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High performance solution-processed green phosphorescent organic light-emitting diodes with high current efficiency and long-term stability

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Abstract

In this study, we design and synthesize a new host and two new highly efficient green-emitting hetroleptic Ir(III) complexes. These new materials are based on an amide-bridged, trifluromethylsubstituted, phenylpyridine skeleton with a longer alkyl chain as the main ligand, and on a containing phosphine oxide symmetrical dipyridinylphosphinate and asymmetrical phenyl(pyridin-2-yl)phosphineate as ancillary ligands. Their thermal. photophysical, electrochemical, and electroluminescent (EL) properties are fully investigated. The solutionprocessed green devices were fabricated using bis[5-ethylhexyl-8-trifluoromethyl-5Hbenzo(c)(1,5)naphthyridin-6-one](dipyridinylphosphiate)iridium(III) as dopant, and (4'-(9H-carb azol-9-yl)-[1,1'-biphenyl]-4-yl)di-o-tolylphosphine oxide (m-CBPPO1) and TPBi as hosts. The optimized devices containing a symmetrical-type ancillary ligand show excellent EL performance with a maximum current efficiency (CE_{max}) of 68.72 cd/A and a maximum external quantum efficiency (EQE_{max}) of 20.82% without compromising the color purity. This is one of the best reported CE_{max} values with high EQE for solution-processed phosphorescent organic lightemitting diodes (PHOLEDs). To the best of our knowledge, this is the first report on green solutionprocessed PHOLEDs with EQE over 20% by using phosphine oxide functionalized symmetrical type ancillary ligand. Furthermore, these devices with symmetrical Ir(III) complexes show better device stability than that of asymmetrical Ir(III) complexes, which is attributed to the formation of undesirable isomers in asymmetrical complexes.

Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have become very popular and are preferred for displays and energy saving solid-state lighting applications in the past decade.¹⁻⁵ Although green, red and blue triplet emitters have reached commercialization, there is still much room for improvement in efficiency, color purity and stability.⁶ In addition, a highly efficient green triplet emitter for PHOLEDs is crucial to generate an efficient white light⁷⁻⁸. Using electroluminescence (EL) efficient green triplet emitters via a wet process attained the maximum benefit in case of commercial products and cost-effective large-area production.⁹⁻¹³ The wellknown and highly efficient commercial green triplet emitter, fac-tris(2-phenylpyridine)iridium $[Ir(ppy)_3]$, is commonly used in AMOLED displays. However, the color purity of $Ir(ppy)_3$ remains low for commercial display applications.^{10,13,14} Furthermore, several research groups have been trying to improve the color purity and stability of green emitting Ir(III) complexes by introducing bulky groups on the 2-phenylpyrdine (ppy) ligands with ancillary ligands such as acetylacetonate, picolinate, triazolates, tetrazolates, or quinolinolates for solution-processed PHOLEDs.¹⁵⁻¹⁷ Moreover, only a few studies and literature reports have examined phosphine oxide containing ancillary ligands to improve the device performance of green triplet emitter in wet-processed PHOLED.¹² In addition to an efficient green emitter, an appropriate host matching the needs of the emitter is also essential to realize high efficiency.^{18,19} Sufficient generation and efficient the transfer of excitons from host to guest are necessary for achieving high efficiency. Thus, both successful host and guest materials need to be developed.

Hence, in this communication, we report a novel approach to improve the efficiency and color purity by introducing, firstly, symmetrical dipyridinylphosphinate (sym) and asymmetrical phenyl(pyridin-2-yl)phosphinate (asym) as ancillary ligands, secondly, an amide-bridged,

trifluromethyl (- CF_3)-substituted, phenylpyridine skeleton with a longer alkyl chain as the main ligand, and, finally, a guest with a new donor-pi-acceptor (D $-\pi$ -A)- type (4'-(9H-carb azol-9-yl)-[1,1'-biphenyl]-4-yl)di-o-tolylphosphine oxide (m-CBPPO1) as host by combining the hole transporting carbazole unit, biphenyl and electron-transporting di-o-tolylphosphine oxide as D, π and A, respectively. The bulky $-CF_3$ group on the ppy main ligand is likely to reduce selfquenching, which could enhance the device performance of solution-processed PHOLEDs. Furthermore, the presence of the high polar phosphoryl (P=O) bond in the ancillary ligand may improve the electron mobility and effectively reduce triplet-triplet annihilation (TTA) and tripletpolaron quenching (TPO) effects.^{12,19} In addition, the presence of a longer alkyl chain in the metal complexes may reduce the intermolecular interaction and improve solubility towards common organic solvents, thereby producing a uniform surface morphology. The solution-processed green devices were fabricated using bis[5-ethylhexyl-8-trifluoromet hyl-5H-benzo(c)(1,5)naphthyridin-6-one](dipyridinylphosphinate)iridium(III) (sym-Ir1) and bis[5-ethylhexyl-8-trifluoromethyl-5Hbenzo(c)(1,5)naphthyridin-6-one](phenyl(pyridin-2-yl)phosphinate)iridium(III) (asym-Ir2) as dopants, and TCTA ((4,4',4''-tris(N-carbazolyl)triphe nylamine) and TPBi (1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene) as hosts. The optimized devices show excellent EL performance with a maximum current efficiency (CE_{max}) of 60.08 cd/A, a maximum external quantum efficiency (EQE_{max}) of 17.23%, and a notable CIE of (0.30, 0.62) when using sym-Ir1, compared to 47.86 cd/A, 13.62%, and (0.29, 0.62) with asym-Ir1, respectively. The phase alternation by line (PAL) color coordinate system for standard green CIE (x, y) is (0.29, 0.60), which is highly pursued despite this PAL standard being hard to achieve with high efficiencies.²⁰ The obtained CIE(x, y) color coordinates of sym-Ir1 and asym-Ir2 are very close to those suggested by the PAL standard for a green emitter. The results suggest that both Ir(III) complexes show high color purity with

high EQE, which is a prerequisite for high performance displays and lightning applications. Furthermore, our synthesized new host, m-CBPPO1, exhibits a high triplet energy (E_T) of 2.68 eV, which renders it a potential host for green and red phosphorescent dopants. Thus, the new host material *m*-CBPPO1 was incorporated into the emissive layer (EML) as host for two green dopants, sym-Ir1 and asym-Ir2, and achieved superior EL performance, with more enhanced EQE and CE, to that of TCTA host. We achieved a CE_{max} of 68.72 cd/A and an EQE_{max} of 20.82%, without compromising the color purity CIE (0.30, 0.62) in solution-processed PHOLEDs for the first time by using *m*-CBPPO1 as the new host material. The balanced charge transportation and high E_T that are favored for efficient energy transfer from host to dopant ensure high EQE and high color purity. The integration of P=O groups successfully increased the electron mobility, resulting in the balanced charge injection and transportation. Introduction of such new ligands dramatically improves the photoluminance quantum yield and improved EL performance by reducing the formation of additional isomers for sym-complex. Additionally, we achieved a highest EQE and CE for green emitting solution-process PHOLEDs with high color purity. As of now, there have been only few reports on the phosphine oxide functionalized green Ir(III) complexes for solution-processed PHOLEDs and their EQE has been surpassed successfully with our new design concept by suppressing the formation of undesired isomers. To the best of our knowledge, this is the highest reported EQE with high color purity in solution-processed PHOLEDs by using phosphine oxide containing symmetrical ancillary ligands (Table S1, Supporting Information). In addition, we also examined the stability of the Ir(III) complexes and found that sym-Ir1 showed better device stability. This difference in device stability might be due to the formation of undesirable isomers of the asymmetrical Ir(III) complex, asym-Ir2. The above results clearly reveal that the symmetrical ancillary ligand-based Ir(III) complex shows better EL

performance than that of the asymmetrical ancillary ligand-containing Ir(III) complex. We therefore conclude that the Ir(III) complexes with dipyridinylphosphinate ancillary ligands could be useful in improving both the performance and color purity of solution-processed PHOLEDs.

Experimental

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General information

¹H NMR spectra were recorded on a Varian Mercury Plus 300 MHz spectrometer in CDCl₃ using tetramethylsilane as an internal reference. The chemical shifts were reported in ppm relative to the singlet of CDCl₃ at 7.26 ppm for the ¹H NMR. UV-visible and the emission spectra were recorded with a JASCO V-570 and Hitachi F-4500 fluorescence spectrophotometers at room temperature. Transient PL measurements were carried out using compact fluorescence lifetime spectrometer C11367 at room temperature. Thermal analyses were carried out on a Mettler Toledo TGA/SDTA 851e analyzer under N₂ atmosphere at a heating rate of 10 °C min⁻¹. Cyclic voltammetry (CV) studies were carried out with a CHI 600C potentiostat (CH Instruments) at a scan rate of 100 mV s⁻¹ in anhydrous dichloromethane (CH₂Cl₂) solvent with 0.1 M TBAClO₄ as supporting electrolyte. A platinum wire was used as the counter electrode and an Ag/AgCl electrode was used as the reference electrode. The potentials were referenced to the ferrocene/ferrocenium redox couple (Fc/Fc⁺)

Synthesis of sodium dipyridinylphosphinate (sym). A solution of *n*-BuLi (6.40 mL, 16.00 mmol) in diethyl ether (Et₂O, 15 mL) was cooled to -78 °C and 2-bromopyridine (2.52 g, 15.94 mmol) in Et₂O (6 mL) at -78 °C was added quickly and the resulting dark red solution was stirred at -78 °C for 4 h. A solution of phosphorus trichloride (0.74 g, 5.40 mmol) in Et₂O (10 mL) was added slowly over 1 h at -78 °C the solution stirred for 2 h at the same temperature, and the reaction mixture was slowly warmed to RT. The tan-colored mixture was extracted with sulfuric acid

(H₂SO₄) (20 mL, 2N) and the extract made alkaline with saturated sodium hydroxide (NaOH) solution. The solid product was collected and recrystallized from acetone/*n*-hexane (1:1, v/v) to get 0.59 g of pure product with 41.09% yield. Then the product (0.59 g, 2.23 mmol) was dissolved in dimethylsulfoxide (DMSO) (4 mL)/H₂O (4 mL) and H₂O₂ (30%, 0.3 g, 2.67 mmol) was added. The mixture was stirred at RT for 1 h. The solid of sodium hydroxide (NaOH) (0.27 g, 6.69 mmol) was added and the mixture was stirred at RT for 12 h. Then the solvent was evaporated off and the residue was extracted with methanol (MeOH) to give the compound **sym** as a white solid (0.72 g). (yield: 70%). ¹H NMR (300 MHz, D₂O, δ): 8.40 (d, J = 4.8 Hz, 2H), 7.91 (t, J = 6.7 Hz, 2H), 7.89 – 7.82 (m, 2H), 7.43 – 7.34 (m, 2H).

Synthesis of sodium phenyl(pyridin-2-yl)phosphinate (asym). A solution of *n*-BuLi (6.40 mL, 16.00 mmol) in (Et₂O, 15 mL) was cooled to -78 °C and 2-bromopyridine (2.52 g, 15.94 mmol) in Et₂O (6 mL) at -78 °C was added quickly and the resulting dark red solution was stirred at -78 °C for 4 h. A solution of dichlorophenylphosphine (1.44 g, 8.04 mmol) in Et₂O (10 mL) was added slowly and the solution was stirred at -78 °C for 2 h and the reaction mixture was slowly warmed to RT. After reaction completion, the tan-colored mixture was extracted with H₂SO₄ (20 mL, 2N) and the extract made alkaline with saturated NaOH solution. The solid product was collected and recrystallized from acetone/*n*-hexane (1:1, v/v) to get 0.84 g of pure product with 39.59% yield. Then the product (0.84 g, 3.17 mmol) was dissolved in DMSO (5 mL)/H₂O (5 mL) and H₂O₂ (30%, 0.43 g, 3.80 mmol) was added. After the mixture was stirred at RT for 1 h, solid NaOH (0.38 g, 9.52 mmol) was added, the mixture was stirred at RT for 12 h, the solvent was evaporated off, and the residue was extracted with MeOH to give the compound **asym** as a white solid (0.72 g). (yield: 60%). ¹H NMR (300 MHz, D₂O, δ): 8.38 (d, J = 4.8 Hz, 1H), 7.87 – 7.71 (m, 2H), 7.66 – 7.52 (m, 2H), 7.43 – 7.26 (m, 4H).

Synthesis of iridium(III) dimer complex. Ligand (1.5 g, 53.91 mmol) and $IrCl_3 \cdot 3H_2O$ (0.76 g, 134.77 mmol) were added to a mixture of 2-ethoxyethanol and water (40 mL, 3:1 v/v). The reaction mixture was stirred at 140 °C for 20 h under nitrogen (N₂) atmosphere and a yellow precipitate was obtained and cooled to RT. The precipitate was filtered and washed with water (60 mL) and MeOH (10 mL) and subsequently dried under vacuum to afford a yellow solid compound.

Synthesis of bis[5-ethylhexyl-8-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one](dipyr idinylphosphinate)iridium(III) (sym-Ir1) complex. Dimer (1 g, 0.51 mmol) and **sym** (0.30 g, 1.27 mmol) were dissolved in 2-ethoxyethanol (30 mL). After being degassed, the reaction was maintained at 140 °C for 24 h under N₂ atmosphere, the solvent was removed and the crude compound purified by column chromatography with MeOH/EtOAc (6:4, v/v) as eluent to afford **sym-Ir1** as a yellow solid. Further purification by high vacuum train sublimation afforded pure product (yield: 50%). ¹H NMR (300 MHz, CDCl₃, δ): 9.51 (s, 1H), 8.66 (s, 1H), 8.32 (d, 1H), 8.16 (s, 1H), 8.04 (d, 1H), 7.77 (m, 6H), 7.68- 7.52 (m, 2H), 7.42 (d, 2H), 7.16 (s, 1H), 6.69 (d, 1H), 6.46 (d, 1H), 4.35 (s, 4H), 1.98 (s, 2H), 1.36 (d, 16H), 1.01-0.84 (m, 12H). ¹³C NMR (75 MHz, CDCl₃, δ): 161.5, 150.6, 149.1, 149.8, 148.1, 147.2, 145.7, 144.2, 144.8, 140.5, 137.3, 134.2, 132.8, 130.8, 129.6, 127.5, 127.1, 127.6, 126.4, 125.3, 125.8, 124.5, 124.1, 123.5, 123.3, 123.0, 119.8, 118.1, 46.6, 46.4, 46.3, 38.0, 37.9, 28.8, 28.7, 23.9, 23.0, 14.1, 14.1, 14.0, 13.9, 10.9, 10.8, 10.8, 10.7, 10.5. FAB⁺ MS (m/z); [M + H]⁺ calcd. for C₅₂H₅₂F₆IrN₆O4P, 1162.33; found, 1163.34.

Synthesis of bis[5-ethylhexyl-8-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one](phen yl(pyridin-2-yl)phosphinate)iridium(III) (asym-Ir2) complex. Dimer (1.5 g, 0.76 mmol) and asym (0.46 g, 1.91 mmol) were dissolved in 2-ethoxyethanol (30 mL). After being degassed, the reaction was maintained at 140 °C for 24 h under N₂ atmosphere, the solvent was removed and the crude compound purified by column chromatography with EtOAc/MeOH (6:4, v/v) as eluent to

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afford **asym-Ir2** as a yellow solid. (yield: 30%) ¹H NMR (300 MHz, CDCl₃, δ): 9.62 (d, 1H), 8.21 – 8.06 (m, 2H), 7.94 – 7.66 (m, 6H), 7.66 – 7.39 (m, 2H), 7.33 (t, 3H), 7.19 (dd, 3H), 6.74 – 6.42 (m, 2H), 4.34 (t, 4H), 1.98 (s, 2H), 1.42 (dd, 8H), 1.24 (s, 8H), 0.96 – 0.85 (m, 12H). ¹³C NMR (75 MHz, CDCl₃, δ): 161.6, 161.4, 150.2, 149.7, 149.6, 147.9, 147.3, 147.3, 146.7, 144.9, 141.7, 140.5, 137.7, 137.6, 134.9, 134.8, 134.5, 134.2, 132.2, 132.1, 131.7, 131.5, 131.3, 131.1, 130.9, 130.7, 130.1, 129.9, 128.3, 128.1, 127.9, 127.3, 126.3, 124.9, 123.8, 123.5, 123.2, 118.9, 118.2, 46.6, 38.1, 38.0, 37.9, 37.8, 29.6, 28.8, 28.7, 14.1, 14.0, 14.0, 13.9, 10.9, 10.8, 10.7, 10.7. FAB⁺ MS (m/z): [M + H]⁺ calcd. for C₅₃H₅₃F₆IrN₅O₄P, 1161.34; found, 1162.34.

Synthesis of 9-(4-bromophenyl)-9H-carbazole (1). 9H-Carbazole (0.3 g, 1.79 mmol), K₂CO₃ (0.74 g, 5.38 mmol), Cu (0.34 g, 5.38 mmol), and 1-bromo-4-iodobenzene (0.55 g, 1.97 mmol) were mixed in dimethylformamide (10 mL) under N₂ atmosphere. The reaction mixture was heated to 130 °C for 48 h. After reaction completion, the reaction mixture was cooled to RT, extracted with methylene chloride (MC), washed with brine solution, and dried over anhydrous Na₂SO₄. The solvent was distilled off and the solid residue was purified by column chromatography on silica gel using EtOAc/*n*-hexane (1:9, v/v) as eluent to afford **1** as a white solid. (yield: 70%). ¹H NMR (300 MHz, CDCl₃, δ): 7.20–7.37 (m, 6H), 7.44 (d, 2H), 7.69 (d, 2H), 8.07 (d, 2H).

Synthesis of 9-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazole(2). *n*-BuLi (5.21 mL, 13.03 mmol) was added to the solution of **1** (2.8 g, 8.69 mmol) at -78 °C in dry tetrahydrofuran. After the mixture was stirred for 2 h at the same temperature, it was slowly warmed to RT, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.42 g, 13.03 mmol) was added and the mixture was stirred at RT for 48 h. After reaction completion, the reaction mixture was quenched by the addition of water (50 mL). Finally, the organic layer was extracted with MC, washed with brine solution and dried over anhydrous Na₂SO₄. The solvent was distilled off, and

Synthesis of (4-bromophenyl)di-o-tolylphosphine oxide (3). 1-Bromo-4-iodobenzene (1 g, 3.53 mmol), di-o-tolylphosphine oxide²¹ (0.81 g, 3.53 mmol), Pd(PPh₃)₄ (0.20 g, 0.17 mmol), and triethylamine (0.35 g, 3.53 mmol) were dissolved in toluene (30 mL) under N₂ for 10 min and the reaction mixture was stirred at 110 °C for 12 h. After reaction completion, the mixture was cooled to RT and water (50 mL) was added. The resulting mixture was extracted with MC (100 mL) and the organic phase was dried over anhydrous Na₂SO₄. The solvent was evaporated off, and the solid residue was purified by column chromatography on silica gel using EtOAc/n-hexane (5:5, v/v) to afford **3** as a white color solid. (yield: 75%). ¹H NMR (300 MHz, CDCl₃, δ): 7.63-7.60 (m, 2H), 7.49-7.43 (m, 4H), 7.31 (m, 2H), 7.14-7.11 (t, 2H), 7.02-6.97 (m, 2H), 2.50 (s, 6H).

Synthesis of (4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)di-o-tolylphosphine oxide (m-CBPP

O1). (4-Bromophenyl)di-o-tolylphosphine oxide **3** (1.5 g, 3.89 mmol) and 9-(4-(4,4,5,5-tetrame thyl-1,3,2-dioxaborolan-2-yl)phenyl)-9H-carbazol **2** (1.5 g, 4.28 mmol) were mixed in a degassed toluene, ethanol, and water (3:1:1) system and heated to 80 °C for 12 h. After reaction completion, the organic layer was extracted with MC, washed with brine solution and dried over anhydrous Na₂SO₄. The solvent was distilled off, and the solid residue was purified by column chromatography on silica gel using EtOAc/*n*-hexane (4:6, v/v) as eluent to afford *m*-CBPPO1 as a white solid. Further purification by high vacuum train sublimation afforded pure product (yield: 95%). ¹H NMR (300 MHz, CDCl₃, δ): 8.14 (s, 2H), 7.76 (dd, 8H), 7.46 (s, 6H), 7.32 (s, 4H), 7.12 (d, 4H), 2.56 (s, 6H). ¹³C NMR (75 MHz, CDCl₃, δ): 143.4, 143.4, 143.3, 141.6, 139.8, 138.7, 133.0,133.9, 133.8, 132.3, 132.1, 132.0, 132.9, 131.4, 131.0, 130.0, 129.6, 127.4, 127.2, 127.0,

126.0, 125.4, 125.3, 123.4, 120.36, 120.1, 110.7, 22.9, 22.8.

Device fabrication and measurement

As the hole injection layer (HIL), poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) was spin coated at 3000 RPM for 30 s onto the UV-ozone-treated (20 min) indium tin oxide-coated glass substrate, followed by annealing in air for 15 min at 150 °C. The EML was then spin coated onto the HILs and annealed at 110 °C for 20 min in N₂ atmosphere. The electron-transporting layer, LiF and Al were sequentially deposited over the EML layer in a vacuum at a pressure of 5 x 10⁻⁶ Torr. All devices were measured under ambient condition at RT. The concentration of the hosts and dopants in solvents were uniformly 1 wt%. The thickness of each layer was measured by an alpha-step IQ surface profiler (KLA Tencor, San Jose, CA). Different devices with different hosts and dopants were fabricated with different RPM with varying time. So, the measured thickness of EML of different optimized devices were approximately 50, 45, 40 and 40 nm for devices A, B, C and D, respectively. The current density and voltage were controlled with a measurement unit (Keithley, model 236) power source. The luminance, CE, EQE, CIE coordinates (x, y), current density characteristics, and EL spectra were measured by a spectra scan CS-1000 photometer (Minolta).

Results and discussion

Synthesis and characterization

Our group has recently reported phosphine oxide (Ph₂P=O) containing symmetrical ancillary ligands as one of the most promising candidates to achieve highly stable and efficient Ir(III) complexes and PHOLEDs. Here, in order to develop highly efficient solution-processed green PHOLEDs and investigate the effect of symmetrical ancillary ligands on the device

performance, two Ir(III) complexes, sym-Ir1 and asym-Ir2, were designed and successfully synthesized according to the route shown in Scheme 1. The main ligand was synthesized by our previously reported synthetic procedure.¹² Most research groups have tried to introduce asymmetrical ancillary ligands containing electron-transporting groups (nitrogen-containing heterocycles, P=O, oxadiazole, etc.) into the Ir(III) metal complexes to improve the PHOLED device performance, whereas symmetrical ancillary ligands with an electron-transporting material in PHOLEDs still remain unexplored.^{22,23}

Based on the above considerations, we developed two novel green emitting Ir(III) complexes with P=O containing sym and asym ancillary ligands. Furthermore, the new green host material *m*-CBPPO1 was also designed and synthesized by Suzuki-coupling reaction, as shown in Scheme 2, and the intermediates synthesis is shown in Scheme S1 of the supporting information. In addition, *m*-CBPPO1 and sym-Ir1 were sublimed via high vacuum train sublimation to achieve high purity. Fig. S1 (supporting information) shows the molecular structures of sym-Ir1, asym-Ir2 and m-CBPPO1 were confirmed by ¹H, ¹³C NMR and mass spectroscopy. The detailed photophysical, electrochemical and thermal properties of sym-Ir1, asym-Ir2 and m-CBPPO1 are summarized in Table 1. Furthermore, Fig. S2 (supporting information) shows the purity of the synthesized Ir(III) complexes was analyzed by high performance liquid chromatography. Sym-Ir1 shows higher purity level without any shoulder peak, whereas asym-Ir2 shows both a shoulder peak and a main peak. We clearly attributed this to the formation of an undesirable isomer in asym-Ir2 due to the asymmetrical structural arrangement of the ancillary ligand. Purifying the mixture of an undesirable isomer in phosphorescent material synthesis remains a very challenging issue in PHOLED fabrication. This challenge is further complicated by high vacuum train sublimation, which is the most prevalent purification method for these materials and which suffers the major

drawback of potential thermal isomerization occurring in situ during sublimation.^{24,25} Moreover, this purification technique often results in an undesirable isomeric mixture that degrades the PHOLED device performance and lifetime. The results show that the asymmetrical structural arrangement of ancillary ligands is not suitable for PHOLED device fabrication. Furthermore, in order to control the undesirable isomer formation, ligands with a symmetrical structural arrangement are highly preferred for PHOLED devices with improved device performance and longer lifetime.

Photophysical and electrochemical properties

Fig. 1a and 1b shows the UV-vis absorption spectra and photoluminescence (PL) of sym-Ir1 and asym-Ir2 in both dichloromethane (CH₂Cl₂) solution and neat film. The strong absorption bands below 340 nm in the ultraviolet region were assigned to ligand-centered (LC) π - π * transitions in the Ir(III) complexes. The weak absorption bands in the low energy region from 400-450 nm were assigned to an admixture of metal-to-ligand charge transfer ¹MLCT and ³MLCT due to the strong spin-orbit coupling. Both emitters show bright green PL emission in CH₂Cl₂ solution at room temperature (RT) with a main emission peak of 509 nm and a weak shoulder peak at 540 nm. The low-temperature spectra of both Ir(III) complexes at 77K exhibit a well-resolved vibronically structured line shape, which reveals the mixing between the ³MLCT and ³ π - π * levels and, further, that the PL emission of both Ir(III) complexes mainly arises from the LC ${}^{3}\pi \rightarrow \pi^{*}$ excited state, and not from ³MLCT or ligand-to-ligand charge transfer (³LLCT), which always shows featureless emission spectra. In neat films, sym-Ir1 and asym-Ir2 show broad and structureless emission and were red shifted compared to the solution, which clearly attributes the broad emission bands in neat films to aggregation effects.²⁶⁻²⁸ Fig. 1c shows the UV-vis absorption, fluorescence and phosphorescence spectra of *m*-CBPPO1 in 2-methyltetrahydrofuran (2-MeTHF) solution at RT and 77 K. The absorption peak at 292 nm and the absorption band from 318 nm to 337 nm were assigned to π - π * transition of the carbazole unit.²⁹ The fluorescence spectra of *m*-CBPPO1 exhibited a featureless emission peak maximum of 396 nm at RT. The E_T was calculated from the first emission peak of the low-temperature phosphorescence spectrum.

The E_T measured for sym-Ir1, asym-Ir2 and *m*-CBPPO1 were 2.47, 2.48 and 2.68 eV, respectively. Fig. 2 shows molecular orbital distributions obtained from the density functional theory (DFT) calculation for sym-Ir1, asy-Ir2 and m-CBPPO1. The observed dihedral angle between the two phenyl groups was 36.54°. No orbital overlap was observed for deep-blue host *m*-CBPPO, whereas an orbital overlap over the phenyl was observed in m-CBPPO1.²⁹ This is due to the presence of methyl in the biphenyl, which induced the twisted conformation of the deep-blue host, while its absence prompted the orbital overlap. The highest occupied molecular orbital (HOMO) and HOMO-1 of sym-Ir1 and asym-Ir2 are mainly distributed over the Ir atom and main ligand, whereas the lowest unoccupied molecular orbital (LUMO) and LUMO+1 are mostly localized on the main ligand and the ancillary ligand. The HOMO of *m*-CBPPO1 is prevailingly localized on the phenylcarbazole unit, whereas HOMO-1 is mainly localized on the carbazole unit. LUMO is mainly distributed over the phosphine oxide unit and the center of the biphenyl system, whereas LUMO+1 is localized only on the phosphine oxide unit. Fig. S3 (supporting information) shows the calculated electrostatic potential surfaces of sym-Ir1, asym-Ir2 and *m*-CBPPO1 molecules, along with the visualization of the E_T states of Ir(III) complexes. Both Ir(III) complexes show a highly electronegative region in the molecules due to the presence of P=O. The PL quantum yields (PLQYs) of sym-Ir1 and asym-Ir2 were measured in degassed CH₂Cl₂ at RT and the well-known green emitter fac-Ir(ppy)₃ was used as a reference. Sym-Ir1 showed higher quantum yield of 78%, compared to 58% for asym-Ir2. The obtained PLQYs were much higher than that of the standard

green emitter *fac*-Ir(ppy)₃ (40%).^{1,30} Furthermore, the study results reveal that the introduction of a symmetrical ancillary ligand into the Ir(III) metal complex not only improves the device performance but also increases the PLQY.

The triplet lifetime (τ) was measured in deaerated CH₂Cl₂ (1 x 10⁻⁴ M), and is shown in Fig. S4 (supporting information). The measured τ values were 0.36 and 0.37 µs for sym-Ir1 and asym-Ir2, respectively. By assuming that the emitting state of the Ir(III) complex represents the unit efficiency, the radiative (k_r) and non-radiative (k_{nr}) rate constants can be calculated using the relationships, $k_r = \Phi_{PL}/\tau$ and $\Phi_{PL} = k_r/(k_r + k_{nr})$, as given in Table 2. The calculated k_r and k_{nr} values were 2.17 x 10⁻⁶ and 6.1 x 10⁻⁷ for sym-Ir1 complex, and 1.57 x 10⁻⁶ and 1.14 x 10⁻⁶ for asym-Ir2, respectively. Sym-Ir1 exhibited higher k_r and lower k_{nr} than asym-Ir2. The possible contributing factors for sym-Ir1 are its high emission quantum yield and high k_r for achieving high EQE.

The electrochemical behaviors of sym-Ir1, asym-Ir2 and *m*-CBPPO1 were investigated by cyclic voltammetry (CV; Fig. S5, Supporting Information). The two Ir(III) complexes show similar oxidation and reduction behaviors, indicating that they possess frontier molecular orbitals with similar energy levels. The oxidation potential was calculated by the onset peak at (0.76 eV) with respect to Fc/Fc+, which was attributed to the metal-centered Ir^{III}/Ir^{IV} oxidation couple. Therefore, as estimated from the optical E_g , HOMO and LUMO were -5.0 and -2.5 eV, respectively.

To further analyze the charge transporting properties of *m*-CBPPO1, we also calculated the reorganization energies (Marcus theory) for *m*-CBPPO1, which is associated with the transport properties of the charge carriers. From Fig. 3, the reorganization energies for *m*-CBPPO1 were calculated as 0.255 eV for hole hopping and 0.418 eV for electron hopping. The lower reorganization energy for hole hopping as compared to that of electron hopping suggests that it

might have relatively capability for hole transporting than for electron hopping. The calculated ratio of rate constants for *m*-CBPPO1 was much higher than unity, showing a possible charge imbalance. The contributions from HOMO \rightarrow LUMO transition to both the lowest singlet transition (S0 \rightarrow S1) and the lowest triplet transition (S0 \rightarrow T1) were large (91–97.2%), and all the S0 \rightarrow T1 transitions for these complexes were assigned to an MLCT character mixed with some contribution from LLCT and $\pi\pi^*$ features (Table S2, Supporting Information). Figure S6 shows the absorption coefficient spectra for sym-Ir1, asym-Ir2 and *m*-CBPPO1 and the corresponding values are tabulated in Table S3 of the supporting information ³⁰.

Thermal properties

In general, the thermal stability of triplet emitters is crucial for developing highly efficient PHOLED devices. The thermal properties of sym-Ir1, asym-Ir2 and *m*-CBPPO1 were investigated under nitrogen (N₂) atmosphere using thermogravimetric analysis and differential scanning calorimetry (DSC) (Fig. S7 and S8, Supporting Information). The decomposition temperature (T_d) of sym-Ir1 is much higher than that of asym-Ir2, and this difference might be due to the formation of undesirable isomers in asym-Ir2; the relevant data are summarized in Table 1. The DSC analysis of sym-Ir1 and asym-Ir2 shows high glass transition temperature (T_g) in the range of 110-180°C, which supports good film morphological stability at RT. Moreover, sym-Ir1 complex clearly has better thermal stability than that of asym-Ir2. In addition, the T_d of *m*-CBPPO1 was 375 °C with a 5% loss of weight. The thermal stability of *m*-CBPPO1 is increased compared to that of our previous reported bipolar host *m*-CBPPO, which was attributed to the *ortho*- substitution of two methyl groups into the phosphine oxide moiety.²⁹ Furthermore, the high T_g of the host material is most useful for improving the operational stability of PHOLEDs. Notably, we observed the high T_g value of *m*-CBPPO1 during DSC measurement and the no exothermic peak related to

crystallization was observed at temperatures up to 250 °C. These observations indicate that the enhanced thermal stability of the amorphous glass states of *m*-CBPPO1 may arise from more crowded arrangement of two alkyl groups around the P=O atom, and prevents the easy intermolecular packing and hence ready crystallization which could improve the carrier transport property in EML. Furthermore, *m*-CBPPO1 shows $T_g > 100$ °C, which was very high compared to that of commonly used high E_T hosts in PHOLEDs device.^{31,32}

Carrier Transport and Surface Analysis

To study the charge carrier transport property of *m*-CBPPO1, we fabricated single carrier devices and their current density-voltage (*J*-V) curve is shown in Fig. 4. From the previously reported host *m*-CBPPO, we observed a bipolar transporting nature from *m*-CBPPO.²⁹ But the single carrier device results showed that the hole mobility was higher than the electron mobility in *m*-CBPPO1, as was observed from the calculated hole and electron carrier mobilities. The hole and electron mobilities of *m*-CBPPO1 were calculated to be 1.08×10^{-5} and $5.75 \times 10^{-6} \text{ cm}^2/\text{Vs}$, respectively. From these carrier mobilities, we assume that the relatively reduced twist angle of the biphenyl in *m*-CBPPO1 led to the imbalance in the carrier transport of the molecule due to partial overlap of molecular orbitals (HOMO and LUMO), whereas the orbitals were completely separated in bipolar *m*-CBPPO with 87.6° twist.

Atomic force microscopy (AFM) was used to measure the morphology of the EML films and Fig. S8 (supporting information) shows the 3D images of mixed *m*-CBPPO1:TPBi and TCTA:TPBi host films containing the symmetrical and asymmetrical Ir(III) complexes. The AFM test results reveal that the sym-Ir1 complex-based films show lower surface roughness with both mixed hosts. The root mean square (RMS) surface roughness values of the spin-coated films with *m*-CBPPO1:TPBi and TCTA:TPBi as mixed hosts were 326 and 658 nm for sym-Ir1 and 393 and 698 nm for asym-Ir2, respectively. In addition, films with *m*-CBPPO1 in the host matrix exhibited a comparatively better surface morphology compared to that of films with TCTA as host. Homogeneous and smooth morphology without any noticeable aggregation was observed for all four films. This negligible aggregation may lower the TTA effect, and result in better roll-off. Remarkable emission redshifts of these Ir(III) complexes were not observed, which was further confirmed from the absence of aggregation.

Electroluminescent Properties of Solution-Processed PHOLEDs

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Further, to understand the EL properties of the Ir(III) complexes, we fabricated devices A (sym-Ir1) and B (asym-Ir2) with TCTA and TPBi as hosts to compare the performance of the two Ir(III) complexes and the device energy level diagram is shown in Fig. 5. TCTA and TPBi were chosen because of their different carrier transporting properties, which could help achieve a balanced transport of carriers and in turn improve device lifetime and prevent charge accumulation in EML.³³ TCTA and TPBi were mixed in a 1:1 ratio doped with 12 wt% of guest Ir(III) complexes. Fig. 6 shows the current density-voltage-luminance (*J*-V-L) characteristic of devices A and B and their key parameters are summarized in Table 3. Devices A and B showed a turn-on voltage (V_{on}) of 5.3 and 5.7 V, respectively. From Fig. 6b, the CE_{max} and PE_{max} of device A were 55.91 cd/A and 47.92 cd/A at 30 mA/cm² and 18.56 lm/W, compared to 47.79 cd/A and 31.07 cd/A at 30 mA/cm² and 16.68 lm/W for device B, respectively. Device A and B achieved an EQE_{max} of 17.75 and 13.63%, respectively.

In addition, to understand the PHOLED performance of the newly designed host, *m*-CBPPO1, we fabricated devices with *m*-CBPPO1 in place of TCTA. Devices C (sym-Ir1) and D

(asym-Ir2) were fabricated with *m*-CBPPO1 and TPBi (7:3) as a mixed host and their performance as PHOLEDs was evaluated. Fig. 7 shows the *J*-V-L characteristic and the efficiency curves of devices C and D versus luminance. Device C exhibited a higher efficiency than that of device D: CE_{max} , PE_{max} and EQE_{max} of 68.72 cd/A, 29.44 lm/W and 20.82% for C, compared to 54.74 cd/A, 18.26 lm/W and 15.62% for D, respectively.

From Fig. 7c, the EL_{max} spectra of sym-Ir1 and asym-Ir2 complexes were measured at 515 and 514 nm. The EL spectra were similar to the observed PL spectra of the Ir(III) complexes in neat film. CIE coordinates of all four PHOLEDs (A, B, C, and D) were recorded at 30 mA cm⁻² and represent standard green color at (0.306, 0.627), which is very close to the suggested PAL standard for a green emitter. The devices with sym-Ir1 complex (A and C) showed better performance than asym-Ir2 complex devices (B and D), which further demonstrates the advantages of the new host and dopant system. The higher efficiency of the devices with sym-Ir1 complex was attributed to the distinctly higher PLQY. Further, the higher k_r and lower k_{nr} calculated using τ and the shorter lifetime of sym-Ir1 complex may account for the superior performance.

However, roll-off in PHOLEDs usually occurs due to the possible quenching process: TTA and TPQ.³⁴ To further analyze this issue, a TTA model was used to fit the *J*-EQE curves using the equation

$$\frac{\eta}{\eta_0} = \frac{J_0}{4J} \left(\sqrt{1 + 8\frac{J}{J_0}} - 1 \right)$$

where η and η_0 refer to EQE with and without TTA, respectively, and J_0 is the critical current density at $\eta = \eta_0/2$. EQE curves fitted for the complexes were in agreement with the TTA model (Fig. S10, supporting information), indicating the TTA process is responsible for the efficient roll-

off at high current densities. When defined as the current density at $\eta = \eta_0/2$, J_0 for devices with sym-Ir1 was 75.9 mA cm⁻². We also studied the reproducibility of the results by fabricating devices with the optimized structures (device C and D). The results show that the materials have notable repeatability (Fig. S11 a and b). Finally, we also studied the long-term stability of the encapsulated devices (C and D) measured at regular intervals. Fig. 8 shows the time versus EQE and luminance of these devices and their stability was measured. The stability was measured at *J* value of 10 mA cm⁻² for both devices and, the EQE and brightness values are shown in Table S4 (supporting information). The results reveal that sym-Ir1 complex has better stability and longer device lifetime than sym-Ir2 complex. Device D exhibited a faster rate of efficiency decline and retained ~50% of initial EQE, compared to ~67% for device C. This difference in device stability might be due to the formation of undesirable isomers in asym-Ir2 complex and may further explain the rapid degradation observed in device D.

Conclusion

In this work, we have introduced a new host material, (4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4yl)di-o-tolylphosphine oxide (*m*-CBPPO1), and two new green dopants, bis[5-ethylhexyl-8trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one](dipyridinylphosphinate)iridium(III) (sym-Ir1), and bis[5-ethylhexyl-8-trifluoromethyl-5H-benzo(c)(1,5)naphthyridin-6-one](phenyl(pyridin-2-yl)phosphineate)iridium(III) (asym-Ir2) for solution-processable green PHOLEDs. The carbazole/di-o-tolylphosphine oxide hybrid compound of *m*-CBPPO1 showed a high E_T of 2.68 eV. Therefore, solution-processed green PHOLEDs were fabricated and we achieved a CE_{max} of 68.72 cd/A and an EQE_{max} of 20.82% without compromising color purity CIE (0.30, 0.62) in solution-processed PHOLEDs for the first time by using our new host material *m*-CBPPO1. This is the highest reported EQE for solution-processed PHOLEDs using phosphine oxide

functionalized symmetrical type ancillary ligand. Our results have demonstrated the potential for this newly developed host and dopant system to be effectively applied for highly efficient solutionprocessed PHOLEDs. From the device lifetime studies, devices with sym-Ir1 complex showed comparatively better stability, which was attributed to the formation of undesirable isomers in asym-Ir2. These results clearly reveal that the symmetrical ancillary ligand-based Ir(III) complex shows better overall EL performance than the asymmetrical ancillary ligand-based Ir(III) complex. Thus, we summarize that Ir(III) complexes with dipyridinylphosphinate ancillary ligands could be useful in improving both the performance and high color purity of solution-processed PHOLEDs.

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References

- H. Shin, J.-H. Lee, C.-K. Moon, J.-S. Huh, B. Sim, J.-J. Kim, *Adv. Mater.*, 2016, 28, 4920.
- 2. M. Kim, J. Y. Lee, ACS Appl. Mater. Interfaces, 2014, 6, 14874.
- Y. Ohmori, H. Kajii, T. Sawatani, H. Ueta and K. Yoshino, *Thin Solid Films.*, 2001, **393**, 407.
- H. K. Kim, S.-H. Cho, J. R. Oh, Y.-H. Lee, J.-H. Lee, J.-G. Lee, S.-K. Kim, Y.-I. Park, J.-W. Park and Y. R. Do, *Org. Electron.*, 2010, **11**, 137.
- 5. L. Wang, Y. Jiang, J. Luo, Y. Zhou, J. Zhou, J. Wang, J. Pei, Y. Cao, Adv. Mater., 2009,

21, 4854.

- M.-J. Kim, S.-J. Yoo, J. Hwang, S.-J. Park, J.-W. Kang, Y.-H. Kim, J.-J. Kim, S.-K. Kwon, *J. Mater. Chem. C*, 2017, 5, 3107.
- 7. G. Wald, Science, 1945, 101, 653.
- 8. L. T. Sharpe, A. Stockman, W. Jagla, H. J ägle, J. Vision., 2005, 5, 948.
- M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature*, 1998, **395**, 151.
- 10. S. Watanabe, N. Ide and J. Kido, Jpn. J. Appl. Phys., 2007, 46, 1186.
- 11. C. Adachi, M. A. Baldo, M. E. Thompson, S. R. Forrest, J. Appl. Phys., 2001, 90, 504
- V. G. Sree, A. Maheshwaran, H. Kim, H.-Y. Park, Y. Kim, J. C. Lee, M. Song, S.-H. Jin, *Adv. Funct. Mater.*, 2018, 28, 1804714.
- V. Cleave, G. Yahioglu, P. Le Barny, R. H. Friend, N. Tessler, *Adv. Mater.*, 1999, 11, 285.
- 14. F.-C. Chen, G. He and Y. Yang, Appl. Phys. Lett., 2003, 82, 1006.
- J. Qiao, L. D. Wang, J. F. Xie, G. T. Lei, G. S. Wu, Y. Qiu, *Chem. Commun.*, 2005, 0, 4560.
- S. Kappaun, S. Sax, S. Eder, K. C. Möller, K. Waich, F. Niedermair, R. Saf, K. Mereiter, J. Jacob, K. Müllen, E. J. W. List, C. Slugovc, *Chem. Mater.*, 2007, **19**, 1209.
- 17. J. H. Park, T.-W. Koh, J. Chung, S. H. Park, M. Eo, Y. Do, S. Yoo, M. H. Lee, Macro

molecules, 2013, 46, 674.

- T. Jiang, F. Wang, C. Tang, X. Zhang, X. Cao, Y. Tao, W. Huang, *Dyes and Pigm.*, 2018, 150, 130.
- 19. H.-H. Chou, C.-H. Cheng, Adv. Mater., 2010, 22, 2468.
- H. J. Bolink, E. Coronado, S. G. Santamaria, M. Sessolo, N. Evans, C. Klein, E. Baranoff, K. Kalyanasundaram, M. Graetzel, Md. K. Nazeeruddin, *Chem. Commun.*, 2007, 3278.
- 21. A. Sui, X. Shi, Y. Geng, F. Wang, Polym. Chem., 2015, 6, 4872.
- 22. W. Qu, F, Zhang, S. Liu, D. Wei, X. Dong, B. Yu, W. Lu, C. Zhang, S. Li, Z. Li, B. Wei,
 B. Zhai, G. Cao, *Dyes and Pigm.*, 2017, 145, 116.
- 23. M. Sarma, W.-L. Tsai, W.-K. Lee, Y. Chi, C.-C. W, S.-H. Liu, P.-T. Chou, K.-T. Wong, *Chem.*, 2017, 3, 461.
- 24. E. Baranoff, S. Suàrez, P. Bugnon, C. Barolo, R. Buscaino, R. Scopelliti, L. Zuppiroli, M. Graetzel and M. K. Nazeeruddin, *Inorg Chem.*, 2008, 47, 6575.
- E. Baranoff, H. J. Bolink, F D. Angelis, S. Fantacci, D. D. Censo, K. Djellab, M. Grätzel and M. K. Nazeeruddin, *Dalton Trans.*, 2010, **39**, 8914.
- 26. C. Xiang, X. Fu, W. Wei, R. Liu, Y. Zhang, V. Balema, B. Nelson, F. So, Adv. Funct. Mater., 2016, 26, 1463.
- 27. C. Murawski, K. Leo, M. C. Gather, Adv. Mater., 2013, 25, 6801.

- W. Cho, G. Sarada, J.-S. Park, Y.-S. Gal, J. H. Lee, S.-H. Jin, Org. Electron., 2014, 15, 2328.
- 29. A. Maheshwaran, V. G. Sree, H.-Y. Park, H. Kim, S. H. Han, J. Y. Lee, S.-H. Jin, *Adv. Funct. Mater.*, 2018, 28, 1802945.
- A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, J. Am. Chem. Soc., 2003, 125, 7377.
- C.-C. Wang, Y.-M. Jing, T.-Y. Li, Q.-L. Xu, S. Zhang, W.-N. Li, Y.-X. Zheng, J.-L. Zuo,
 X.-Z. You, X.-Q. Wang, *Eur. J. Inorg. Chem.*, 2013, 33, 5683.
- 32. Y. P. Jeon, K. S. Kim, K. K. Lee, I. K. Moon, D. C. Choo, J. Y. Lee, T. W. Kim, J. Mater. Chem. C, 2015, 3, 6192.
- M. Gantenbein, M. Hellstern, L. L. Pleux, M. Neuburger, M. Mayor, *Chem. Mater.*, 2015, 27, 1772.
- 34. B. D. Chin, J. Phys. D: Appl. Phys., 2011, 44, 115103.



Scheme 1. Synthesis of Ir(III) complexes.



Scheme 2. Synthesis of green-host *m*-CBPPO1.

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Fig. 1. UV-vis and PL spectra of (a) sym-Ir1, (b) asym-Ir2 and (c) *m*-CBPPO1 in solution and in film state.



Fig. 2. Contours and contributions of the frontier molecular orbitals of the studied molecules.

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Fig. 3. *m*-CBPPO1 energetics for the reorganization energies for hole and electron transfer calculated by DFT method.

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Fig. 4. *J*-electric field calculated from single carrier devices: (a) hole and (b) electron. J-V calculated from hole-only and electron-only devices for *m*-CBPPO1 (c) hole-only and electron-only.



Fig. 5. Energy level diagram of PHOLEDs using solution-process device fabrication.

Luminance (cd/m

View Article Online DOI: 10.1039/C9TC03559A



Fig. 6. (a) L–V–*J* characteristics, and (b) current efficiency, power efficiency and EQE curves versus luminance of devices A and B.

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Fig. 7. (a) L–V–*J* characteristics, (b) current efficiency, power efficiency and EQE curves versus luminance, and (c) EL spectra of devices C and D.

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Fig. 8. Lifetime of devices measured for complexes sym-Ir1 and asym-Ir2 (with encapsulation).

		$\lambda_{PL}{}^{a)}$		λ_{PL}^{d}				
	T _g /T _d	[nm]			НОМО	LUMO	E _g ^{b)}	E _T
Complexes				[nm]				
	[°C]			[eV]	[eV]	[eV]	[eV]	
		CH_2Cl_2	neat film	77 K				
sym-Ir1	176/374	509	517	498	-5.1 ^{b)} /-5.1 ^{c)}	-2.6 ^{b)} /-1.8 ^{c)}	2.5	2.47^{e} / 2.46^{c})
asym-Ir2	112/300	509	515	498	-5.1 ^{b)} /-5.2 ^{c)}	-2.5 ^{b)} /-1.9 ^{c)}	2.6	2.48^{e} / 2.45^{c})
<i>m</i> -CBPPO1	103/375	396	400	461, 490	-5.7 ^{b)} /-5.4 ^{c)}	$-2.2^{b)}/1.4^{c)}$	3.5	2.68 ^e)/2.57 ^c)

^{a)}Measured in CH₂Cl₂ solution at RT (1×10^{-5} M).

^{b)}HOMO is calculated from the onset oxidation potentials from CV, LUMO = E_g (optical) + HOMO.

^{c)}Calculated from DFT.

^{d)}Measured in 2-MeTHF solution.

 $^{e)}\!E_{T}$ measured from low-temperature phosphorescence spectra.

	fPLQY	^g t	hlz	ⁱ k _{nr} x 10 ⁻⁶	
Complexes	[%]	[µs]	κ _r		
	CH_2Cl_2	CH_2Cl_2	x 10 ⁻⁶		
sym-Ir1	78	0.36	2.17	0.61	
asym-Ir2	58	0.37	1.57	1.14	

Table 2. PLQY, lifetimes and radiative/non-radiative rate constants for Ir(III) complexes.

f)Relative PLQY.

^{g)}Decay time measured in solution under N₂ atmosphere.

 $^{h)}Radiative$ rate constant calculated from k_{r} = $\Phi_{PL}/\tau.$

ⁱ⁾Non-radiative rate constant calculated from $\Phi_{PL} = k_r/(k_r + k_{nr})$.

Page 37 of 38

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$ \begin{array}{c} {} {} {} {} {} {} {} {} {} {} {} {} {}$			-	-						
DeviceEmitter $[nm]$ $[V]$ $[\%]$ $[cd/A]$ $[lm/W]$ $[x,y]$ $[cd/A]$ Asym-Ir1515 $5.3^{a}/8.3^{c}/10.3^{d}$ $17.75^{b}/14.48^{c}$ $55.91^{b}/47.92^{c}$ $18.56^{b}/16.34^{c}$ $(0.305, 0.625)$ 3.63^{c} Basym-Ir2515 $5.7^{a}/8.0^{c}/9.5^{d}$ $13.63^{b}/8.50^{c}$ $47.79^{b}/31.07^{c}$ $16.68^{b}/11.90^{c}$ $(0.307, 0.626)$ 5 Csym-Ir1515 $4.8^{a}/7.4^{c}/9.5^{d}$ $20.82^{b}/15.57^{c}$ $68.72^{b}/52.91^{c}$ $29.44^{b}/18.95^{c}$ $(0.306, 0.627)$ 2 Dasym-Ir2514 $5.1^{a}/8.3^{c}/9.9^{d}$ $15.62^{b}/15.05^{c}$ $54.74^{b}/52.88^{c}$ $18.26^{b}/16.05^{c}$ $(0.299, 0.627)$ 4				λ_{ELmax}	V _{on}	EQE	CE	PE	CIE	Brightness
Asym-Ir1515 $5.3^{a}/8.3^{c}/10.3^{d}$ $17.75^{b}/14.48^{c}$ $55.91^{b}/47.92^{c}$ $18.56^{b}/16.34^{c}$ $(0.305, 0.625)$ $3.56^{b}/16.34^{c}$ Basym-Ir2 515 $5.7^{a}/8.0^{c}/9.5^{d}$ $13.63^{b}/8.50^{c}$ $47.79^{b}/31.07^{c}$ $16.68^{b}/11.90^{c}$ $(0.307, 0.626)$ 5 Csym-Ir1 515 $4.8^{a}/7.4^{c}/9.5^{d}$ $20.82^{b}/15.57^{c}$ $68.72^{b}/52.91^{c}$ $29.44^{b}/18.95^{c}$ $(0.306, 0.627)$ 2 Dasym-Ir2 514 $5.1^{a}/8.3^{c}/9.9^{d}$ $15.62^{b}/15.05^{c}$ $54.74^{b}/52.88^{c}$ $18.26^{b}/16.05^{c}$ $(0.299, 0.627)$ $4.56^{b}/16.05^{c}$	Device	Emitter	[nm]	[V]	[%]	[cd/A]	[lm/W]	[x,y]	[cd/m ²]	
Basym-Ir2 515 $5.7^{a}/8.0^{c}/9.5^{d}$ $13.63^{b}/8.50^{c}$ $47.79^{b}/31.07^{c}$ $16.68^{b}/11.90^{c}$ $(0.307, 0.626)$ 5 Csym-Ir1 515 $4.8^{a}/7.4^{c}/9.5^{d}$ $20.82^{b}/15.57^{c}$ $68.72^{b}/52.91^{c}$ $29.44^{b}/18.95^{c}$ $(0.306, 0.627)$ 2 Dasym-Ir2 514 $5.1^{a}/8.3^{c}/9.9^{d}$ $15.62^{b}/15.05^{c}$ $54.74^{b}/52.88^{c}$ $18.26^{b}/16.05^{c}$ $(0.299, 0.627)$ $430^{c}/45^$		А	sym-Ir1	515	5.3 ^a /8.3 ^c /10.3 ^d)	17.75 ^b /14.48 ^c)	55.91 ^{b)} /47.92 ^{c)}	18.56 ^b /16.34 ^c)	(0.305, 0.625)	33145
Csym-Ir1515 $4.8^{a}/7.4^{c}/9.5^{d}$ $20.82^{b}/15.57^{c}$ $68.72^{b}/52.91^{c}$ $29.44^{b}/18.95^{c}$ $(0.306, 0.627)$ 2 Dasym-Ir2514 $5.1^{a}/8.3^{c}/9.9^{d}$ $15.62^{b}/15.05^{c}$ $54.74^{b}/52.88^{c}$ $18.26^{b}/16.05^{c}$ $(0.299, 0.627)$ 4^{c}		В	asym-Ir2	515	$5.7^{a}/8.0^{c}/9.5^{d}$	13.63 ^{b)} /8.50 ^{c)}	47.79 ^{b)} /31.07 ^{c)}	16.68 ^{b)} /11.90 ^{c)}	(0.307, 0.626)	51421
D asym-Ir2 514 $5.1^{a}/8.3^{c}/9.9^{d}$ $15.62^{b}/15.05^{c}$ $54.74^{b}/52.88^{c}$ $18.26^{b}/16.05^{c}$ (0.299, 0.627) 4		С	sym-Ir1	515	$4.8^{a}/7.4^{c}/9.5^{d}$	20.82 ^{b)} /15.57 ^{c)}	68.72 ^{b)} /52.91 ^{c)}	29.44 ^{b)} /18.95 ^{c)}	(0.306, 0.627)	21454
		D	asym-Ir2	514	5.1 ^{a)} /8.3 ^{c)} /9.9 ^{d)}	15.62 ^{b)} /15.05 ^{c)}	54.74 ^{b)} /52.88 ^{c)}	18.26 ^{b)} /16.05 ^{c)}	(0.299, 0.627)	41944

Table 3. Device performance of green PHOLEDs using sym-Ir1 and asym-Ir2 complexes.

a)Operation voltage (V_{on}) at 1 cd/m².

^{b)}Maximum.

^{c)}At 1,000 cd/m².

^{d)}At 10,000 cd/m².

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Graphical Abstract

Highly efficient (D-\pi-A)-type host and green phosphorescent Ir(III) complexes are introduced for solution-processed green PHOLEDs that achieve high CE with considerably high EQE. Introduction of a symmetrical ancillary ligand to the Ir(III) complex increases the quantum yield and improves the EL performance. Additionally, the devices with symmetrical complexes are more stable than those with asymmetrical complexes.

