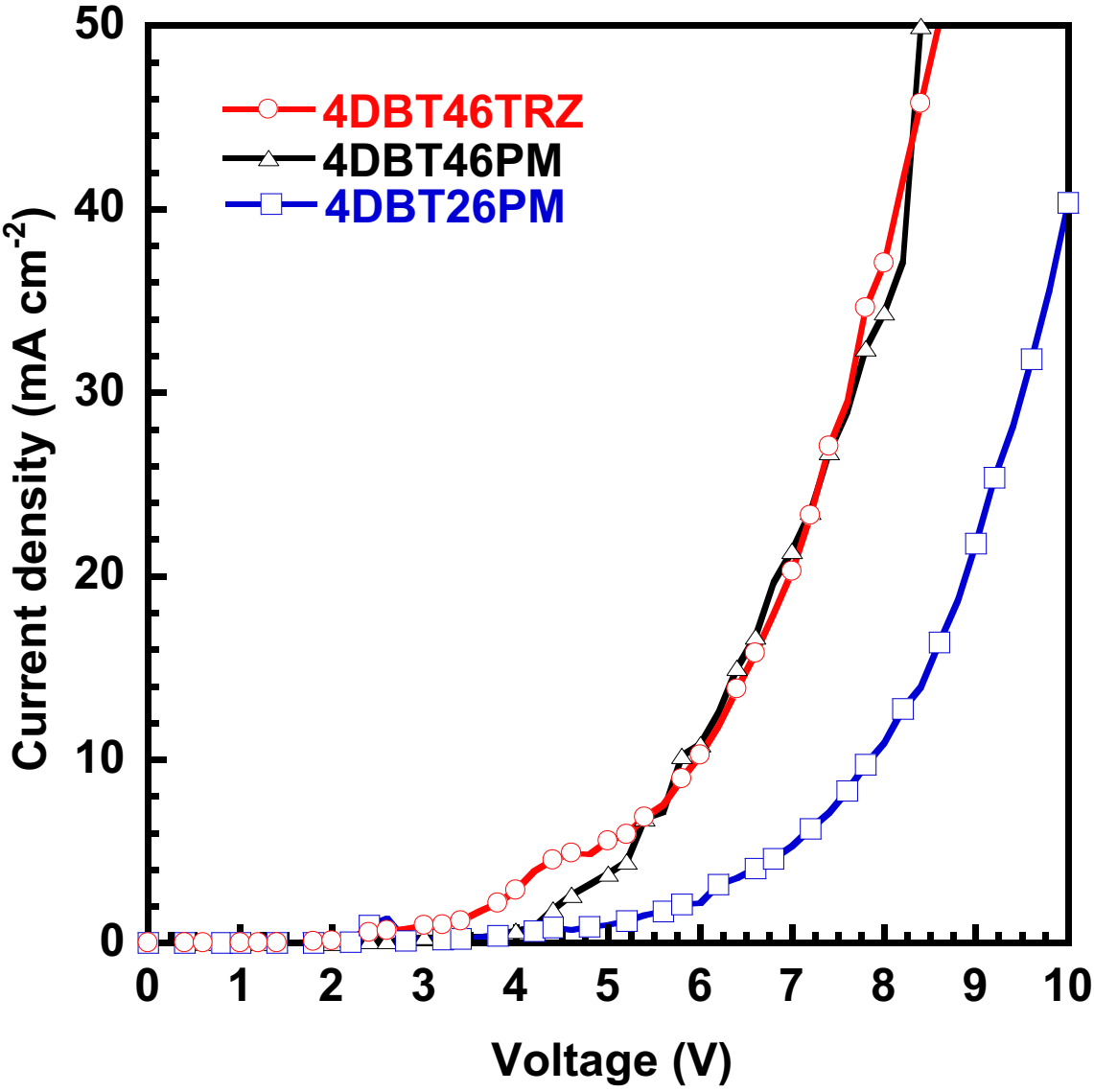


Fig. S8. J-V characteristics of electron only device.

Table **S1**. Summary of the performances in deep-red OLEDs.

	λ_{EL} [nm]	V_{on} [V]	EQE_{max} [%]
This work	671	2.61	15.0
	671	3.66	16.6
	671	2.41	17.9
Ref 5a	675	-	10.2
Ref 5b	688	3.0	11.2
Ref 5c	668	-	9.8
Ref 5d	657, 730	-	8.2
Ref 5e	666	3.2	1.36
	662	3.7	1.66
	657	3.6	2.09
Ref 5f	ca. 610	ca. 3.7 V	16
	ca. 750	-	5