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Supporting Information

Single molecule white emission by intra- and inter- molecular charge transfer

Ha Lim Lee, Ho Jin Jang, Jun Yeob Lee*

School of Chemical Engineering, Sungkyunkwan University

2066, Seobu-ro, Jangan-gu, Suwon-si, Gyeonggi-do, 440-746, Korea

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Experimental

General information

2,4-Dichloro-6-phenyl-1,3,5-triazine, tri-tert-butylphosphine, tetrakis(triphenylphosphine) palladium(0) and tris(dibenzylideneacetone)dipalladium(0) were products of P&H Tech Co. 1-Bromo-4-fluorobenzene, (4-bromophenyl)boronic acid, and sodium tert-butoxide were purchased from Alfa Aesar, Thermo Fisher Scientific Inc. 5H-Benzofuro[3,2-c]carbazole was reported in our previous work. 1,3-Dibromo-5-methoxybenzene, 10H-phenothiazine, sodium hydride and iodine were bought from Tokyo Chemical Industry Co. Magnesium turning, picolinic acid and boron tribromide were products of Sigma Aldrich Co. Potassium carbonate, potassium phosphate tribasic, dimethyl sulfoxide (DMSO) and N,N-dimethylformamide (DMF) were supplied from Daejung Chemical & Metal Co. n-Hexane, ethyl acetate, methylene chloride (MC), tetrahydrofuran (THF) and toluene were products from Samchun Pure Chemical Co., Ltd. Toluene and THF were distilled over sodium and calcium hydride before use.

The UV-vis absorption spectra and emission spectra of the synthesized compounds were recorded by UV-Vis spectrophotometer (JASCO, V-730) and fluorescence spectrophotometer (PerkinElmer, LS-55), respectively. The fluorescent and phosphorescent spectra were measured at 77 K in THF matrix. The fluorescent spectrum was measured without any delay time, while the phosphorescent spectrum was recorded with 2 ms delay time after the excitation. Time-resolved PL spectra and transient PL decay curves were measured with Quantaurus-Tau system (Hamamatsu, C11367-31) under a nitrogen atmosphere. The chemical structures of intermediates and final products were analyzed by nuclear magnetic resonance (NMR) (Oxford 300 NMR (VARIAN, 300 MHz) and AVNACE III HD (Bruker, 500 MHz)) and mass spectroscopy (Advion, Expresion^{L} CMS spectrometer with APCI mode and JMS-700 (JEOL) with high resolution fast atom bombardment (FAB) mode).

Synthesis

2-Chloro-4-(4-fluorophenyl)-6-phenyl-1,3,5-triazine

Magnesium turning (0.52 g, 21.2 mmol) and iodine (0.67g, 2.65 mmol) were poured into a 250 ml 2-neck round-bottomed (RB) flask. The RB flask was connected to manifold and maintained in vacuum state using a vacuum pump. Then, the RB flask was heated with heat gun during 20 seconds and begun to purge with nitrogen. The distilled THF (5 ml) was added into the RB flask and the mixture was stirred for 30 minutes. After that, 1-bromo-4-fluorobenzene (3.48 g, 19.9 mmol) in THF solution (22 ml) was added dropwisely into an activated magnesium mixture. The solution was stirred and refluxed for 1 hour. After cooling down to room temperature, a Grignard reagent was slowly added into a 2,4-dichloro-6-phenyl-1,3,5-triazine (3.00 g, 13.3 mmol) solution in THF (30 ml). The reaction mixture was stirred and refluxed during overnight. After the reaction, sodium thiosulfate solution was poured into the mixture to quench residual iodine. Extraction was proceeded using MC and deionized water (DW) several times. Extracted organic layer was evaporated and adsorbed into a silica gel. The adsorbed crude product was purified by column chromatography suing MC: n-hexane eluent (1:4). The purified product was a white solid. (1.65 g, Yield 44%)

^{1}H NMR (300 MHz, DMSO-d_6) : δ 8.60-8.43 (m, 4H), 7.73-7.69 (t, J_1=7.20 Hz, J_2=7.50 Hz, 1H), 7.63-7.58 (t, J_1=7.80 Hz, J_2=7.20 Hz, 2H), 7.46-7.40 (t, J_1=8.70 Hz, J_2=9.00 Hz, 2H), MS (APCI) m/z : Found 285.96 [(M + H)+]. Calculated For $C_{15}H_9ClFN_3$: 286.05

2-(4-Bromophenyl)-4-(4-fluorophenyl)-6-phenyl-1,3,5-triazine

2-Chloro-4-(4-fluorophenyl)-6-phenyl-1,3,5-triazine (1.00 g, 3.50 mmol) and (4-bromophenyl)boronic acid (0.74 g, 3.68 mmol) were dissolved in THF (20 ml) and added into a 100 ml RB flask. The reaction mixture was slightly heated with stirring and 2M of potassium carbonate solution (10 ml) was poured into the RB flask. After that, tetrakis(triphenylphosphine) palladium(0) (0.12 g, 0.11 mmol) was added into the reaction mixture. The reaction was proceeded for 1 hour and the mixture was cooled down to room temperature. The crude product was extracted with MC and DW. The mixed solution was evaporated and adsorbed into a silica gel for column purification using a mixed solvent of MC : n-hexane (1:4). The purified product was a white solid. (1.02 g, Yield 72%)

^{1}H NMR (300 MHz, $CDCl_3$) : δ 8.78-8.70 (m, 4H), 8.62-8.59 (d, J=8.70 Hz, 2H), 7.71-7.68 (d, J=8.70 Hz, 2H) 7.63-7.54 (m, 3H), 7.25-7.20 (t, J_1=8.70 Hz, J_2=8.70 Hz, 2H), MS (APCI) m/z : Found 405.94 [(M + H)+]. Calculated For $C_{21}H_{13}BrFN_3$: 406.04

5-(4-(4-(4-Bromophenyl)-6-phenyl-1,3,5-triazin-2-yl)phenyl)-5H-benzofuro[3,2-c]carbazole

Sodium hydride (60% shielded in mineral oil) (0.18 g, 7.38 mmol) in DMF (3 ml) was added into a 100 ml RB flask and begun to purge with nitrogen. After that, 5H-benzofuro[3,2-c]carbazole (0.95 g, 3.69 mmol) dissolved in DMF (5 ml) was slowly added into the 100 ml RB flask. The mixture was stirred for 30 minutes. At the end of nitrogen atom activation, 2-(4-bromophenyl)-4-(4-fluorophenyl)-6-phenyl-1,3,5-triazine (1.00 g, 2.46 mmol) in DMF (15 ml) was added into the solution. The mixture was stirred and heated at 100 °C for 6 hours. The reaction mixture was cooled down to room temperature and DW was poured into the RB flask to quench excess sodium hydride. After quenching process, the extraction was proceeded using MC and DW. The crude solution was evaporated using a rotary evaporator and adsorbed into a silica gel. The crude product adsorbed into the silica gel was purified by column purification using chloroform : n-hexane mixed solvent (1:1). The purified product showed bright green color. (0.62 g, Yield 39%)

^{1}H NMR (300 MHz, $CDCl_3$) : δ 9.02-8.99 (d, J=8.70 Hz, 2H), 8.81-8.77 (dd, J_1=7.80 Hz, J_2=1.50 Hz, 2H), 8.68-8.65 (d, J=8.70 Hz, 2H), 8.61-8.58 (dd, J_1=6.90 Hz, J_2=1.50 Hz, 1H), 7.99-7.94 (t, J_1=7.20 Hz, J_2=8.40 Hz, 2H), 7.87-7.84 (d, J=8.70 Hz, 2H), 7.76-7.37 (m. 12H), MS (APCI) m/z : Found 643.17 [(M + H)+]. Calculated For $C_{39}H_{23}BrN_4O$: 643.11

10,10'-(5-Methoxy-1,3-phenylene)bis(10H-phenothiazine)

1,3-Dibromo-5-methoxybenzene (3.00 g, 11.3 mmol), 10H-phenothiazine (4.95 g, 24.8 mmol), sodium tert-butoxide (6.50 g, 67.7 mmol) and tris(dibenzylideneacetone)dipalladium(0) (1.03 g, 1.13 mmol) were poured into a 250 ml RB flask. The distilled toluene (120 ml) was added into the mixture and tri-tert-butylphosphine (2.26 mmol) was slowly added into the stirred reaction mixture. The reaction was proceeded under a reflux condition during overnight. When the reaction solution was cooled down to room temperature, MC was poured into the mixture and the solution was filtered using celite/silca gel. The filtrate was concentrated and adsorbed into the silica gel. The crude product in silica gel was purified by column purification using an eluent of MC: n-hexane (1:9). The product product was a white powder. (4.14 g, Yield 73%)

^{1}H NMR (300 MHz, DMSO-d_6) : δ 7.13-7.10 (dd, J_1=7.50 Hz, J_2=1.50 Hz, 4H), 7.06-6.99 (m, 6H), 6.93-6.88 (t, J_1=7.20 Hz, J_2=7.50 Hz, 4H), 6.79 (s, 1H), 6.52-6.50 (d, J=8.10 Hz, 4H), 3.80 (s, 3H), MS (APCI) m/z : Found 503.08 [(M + H)+]. Calculated For $C_{31}H_{22}N_2OS_2$: 503.13

3,5-Di(10H-phenothiazin-10-yl)phenol

10,10'-(5-Methoxy-1,3-phenylene)bis(10H-phenothiazine) (2.00 g, 3.98 mmol) was added into a 2-neck 100 ml RB flask and connected to vacuum pump for removal of moisture. The RB flask was connected to manifold under nitrogen. The anhydrous MC (20 ml) was added to dissolve the reactants, and the solution was cooled down to -78 °C using an acetone/dry ice cold bath. After 30 minutes, boron tribromide (1.99 g, 7.96 mmol) was added very slowly using a syringe. The reaction was proceeded overnight after adding boron tribromide while slow heating to room temperature. Excess boron tribromide was quenched with sodium bicarbonate solution using a pH meter. The quenched solution was extracted with MC and DW, and evaporated using a rotary evaporator and adsorbed into a silica gel. The adsorbed product was purified with column chromatography using a mixed solvent of ethyl acetate : n-hexane (1:9). The purified product was a white solid. (1.21 g, Yield 65%)

^{1}H NMR (300 MHz, DMSO-d_6) : δ 10.23 (s, 1H), 7.13-7.10 (dd, J_1=7.50 Hz, J_2=1.50 Hz, 4H), 7.07-7.01 (td, J_1=7.80 Hz, J_2=7.80 Hz, J_3=1.80 Hz, 4H), 6.93-6.88 (td, J_1=7.20 Hz, J_2=7.50 Hz, J_3=1.50 Hz, 4H), 6.76-6.75 (sd, J=1.80 Hz, 2H), 6.63-6.62 (st, J_1=2.10 Hz, J_2=1.80 Hz, 1H), 6.55-6.52 (dd, J_1=8.10 Hz, J_2=1.50 Hz, 4H), MS (APCI) m/z : Found 489.07 [(M + H)+]. Calculated For $C_{30}H_{20}N_2OS_2$: 489.11

5-(4-(4-(4-(3,5-Di(10H-phenothiazin-10-yl)phenoxy)phenyl)-6-phenyl-1,3,5-triazin-2-yl)phenyl)-5H-benzofuro[3,2-c]carbazole (PT-CzTrz)

5-(4-(4-(4-Bromophenyl)-6-phenyl-1,3,5-triazin-2-yl)phenyl)-5H-benzofuro[3,2-c]carbazole (0.50 g, 0.78 mmol), 3,5-di(10H-phenothiazin-10-yl)phenol (0.57 g, 1.17 mmol), copper iodide (0.15 g, 0.78 mmol), picolinic acid (0.19 g, 1.55 mmol) and potassium phosphate tribasic (0.99 g, 4.66 mmol) were added into a 100 ml pressure tube. After that, dimethyl sulfoxide (20 ml) was added and the mixture was stirred and refluxed during overnight. The reaction solution was cooled down and extracted with MC and DW. The extracted crude solution was evaporated and adsorbed into a silica gel. The crude product was purified with column purification and further purified by recrystallization using toluene. The purified product was a slightly green powder. (0.32 g, Yield 45%)

^{1}H NMR (500 MHz, $CDCl_3$) : δ 9.01-8.99 (d, J=8.50 Hz, 2H), 8.79-8.77 (d, J=9.00 Hz, 4H), 8.59-8.58 (d, J=7.50 Hz, 1H), 7.98-7.96 (d, J=7.50 Hz, 1H), 7.95-7.94 (d, J=8.50 Hz, 1H), 7.84-7.83 (d, J=8.50 Hz, 2H), 7.75-7.73 (d, J=8.00 Hz, 1H), 7.63-7.57 (m, 4H), 7.51-7.48 (m, 2H), 7.46-7.43 (t, J_1=7.00 Hz, J_2=8.00 Hz, 2H), 7.40-7.37 (t, J_1=7.50 Hz, J_2=7.00 Hz, 1H), 7.24-7.22 (d, J=9.00 Hz, 2H), 7.16-7.14 (dd, J_1=7.50 Hz, J_2=1.00 Hz, 4H), 7.08-7.04 (t, J_1=8.00 Hz, J_2=7.50 Hz, 4H), 6.97-6.93 (m, 7H), 6.75-6.73 (d, J=8.00 Hz, 4H), ^{13}C NMR (125 MHz, $CDCl_3$) : δ 171.9, 171.2, 170.9, 160.5, 159.5, 156.5, 151.4, 146.0, 143.2, 141.7, 141.1, 140.4, 136.3, 135.5, 132.9, 131.7, 131.4, 130.9, 129.2, 128.9, 127.8, 127.6, 127.4, 127.3, 127.2, 126.2, 125.6, 125.3, 125.2, 124.2, 123.9, 123.1, 123.1, 121.6, 121.3, 120.0, 119.8, 119.2, 118.8, 118.4, 118.3, 117.1, 113.8, 111.9, 110.1, 109.3, 105.8, MS (HR-FAB) m/z : Found 1051.2900 [(M + H)+]. Calculated For $C_{69}H_{42}N_6O_2S_2$: 1051.2889

Device Fabrication

Doped and non-doped OLEDs were fabricated using the following device structure : indium tin oxide (ITO) (50 nm) / PEDOT:PSS (60 nm) / PVK (10 nm) / DPOBBPE : PT-CzTrz (30 nm : X wt%)) / TSPO1 (35nm) / LiF (1 nm) /Al (200 nm). The PVK solution (0.3 wt% chlorobenzene solution) was spin-coated at a spin speed of 2000 rpm for 30 min. The coated film was annealed at 150 °C for 30 min. The emitting layer solution was a mixed solution of 0.7w% toluene solution of DPOBBPE and 0.7 wt% toluene solution of PT-CzTrz, and it was spin-coated at a spin speed of 2000 rpm for 30 s followed by annealing at 80 °C for 20 min. The doping concentrations were 5, 10, 30, 50, 100 wt% (non-doped). All solution process was conducted in the nitrogen filled glove box. Electron transporting materials were thermally deposited at a deposition rate of 1.0 Å/s under a high vacuum ($\sim 10^{-7}$ torr), and LiF and Al were deposited at a rate of 0.1 Å/s and 1.0 Å/s, respectively. After deposition of cathode, devices were protected from oxygen and moisture by encapsulating with an encapsulation glass, CaO getter, and epoxy adhesive. Electrical and optical analyses were performed using a Keithley 2400 source measurement unit and a CS2000 spectroradiometer.

List of Table

Table S1.

	1 wt%	5 wt%	10 wt%	30 wt%	50 wt%	100 wt%
Total (%)	34	33	34	35	32	34
Blue (%)	34	13	7	1	1	-
Orange (%)	-	20	27	34	31	34

List of Figure

Figure S1. Temperature dependent transient PL decay curves of (a) blue prompt, (b) blue delayed, (c) yellow prompt and (d) yellow delayed components.

Figure S2. Time resolved PL spectra of 30 wt% PT-CzTrz doped film.

Figure S3. The energy diagram of the solution processed device.

Figure S4. (a) Current density-voltage curves and (b) luminance-voltage curves and (c) quantum efficiency-luminance curves of the PT-CzTrz device according to doping concentration

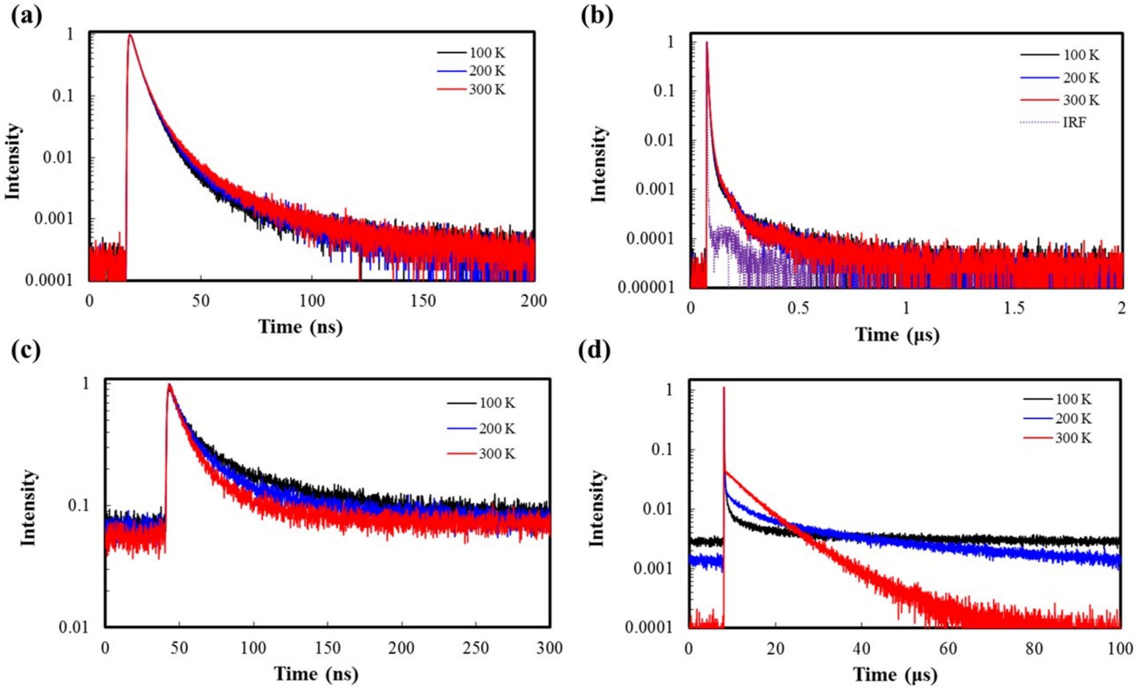
(a)
Intensity
1
0.1
0.01
0.001
0.0001
0
50
100
150
200
Time (ns)
100 K
200 K
300 K
(b)
Intensity
1
0.1
0.01
0.001
0.0001
0.00001
0
0.5
1
1.5
2
Time (μs)
100 K
200 K
300 K
IRF
(c)
Intensity
1
0.1
0.01
0
50
100
150
200
250
300
Time (ns)
100 K
200 K
300 K
(d)
Intensity
1
0.1
0.01
0.001
0.0001
0
20
40
60
80
100
Time (μs)
100 K
200 K
300 K

Figure S1.

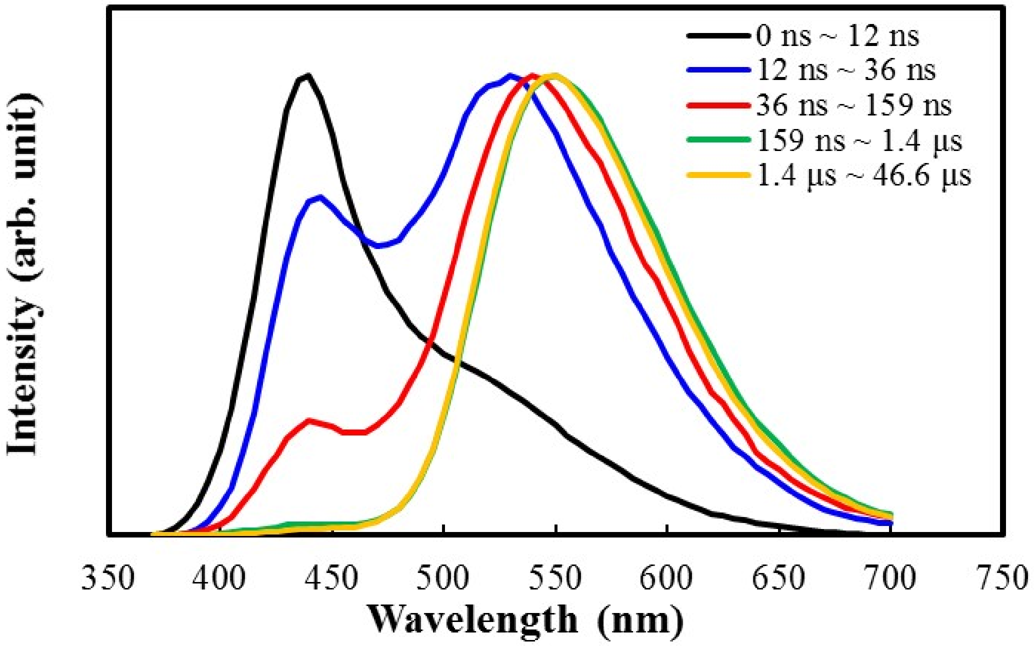
0 ns ~ 12 ns
12 ns ~ 36 ns
36 ns ~ 159 ns
159 ns ~ 1.4 μs
1.4 μs ~ 46.6 μs
Intensity (arb. unit)
350
400
450
500
550
600
650
700
750
Wavelength (nm)

Figure S2.

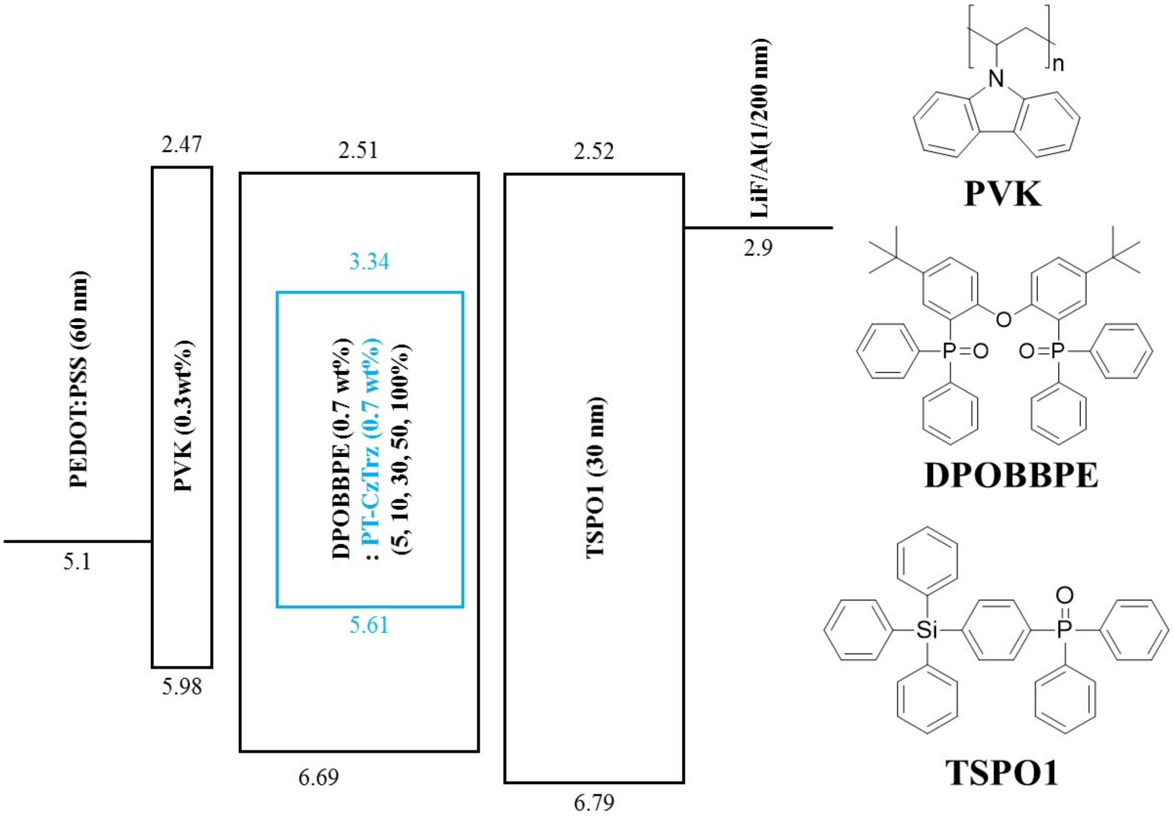
PEDOT:PSS (60 nm)
5.1
2.47
PVK (0.3wt%)
5.98
2.51
3.34
DPOBBPE (0.7 wt%)
: PT-CzTrz (0.7 wt%)
(5, 10, 30, 50, 100%)
5.61
6.69
2.52
TSPO1 (30 nm)
6.79
LiF/Al(1/200 nm)
2.9
PVK
DPOBBPE
TSPO1

Figure S3.

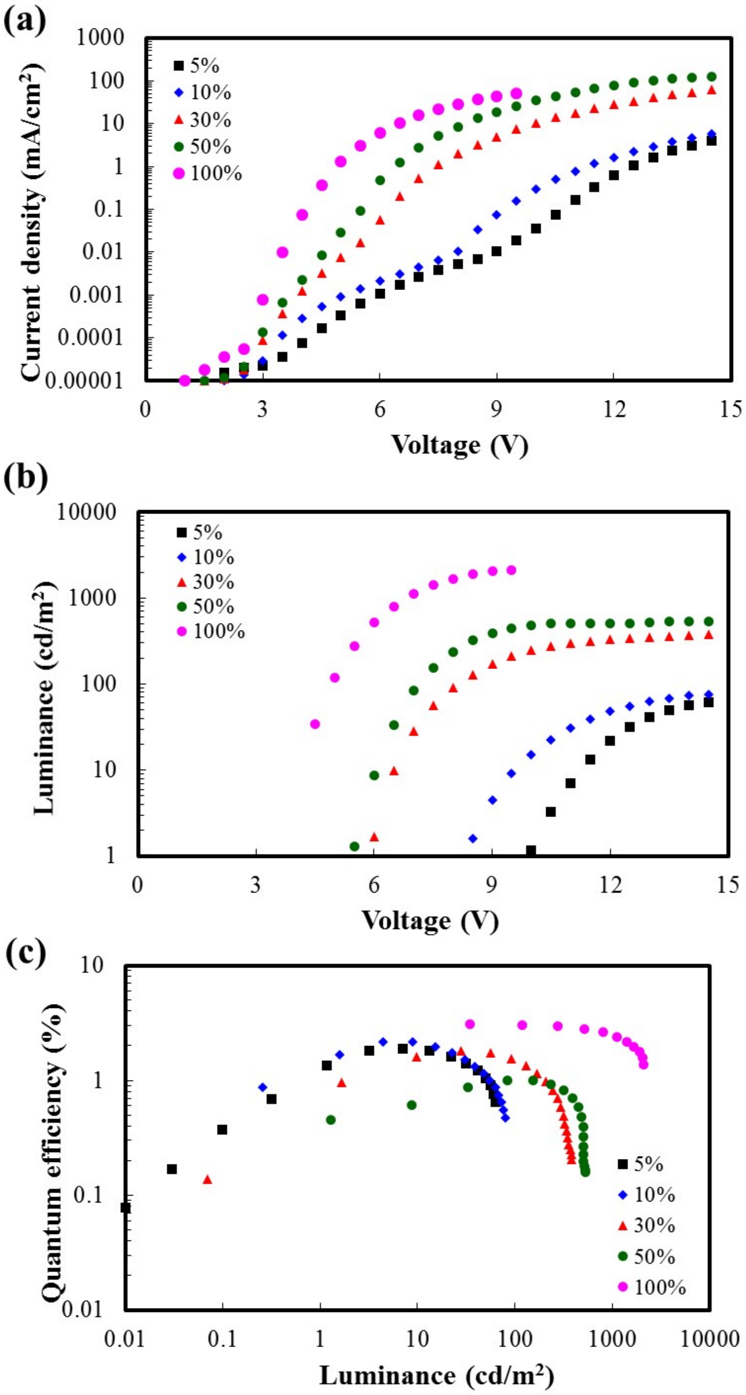
(a)
Current density (mA/cm²)
1000
100
10
1
0.1
0.01
0.001
0.0001
0.00001
0
3
6
9
12
15
Voltage (V)
5%
10%
30%
50%
100%
(b)
Luminance (cd/m²)
10000
1000
100
10
1
0
3
6
9
12
15
Voltage (V)
5%
10%
30%
50%
100%
(c)
Quantum efficiency (%)
10
1
0.1
0.01
0.01
0.1
1
10
100
1000
10000
Luminance (cd/m²)
5%
10%
30%
50%
100%

Figure S4.