

Supplementary Information

Ancillary ligand increases the efficiency of heteroleptic Ir-based triplet emitters in OLED devices

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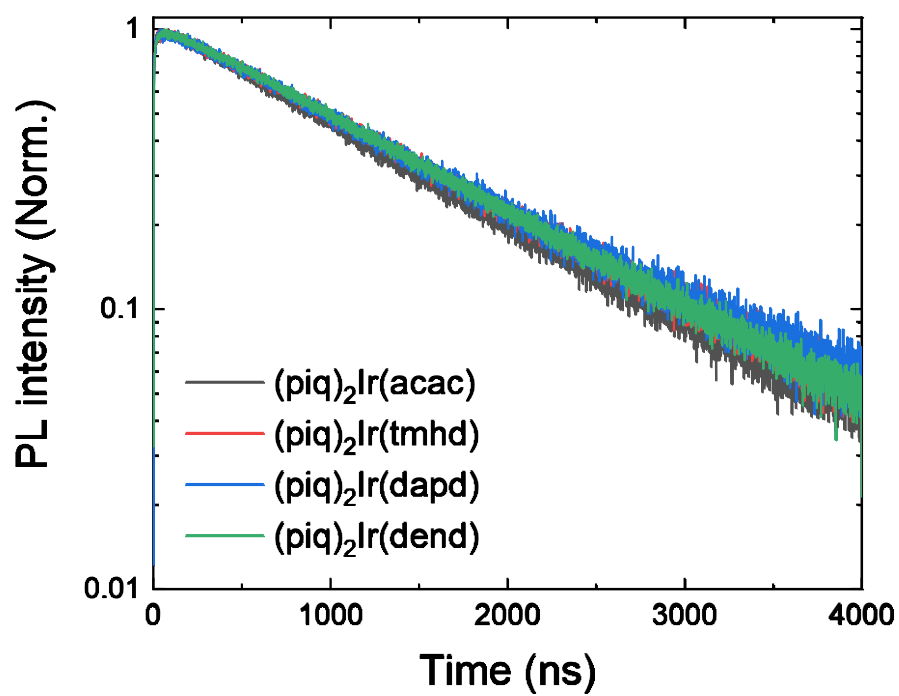
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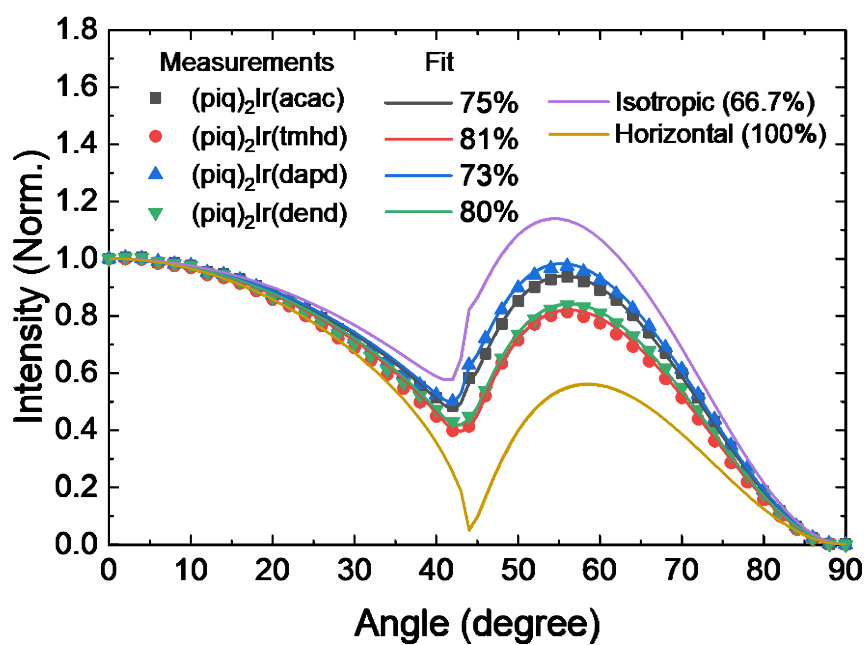
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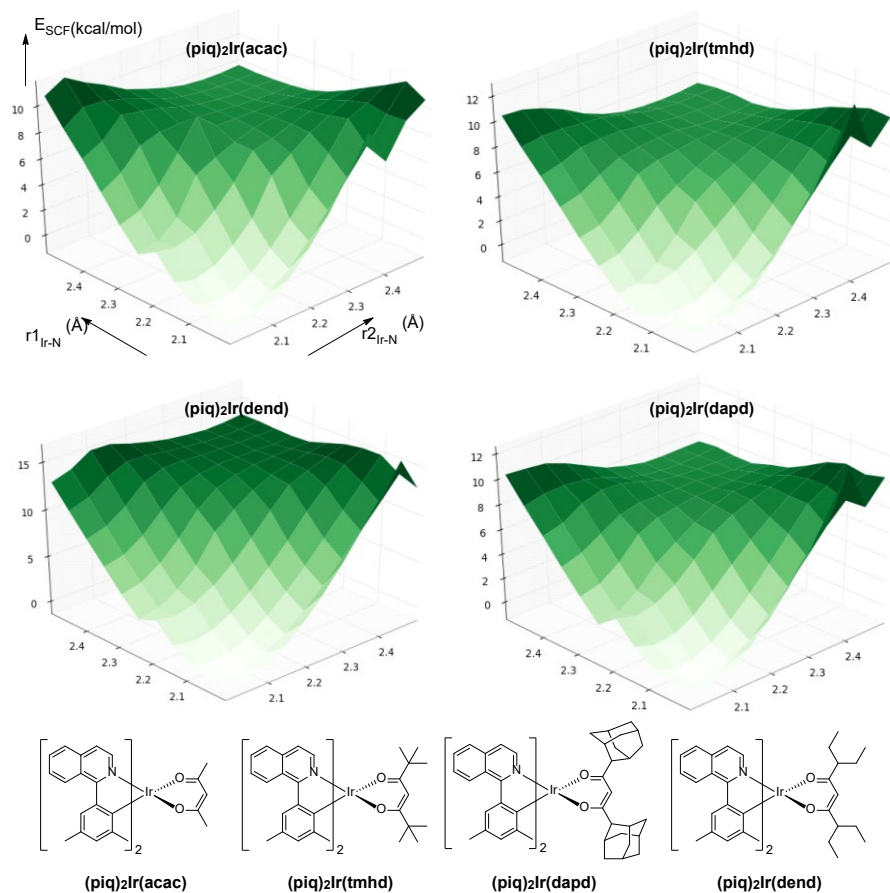
Supplementary Figures



Supplementary Figure 1 | Time-resolved PL decay curves



Supplementary Figure 2 | Angle-dependent PL intensities and fitting data



Supplementary Figure 3 | The relaxed coordinate scan results of four dopants

Supplementary Tables

DFT-optimized structure's energy components

Supplementary Table 1 | Computed energy components for DFT-optimized structures.

	E(SCF)/(eV) LACVP**	E(SCF)/(eV) cc-pVTZ(-f)
acac-S₀	-50904.508	-50917.344
acac-T₁	-50902.473	-50915.355
acac-T₂	-50902.172	-50914.902
tmhd-T₁	-57316.414	-57330.938
tmhd-T₂	-57316.051	-57330.457
dend-T₁	-59454.523	-59469.535
dend-T₂	-59453.898	-59468.84
dapd-T₁	-69948.523	-69965.977
dapd-T₂	-69948.133	-69965.508

Benchmark of functionals

Supplementary Table 2 | The calculated energy gaps of Ir(III) red dopants in various functionals

$\Delta E(T_2-T_1)$ (kcal/mol)	(piq) ₂ Ir(acac)	(piq) ₂ Ir(tmhd)	(piq) ₂ Ir(dapd)	(piq) ₂ Ir(dend)
M06	10.45	11.09	10.82	16.03
B3LYP	12.71	12.43	12.25	15.31
B3LYP-D3	24.05	23.31	23.25	27.28
PBE0	24.14	25.34	25.04	28.02

Cartesian coordinates of the optimized geometries

Supplementary Table 3 | Cartesian Coordinates of the Optimized Geometries.

=====	C	-4.612878323	2.073492765	-2.815419197
acac-S ₀	H	-3.021486521	-0.774721503	-1.791321754
=====	H	-5.335073948	0.130780175	-2.134935856
Ir	N	1.552441597	-0.025487367	-0.989003241
N	C	2.124295712	0.744950533	-0.037020743
C	C	1.926201582	-1.323952317	-1.176595926
C	C	3.088302612	0.261943758	0.797771752
C	C	2.779122591	-1.951729059	-0.212993905
C	C	3.411339283	-1.123107433	0.763098419
C				
-0.215958565				
0.436672270				
-1.915432572				
-2.098595381				
0.903702080				
-2.557803392				
-2.181546926				
2.149422646				
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-3.205173492				
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-2.211063147				
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-3.141947746				
-4.458876610				
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-2.385388136				

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acac-T1

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acac-T2

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tmhd-T1

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dapd-T2

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C	-4.315142632	5.256533623	1.700672626	H	-1.095357299	4.410224438	0.676494420

Supplementary Discussion

Benchmark of functionals To ensure our calculation results are not only valid for the given DFT methods, we re-calculated all structures using PBE0, B3LYP and B3LYP-D3. The calculated energy gaps between two triplet states with different functionals are summarized in Supplementary Figure 2. The results showed that our conclusions can be reproduced with any of these methods: In all cases, the (piq)₂Ir(dend) exhibits a meaningfully large energy gap compared with other dopants indicating that the direct bulkiness of 3,7-diethylnonane-4,6-dione(dend) ligand is valid.

Conformational Isomers Search on the dend ligand To understand the different dend ligand effects as a function of the conformations, we calculated gauche conformers of 3-pentyl substituents in the dend ligand. Not surprisingly, the calculated 3MLCT structure and 3MC structure of gauche conformers have 4.8 kcal/mol and 2.6 kcal/mol higher energies, respectively, than the anti-conformer. Of course, this leads to the slightly decreased energy gap between the two-state of 14.7 kcal/mol, but it is still higher than what was found with the other ligands. The triplet state of the other gauche conformer is higher in energy than the anti conformer with a similar energy gap of 16.4 kcal/mol. These results suggest that the effect of the dend ligand still exists in its various conformational isomers.

Relaxed coordinate scan of dopants To understand whether the transition state between 3MLCT and 3MC state exist or not, we performed the linear scan calculation by elongating two Ir–N bonds in four dopants. The calculated results clearly show that the transition state between 3MLCT and 3MC state cannot be found through a simple PES scan, although two excited states are clearly optimized having the highest energy gap in the (piq)₂Ir(dend) dopant.

Supplementary Methods

General Commercially available chemicals were used without further purification after purchase from Sigma-Aldrich and Tokyo Chemical Industry (TCI). NMR spectra recorded on Bruker ASCEND 500 (500MHz for ^1H NMR, 125 MHz for ^{13}C NMR). Chemical shift are given in ppm with the residual solvent signal as internal standard (dichloromethane at 5.32 ppm and 54.00 ppm, respectively). Mass spectrometry (MS) analysis was performed with LCMS-IT-TOF.

Synthesis of $(\text{piq})_2\text{Ir}(\text{acac})$ The mixture of $(\text{piq})_2\text{Ir}$ dimer 1.37g (1.0 mmol), Na_2CO_3 1.05g (9.9 mmol), acac 0.99g (9.9 mmol) and 2-ethoxyethanol (50 mL) was stirred at 80 °C for 12 hours. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (100 mL). The combined organic phases were washed with brine, dried over anhydrous MgSO_4 , filtered, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography (CH_2Cl_2 : Hexane = 4:6) and dried under vacuum to afford desired products as red solid (0.45g, 30%). ^1H -NMR (500MHz, CD_2Cl_2): δ (ppm) = 8.99-8.98 (m, 2H), 8.25 (d, 2H, 6.5Hz), 7.98(s, 2H), 7.90-7.88(m, 2H), 7.72-7.70(m, 4H), 7.32(d, 2H, 6Hz), 6.55(s, 2H), 4.93(s, 1H), 2.34(s, 6H), 1.56(s, 6H), 1.39(s, 6H). ^{13}C -NMR (125MHz, CD_2Cl_2): δ (ppm) = 185.20, 169.64, 149.22, 147.35, 144.51, 141.35, 137.55, 131.38, 130.98, 130.70, 128.78, 127.79, 127.56, 126.87, 118.46, 100.27, 28.58, 24.18, 21.35. MS(m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{39}\text{H}_{36}\text{IrN}_2\text{O}_2$, 757.240; found, 759.240.

Synthesis of $(\text{piq})_2\text{Ir}(\text{tmhd})$ This complex was synthesized by the same method for the $(\text{piq})_2\text{Ir}(\text{acac})$, except that tmhd was used instead of acac. ^1H -NMR (500MHz, CD_2Cl_2): δ (ppm) = 8.97-8.95 (m, 2H), 8.13 (d, 2H, 6.5Hz), 7.96(s, 2H), 7.86-7.83(m, 2H), 7.67-7.66(m, 4H), 7.24 (d, 2H, 6Hz), 6.57(s, 2H), 5.18(s, 1H), 2.35(s, 6H), 1.42(s, 6H), 0.62(s, 18H). ^{13}C -NMR (125MHz, CD_2Cl_2): δ (ppm) = 196.64, 169.73, 149.27, 147.29, 145.93, 141.37, 137.39, 131.00, 130.74, 130.30, 128.65, 127.60, 127.45, 127.36, 126.96, 118.08, 89.75, 41.41, 28.16, 24.27, 21.41. MS(m/z): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{45}\text{H}_{48}\text{IrN}_2\text{O}_2$, 841.334; found, 841.334.

Synthesis of $(\text{piq})_2\text{Ir}(\text{dapd})$ This complex was synthesized by the same method for the $(\text{piq})_2\text{Ir}(\text{acac})$, except that dapd was used instead of acac. ^1H -NMR (500MHz, CD_2Cl_2): δ (ppm) = 8.98-8.96 (m, 2H), 8.08 (d, 2H, 6.5Hz), 7.95(s, 2H), 7.85-7.83(m, 2H), 7.69-7.65(m, 4H), 7.23 (d, 2H, 6.5Hz), 6.57(s, 2H), 5.02(s, 1H), 2.36(s, 6H), 1.64(s, 6H), 1.49(d, 6H, 12Hz), 1.42(s, 6H), 1.36(d, 6H, 11.5Hz), 1.20(s, 12H). ^{13}C -NMR (125MHz, CD_2Cl_2): δ (ppm) = 194.00,

169.76, 149.30, 147.22, 146.14, 141.50, 137.40, 130.85, 130.67, 130.25, 128.72, 127.52, 127.48, 127.29, 127.05, 118.01, 89.24, 43.46, 40.06, 37.12, 29.03, 24.24, 21.39. MS(m/z):[M+H]⁺ calculated for C₅₇H₆₀IrN₂O₂, 997.428; found, 997.428.

Synthesis of (piq)₂Ir(dend) This complex was synthesized by the same method for the (piq)₂Ir(acac), except that dend was used instead of acac. ¹H-NMR (500MHz, CD₂Cl₂) : δ (ppm) = 8.96-8.94 (m, 2H), 8.21 (d, 2H, 6.5Hz), 7.98(s, 2H), 7.84-7.82(m, 2H), 7.69-7.67(m, 4H), 7.24(d, 2H, 6.5Hz), 6.57(s, 2H), 4.89(s, 1H), 2.35(s, 6H), 1.61-1.55 (m, 2H), 1.41 (s, 6H), 1.30-1.24(m, 2H), 1.18-1.11(m, 2H), 0.94-0.87(m, 4H), 0.40(t, 6H, 7.5Hz), -0.11(t, 6H, 7.5H). ¹³C-NMR (125MHz, CD₂Cl₂): δ (ppm) = 190.60, 169.68, 149.33, 147.47, 145.57, 141.59, 137.84, 131.10, 130.79, 130.59, 128.83, 127.66, 127.45, 127.35, 127.10, 118.01, 100.96, 55.70, 27.23, 26.82, 24.27, 21.40, 12.01, 11.62. MS(m/z):[M+H]⁺ calculated for C₄₇H₅₂IrN₂O₂, 869.365; found, 869.365.