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Supporting information

Ancillary ligand-assisted robust deep-red emission in iridium(III)

complexes for solution-processable phosphorescent OLEDs

Hae Un Kim,^{a‡} Ho Jin Jang,^{b‡} Wanuk Choi,^c Minjun Kim,^a Sungjin Park,^a Taiho Park,^{a*} Jun Yeob Lee,^{b*} and K. S. Bejoymohandas^{a*}

^aDepartment of Chemical Engineering, Pohang University of Science and Technology, 77 Cheongam-Ro, Nam-Gu, Pohang, Gyeongbuk 37673, Korea

^bSchool of Chemical Engineering, Sungkyunkwan University 2066, Seobu-ro, Jangan-gu, Seobu-ro, Suwon, Gyeonggi, 16419, Korea

^cDivision of Environmental Science and Engineering, Pohang University of Science and Technology, 77 Cheongam-Ro, Nam-Gu, Pohang, Gyeongbuk 37673, Korea

*E-mail: taihopark@postech.ac.kr, leej17@skku.edu, bejoymohan@postech.ac.kr

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EXPERIMENTAL SECTION

Materials and Physical Measurements. A 400 MHz Bruker NMR spectrometer was used to record the ¹H, ¹⁹F and ¹³C NMR spectra of the iridium(III) complex in CDCl₃ solution. The chemical shifts (δ) of the signals are given in ppm and referenced to the internal standard tetramethylsilane [Si(CH₃)₄]. The signals splitting is abbreviated as follows: s = singlet; d =doublet; t = triplet; dd = doublet of doublets; dq = doublet of quintets; td = triplet of doublets; dd= doublet of doublets; m = multiplet. Coupling constants (J) are given in Hertz (Hz). Magnesium sulphate (anhydrous), sodium carbonate, $IrCl_3 \cdot x(H_2O)$ and 2-picolinic acid were employed in the synthesis of the iridium(III) complex (Ir1-pic and Ir2-pic). These chemicals were purchased from Sigma Aldrich and were used without any further purification. The cyclometalated ligands, namely, 2-(benzo[b]thiophen-2-yl)-4-methylquinoline (L1), 2-(benzo[b]thiophen-2yl)quinoline (L2), were synthesized and fully characterized as per our earlier reports.¹ The synthesis of the iridium dimer complex $[(C^N)_2 Ir(\mu-Cl)]_2$ was carried out by a standard procedure proposed by Watts and co-workers,² using $IrCl_3 \cdot x(H_2O)$ and cyclometalating ligands (L1 and L2) in a mixture of 2-ethoxyethanol and water. Thin-layer chromatography (TLC) was used to monitor the reaction progress (silica gel 60 F254, Merck Co.) and the spots were observed under UV light at 254 and 365 nm. Silica column chromatography was performed using silica gel (230-400 mesh, Merck Co.). The dry solvents are purified using J.C. Metyer solvent drying system. All other reagents are of analytical grade and used as received from Aldrich, Alfa Aesar and Samchun chemicals unless otherwise specified.

Synthesis of iridium(III) dimer complex $[(L1)_2Ir(\mu-Cl)]_2$. IrCl₃·xH₂O (170 mg, 0.57 mmol) and 2-(benzo[b]thiophen-2-yl)-4-methylquinoline (L1) (350 mg, 1.27 mmol) were dissolved in 20 mL of 2-ethoxyethanol and water (3:1) mixture and refluxed at 140 °C for 24 h. After cooling the reaction mixture, the addition of 20 mL of H₂O gave a red precipitate that was filtered and washed with diethyl ether. The crude product was used for the next reaction without further purification (yield: 88%).

Synthesis of iridium(III) dimer complex $[(L2)_2Ir(\mu-Cl)]_2$. IrCl₃·xH₂O (180 mg, 0.66 mmol) and 2-(benzo[b]thiophen-2-yl)quinoline (L2) (350 mg, 1.33 mmol) were dissolved in 20 mL of 2-ethoxyethanol and water (3:1) mixture and refluxed at 140 °C for 24 h. After cooling the reaction

mixture, the addition of 20 mL of H_2O gave a dark red precipitate that was filtered and washed with diethyl ether. The crude product was used for the next reaction without further purification (yield: 85%).

General synthesis procedure for complexes Ir1-pic and Ir2-pic.

A mixture of one equivalent of the corresponding dimer, 2.6 equivalents of picolinic and 11 equivalents of sodium carbonate were stirred overnight in a 3:1 mixture of dichloromethane and ethanol (40 mL) at 60 °C under argon atmosphere. The solvent was removed by evaporation under reduced pressure. The crude product obtained was poured into water and extracted with ethyl acetate (3×50 mL). The combined organic layer was dried over Na₂SO₄. The solvent was removed under reduced pressure to give a crude residue. The crude product was purified by using silica gel column chromatography with CH₂Cl₂: methanol in 9:1 ratio as eluent, giving the desired complex as dark red powder with the following yields: **Ir1-pic** (82%) and **Ir2-pic** (89%). All purified samples were recrystallized and dried before conducting all analysis.

Spectral data of bis[2-(*benzo*[*b*]*thiophen-2-yl*)-4-*methy*]*quinoline*]*iridium*(*III*) (*picolinate*): (*btmq*)₂*Ir*(*pic*) = *Ir1-pic*. Yield: 82%. Anal. Calcd (%) for C₄₂H₂₈IrN₃O₂S₂: C, 58.45; H, 3.27; N, 4.87, S, 7.43, Found: C, 58.59; H, 3.21; N, 4.59, S, 7.55. ¹H NMR 400 MHz, Chloroform-*d*) δ 8.42 (d, *J* = 8.6 Hz, 1H), 8.11 (d, *J* = 5.4 Hz, 1H), 7.81 (t, *J* = 7.3 Hz, 2H), 7.79 – 7.72 (m, 3H), 7.72 – 7.67 (m, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.34 (dt, *J* = 21.3, 7.1 Hz, 3H), 7.19 – 7.06 (m, 2H), 6.97 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.69 – 6.61 (m, 2H), 6.49 (t, *J* = 7.7 Hz, 1H), 6.05 (d, *J* = 8.2 Hz, 1H), 2.89 (d, *J* = 5.6 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 177.06, 166.32, 166.25, 149.33, 149.16, 148.62, 147.46, 147.36, 147.21, 147.09, 145.44, 142.00, 138.93, 131.71, 131.01, 130.39, 128.47, 127.92, 126.53, 126.41, 125.71, 125.45, 125.41, 125.35, 125.06, 124.73, 123.98, 123.83, 123.68, 123.63, 122.42, 122.39, 118.23, 118.03, 91.57, 19.19, 19.15. (MALDI-TOF-MS) [C₄2H₂₈IrN₃O₂S₂]: calcd, m/z = 863.04; found, m/z = 863.13 [M+].

Spectral data of bis[2-(*benzo*[*b*]*thiophen-2-yl*)*quinoline*]*iridium*(*III*) (*picolinate*)*:* (*btq*)₂*Ir*(*pic*) = *Ir2-pic*. Yield: 89%. Anal. Calcd (%) for C₄₀H₂₄IrN₃O₂S₂: C, 57.54; H, 2.90; N, 5.03, S, 7.68, Found: C, 57.34; H, 2.82; N, 4.83, S, 7.78. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.6 Hz, 1H), 8.15 – 8.09 (m, 2H), 7.87 (t, *J* = 8.6 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.73 – 7.60 (m, 4H), 7.39 (ddd, *J* = 8.7, 6.9, 1.6 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.19 – 7.08 (m, 2H), 6.98 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 6.01 (d, *J* = 8.2 Hz, 1H). 6.68 (qd, *J* = 6.3, 5.9, 1.3 Hz, 3H), 6.49 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 6.01 (d, *J* = 8.2 Hz, 1H).

¹³C NMR (151 MHz, CDCl₃) δ 171.86, 167.74, 166.17, 153.56, 152.42, 151.21, 149.69, 148.61, 146.97, 146.82, 146.10, 142.95, 142.77, 140.33, 139.43, 139.31, 138.03, 137.99, 132.18, 129.63, 128.95, 127.67, 127.47, 127.44, 127.30, 126.48, 126.42, 126.20, 125.91, 125.81, 125.56, 125.42, 124.73, 124.21, 124.18, 123.53, 122.62, 122.56, 118.38, 116.99. (MALDI-TOF-MS) [C₄₀H₂₄IrN₃O₂S₂]: calcd, m/z = 834.99; found, m/z = 835.10 [M+].

X-Ray crystallographic analysis. Synchrotron single crystal X-ray diffraction (XRD) data for two different tris-Heteroleptic Iridium complex (**Ir1-pic** and **Ir2-pic**) were measured at -173 °C on the 2D beamline of the Pohang Acceleration Laboratory (PAL; Pohang, Korea) using MX225-HS CCD area detector with monochromated X-ray in a scan width of 1° around omega axis by collecting 360 frames. The raw data were processed and scaled using the programs HKL3000 and DENZO.³ Corrections for the Lorentz and polarization effects, along with an empirical absorption correction, were applied. The space group was determined by the program XPREP,⁴ and the structure was solved by direct methods using SHELXS.⁵ The structure refinement was carried out with full-matrix least-squares refinements on F^2 using the program SHELXL2018.⁵ The data collection conditions and crystallographic parameters are summarized in Table S1.

Thermal analysis. Thermo-gravimetric analyses were performed on an TG/DTA Q500 (TA Instrument) heated from 30 to 900°C in flowing of nitrogen at the heating rate of 10 °C min⁻¹. Temperature at which a 5% weight loss occurred has been considered as the decomposition temperature (T_d). Differential scanning calorimetry was performed using a Perkin-Elmer Pyris DSC 4000 instrument in sealed aluminum pans under nitrogen flow at a heat/cooling rate of 5°C/min. The endothermic peak observed in the second heating cycle has been considered as the glass transition temperature (T_g).

Cyclic voltammetry. Cyclic voltammetry experiments were carried out with a PowerLab/AD instrument model system using three electrode cell assemblies. Platinum wires were used for counter electrodes, a silver wire was used as Ag/Ag⁺ quasi reference electrode and a platinum electrode was used as a working electrode. Measurements were carried out in dichloromethane solution with tetrabutylammonium hexafluorophosphate as supporting electrolyte at a scan rate of 100 mV/s. Concentrations of iridium(III) complex and supporting electrolyte were 5×10^{-3} and 0.2 M, respectively. The ferrocenium/ferrocene couple (FeCp₂⁺/FeCp₂⁰) was used as an internal reference. The energy level of FeCp₂⁺/FeCp₂⁰ was assumed at -4.8 eV to vacuum.⁶ All solutions

for the electrochemical studies were deaerated with pre-purified argon gas prior to the measurements.

Computational methods. The geometrical structures of the singlet ground state (S_0) and the lowest lying triplet excited state (T_1) were optimized by using density functional theory (DFT) based on a method with Perdew-Burke-Ernzerhof (PBE0) hybrid functional with LANL2DZ basis set for the Iridium (Ir) atom and 6-31G* for the rest of the atoms. Frequency calculations were also executed at the same level of theory. The optimizations and the vibrational data confirmed that the structures were true minima on the potential energy surface because there were no imaginary frequencies. On the basis of the optimized ground and excited state geometry structures, the absorption spectral properties in dichloromethane media were calculated by time-dependent density functional theory (TD-DFT) approach with B3LYP/6-31G*. As solvent effects are known to play a crucial role in predicting the absorption and emission spectra, the same was incorporated in the TD-DFT calculations within the PCM framework. The adopted methodology was validated by reproducing the experimental spectra via calculation of the first vertical triplet and singlet excitations. The Swizard program has been employed to evaluate the contribution of singly excited state configurations to each electronic transition.⁷ All calculations were carried out with Gaussian 16 package.⁸

Photophysical characterization. The electronic absorption spectrum of the complex was measured on a Mecasys Optizen Pop UV/vis spectrophotometer. The photoluminescence (PL) spectrum of the iridium(III) complex was recorded on a spectrofluorimeter (FP-6500, JASCO). Emission and excitation spectra were corrected for source intensity (lamp and grating) by standard correction curves. Phosphorescence lifetimes were measured using time correlated single photon counting (TCSPC) system (HAMAMATSU/C11367-31). The luminescence quantum efficiencies in the solution as well as film states were calculated by Quantaurus-QY Absolute PL quantum yield spectrometer (C11347-11).

PhOLED device fabrication. The structure of the fabricated device was Indium tin oxide(ITO) 50nm / poly(3,4-ethylenedioxythiophene) polystyrene sulfonate(PEDOT:PSS) 60nm / Poly vinyl carbazole (PVK) / 4,4'-di(9 H-carbazol-9-yl)biphenyl(CBP) : 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene (TPBi) : Dopant (75:25:X%) / TPBi (45 nm) /LiF (1 nm) / Al (200 nm). HTL and EML processed in solution process by spincoating. PVK solution which was 10mg/ml of chlorobenzene solution was spin-coated at 2000rpm for 30s, and annealed at 150°C for 30min.

EML host was mixed with CBP solution which was 10mg/ml of toluene solution and TPBi solution which was 10mg/ml of toluene solution in 75%:25% respectively. Dopants were **Ir1-pic** and **Ir2-pic** and they were dissolved in chloroform in 5mg/ml. Each dopant was doped in host for 10%, 15%, and 20%. Mixed EML solution was spin-coated at 2000 rpm for 30s, and annealed at 80°C for 20min. ETL, and EIL were thermally evaporated under a high vacuum (~10⁻⁷ torr). ETL was TPBi and thermally deposited at 1 Å/s and LiF at 0.1Å/s. Al was deposited as cathode at 1Å/s under ~10⁻⁶ torr. After deposition of cathode, devices were protected from oxygen and moisture by encapsulating with an encapsulation glass, CaO getter, and epoxy adhesive.



Figure S1 ¹H-NMR spectrum of bis[2-(benzo[b]thiophen-2-yl)-4-methylquinoline] iridium(III) (picolinate): (btmq)₂Ir(pic) (Ir1-pic).



Figure S2 ¹³C-NMR spectrum of bis[2-(benzo[b]thiophen-2-yl)-4-methylquinoline] iridium(III) (picolinate): (btmq)₂Ir(pic) (Ir1-pic).



Figure S3 MALDI spectrum of bis[2-(benzo[b]thiophen-2-yl)-4-methylquinoline] iridium(III) (picolinate): (btmq)₂Ir(pic) (Ir1-pic).



Figure S4 ¹H-NMR spectrum of bis[2-(benzo[b]thiophen-2-yl)quinoline] iridium(III) (picolinate): (btq)₂Ir(pic) (Ir2-pic).



Figure S5 ¹³C-NMR spectrum of bis[2-(benzo[b]thiophen-2-yl)quinoline] iridium(III) (picolinate): (btq)₂Ir(pic) (Ir2-pic).



Figure S6 MALDI TOF MASS spectrum of bis[2-(benzo[b]thiophen-2-yl)quinoline] iridium(III) (picolinate): (btq)₂Ir(pic) (Ir2-pic).



Figure S7 Thermogravimetric curves for complex Ir1-pic and Ir2-pic under nitrogen atmosphere.



Figure S8 Differential scanning calorimetric curves for complex Ir1-pic and Ir2-pic under N₂ atmosphere.



Figure S9 General structure of the complexes shows the label used for selected atoms as used in Table S2.



Figure S10 Crystal Structure of **Ir1-pic**, **Ir2-pic**, **Ir1-tta** and **Ir2-tta** displaying torsion angle between the benzothiophene and quinolinate moity of the cyclometalating ligands. Green arrow serves to indicate the cyclometalating ligand para to the coordinating nitrogen atom of picolinate.



Figure S11 Intermolecular hydrogen bonding interactions between adjacent complex of (a) Ir1-pic and (b) Ir2-pic.



Figure S12 Intermolecular short contact between adjacent complex of (a) **Ir1-pic** and (b) **Ir2-pic**. Blue dotted lines represent carbon carbon contact near sum of vdW distance of aromatic carbon, 3.54 Å. The atom labels and distances indicate shortest contact in each system. (c) Parallel view of **Ir2-pic** packing diagram along c-axis. Carbon atoms are shown in gray, nitrogen in blue, oxygen in red, sulfur in yellow, chlorine in green, and iridium in aqua. Hydrogen atoms are omitted for clarity.



Ir2-pic (singlet)



Figure S13 Singlet and Triplet Optimized geometries of Ir1-pic and Ir2-pic at the PBE1PBE/6-31G* level



Figure S14 Comparison of experimental (red line) and Calculated absorption spectra (TD-DFT) for **Ir1-pic** and **Ir2-pic**. The vertical segments are the calculated absorption wavelengths and their size is proportional to the oscillator strength. The calculated spectral lines are the convolution of the transitions with a gaussian smearing of 0.15eV.



Figure S15 Cyclic voltammograms of redox processes of complexes Ir1–pic, Ir1-tta, Ir2-pic and Ir2-tta (conditions: GC as working electrode, sweep rate v = 100 mV/s, 0.2 M Bu₄NPF₆ in CH₂Cl₂vs) Ag/AgCl. (Ir1-tta and Ir2-tta data values are used from ref 1)



Figure S16 Comparison of the normalized emission spectra of complexes Ir1–pic, Ir1-tta, Ir2-pic and Ir2-tta in the CH₂Cl₂ solution, 5 wt% doped PMMA film at 298 K and freez 2-methyl tetrahydrofuran at 77 K. (Ir1-tta and Ir2-tta spectral data are used from ref 1)



Figure S17 Comparison of lifetime decay profiles of complex Ir1–pic, Ir1-tta, Ir2-pic and Ir2-tta in degassed dichloromethane solution ($c = 2 \times 10^{-5}$ M) and 5 wt% doped PMMA films at 298 K ($\lambda_{exc} = 464$ nm). (Ir1-tta and Ir2-tta lifetime values are used from ref 1)



Figure S18 Singlet and triplet optimized geometries along with spin densities of the triplet excited states for complexes Ir1–pic, Ir1-tta, Ir2-pic and Ir2-tta obtained at the B3LYP/LANL2DZ/6-31G(d,p) level of theory (isosurface value = 0.003, red for positive and yellow for negative, Ir1-tta and Ir2-tta geometries are used from ref 1).



Figure S19 Comparison of experimental FT-IR spectrum with the IR intensity obtained from the optimized triplet and singlet geometries of **Ir1-pic**, **Ir1-tta**, **Ir2-pic** and **Ir2-tta**. (**Ir1-tta** and **Ir2-tta** values are used from ref 1)

	Ir1-pic	Ir2-pic
Formula	C ₄₂ H ₂₈ Ir N ₃ O ₂ S ₂	C ₄₀ H ₂₄ Ir N ₃ O ₂ S ₂ , 0.5 (C ₆ H ₁₄), 0.992 (CH ₂ Cl ₂)
Formula weight	862.99	962.95
Temp (K)	100	100
Wavelength (Å)	0.62000	0.62000
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	I 2/a
Hall group	-P 2ybc	-I 2ya
Crystal size (mm ³)	$0.070\times0.040\times0.020$	$0.120\times0.120\times0.050$
<i>a</i> [Å]	25.602 (5)	19.425 (4)
<i>b</i> [Å]	15.186 (3)	17.305 (3)
<i>c</i> [Å]	17.506 (4)	22.923 (10)
α [°]	90.00	90.00
β [°]	91.37	109.86
γ [°]	90.00	90.00
<i>V</i> [Å ³]	6804 (2)	7247 (4)
Z	8	8
$ ho_{ m calc}[m g/cm^3]$	1.685	1.765
μ (Mo K α) [mm ⁻¹]	2.865	2.791
<i>h</i> , <i>k</i> , <i>l</i> max	38, 23, 24	30, 26, 36
Total reflections	43085	26838
Unique reflections	22369	14396
$R_{\rm F}, R_{\rm w}({\rm F}^2) [{\rm I} > 2\sigma({\rm I})]$	0.1327, 0.2588	0.0481, 0.1221
GOF on F^2	1.094	1.080
CCDC	1873937	1873938

 Table S1 Crystallographic and refinement data for complexes Ir1-pic and Ir2-pic.

	Ir1-pic		^a Ir1-tta			Ir2-pic		^a Ir2-tta				
	S ₀	T_1	Exp	S ₀	T ₁	Exp	S ₀	T_1	Exp	S ₀	T ₁	Exp
Bond length ((Å)											
Ir-L	2.14502	2.16402	2.133	2.15528	2.11576	2.145	2.14624	2.16554	2.153	2.15492	2.11375	2.159
Ir-X	2.14980	2.14104	2.140	2.15693	2.06156	2.136	2.14805	2.13947	2.148	2.15691	2.06003	2.113
Ir-N1	2.08200	2.07791	2.118	2.07889	2.08585	2.101	2.08058	2.07627	2.074	2.07917	2.08522	2.065
Ir-N2	2.08719	2.07054	2.093	2.07810	2.08034	2.086	2.08699	2.07022	2.093	2.07611	2.08002	2.060
Ir-C1	1.98949	1.98131	1.981	1.98156	1.98855	1.970	1.98921	1.98089	1.979	1.98126	1.98929	1.960
Ir-C5	2.00194	1.97013	1.952	1.98085	1.98314	1.975	2.00120	1.96966	1.996	1.98083	1.98296	1.973
Bond angle(d	eg)											
N1-Ir-C1	80.095	81.167	80.10	80.472	81.010	80.18	80.201	81.241	79.86	80.595	81.064	79.58
N2-Ir-C5	80.173	81.225	80.04	80.497	80.968	80.13	80.269	81.294	79.84	80.612	81.074	80.45
L-Ir-X	76.645	76.504	76.32	84.781	84.682	86.55	76.672	76.497	76.00	84.843	84.537	86.09
N1-Ir-N2	177.382	177.862	176.30	179.039	178.669	179.23	177.296	177.753	177.52	178.876	178.577	179.85
C5-Ir-L	167.762	169.651	170.53	174.154	178.280	174.87	167.715	169.500	168.73	173.925	178.440	175.92
C1-Ir-X	174.098	174.169	172.03	174.642	171.589	173.63	174.036	174.128	173.21	174.739	171.303	176.40
Interligand A	ngle (deg)											
N1-Ir-L	83.877	82.300	98.19	80.301	79,707	97.11	83.878	82.340	82.15	80,194	79.923	79.44
N1-Ir-C5	97.598	98.192	101.78	100.386	100.309	80.18	97.498	98.172	97.71	100.473	100.288	99.42
Dihedral Angle (deg)												
C1-C2-C3-	177.599	179.863	175.60	179.831	177.585	179.20	177.463	179.831	177.26	179.981	178.403	179.44
C4 C5-C6-C7- C8	177.242	176.977	178.80	178.949	179.716	177.46	177.657	177.325	172.22	178.399	179.372	178.66

Table S2 Selected bond distances, bond angles and dihedral angles from the optimized ground (S_0) and triplet state (T_1) geometry for the complexes Ir1-pic, Ir1-tta, Ir2-pic and Ir2-tta together with the experimental values.

^aValues from ref 1.

Table S3 Optimized geometries, HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1 and LUMO+2 contour plots of **Ir1-pic** and **Ir2-pic** at the PBE1PBE/6-31G* level



Complex	Orbital	E (eV)	Iridium	Substituted Quinolinate moiety	Benzothiophene moiety	Ancillary (pic)
Ir1-pic	HOMO-3	-5.883	13.58	23.25	53.97	9.2
	HOMO-2	-5.752	34.1	15.54	38.78	11.58
	HOMO-1	-5.385	3.49	25.35	67.53	3.62
	НОМО	-4.835	26.44	17.76	53.45	2.36
	LUMO	-1.958	6.84	64.86	21.43	6.87
	LUMO+1	-1.923	4	66.6	19.44	9.96
	LUMO+2	-1.596	4.36	12.5	2.17	80.97
	LUMO+3	-1.131	1.16	25.42	5.42	68
Ir2-pic	HOMO-3	-5.95	14.86	21.95	52.19	11
	HOMO-2	-5.824	31.23	13.99	43.91	10.87
	HOMO-1	-5.451	3.29	24.47	68.52	3.72
	НОМО	-4.904	26.14	17.79	53.75	2.32
	LUMO	-2.039	7.08	64.9	21.57	6.45
	LUMO+1	-2	4.39	66.88	19.76	8.97
	LUMO+2	-1.655	4.26	11.24	1.81	82.69
	LUMO+3	-1.199	1.03	30.79	7.61	60.58

Table S4 Calculated energy levels of the HOMO, HOMO-1, HOMO-2, LUMO, LUMO+1, and LUMO+2 and percentage of contribution of iridium metal (Ir), benzothiophenequinolinate derivatives and picolinate (pic) ligands.

	State	$\lambda(nm)/E(eV)$	Oscillator	Main configuration	Assign	λ_{exp} (nm)
Ir1-pic	$S_{1(triplet)}$	652/1.90	f=0.00001	H→L (58%)	btp/ Ir \rightarrow CH ₃ Qn (ILCT/ MLCT)	630
	$S_{2(triplet)}$	643/1.92	f=0.00001	H→L+1 (57%)	btp/ Ir \rightarrow CH ₃ Qn (ILCT/ MLCT/LLCT)	
	$S_{3(singlet)}$	520/2.38	f=0.0387	H→L (70%)	btp/ Ir \rightarrow CH ₃ Qn (MLCT/ ILCT)	522
	$S_{4(singlet)}$	516/2.40	f=0.1379	H→L+1 (70%)	btp/ Ir \rightarrow CH ₃ Qn (MLCT/ LLCT)	
	$S_{8(singlet)}$	458/2.70	f=0.0122	H→L+2(70%)	btp/ Ir \rightarrow pic (MLCT/ LLCT)	
	S _{11(singlet)}	415/2.98	f=0.1442	H-1→L (68%)	$btp \rightarrow CH_3Qn (ILCT)$	414
	S _{12(singlet)}	412/3.01	f=0.0717	H-1→L+1 (68%)	$btp \rightarrow CH_3Qn (LLCT)$	
	S _{16(singlet)}	386/ 3.20	f=0.0903	H-2→L (60%)	btp/ pic/ Ir \rightarrow CH ₃ Qn (MLCT/ LLCT/ILCT)	
	S _{17(singlet)}	380/ 3.26	f=0.0019	H-2→L+1 (55%)	btp/ pic/ Ir \rightarrow CH ₃ Qn (ILCT/ MLCT/LLCT)	
	$S_{18(singlet)}$	378/3.28	f=0.0294	H→L+3 (66%)	btp/ Ir \rightarrow pic (MLCT/ LLCT)	377
	$S_{19(singlet)}$	372/3.33	f=0.0102	H-1→L+2 (63%)	$btp \rightarrow pic (LLCT)$	
	S _{20(singlet)}	366/3.38	f=0.0115	H-3→L (45%)	btp/ Ir \rightarrow CH ₃ Qn (MLCT/ ILCT)	337
Ir2-pic	$S_{1(triplet)}$	659/1.88	f=0.00001	H→L (58%)	btp/ Ir \rightarrow Qn (ILCT/ MLCT)	634
	S _{2(triplet)}	650/1.90	f=0.00001	H→L+1 (57%)	btp/ Ir \rightarrow Qn (ILCT/ MLCT/ LLCT)	
	$S_{3(singlet)}$	524/2.36	f=0.0284	H→L (70%)	btp/ Ir \rightarrow Qn (ILCT/ MLCT)	530
	$S_{4(singlet)}$	520/2.38	f=0.1351	H→L+1 (69%)	btp/ Ir \rightarrow Qn (ILCT/ MLCT/ LLCT)	
	$S_{8(singlet)}$	456/2.71	f=0.0099	H→L+2 (69%)	btp/ Ir \rightarrow Qn/pic (ILCT/ MLCT/ LLCT)	
	S _{11(singlet)}	417/2.96	f=0.1470	H-1→L (67%)	$btp \rightarrow Qn (ILCT/LLCT)$	420
	S _{12(singlet)}	414/2.99	f=0.0673	H-1→L+1 (68%)	$btp \rightarrow Qn (ILCT/LLCT)$	
	S _{16(singlet)}	387/ 3.19	f=0.0605	H-2→L (59%)	btp/ Ir \rightarrow Qn (ILCT/ MLCT)	
	S _{17(singlet)}	380/ 3.26	f=0.0063	H-2→L+1 (53%)	btp/ Ir \rightarrow Qn (ILCT/ MLCT/ LLCT)	
	S _{18(singlet)}	378/3.28	f=0.0314	H→L+3 (64%)	btp/ Ir \rightarrow Qn/pic (ILCT/ MLCT/ LLCT)	380
	S _{19(singlet)}	371/3.34	f=0.0077	H-1→L+2 (65%)	$btp \rightarrow Qn/pic (ILCT / LLCT)$	
	S _{20(singlet)}	367/3.37	f=0.0179	H-3→L (39%)	btp/ Ir \rightarrow Qn (ILCT/ MLCT/ LLCT)	

Table S5 Calculated Absorption of Ir1-pic and Ir2-pic in CH₂Cl₂ Media at TD-B3LYP Level together with Experimental Values

		Ir1-pic	^a Ir1-tta	Ir2-pic	^a Ir2-tta
	$E_{oxd}(V)$	0.98	0.72	1.03	0.76
	$E_{red}(V)$	-1.47	-1.64	-1.45	-1.61
	HOMO (eV)	-5.09	-4.83	-5.14	-4.87
Electrochemical properties	LUMO (eV)	-2.92	-2.68	-2.99	-2.75
	$E_{g}(elec) (eV)$	2.46	2.37	2.49	2.38
	E(opt) (eV)	2.17	2.15	2.15	2.12
	Triplet energy (eV)	1.99	1.99	1.98	1.96
Decomposition temperature	T_d (°C)	435	333	350	340
Absorbance at 298 K in CH ₂ Cl ₂ Solution	Absorption λ_{max} (nm) ($\epsilon \times 10^3$ M ⁻¹ cm ⁻¹)	293 (38), 337 (21), 358 (20), 523 (8.4), 632 (0.2)	294 (47), 336 (32), 359 (28), 522 (9), 640 (0.2)	294 (35), 340 (20), 359 (18), 531 (7.6), 634 (0.2)	295 (46), 338 (32), 361 (27), 531 (8), 649 (0.2)
	$\lambda_{max} (nm)$	651	655	660	665
	$\Phi_{ m PL}$	0.485	0.02	0.372	0.081
Emission at 298 K in CH_2Cl_2	$\tau_{obs}(\mu s)$	5.22	0.11	4.25	0.67
Solution	$k_r 10^5 \ S^{-1}$	0.09	0.18	0.08	0.12
	k _{nr} 10 ⁵ S ⁻¹	0.1	8.9	0.14	1.44
	^b E _{em(0-0)} nm)	636	638	641	645
Expited state properties at 77K	$^{c}\Delta v_{1/2} (cm^{-1})$	462	411	415	456
Excited-state properties at 77K	$^{\mathrm{d}}\hbar\omega_{\mathrm{M}}~(\mathrm{cm}^{-1})$	1384	1408	1390	1439
	^e S _M	0.24	0.2	0.22	0.2
	$\lambda_{max} nm$)	651	655	660	665
Emission at 5 wt % doned PMMA	$\Phi_{ ext{PL}}$	0.492	0.24	0.39	0.305
film	$ au_{ m obs}(\mu s)$	4.59	1.85	3.88	2.38
111111	k _r 10 ⁵ S ⁻¹	0.1	0.13	0.1	0.13
	$k_{nr} 10^5 \ S^{-1}$	0.11	0.41	0.16	0.29

 Table S6 Comparison of electrochemical, thermal and photophysical properties of Ir1-pic, Ir1-tta, Ir2-pic and Ir2-tta.

^aValues from ref 1, ^bObtained from the peak emission wavelength in 2-methyl tetrahydrofuran at 77 K. ^cFWHM for the (0–0) band obtained from the emission spectra at 77 K. ^dFrom the energy difference of the first two emission peaks at 77 K. ^eThe Huang–Rhys factor (S_M) was estimated from the peak heights and energies of the first two peaks of the emission spectra at 77 K [$S_M = (I_{0,1}/I_{0,0})$ ($\overline{v}_{0,0}/\overline{v}_{0,1}$)].

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