

Indolo [3,2-*b*]carbazole/Benzimidazole Hybrid Bipolar Host Materials for Highly Efficient Red, Yellow, and Green Phosphorescent Organic Light Emitting Diodes

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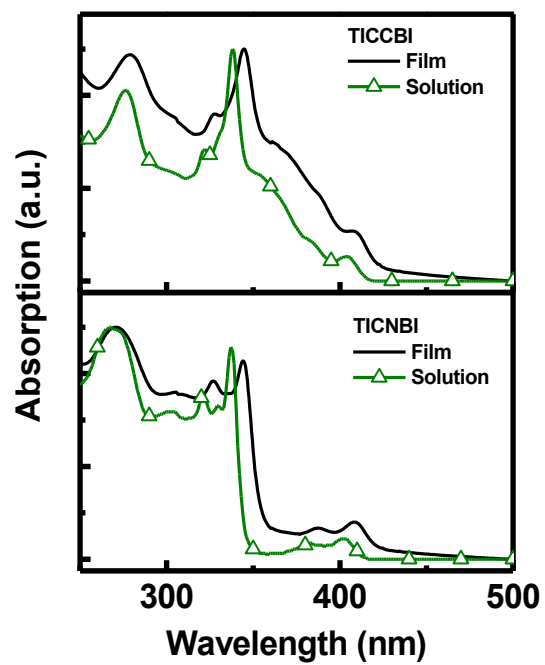


Fig. S-1. Room-temperature absorption spectra of **TICCBI** and **TICNBI** in CH_2Cl_2 solutions and in neat films.

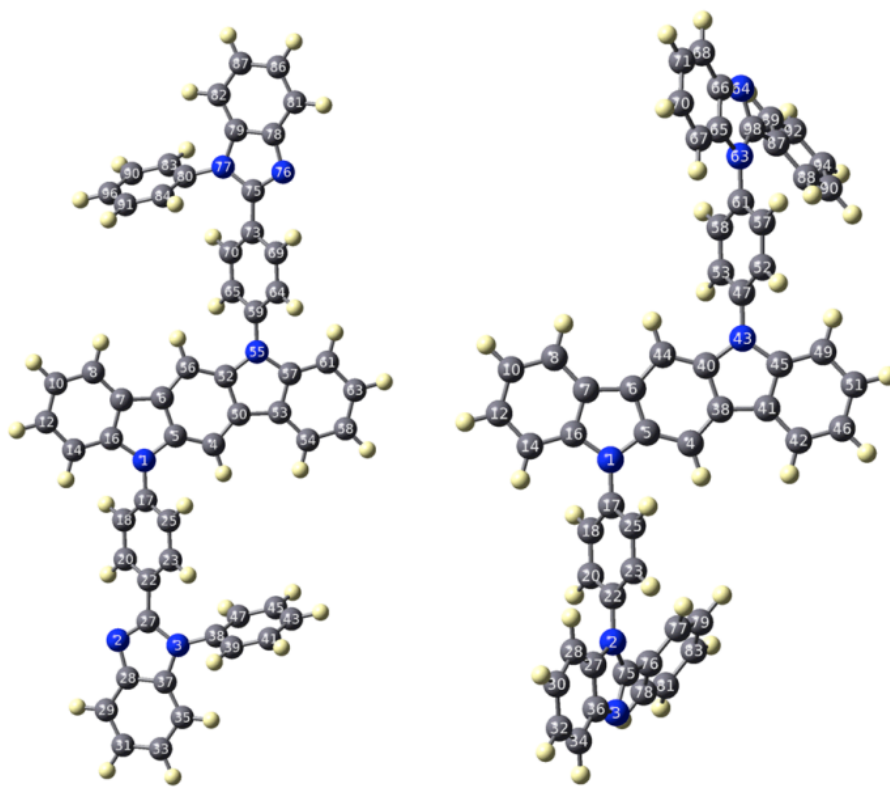


Fig. S-2. Atomic numbers in **TICCBI** (left) and **TICNBI** (right).

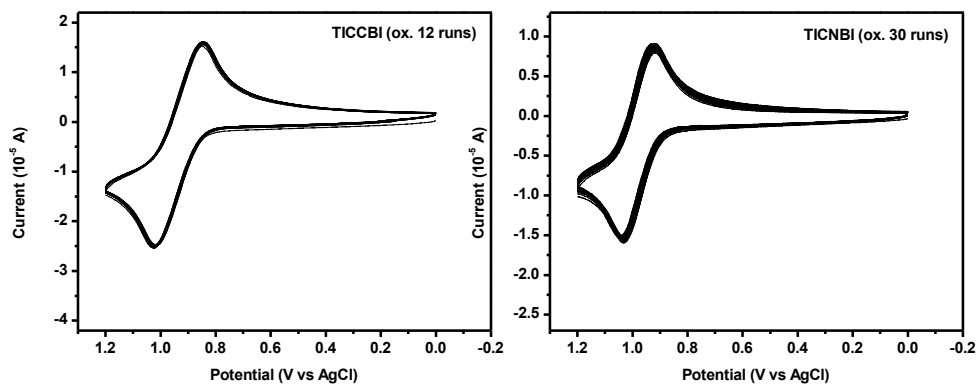


Fig. S-3. Multiple cycles of CV scan in **TICCBI** and **TICNBI**.

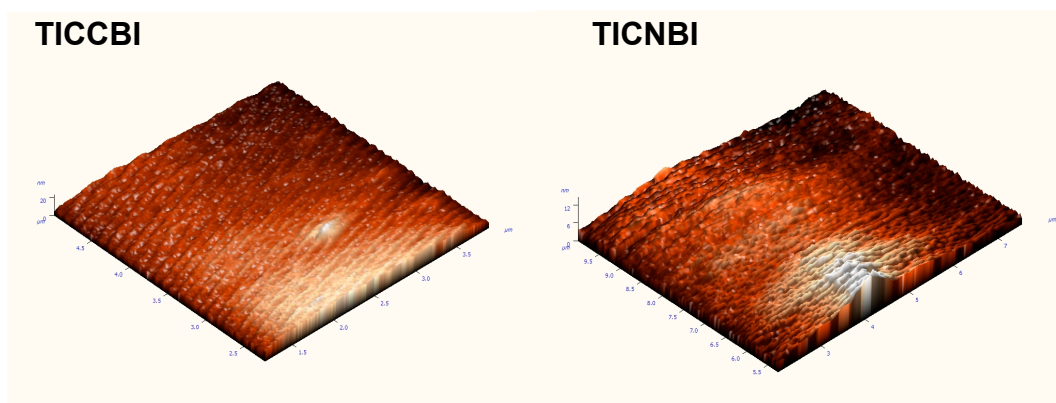


Fig. S4. AFM images of **TICCBI** and **TICNBI** film surfaces after heating at 100 °C for 30 min under nitrogen atmosphere.

Table S1. Bond lengths (r) and dihedral angles (Φ) for DFT B3LYP/6-31G(d) ground states (S_0) and CIS/6-31G(d) excited states (S_1) of **TICCBI** and **TICNBI**, along with x-ray structures for comparison.

TICCBI	S_0			S_1	TICNBI	S_0			S_1
	DFT	x-ray	% diff ^a	CIS		DFT	x-ray	% diff ^a	CIS
r(1,5)	1.406	1.4007	0.0038	1.38988	r(1,5)	1.4059	1.3946	0.0081	1.39621
r(1,16)	1.3998	1.4006	-0.0005	1.39146	r(1,16)	1.4004	1.3922	0.0059	1.38165
r(16,7)	1.4183	1.4001	0.0131	1.40558	r(16,7)	1.418	1.4098	0.0058	1.42819
r(5,6)	1.4258	1.4154	0.0074	1.41366	r(5,6)	1.4258	1.4196	0.0044	1.43744
r(7,6)	1.4476	1.4499	-0.0016	1.44315	r(7,6)	1.4478	1.4418	0.0042	1.40035
r(5,4)	1.3919	1.3908	0.0008	1.39113	r(5,4)	1.3917	1.3866	0.0036	1.36013
r(6,56)	1.3982	1.3909	0.0053	1.39169	r(6,44)	1.3982	1.3955	0.0019	1.43416
r(7,8)	1.3996	1.3916	0.0058	1.39294	r(7,8)	1.3997	1.3949	0.0034	1.41443
r(14,16)	1.3978	1.3946	0.0023	1.38747	r(14,16)	1.3974	1.3925	0.0035	1.37834
r(12,14)	1.3937	1.3801	0.0098	1.38496	r(12,14)	1.3938	1.3817	0.0087	1.39313
r(10,8)	1.3919	1.3855	0.0046	1.38078	r(10,8)	1.3919	1.3828	0.0066	1.37353
r(1,17)	1.4166	1.4158	0.0006	1.40297	r(1,17)	1.4164	1.4202	-0.0027	1.41612
r(22,27)	1.4166	1.4759	-0.0402	1.45905	r(2,22)	1.4257	1.4302	-0.0031	1.42115
r(2,27)	1.3168	1.312	0.0037	1.3015	r(2,75)	1.4017	1.3842	0.0126	1.38127
r(3,27)	1.3999	1.3776	0.0162	1.38687	r(3,75)	1.3157	1.3141	0.0013	1.28568
r(3,38)	1.4286	1.4363	-0.0053	1.42378	r(76,75)	1.4731	1.4743	-0.0008	1.48108
$\Phi(16,1,17,18)$	52.086	58.152	-0.1043	55.07389	$\Phi(16,1,17,18)$	53.842	60.256	-0.1064	68.64336
$\Phi(20,22,27,2)$	-28.17	-31.205	-0.0973	-19.4863	$\Phi(20,22,2,27)$	-113.99	-58.164	0.9599	-108.43129
$\Phi(27,3,38,47)$	-57.507	-52.994	0.0852	-63.78413	$\Phi(23,22,2,75)$	-126.04	-60.505	1.0832	-121.54444
$\Phi(37,3,38,39)$	-67.112	-60.963	0.1009	-76.42921	$\Phi(2,75,76,77)$	30.583	-38.498	-1.7944	39.11275

^a difference defined as $(R_{\text{DFT}} - R_{\text{x-ray}}) / R_{\text{x-ray}} \times 100 \%$

Table S2. The crystal data of **TICCBI** and **TICNBI**.

	TICCBI	TICNBI
empirical formula	C ₆₀ H ₄₈ N ₆ O ₂ S ₂	C ₅₆ H ₃₆ N ₆
formula weight	949.16	792.91
crystal system	Monoclinic	Triclinic
space group	P2 ₁ /n	P1
<i>a</i> (Å)	13.9165(2)	9.3415
<i>b</i> (Å)	12.2744(2)	10.0537
<i>c</i> (Å)	14.5110(2)	11.5245
α (deg)	90	106.117
β (deg)	100.017(2)	99.662
γ (deg)	90	93.529
cell volume (Å) ³	2440.94(6)	1018.35(13)
<i>Z</i>	2	1
density (calc) Mg/m ³	1.291	1.293
<i>F</i> (000)	996	414
Temperature (K)	295(2)	295(2)
Wavelength (Å)	1.54178	1.54178
Reflections collected	9125	6496
Independent reflns (<i>R</i> _{int})	4436 (0.0196)	3701 (0.0255)
<i>R</i> (<i>F</i>), <i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)]	0.0573, 0.1689	0.0470, 0.1332
<i>R</i> (<i>F</i>), <i>wR</i> 2 (all data)	0.0730, 0.1784	0.0617, 0.1538

Experimental Section

Synthesis of **TICCBI**

An oven-dried 50-mL double-necked round bottom flask was charged with Indolo [3,2-*b*] carbazole **1** (256 mg, 1.00 mmol, 1.0 equiv.), 2-(4-iodophenyl)-1-phenyl benzimidazole **2** (872 mg, 2.20 mmol, 2.2 equiv.), K₂CO₃ (691 mg, 5.00 mmol, 5.0 equiv.), Cu powder (140 mg, 2.20 mmol, 2.2 equiv.) and few 18-crown-6. The flask, equipped with a condenser, was capped and then evacuated and backfilled with argon. The degassed 1,2-dichlorobenzene (20 mL) was added via syringe, through the septum and reaction mixture was heated to reflux for 48 h. The reaction mixture was then cooled to room temperature, filter through Celite/Al₂O₃ and elute with CHCl₃. The eluent was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified via column chromatography followed by sublimation under the pressure of 10⁻⁶ torr to provide the compound **TICCBI** as a yellow crystal. (201 mg, 25%). ¹H NMR (CDCl₃, 400 MHz): δ 8.09 (d, *J* = 4.0 Hz, 2H), 8.08 (s, 2H), 7.95 (d, *J* = 4.0 Hz, 2H), 7.89 (d, *J* = 4.0 Hz, 4H), 7.55-7.68 (m, 10H), 7.38-7.50 (m, 10H), 7.27-7.33 (m, 6H); ¹³C NMR (CDCl₃, 500 MHz) δ 141.51, 136.66, 131.05, 130.17, 129.07, 127.57, 126.65, 126.23, 123.74, 123.64, 123.36, 120.30, 119.95, 110.63, 109.57, 100.05; MS (*m/z*, FAB+) 792.9 (10); HRMS (*m/z*, FAB+) calcd for C₅₆H₃₆N₆ 792.3001, found 792.2988. IR (KBr) 3059 (m), 1901 (w), 1701 (w), 1604 (s), 1529 (s), 1500 (s), 1320(s), 1232(m) cm⁻¹

Synthesis of **TICNBI**

An oven-dried 50-mL double-necked round bottom flask was charged with Indolo [3,2-*b*] carbazole **1** (128 mg, 0.50 mmol, 1.0 equiv.), 1-(4-iodophenyl)-2-phenyl benzimidazole **3** (436 mg, 1.10 mmol, 2.2 equiv.), K₂CO₃ (345 mg, 2.50 mmol, 5.0 equiv.), Cu powder (70 mg, 1.10 mmol, 2.2 equiv.) and few 18-crown-6. The flask, equipped with a condenser, was capped and then evacuated and backfilled with argon. The degassed 1,2-dichlorobenzene (25 mL) was added via syringe, through the septum and reaction mixture was heated to reflux for 48 h. The reaction mixture was then cooled to room temperature, filter through Celite/Al₂O₃ and elute with CHCl₃. The eluent was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified via column chromatography followed by sublimation under the pressure of 10⁻⁶ torr to provide the compound **TICNBI** as a bright yellow crystal. (160 mg, 40%). ¹H NMR (CDCl₃, 400 MHz): δ 8.19 (d, *J* = 4.0 Hz, 2H), 7.97 (d, *J* = 6.6 Hz, 2H), 7.87 (d, *J* = 4.0 Hz, 4H), 7.73 (dd, *J* = 8.0 Hz, 4H), 7.65 (d, *J* = 8.0 Hz, 4H), 7.32-7.53 (m, 18H); ¹³C NMR (CDCl₃, 500 MHz) δ 141.58, 136.76, 129.88, 129.05, 128.80, 128.39, 126.58, 123.81, 123.76, 120.45, 120.30, 110.78,

109.44, 99.96, 96.11; MS (m/z, FAB+) 792.9 (1); HRMS (m/z, FAB+) calcd for C₅₆H₃₆N₆ 792.3001, found 792.2997. IR (KBr) 3046 (m), 1687 (w), 1608 (s), 1517 (s), 1477 (s), 1452 (s), 1372(s), 1233(s) cm⁻¹

Synthesis of 1-chloro-6-fluoroisoquinoline (**5**).

To a solution (250 ml: 50 ml= EtOH: H₂O) of 4-fluoro-2-((trimethylsilyl) ethynyl) benzaldehyde oxime (20 g, 85 mmole) was added K₂CO₃ (11.73 g, 85 mmole) and stirred at 60 °C for 1 hour, the color of the solution was change to black. The mixture was extracted with dichloromethane three times and the combined organic layer was dried over MgSO₄. The solution was evaporated to give purplish black solid. The crude product was dissolved in dry CHCl₃ (100ml) under nitrogen at 0 °C and POCl₃ (9.3 ml,102 mmole) was added dropwise and stirred for 30 min .Further, Et₃N was added and the resulting solution was reflux for 4 h. Na₂CO₃(aq) (1M) was added to neutralize the solution and then extracted by ethyl acetate, dried over MgSO₄ and concentrated under reduced pressure. The residue was eluted through a silica column to afford the desired product compound **5** (4.51 g, 30% over 2 steps). ¹H NMR(400MHz, CDCl₃); δ 8.13 ~ 8.08 (m, 2 H), 7.37 (d, *J* = 5.6 Hz, 1 H), 7.26 ~ 7.21 (m, 2 H); ¹³C NMR (100MHz, CDCl₃); δ 163.3 (d, *J* = 254 Hz), 151.0, 142.03 , 138.9(d, *J* = 11 Hz), 129.3 (d, *J* = 10 Hz), 123.6 , 120.8 (d, *J* = 4 Hz), 118.5 (d, *J* = 25 Hz), 110.1 (d, *J* = 21 Hz); HRMS calcd. for C₉H₅ClFN: 181.0095, found: 181.0043.

Synthesis of 1-(4-tert-butylphenyl)-6-fluoroisoquinoline (*6f-1p-tBu-piq*) **5a**

The compound **5** (2.5 g, 13.8 mmole), 4-tert-butylphenylboronic acid (3.68 g, 20.7 mmole), PPh₃ (0.036 g, 0.14 mmole), Pd(OAc)₂ (0.077 g, 0.34 mmole) and K₂CO₃ (2.85 g, 20.7 mmole) were dissolved in a mixed solution of DME (60 ml) and H₂O (40 ml); The resulting mixture was heated to 80 °C for 4 h. The solution was cooled to room temperature, extracted with ethyl acetate, dried over MgSO₄ and concentrated under reduced pressure. The residue was eluted through a silica column to afforded desired product compound **5a** (2.77 g, 72%). ¹H NMR(400MHz, CDCl₃); δ 8.57 (d, *J* = 5.6 Hz 1 H), 8.17 (dd, *J* = 8.8, 5.2 Hz, 1 H), 7.62 ~ 7.60 (m, 2 H), 7.56 ~ 7.53 (m, 3 H), 7.43 (dd, *J* = 9.2, 2.4 Hz, 1 H), 7.25 (dt, *J* = 2.8, 8.8 Hz, 1 H), 1.39 (s, 9 H); ¹³C NMR (100MHz, CDCl₃); δ162.7 (d, *J* = 252 Hz), 160.6, 151.7, 143.0, 138.3 (d, *J* = 9.7 Hz),136.3,130.9 (d, *J* = 9.7 Hz), 129.5 , 125.3, 123.8, 119.1 (d, *J* = 5.2 Hz), 117.2 (d, *J* = 24.6 Hz), 110.0 (d, *J* = 20 Hz), 34.6, 31.2; HRMS calcd. for C₁₉H₁₈FN: 279.1423, found: 279.1469.

Synthesis of 1-(3,5-dimethylphenyl)-6-fluoroisoquinoline (*6f-1p-35dm-piq*) **5b**

The preparation procedure of **5b** was similar to compound **5a**. 85% yield. ^1H NMR(400MHz, CDCl_3); δ 8.55 (d, $J = 5.6$ Hz, 1H), 8.12 (dd, $J = 8.8, 5.2$ Hz, 1 H), 7.54 (d, $J = 5.6$ Hz, 1 H), 7.42 (dd, $J = 5.6, 9.2$ Hz, 1 H), 7.26 ~ 7.22 (m, 3 H), 7.11 (s, 1 H), 2.38 (s, 6 H); ^{13}C NMR (100MHz, CDCl_3); δ 162.8 (d, $J = 251$ Hz), 161.0, 142.8, 138.9, 138.3 (d, $J = 11$ Hz), 137.8, 131.0 (d, $J = 9.4$ Hz), 130.3, 127.5, 123.9, 121.0, 119.3 (d, $J = 4.6$ Hz), 117.3 (d, $J = 25.0$ Hz), 109.9 (d, $J = 20.5$ Hz), 21.2; HRMS calcd. for $\text{C}_{17}\text{H}_{14}\text{FN}$: 251.1110, found: 251.1345.

Synthesis of (4tBuPh-6Fiq) $_2$ Ir(acac) **i6**

The compound **5a** (2 g, 7.16 mmole) and $\text{IrCl}_3 \cdot n\text{H}_2\text{O}$ (1.04 g, 3.49 mmole) were dissolved in a mixed solution of 2-ethoxyethanol (18 ml) and H_2O (6 ml); The resulting mixture was heated to 100 °C for 12 h. The solvent was removed by vacuum and the residues were washed by hexane and water. The dried crude product and acetylacetone (1.25 g, 12.5 mmole) were dissolved in 2-ethoxyethanol (18 ml). Then, Na_2CO_3 (0.95 g, 9 mmole) was added to this solution and stirred for 24 h at 100 °C. The solvent was removed by vacuum and the residues were eluted through a silica column (1:3 = CH_2Cl_2 : Hexane) to give a red solid. Further the crude product was washed by mixture solution (EA: Hexane = 5: 95) to afford the desired product compound (4tBuPh-6Fiq) $_2$ Ir(acac) **i6** (1.81 g, 60% over two steps). ^1H NMR(400MHz, CDCl_3); δ 8.95 (dd, $J = 9.6, 5.6$ Hz, 2 H), 8.45 (d, $J = 6.4$ Hz, 2 H), 7.98 (d, $J = 8.4$ Hz, 2 H), 7.50 (d, $J = 9.2$ Hz, 2 H), 7.42 ~ 7.38 (m, 4 H), 6.90 (dd, $J = 2.0, 8.4$ Hz, 2 H), 6.26 (d, $J = 2.0$ Hz, 2 H), 5.26 (s, 1 H), 1.79 (s, 6 H), 0.93 (s, 18 H); ^{13}C NMR (100MHz, CDCl_3); δ 184.7, 169.7, 163.4 (d, $J = 252$ Hz), 160.6, 151.5, 143.4, 141.6, 138.8 (d, $J = 10$ Hz), 130.1, 130.0 (d, $J = 9.2$ Hz), 129.2, 123.1, 118.5, 117.9, 117.4 (d, $J = 24.4$ Hz), 110.5 (d, $J = 20.6$ Hz), 110.6, 34.0, 30.9, 28.6; HRMS calcd. for $\text{C}_{43}\text{H}_{41}\text{F}_2\text{IrN}_2\text{O}_2$: 848.2765, found: 848.2831. Anal. calcd for $\text{C}_{43}\text{H}_{41}\text{F}_2\text{IrN}_2\text{O}_2$: C, 60.90; H, 4.87; N, 3.30. Found: C, 60.83. H, 4.92; N, 3.31.

Synthesis of (35dmPh-6Fiq) $_2$ Ir(acac) **i3**

The preparation procedure of (35dmPh-6Fiq) $_2$ Ir(acac) **i3** was similar to compound (4tBuPh-6Fiq) $_2$ Ir(acac) **i6**. 25% yield (over two steps). ^1H NMR(400MHz, CDCl_3); δ 9.01 (dd, $J = 10.0, 5.6$ Hz, 2 H), 8.26 (d, $J = 6.4$ Hz, 2 H), 7.88 (s, 2 H), 7.45 ~ 7.42 (m, 4 H), 7.20 (d, $J = 6.4$ Hz, 2 H), 6.57 (s, 2 H), 4.88 (s, 1 H), 2.32 (s, 6 H), 1.53 (s, 6 H), 1.44 (s, 6 H); ^{13}C NMR (100MHz, CDCl_3); δ 184.6, 169.5, 163.3 (d, $J = 251$ Hz), 148.1, 147.0, 144.3, 141.7, 138.7 (d, $J = 10$ Hz), 131.6, 130.3 (d, $J = 9.2$ Hz), 130.2, 128.2, 123.3, 117.2, 116.9, 110.4 (d, $J = 20.6$ Hz), 99.8, 28.3, 23.9, 21.1; HRMS calcd. for $\text{C}_{39}\text{H}_{33}\text{F}_2\text{IrN}_2\text{O}_2$: 792.2139, found: 792.2267. Anal. calcd for $\text{C}_{39}\text{H}_{33}\text{F}_2\text{IrN}_2\text{O}_2$: C, 59.15; H, 4.20; N, 3.54. Found: C, 59.01. H, 4.32; N, 3.21.

Photophysical measurements

Steady state spectroscopic measurements were conducted both in solution and solid films prepared by vacuum (2×10^{-6} torr) deposition on a quartz plate (1.6 x 1.0 cm). Absorption spectra were recorded with a U2800A spectrophotometer (Hitachi). Fluorescence spectra at 300 K and phosphorescent spectra at 77 K were measured on a Hitachi F-4500 spectrophotometer upon exciting at the absorption maxima. The experimental values of HOMO levels were determined with a Riken AC-2 photoemission spectrometer (PES), and those of LUMO levels were estimated by subtracting the optical energy gap from the measured HOMO.

Cyclic Voltammetry

The oxidation potential was determined by cyclic voltammetry (CV) in CH_2Cl_2 solution (1.0 mM) containing 0.1 M tetra *n*-butylammonium hexafluorophosphate (TBAPF6) as a supporting electrolyte at a scan rate of 100 mV s^{-1} . The reduction potential was recorded in THF solution (1.0 mM) containing 0.1M tetra-*n*-butylammonium perchlorate (TBAClO₄) as a supporting electrolyte at a scan rate of 100 mV s^{-1} . A glassy carbon electrode and platinum wire were used as the working and counter electrodes, respectively. All potentials were recorded versus Ag/AgCl (saturated) as a reference electrode.

Time-of-flight (TOF) mobility measurements

Carrier-transport properties were studied in vapor-deposited glasses of compounds by the time-of-flight (TOF) transient photocurrent technique. The samples for the TOF measurement were prepared by vacuum deposition using the structure: ITO glass/compounds /Al (150 nm), and then placed inside a cryostat and kept under vacuum. The thickness of organic film was monitored in situ with a quartz crystal sensor and calibrated by a thin film thickness measurement (K-MAC ST2000). A pulsed nitrogen laser was used as the excitation light source through the transparent electrode (ITO) induced photogeneration of a thin sheet of excess carriers. Under an applied dc bias, the transient photocurrent was swept across the bulk of the organic film toward the collection electrode (Al), and then recorded with a digital storage oscilloscope. Depending on the polarity of the applied bias, selected carriers (holes or electrons) are swept across the sample with a transit time of t_T . With the applied bias V and the sample thickness D , the applied electric field E is V/D , and the carrier mobility is then given by $\mu = D/(t_T E) = D^2/(Vt_T)$, in which the carrier transit time, t_T , can be extracted from the intersection point of two asymptotes to the plateau and the tail sections in double-logarithmic plots.

OLED device fabrications

All chemicals were purified through vacuum sublimation prior to use. The OLEDs were fabricated through vacuum deposition of the materials at 10^{-6} Torr onto ITO-coated glass substrates having a sheet resistance of $15 \Omega \text{ sq}^{-1}$. The ITO surface was cleaned ultrasonically –sequentially with acetone, methanol, and deionized water – and then it was treated with UV-ozone. The deposition rate of each organic material was ca. $1\text{--}2 \text{ \AA s}^{-1}$. Subsequently, LiF was deposited at 0.1 \AA s^{-1} and then capped with Al (ca. 5 \AA s^{-1}) through shadow masking without breaking the vacuum. The $J\text{--}V\text{--}L$ characteristics of the devices were measured simultaneously in a glove-box using a Keithley 6430 source meter and a Keithley 6487 picoammeter equipped with a calibration Si-photodiode. EL spectra were measured using a photodiode array (OTO SD1200).