

Supporting Information

Electron transporting unit linked multifunctional heteroleptic Ir(III) complex: A promising strategy to improve the performance of solution-processed phosphorescent organic light-emitting diodes

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Experimental section

General Information

All chemicals and reagents were purchased from Aldrich Chemical Co., and it was used without further purification. The dimer (**4**) was synthesized using the procedure we have developed previously¹ and 4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenol (**9**) was synthesized by the reported procedure.² All reactions were systematically monitored by thin layer chromatography with Merck precoated aluminum plates. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer in CDCl₃ using tetramethylsilane as an internal standard. High resolution mass spectra were obtained from the Korea Basic Science and Institute, Daegu Center (HR-ESI Mass). TGA and DSC thermograms were obtained with Mettler Toledo TGA/SDTA 851e and DSC 822e analyzer under N₂ atmosphere at a heating rate of 10 °C/min, respectively. The UV–visible absorption and the fluorescence spectra were recorded with a JASCO V–570 and Hitachi F–4500 fluorescence spectrophotometers at room temperature, respectively. Cyclic voltammetry (CV) measurements were performed with a CHI 600C potentiostat (CH Instruments), which is equipped with a platinum disc as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl as the reference electrode, at a scan rate of 100 mV/s using anhydrous methylene chloride (MC) and 0.1 M tetrabutylammonium tetrafluoroborate (TBABF₄) as the solvent and electrolyte, respectively. The potentials were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc⁺). It was assumed that the redox potential of Fc/Fc⁺ had an absolute energy level of –4.8 eV under vacuum. All electrochemical experiments were carried out at room temperature.

Synthesis of (4-phenyl-2-(thiophen-2-yl)quinoline) (3)

A mixture of 1-(thiophen-2-yl)ethanone (3 g, 23.78 mmol), 2-aminobenzophenone (4.69 g, 23.78 mmol), diphenyl phosphate (5.95 g, 23.78 mmol), and *m*-cresol (30 mL) was flushed with N₂ while stirring at room temperature for 30 min and then refluxed for 12 hr at 140 °C. The reaction mixture was distilled to remove *m*-cresol, residue was diluted with MC and washed with 10% sodium hydroxide solution. The reaction mixture was washed with sodium chloride solution and the resulting organic layer was dried over anhydrous MgSO₄ and evaporated the solvent. The residue was then purified by column chromatography on silica gel (hexane:ethyl acetate (EA), 9:1 v/v) to furnish an off-white powder **3** (5.1 g, 74%).

¹H NMR (300 MHz, CDCl₃): δ (ppm) 8.19-8.16 (d, 1H), 8.06-8.05 (dd, 1H), 7.90-7.86 (m, 2H), 7.74-7.69 (m, 2H), 7.56-7.51 (m, 5H), 7.48-7.43 (m, 2H); ¹³C NMR (300 MHz, CDCl₃): δ (ppm) 152.11, 149.29, 148.88, 145.64, 138.42, 129.88, 129.74, 128.84, 128.78, 128.70, 128.30, 126.36, 126.11, 125.91, 118.14. HRESI-MS [M+H]⁺: m/z Found 288.08, Calcd for 287.38.

General procedure for the synthesis of cyclometalated Ir(III) μ-chloride bridged dimer (4**)**

The general procedure for the synthesis of cyclometalated Ir(III) μ-chloride bridged dimer complexes is as follows: the compound **3** (5 g, 17.40 mmol) and IrCl₃·H₂O (2.08 g, 6.96 mmol) were added to a mixture of 2-ethoxyethanol and water (80 mL, 3:1 v/v). The resulting mixture was refluxed at 140 °C for 20 hr under an N₂ atmosphere and cooled to room temperature. The formed red solid was filtered, washed with water followed by methanol. Subsequently, the solid was dried under vacuum at 120 °C to afford cyclometalated Ir(III) μ-chloride bridged dimer (**4**) as a red solid (3.36 g, 60 %).

Synthesis of bis[4-phenyl-2-(thiophen-2-yl)quinoline]iridium picolinate (TPQIr)

The compound **4** (1 g, 0.62 mmol), picolinic acid (0.23 g, 1.87 mmol), and K₂CO₃ (0.86 g, 6.2 mmol) in 2-ethoxyethanol (20 mL) was stirred at room temperature for 8 hr under a N₂

atmosphere. After completing the reaction, the mixture was poured into water and extracted with MC. The organic layer was dried over anhydrous MgSO_4 , filtered, and removed the solvent under reduced pressure. The crude product was purified by silica gel column chromatography using ethylacetate (EA):MC:hexane (2:4:4, v/v/v) as an eluent to furnish a red powder **TPQIr** (0.3 g, 54%).

^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.80-8.77 (d, 1H), 7.98-7.95 (m, 2H), 7.76-7.68 (m, 4H), 7.63 (s, 1H), 7.59-7.57 (m, 11H), 7.42-7.30 (m, 4H), 7.20-7.12 (q, 3H), 6.86 (t, 1H), 6.67-6.66 (d, 1H), 6.20-6.18 (d, 1H); ^{13}C NMR (300 MHz, CDCl_3): δ (ppm) 172.53, 166.72, 165.35, 153.67, 153.59, 153.04, 151.39, 151.35, 149.93, 149.02, 147.03, 141.58, 139.31, 137.95, 137.48, 137.44, 134.84, 133.61, 132.09, 130.90, 130.03, 129.88, 129.21, 129.08, 128.95, 127.97, 127.70, 127.55, 126.48, 126.38, 125.76, 125.64, 124.85, 124.64, 124.14, 117.97, 116.99. IR (NaCl cell, cm^{-1}): 3057, 2355, 1663, 1593, 1541, 1496, 1450, 1427, 1335, 1243, 1145, 1070, 887, 772, 726, 698, 588. Calcd for $\text{C}_{44}\text{H}_{28}\text{IrN}_3\text{O}_2\text{S}_2$: C, 59.58; H, 3.18; N, 4.74. Found: C, 59.54; H, 3.12; N, 4.72. HRESI-MS $[\text{M}+\text{H}]^+$: m/z Found 887.1254, Calcd for 887.1251.

Synthesis of bis[4-phenyl-2-(thiophen-2-yl)quinoline]iridium-4-Cl-picolinate (5)

The compound **4** (2.3 g, 1.44 mmol), 4-chloropicolinic acid (0.68 g, 4.31 mmol), and K_2CO_3 (1.99 g, 14.4 mmol) in 2-ethoxyethanol (20 mL) was stirred at room temperature for 8 hr under a N_2 atmosphere. After completing the reaction, the mixture was poured into water and extracted with MC. The organic layer was dried over anhydrous MgSO_4 , filtered, and removed the solvent under reduced pressure. The crude product was purified by silica gel column chromatography using EA:MC:hexane (1:5:4, v/v/v) as an eluent to afford a red powder **5** (0.84 g, 63%).

^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.73-8.70 (d, 1H), 7.96 (s, 1H), 7.85-7.83 (d, 1H), 7.75-7.72 (d, 2H), 7.67-7.63 (m, 3H), 7.61-7.55 (m, 10H), 7.39-7.33 (m, 3H), 7.22-7.15 (m, 3H), 6.96-

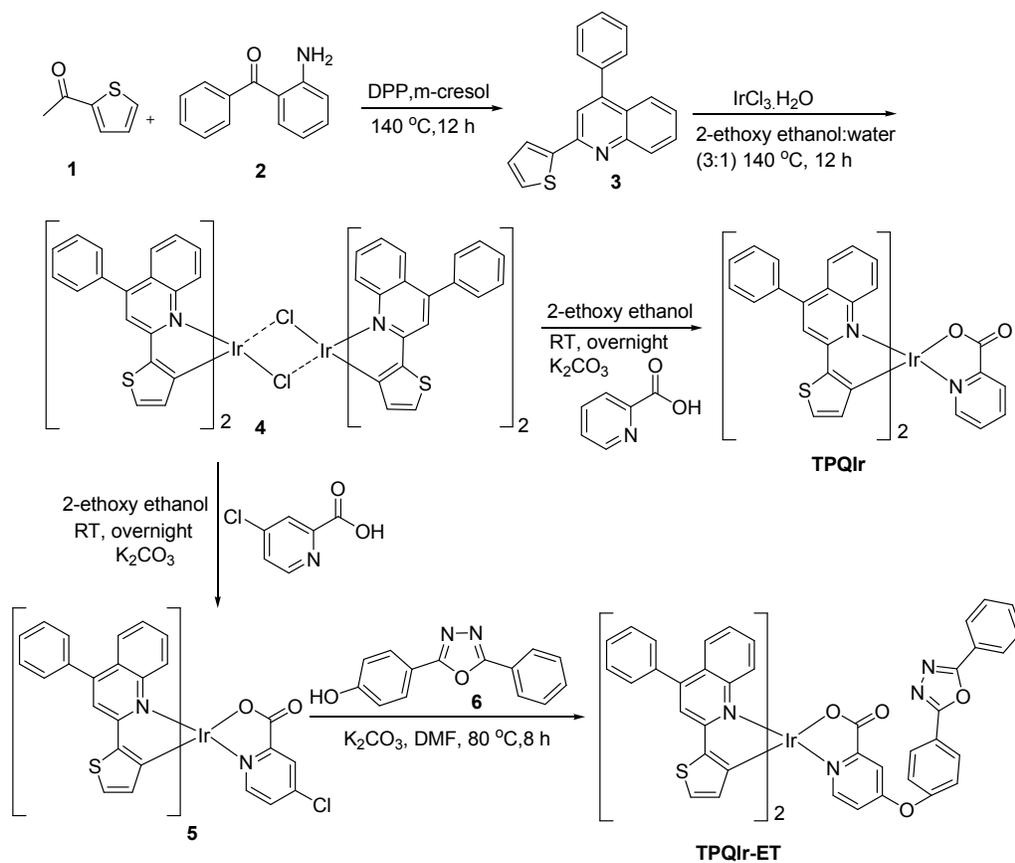
6.95 (m, 1H), 6.66-6.64 (m, 1H), 6.19-6.17 (m,1H); ^{13}C NMR (300 MHz, CDCl_3): δ (ppm) 171.8, 166.6, 165.2, 154.38, 152.91, 152.82, 151.57, 149.80, 148.96, 147.64, 146.51, 141.52, 139.29, 137.40, 137.36, 134.79,133.5, 132.20, 130.99, 130.09, 130.01, 129.87, 129.27, 129.13, 128.98, 128.34, 128.27, 126.52, 126.36, 125.88, 125.68, 124.94, 124.79, 117.98, 116.9. Calcd for $\text{C}_{44}\text{H}_{27}\text{ClIrN}_3\text{O}_2\text{S}_2$: C, 57.35; H, 2.95; N, 4.56. Found: C, 57.24; H, 2.82; N, 4.52. HRESI-MS $[\text{M}+\text{H}]^+$: m/z Found 921.4926, Calcd for 921.4922.

Synthesis of bis[4-phenyl-2-(thiophen-2-yl)quinoline]iridium-4-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenoxy)picolinate (TPQIr-ET)

The compound **5** (1 g, 0.57 mmol), 4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenol (**6**) (1 g, 0.57 mmol), and K_2CO_3 (0.60 g, 5.7 mmol) in DMF (10 mL) was stirred at 80 °C over night under a N_2 atmosphere. After completing the reaction, the mixture was cooled, poured into water and extracted with MC. The organic layer was dried over anhydrous MgSO_4 , filtered, and removed the solvent under reduced pressure. The crude product was purified by silica gel column chromatography using EA:MC:hexane (3:5:2, v/v/v) as an eluent to furnish a red powder **TPQIr-ET** (0.36 g, 59%).

^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.80-8.77 (d, 1H), 8.17-8.15 (m, 4H), 7.87-7.85 (d, 1H), 7.81-7.77 (m, 3H), 7.71 (s, 1H), 7.65-7.57 (m, 16H), 7.41-7.36 (m, 3H), 7.19-7.17 (m, 3H), 7.07-7.02 (m, 2H), 6.70-6.69 (d, 1H), 6.21-6.19 (d,1H); ^{13}C NMR (300 MHz, CDCl_3): δ (ppm) 171.81, 166.86, 165.55, 155.96, 153.57, 151.40, 150.04, 149.05, 139.25, 137.49, 133.62, 132.11, 130.94, 129.88, 129.55, 129.36, 129.03, 128.98, 127.24, 126.63, 126.41, 125.76, 124.93, 124.02, 122.12, 121.69, 115.24. IR (NaCl cell, cm^{-1}): 3057, 2355, 1652, 1596, 1539, 1495, 1452, 1425, 1325, 1290, 1242, 1203, 885, 846, 767, 732, 702, 584. Calcd for $\text{C}_{58}\text{H}_{36}\text{IrN}_5\text{O}_4\text{S}_2$: C, 62.02; H,

3.23; N, 6.23. Found: C, 62.01; H, 3.21; N, 6.20. HRESI-MS $[M+H]^+$: m/z Found 1123.2761, Calcd for 1123.2760.



Scheme S1. Synthesis of **TPQIr** and **TPQIr-ET**.

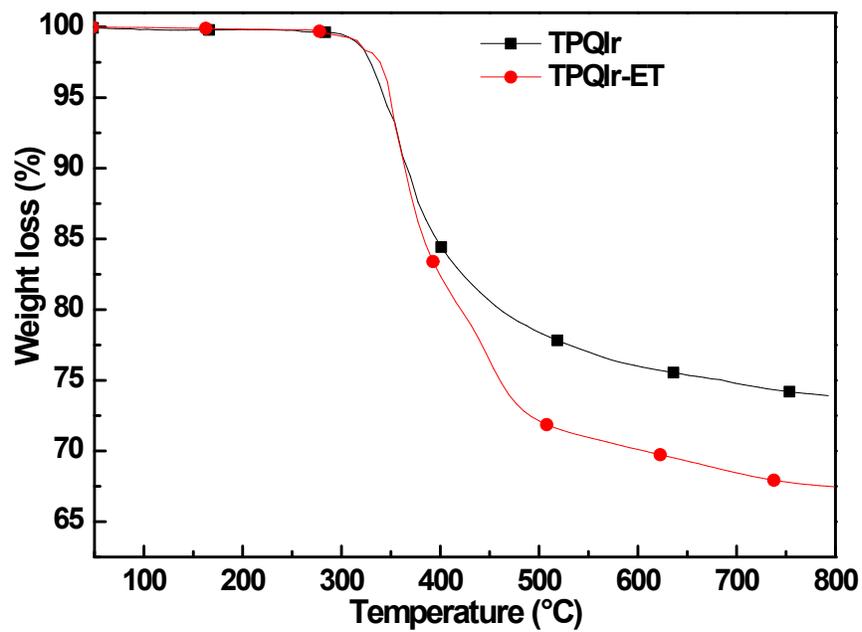


Fig. S1. TGA thermograms of TPQIr and TPQIr-ET measured at 10 °C/min under N₂.

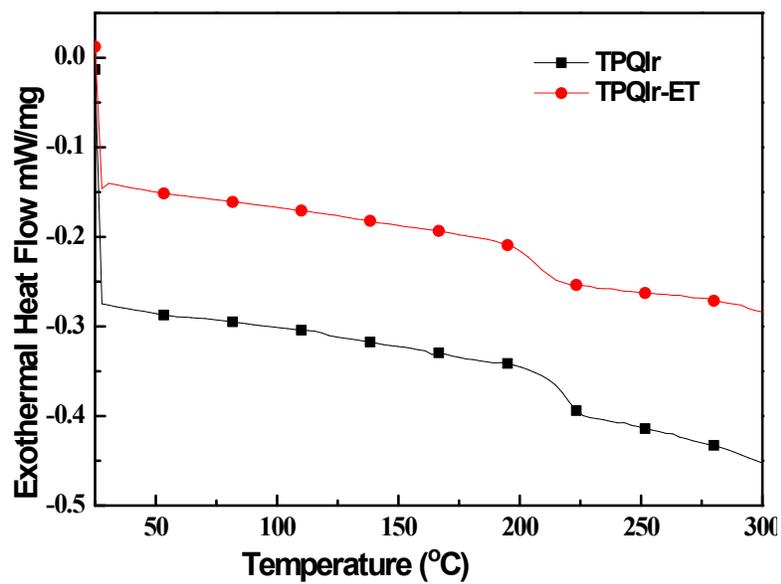


Fig. S2. DSC thermograms of TPQIr and TPQIr-ET measured at 10 °C/min under N₂.

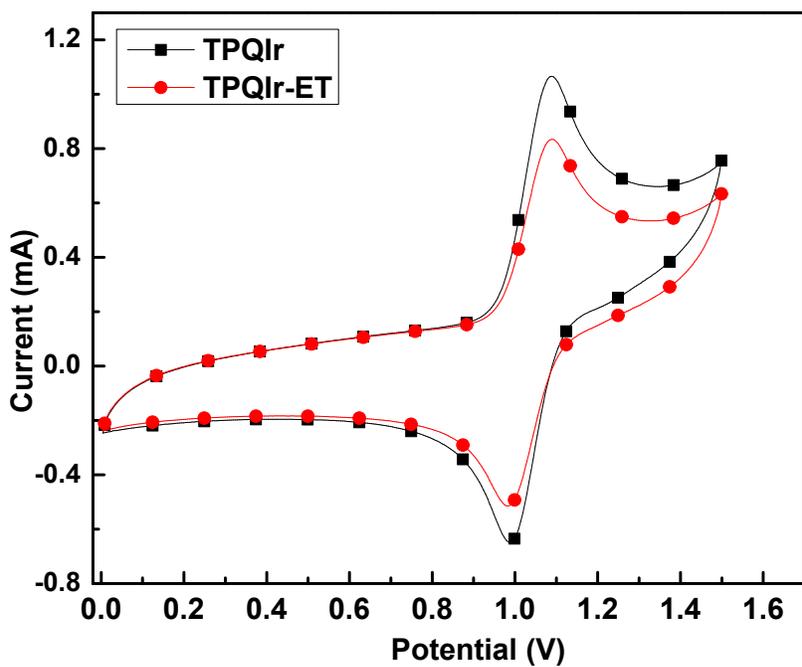


Fig. S3. Cyclic voltammograms of **TPQIr** and **TPQIr-ET** measured in MC at a scan rate of 100 mV/s.

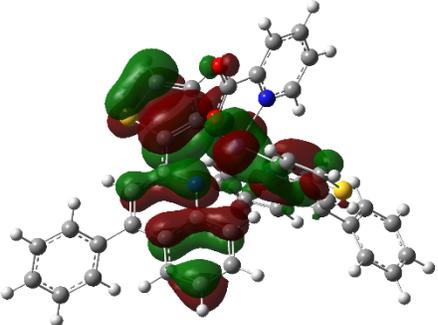
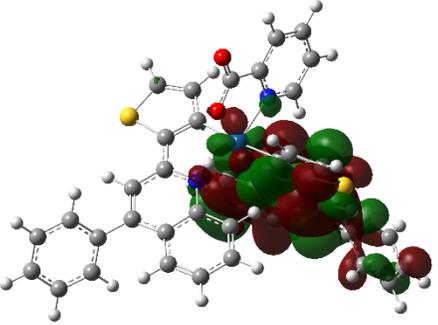
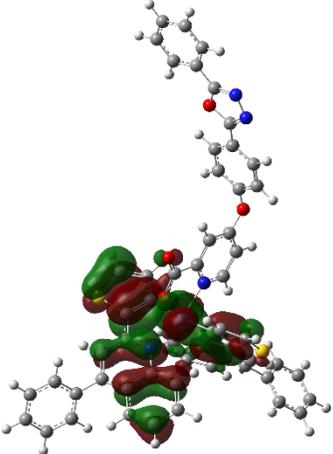
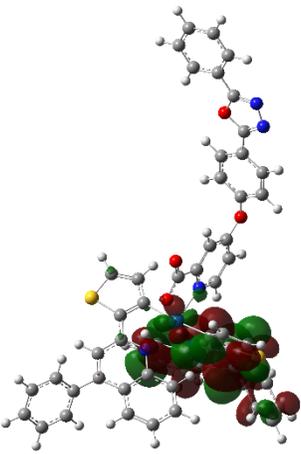
Complex	HOMO	LUMO
TPQIr		
TPQIr-ET		

Fig. S4. Calculated HOMOs and LUMOs of **TPQIr** and **TPQIr-ET**.

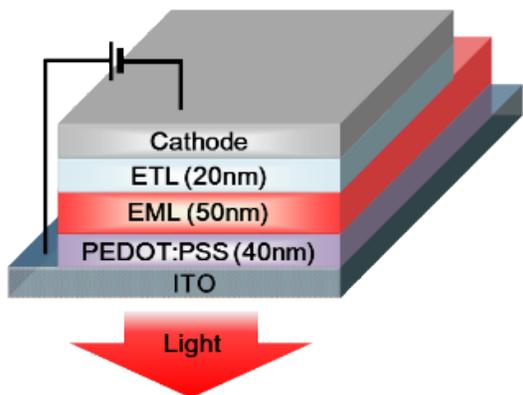


Fig. S5. Schematic illustration of solution-processed deep-red PhOLEDs.

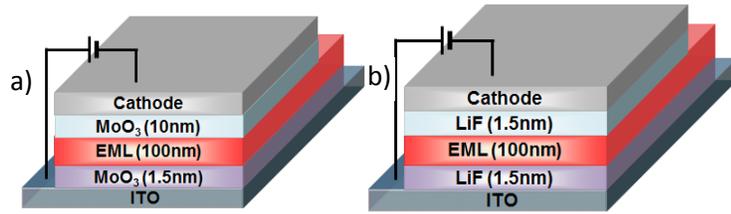


Fig. S6. Device configuration of a) hole [ITO/MoO₃/TPQIr or TPQIr-ET/MoO₃/Al (100 nm)] and b) electron [ITO/LiF/TPQIr or TPQIr-ET/LiF/Al (100 nm)] only devices.

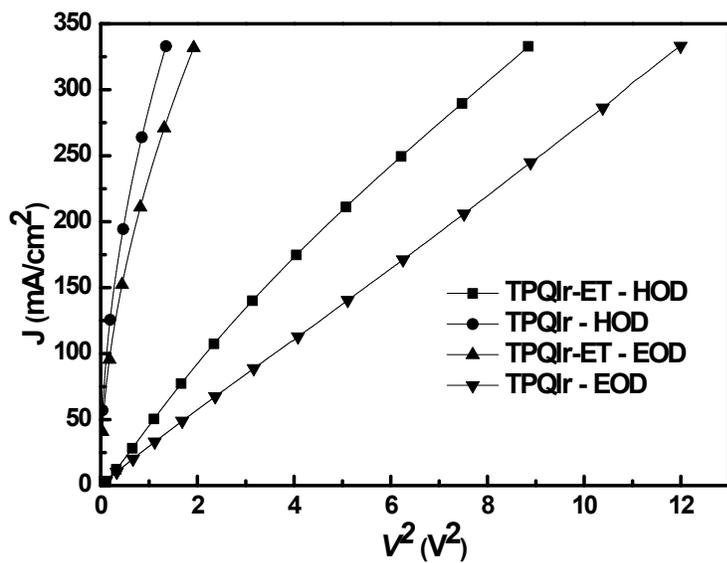


Fig S7. J-V characteristics of hole and electron only devices of TPQIr or TPQIr-ET.

Table S1. Mobility data for **TPQIr** or **TPQIr-ET**

Mobility (μ)	TPQIr	TPQIr-ET
hole (μ_h , cm ² /Vs) ^a	1.3 × 10 ⁻⁴	4.4 × 10 ⁻⁵
electron (μ_e , cm ² /Vs) ^a	4.2 × 10 ⁻⁶	3.5 × 10 ⁻⁴

^athe mobility was calculated from the space charge limited current (SCLC).

Table S2. Comparison of our work with previous literature.

Year	Previous Literature	CIE coordinates (CIE _x , CIE _y)	Luminous/Power Efficiency	EQE
2007	Ref. 3	(0.65, 0.34)	3 lm/W	6.3%
2007	Ref. 4	-	6.4 cd/A /3.2 lm/W	-
2007	Ref. 5	(0.61, 0.38)	12.62 cd/A	8.60 %
2007	Ref. 6	(0.65, 0.33)	12.7 cd/A,	15.1%
2008	Ref. 7	(0.60, 0.29)	1.95 cd/A	-
2008	Ref. 8	(0.64, 0.36)	4.6 cd/A /0.67 lm/W	-
2009	Ref. 9	(0.61, 0.32)	1.66 cd/A	-
2010	Ref. 10	(0.61, 0.38)	4.2 cd/A	3.2%
2010	Ref. 11	(0.62, 0.36)	7.2 cd/A /2.3 lm/W	-
2010	Ref. 12	(0.59, 0.39)	21 cd/A /11 lm/W	14.2%
2011	Ref. 13	(0.64, 0.36)	13.3 cd/A /8.6 lm/W	10.2%
2011	Ref. 14	-	17 cd/A /10 lm/W	8.8%
2012	Ref. 15	(0.65, 0.35)	12 cd/A /7.9 lm/W	10.8%
2013	Ref. 16	(0.65, 0.34)	7.8 cd/A /5.4 lm/W	6.9%
2012	Ref. 17	(0.61, 0.39)	~12.2 cd/A /~5.1 lm/W	~15.3%
2014	Our work	(0.67, 0.32)	~17.20 cd/A /~6.72 lm/W	~20.59%

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