Electronic Supplementary Material (ESI) for RSC Advances


# Supporting Information

# Tuning the electronic properties and quantum efficiency of blue Ir(III) carbene complexes via different azole-pyridine-based N^N' ligands

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**Table S1** Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **1a**

| MO[a] | Energy/eV | MO composition(%)[b] | | | | Assign |
|---|---|---|---|---|---|---|
| | | Ir | fpmi1 | fpmi2 | pyN1 | |
| L+5 | 0.64 | 7 | 21 | 70 | 2 | π*(fpmi) |
| L+4 | 0.37 | 6 | 69 | 22 | 3 | π*(fpmi) |
| L+3 | 0.13 | 5 | 24 | 70 | 0 | π*(fpmi) |
| L+2 | -0.02 | 7 | 65 | 22 | 5 | π*(fpmi) |
| L+1 | -0.32 | 1 | 3 | 2 | 94 | π*(pyN1) |
| L | -0.76 | 3 | 0 | 1 | 96 | π*(pyN1) |
| H | -5.00 | 3 | 1 | 1 | 94 | π(pyN1) |
| H-1 | -5.21 | 35 | 17 | 34 | 13 | d(Ir)+π(fpmi+pyN1) |
| H-2 | -5.40 | 32 | 21 | 10 | 36 | d(Ir)+π(fpmi+pyN1) |
| H-3 | -5.75 | 11 | 42 | 34 | 12 | d(Ir)+π(fpmi+pyN1) |
| H-4 | -5.95 | 26 | 22 | 43 | 9 | d(Ir)+π(fpmi) |
| H-5 | -6.27 | 27 | 47 | 20 | 5 | d(Ir)+π(fpmi) |

[a] H = HOMO; L= LUMO. [b] fpmi1 and fpmi2 are the same ligands, but in different positions, Fig. 1. pyN1 = 2-(1*H*-pyrrol-2-yl)pyridinato, Scheme 1.

**Table S2** Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **2a**

| MO[a] | Energy/eV | MO composition(%)[b] | | | | Assign |
|---|---|---|---|---|---|---|
| | | Ir | fpmi1 | fpmi2 | pyN2 | |
| L+5 | 0.71 | 6 | 10 | 82 | 1 | π*(fpmi) |
| L+4 | 0.35 | 6 | 80 | 11 | 3 | π*(fpmi) |
| L+3 | 0.17 | 6 | 5 | 88 | 1 | π*(fpmi2) |
| L+2 | -0.05 | 8 | 86 | 4 | 2 | π*(fpmi1) |
| L+1 | -0.61 | 1 | 1 | 1 | 97 | π*(pyN2) |
| L | -1.07 | 3 | 1 | 1 | 96 | π*(pyN2) |
| H | -5.20 | 33 | 15 | 46 | 5 | d(Ir)+π(fpmi) |
| H-1 | -5.45 | 32 | 19 | 14 | 34 | d(Ir)+π(fpmi+pyN2) |
| H-2 | -5.69 | 11 | 26 | 23 | 40 | d(Ir)+π(fpmi+pyN2) |
| H-3 | -5.90 | 7 | 18 | 11 | 65 | π(fpmi+pyN2) |
| H-4 | -5.94 | 25 | 23 | 44 | 8 | d(Ir)+π(fpmi) |
| H-5 | -6.27 | 25 | 43 | 24 | 7 | d(Ir)+π(fpmi) |

[a] H = HOMO; L= LUMO. [b] fpmi1 and fpmi2 are the same ligands, but in different positions, Fig. 1. pyN2 = 2-(1*H*-pyrazol-5-yl)pyridinato, Scheme 1.

**Table S3** Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **3a**

| MO[a] | Energy/eV | MO composition(%)[b] | | | | Assign |
|---|---|---|---|---|---|---|
| | | Ir | fpmi1 | fpmi2 | pyN3 | |
| L+5 | 0.59 | 6 | 10 | 82 | 1 | π*(fpmi) |
| L+4 | 0.23 | 6 | 79 | 12 | 3 | π*(fpmi) |
| L+3 | 0.05 | 6 | 6 | 87 | 1 | π*(fpmi2) |
| L+2 | -0.16 | 8 | 85 | 4 | 3 | π*(fpmi1) |
| L+1 | -0.73 | 1 | 1 | 1 | 97 | π*(pyN3) |
| L | -1.23 | 3 | 1 | 1 | 96 | π*(pyN3) |
| H | -5.34 | 33 | 17 | 47 | 3 | d(Ir)+π(fpmi) |
| H-1 | -5.65 | 29 | 26 | 22 | 23 | d(Ir)+π(fpmi+pyN3) |
| H-2 | -5.86 | 15 | 28 | 24 | 33 | d(Ir)+π(fpmi+pyN3) |
| H-3 | -6.08 | 22 | 25 | 41 | 12 | d(Ir)+π(fpmi+pyN3) |
| H-4 | -6.33 | 23 | 28 | 17 | 32 | d(Ir)+π(fpmi+pyN3) |
| H-5 | -6.43 | 22 | 23 | 35 | 20 | d(Ir)+π(fpmi+pyN3) |

[a] H = HOMO; L= LUMO. [b] fpmi1 and fpmi2 are the same ligands, but in different positions, Fig. 1. pyN3 = 2-(1*H*-1,2,4-triazol-5-yl)pyridinato, Scheme 1.

**Table S4** Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **4a**

| MO[a] | Energy/eV | MO composition(%)[b] | | | | Assign |
|---|---|---|---|---|---|---|
| | | Ir | fpmi1 | fpmi2 | pyN4 | |
| L+4 | 0.08 | 6 | 79 | 12 | 3 | π*(fpmi) |
| L+3 | -0.09 | 7 | 7 | 86 | 1 | π*(fpmi2) |
| L+2 | -0.32 | 9 | 84 | 4 | 2 | π*(fpmi1) |
| L+1 | -1.00 | 1 | 1 | 1 | 97 | π*(pyN4) |
| L | -1.50 | 3 | 1 | 1 | 96 | π*(pyN4) |
| H | -5.50 | 31 | 18 | 48 | 3 | d(Ir)+π(fpmi) |
| H-1 | -5.87 | 20 | 38 | 37 | 4 | d(Ir)+π(fpmi) |
| H-2 | -6.15 | 33 | 34 | 24 | 9 | d(Ir)+π(fpmi) |
| H-3 | -6.33 | 27 | 11 | 45 | 17 | d(Ir)+π(fpmi+pyN4) |
| H-4 | -6.54 | 27 | 45 | 20 | 8 | d(Ir)+π(fpmi) |
| H-5 | -6.77 | 3 | 3 | 19 | 76 | π(fpmi2+pyN4) |
| H-6 | -6.83 | 4 | 63 | 25 | 7 | π(fpmi) |

[a] H = HOMO; L= LUMO. [b] fpmi1 and fpmi2 are the same ligands, but in different positions, Fig. 1. pyN4 = 2-(1*H*-tetrazol-5-yl)pyridinato, Scheme 1.

**Table S5** Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **1a'**

| MO[a] | Energy/eV | MO composition(%)[b] | | | | Assign |
|---|---|---|---|---|---|---|
| | | Ir | fpmi | $pyN1_a$ | $pyN1_b$ | |
| L+3 | -0.29 | 1 | 15 | 3 | 81 | π*(fpmi+$pyN1_b$) |
| L+2 | -0.36 | 1 | 8 | 91 | 1 | π*($pyN1_a$) |
| L+1 | -0.80 | 4 | 0 | 5 | 91 | π*($pyN1_b$) |
| L | -0.89 | 3 | 1 | 92 | 4 | π*($pyN1_a$) |
| H | -4.91 | 3 | 1 | 3 | 93 | π($pyN1_b$) |
| H-1 | -5.09 | 2 | 1 | 93 | 4 | π($pyN1_a$) |
| H-2 | -5.32 | 31 | 3 | 26 | 40 | d(Ir)+π(pyN1) |
| H-3 | -5.71 | 26 | 68 | 2 | 4 | d(Ir)+π(fpmi) |
| H-4 | -5.93 | 3 | 3 | 54 | 40 | π(pyN1) |
| H-5 | -6.22 | 39 | 48 | 7 | 7 | d(Ir)+π(fpmi) |
| H-6 | -6.53 | 29 | 63 | 6 | 2 | d(Ir)+π(fpmi) |

[a] H = HOMO; L= LUMO. [b] $pyN1_a$ and $pyN1_b$ are the same ligands, but in different positions, Fig. 1. pyN1 = 2-(1*H*-pyrrol-2-yl)pyridinato, Scheme 1.

**Table S6** Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **2a'**

| MO[a] | Energy/eV | MO composition(%)[b] | | | | Assign |
|---|---|---|---|---|---|---|
| | | Ir | fpmi | $pyN2_a$ | $pyN2_b$ | |
| L+6 | 0.76 | 15 | 74 | 5 | 6 | d(Ir)+π*(fpmi) |
| L+5 | 0.26 | 5 | 91 | 2 | 2 | π*(fpmi) |
| L+4 | -0.26 | 7 | 89 | 2 | 3 | π*(fpmi) |
| L+3 | -0.46 | 1 | 2 | 7 | 91 | π*($pyN2_b$) |
| L+2 | -0.47 | 1 | 4 | 90 | 6 | π*($pyN2_a$) |
| L+1 | -1.00 | 4 | 0 | 28 | 68 | π*(pyN2) |
| L | -1.07 | 3 | 1 | 68 | 28 | π*(pyN2) |
| H | -5.36 | 29 | 3 | 24 | 44 | d(Ir)+π(pyN2) |
| H-1 | -5.66 | 13 | 15 | 11 | 60 | d(Ir)+π(fpmi+pyN2) |
| H-2 | -5.76 | 12 | 31 | 49 | 9 | d(Ir)+π(fpmi+$pyN2_a$) |
| H-3 | -5.88 | 7 | 30 | 37 | 25 | π(fpmi+pyN2) |
| H-4 | -6.17 | 4 | 5 | 54 | 37 | π(pyN2) |
| H-5 | -6.30 | 34 | 45 | 10 | 12 | d(Ir)+π(fpmi+pyN2) |
| H-6 | -6.60 | 25 | 62 | 5 | 7 | d(Ir)+π(fpmi) |

[a] H = HOMO; L= LUMO. [b] $pyN2_a$ and $pyN2_b$ are the same ligands, but in different positions, Fig. 1. pyN2 = 2-(1*H*-pyrazol-5-yl)pyridinato, Scheme 1.

**Table S7** Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **3a'**

| MO[a] | Energy/eV | MO composition(%)[b] | | | | Assign |
|---|---|---|---|---|---|---|
| | | Ir | fpmi | $pyN3_a$ | $pyN3_b$ | |
| L+5 | 0.02 | 5 | 92 | 2 | 2 | π*(fpmi) |
| L+4 | -0.51 | 7 | 89 | 2 | 2 | π*(fpmi) |
| L+3 | -0.72 | 1 | 0 | 66 | 32 | π*(pyN3) |
| L+2 | -0.74 | 1 | 5 | 30 | 64 | π*(pyN3) |
| L+1 | -1.31 | 4 | 0 | 31 | 64 | π*(pyN3) |
| L | -1.38 | 3 | 1 | 65 | 32 | π*(pyN3) |
| H | -5.79 | 25 | 3 | 23 | 49 | d(Ir)+π(pyN3) |
| H-1 | -6.03 | 23 | 69 | 5 | 3 | d(Ir)+π(fpmi) |
| H-2 | -6.13 | 4 | 7 | 53 | 36 | π(pyN3) |
| H-3 | -6.56 | 32 | 48 | 12 | 8 | $d(Ir)+\pi(fpmi+pyN3_a)$ |
| H-4 | -6.64 | 24 | 8 | 31 | 37 | d(Ir)+π(pyN3) |
| H-5 | -6.87 | 27 | 62 | 7 | 5 | d(Ir)+π(fpmi) |

[a] H = HOMO; L= LUMO. [b] $pyN3_a$ and $pyN3_b$ are the same ligands, but in different positions, Fig. 1. pyN3 = 2-(1*H*-1,2,4-triazol-5-yl)pyridinato, Scheme 1.

**Table S8** Frontier molecular orbital energies (eV) and compositions (%) of different fragments in the ground state for complex **4a'**

| MO[a] | Energy/eV | MO composition(%)[b] | | | | Assign |
|---|---|---|---|---|---|---|
| | | Ir | fpmi | $pyN4_a$ | $pyN4_b$ | |
| L+5 | -0.29 | 4 | 93 | 2 | 1 | π*(fpmi) |
| L+4 | -0.83 | 7 | 90 | 1 | 2 | π*(fpmi) |
| L+3 | -1.12 | 1 | 1 | 83 | 15 | π*(pyN4) |
| L+2 | -1.15 | 0 | 3 | 14 | 82 | π*(pyN4) |
| L+1 | -1.74 | 4 | 0 | 41 | 55 | π*(pyN4) |
| L | -1.80 | 3 | 1 | 56 | 41 | π*(pyN4) |
| H | -6.35 | 20 | 74 | 3 | 3 | d(Ir)+π(fpmi) |
| H-1 | -6.60 | 37 | 5 | 22 | 37 | d(Ir)+π(pyN4) |
| H-2 | -6.79 | 28 | 34 | 17 | 21 | d(Ir)+π(fpmi+pyN4) |
| H-3 | -6.99 | 7 | 9 | 32 | 52 | π(pyN4) |
| H-4 | -7.04 | 12 | 35 | 24 | 29 | d(Ir)+π(fpmi+pyN4) |
| H-5 | -7.18 | 14 | 7 | 37 | 42 | d(Ir)+π(pyN4) |

[a] H = HOMO; L= LUMO. [b] $pyN4_a$ and $pyN4_b$ are the same ligands, but in different positions, Fig. 1. pyN4 = 2-(1*H*-tetrazol-5-yl)pyridinato, Scheme 1.

**Table S9** Selected calculated wavelength ($\lambda$, in nm)/energies ($E$, in eV), oscillator strength ($f$), major contribution and transition characters for the $(fpmi)_2Ir(N^N)$ complexes in $CH_2Cl_2$ media, along with the experimental data for **2a**

| | state | $\lambda/E$ | $f$ | Configuration[a] | Assignment | Exptl[b] |
|---|---|---|---|---|---|---|
| **1a** | $S_1$ | 347/3.57 | 0.0908 | H→L(81%) | π(pyN1)→π*(pyN1)/IL | |
| | $S_3$ | 320/3.88 | 0.0526 | H-2→L(95%) | d(Ir)+π(fpmi+pyN1)→π*(pyN1)/MLCT/LLCT/IL | |
| | $S_4$ | 306/4.05 | 0.1541 | H→L+1(71%) | π(pyN1)→π*(pyN1)/IL | |
| | $S_7$ | 288/4.31 | 0.0735 | H-1→L+3(26%) | d(Ir)+π(fpmi+pyN1)→π*(fpmi)/MLCT/LLCT/IL | |
| | | | | H→L+3(18%) | π(pyN1)→π*(fpmi)/LLCT | |
| | | | | H-3→L(18%) | d(Ir)+π(fpmi+pyN1)→π*(pyN1)/MLCT/LLCT/IL | |
| | $S_{10}$ | 285/4.36 | 0.0702 | H-2→L+1(66%) | d(Ir)+π(fpmi+pyN1)→π*(pyN1)/MLCT/LLCT/IL | |
| | $S_{15}$ | 270/4.60 | 0.0694 | H-1→L+4(50%) | d(Ir)+π(fpmi+pyN1)→π*(fpmi)/MLCT/LLCT/IL | |
| | | | | H→L+4(28%) | π(pyN1)→π*(fpmi)/LLCT | |
| | $S_{19}$ | 256/4.84 | 0.0624 | H-3→L+2(47%) | d(Ir)+π(fpmi+pyN1)→π*(fpmi)/MLCT/LLCT/IL | |
| | | | | H-2→L+4(17%) | d(Ir)+π(fpmi+pyN1)→π*(fpmi)/MLCT/LLCT/IL | |
| | $T_1$ | 463/2.68 | 0.0000 | H→L(74%) | π(pyN1)→π*(pyN1)/IL | |
| **2a** | $S_1$ | 357/3.48 | 0.0043 | H→L(96%) | d(Ir)+π(fpmi)→π*(pyN2)/MLCT/LLCT | 379 |
| | $S_2$ | 338/3.67 | 0.0530 | H-1→L(93%) | d(Ir)+π(fpmi+pyN2)→π*(pyN2)/MLCT/LLCT/IL | |
| | $S_3$ | 311/3.98 | 0.0607 | H-2→L(85%) | d(Ir)+π(fpmi+pyN2)→π*(pyN2)/MLCT/LLCT/IL | |
| | $S_5$ | 296/4.19 | 0.0640 | H-3→L(45%) | π(fpmi+pyN2)→π*(pyN2)/LLCT/IL | 304 |
| | | | | H→L+2(35%) | d(Ir)+π(fpmi)→π*(fpmi1)/MLCT/LLCT/IL | |
| | $S_{11}$ | 274/4.53 | 0.1100 | H-2→L+1(70%) | d(Ir)+π(fpmi+pyN2)→π*(pyN2)/MLCT/LLCT/IL | |
| | $S_{15}$ | 262/4.74 | 0.0641 | H-3→L+1(62%) | π(fpmi+pyN2)→π*(pyN2)/LLCT/IL | |
| | $S_{16}$ | 260/4.77 | 0.1239 | H-2→L+2(50%) | d(Ir)+π(fpmi+pyN2)→π*(fpmi1)/MLCT/LLCT/IL | 280 |
| | $T_1$ | 417/2.97 | 0.0000 | H-2→L(34%) | d(Ir)+π(fpmi+pyN2)→π*(pyN2)/MLCT/LLCT/IL | 432 |
| **3a** | $S_1$ | 366/3.39 | 0.0012 | H→L(97%) | d(Ir)+π(fpmi)→π*(pyN3)/MLCT/LLCT | |
| | $S_2$ | 338/3.67 | 0.0660 | H-1→L(86%) | d(Ir)+π(fpmi+pyN3)→π*(pyN3)/MLCT/LLCT/IL | |
| | $S_6$ | 292/4.24 | 0.0560 | H-3→L(72%) | d(Ir)+π(fpmi+pyN3)→π*(pyN3)/MLCT/LLCT/IL | |
| | $S_9$ | 279/4.44 | 0.0612 | H-4→L(80%) | d(Ir)+π(fpmi+pyN3)→π*(pyN3)/MLCT/LLCT/IL | |
| | $S_{13}$ | 265/4.68 | 0.1405 | H→L+4(63%) | d(Ir)+π(fpmi)→π*(fpmi)/MLCT/LLCT/IL | |
| | $S_{15}$ | 259/4.80 | 0.1112 | H-2→L+2(64%) | d(Ir)+π(fpmi+pyN3)→π*(fpmi1)/MLCT/LLCT/IL | |
| | $T_1$ | 413/3.00 | 0.0000 | H-2→L(25%) | d(Ir)+π(fpmi+pyN3)→π*(pyN3)/MLCT/LLCT/IL | |
| **4a** | $S_1$ | 376/3.30 | 0.0005 | H→L(97%) | d(Ir)+π(fpmi)→π*(pyN4)/MLCT/LLCT | |
| | $S_2$ | 338/3.67 | 0.0465 | H-1→L(87%) | d(Ir)+π(fpmi)→π*(pyN4)/MLCT/LLCT | |
| | $S_6$ | 294/4.22 | 0.0443 | H-3→L(75%) | d(Ir)+π(fpmi+pyN4)→π*(pyN4)/MLCT/LLCT/IL | |
| | $S_{13}$ | 263/4.71 | 0.2014 | H→L+4(45%) | d(Ir)+π(fpmi)→π*(fpmi)/MLCT/LLCT/IL | |
| | | | | H-6→L(25%) | π(fpmi)→π*(pyN4)/LLCT | |
| | $S_{16}$ | 257/4.82 | 0.1255 | H-2→L+2(71%) | d(Ir)+π(fpmi)→π*(fpmi1)/MLCT/LLCT/IL | |
| | $T_1$ | 392/3.16 | 0.0000 | H→L(40%) | d(Ir)+π(fpmi)→π*(pyN4)/MLCT/LLCT | |

[a] H = HOMO; L= LUMO. [b] Experimental data from Ref. 11.

**Table S10** Selected calculated wavelength ($\lambda$, in nm)/energies ($E$, in eV), oscillator strength ($f$), major contribution and transition characters for the $(N^N)_2Ir(fpmi)$ complexes in $CH_2Cl_2$ media

| | state | $\lambda/E$ | $f$ | Configuration[a] | Assignment |
|---|---|---|---|---|---|
| **1a'** | $S_1$ | 360/3.44 | 0.0972 | H→L(64%) | $\pi(pyN1_b)\rightarrow\pi^*(pyN1_a)$/LLCT |
| | | | | H→L+1(19%) | $\pi(pyN1_b)\rightarrow\pi^*(pyN1_b)$/IL |
| | $S_5$ | 336/3.69 | 0.0647 | H-2→L(82%) | $d(Ir)+\pi(pyN1)\rightarrow\pi^*(pyN1_a)$/MLCT/LLCT/IL |
| | $S_{10}$ | 302/4.10 | 0.1320 | H→L+3(37%) | $\pi(pyN1_b)\rightarrow\pi^*(fpmi+pyN1_b)$/LLCT/IL |
| | | | | H-3→L+1(34%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN1_b)$/MLCT/LLCT |
| | $S_{11}$ | 298/4.16 | 0.1778 | H-1→L+2(61%) | $\pi(pyN1_a)\rightarrow\pi^*(pyN1_a)$/IL |
| | $S_{19}$ | 281/4.41 | 0.1384 | H-4→L+1(77%) | $\pi(pyN1)\rightarrow\pi^*(pyN1_b)$/LLCT/IL |
| | $S_{22}$ | 273/4.54 | 0.0911 | H-5→L+1(58%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN1_b)$/MLCT/LLCT |
| | $S_{29}$ | 254/4.88 | 0.0935 | H-6→L(70%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN1_a)$/MLCT/LLCT |
| | $T_1$ | 478/2.59 | 0.0000 | H→L+1(54%) | $\pi(pyN1_b)\rightarrow\pi^*(pyN1_b)$/IL |
| **2a'** | $S_1$ | 356/3.48 | 0.0607 | H→L(97%) | $d(Ir)+\pi(pyN2)\rightarrow\pi^*(pyN2)$/MLCT/LLCT/IL |
| | $S_5$ | 310/4.00 | 0.0899 | H-2→L(89%) | $d(Ir)+\pi(fpmi+pyN2_a)\rightarrow\pi^*(pyN2)$/MLCT/LLCT/IL |
| | $S_6$ | 307/4.04 | 0.0758 | H-2→L+1(88%) | $d(Ir)+\pi(fpmi+pyN2_a)\rightarrow\pi^*(pyN2)$/MLCT/LLCT/IL |
| | $S_{12}$ | 286/4.33 | 0.0565 | H-4→L+1(56%) | $\pi(pyN2)\rightarrow\pi^*(pyN2)$/LLCT/IL |
| | | | | H-4→L(22%) | $\pi(pyN2)\rightarrow\pi^*(pyN2)$/LLCT/IL |
| | $S_{14}$ | 277/4.47 | 0.0791 | H-1→L+2(52%) | $d(Ir)+\pi(fpmi+pyN2)\rightarrow\pi^*(pyN2_a)$/MLCT/LLCT/IL |
| | | | | H-1→L+3(26%) | $d(Ir)+\pi(fpmi+pyN2)\rightarrow\pi^*(pyN2_b)$/MLCT/LLCT/IL |
| | $S_{21}$ | 261/4.75 | 0.1438 | H-2→L+2(27%) | $d(Ir)+\pi(fpmi+pyN2_a)\rightarrow\pi^*(pyN2_a)$/MLCT/LLCT/IL |
| | | | | H→L+6(19%) | $d(Ir)+\pi(pyN2)\rightarrow\pi^*(fpmi)$/MLCT/LLCT |
| | $S_{22}$ | 260/4.77 | 0.1692 | H-6→L(34%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN2)$/MLCT/LLCT |
| | | | | H-2→L+3(24%) | $d(Ir)+\pi(fpmi+pyN2_a)\rightarrow\pi^*(pyN2_b)$/MLCT/LLCT |
| | | | | H→L+6(22%) | $d(Ir)+\pi(pyN2)\rightarrow\pi^*(fpmi)$/MLCT/LLCT |
| | $T_1$ | 423/2.93 | 0.0000 | H-2→L(17%) | $d(Ir)+\pi(fpmi+pyN2_a)\rightarrow\pi^*(pyN2)$/MLCT/LLCT/IL |
| | | | | H→L(15%) | $d(Ir)+\pi(pyN2)\rightarrow\pi^*(pyN2)$/MLCT/LLCT/IL |
| | | | | H-2→L+1(15%) | $d(Ir)+\pi(fpmi+pyN2_a)\rightarrow\pi^*(pyN2)$/MLCT/LLCT/IL |
| **3a'** | $S_1$ | 345/3.60 | 0.0539 | H→L(67%) | $d(Ir)+\pi(pyN3)\rightarrow\pi^*(pyN3)$/MLCT/LLCT/IL |
| | | | | H-1→L(28%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN3)$/MLCT/LLCT |
| | $S_3$ | 332/3.74 | 0.0738 | H-1→L(66%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN3)$/MLCT/LLCT |
| | | | | H→L(29%) | $d(Ir)+\pi(pyN3)\rightarrow\pi^*(pyN3)$/MLCT/LLCT/IL |
| | $S_5$ | 304/4.08 | 0.0495 | H-2→L(85%) | $\pi(pyN3)\rightarrow\pi^*(pyN3)$/LLCT/IL |
| | $S_9$ | 282/4.40 | 0.1516 | H→L+2(41%) | $d(Ir)+\pi(pyN3)\rightarrow\pi^*(pyN3)$/MLCT/LLCT/IL |
| | | | | H-1→L+2(28%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN3)$/MLCT/LLCT |
| | | | | H-3→L+1(20%) | $d(Ir)+\pi(fpmi+pyN3_a)\rightarrow\pi^*(pyN3)$/MLCT/LLCT/IL |
| | $S_{13}$ | 273/4.54 | 0.0342 | H→L+4(84%) | $d(Ir)+\pi(pyN3)\rightarrow\pi^*(fpmi)$/MLCT/LLCT |
| | $S_{18}$ | 264/4.69 | 0.0596 | H-5→L+1(74%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN3)$/MLCT/LLCT |
| | $S_{21}$ | 255/4.86 | 0.2550 | H-2→L+3(68%) | $\pi(pyN3)\rightarrow\pi^*(pyN3)$/LLCT/IL |
| | $T_1$ | 417/2.97 | 0.0000 | H→L(18%) | $d(Ir)+\pi(pyN3)\rightarrow\pi^*(pyN3)$/MLCT/LLCT/IL |
| **4a'** | $S_1$ | 343/3.62 | 0.0164 | H→L(96%) | $d(Ir)+\pi(fpmi)\rightarrow\pi^*(pyN4)$/MLCT/LLCT |

| | | | | |
|---|---|---|---|---|
| $S_3$ | 313/3.96 | 0.0727 | H-2→L(87%) | d(Ir)+π(fpmi+pyN4)→π*(pyN4)/MLCT/LLCT/IL |
| $S_6$ | 302/4.11 | 0.0454 | H-1→L+1(77%) | d(Ir)+π(pyN4)→π*(pyN4)/MLCT/LLCT/IL |
| $S_{13}$ | 266/4.67 | 0.1228 | H-4→L+1(58%) | d(Ir)+π(fpmi+pyN4)→π*(pyN4)/MLCT/LLCT/IL |
| $S_{19}$ | 253/4.91 | 0.1197 | H-1→L+3(44%) | d(Ir)+π(pyN4)→π*(pyN4)/MLCT/LLCT/IL |
| | | | H-5→L(30%) | d(Ir)+π(pyN4)→π*(pyN4)/MLCT/LLCT/IL |
| $T_1$ | 389/3.19 | 0.0000 | H-1→L(10%) | d(Ir)+π(pyN4)→π*(pyN4)/MLCT/LLCT/IL |
| | | | H→L(9%) | d(Ir)+π(fpmi)→π*(pyN4)/MLCT/LLCT |

[a] H = HOMO; L= LUMO.

**Table S11** Calculated phosphorescent emission of the studied complexes in CH3CN media at TDDFT/M06-2X level of theory ($\lambda$, in nm; $E$, in eV)

| | ***λ*/*E*** | **Configuration[a]** | **Nature** | **Exptl[b]** |
|---|---|---|---|---|
| **1a** | 497/2.49 | H→L(95%) | IL | |
| **2a** | 459/2.70 | H→L(65%); H-1→L(22%) | MLCT/IL | 468 |
| **3a** | 460/2.70 | H→L(36%); H-1→L(36%); H-2→L(16%) | MLCT/IL | |
| **4a** | 421/2.95 | H-3→L(42%); H-2→L(17%); H-4→L(17%) | MLCT/IL | |
| **1a'** | 462/2.68 | H→L(54%); H-1→L+1(32%) | LLCT/IL | |
| **2a'** | 466/2.66 | H→L(87%) | MLCT/IL | |
| **3a'** | 470/2.64 | H→L(86%) | MLCT/IL | |
| **4a'** | 440/2.82 | H-1→L(82%) | MLCT/IL | |

[a] H = HOMO; L= LUMO. [b] Experimental data from Ref. 11.

**Table S12** Calculated phosphorescent emission of the studied complexes in toluene media at TDDFT/M06-2X level of theory ($\lambda$, in nm; $E$, in eV)

| | ***λ*/*E*** | **Configuration[a]** | **Nature** | **Exptl[b]** |
|---|---|---|---|---|
| **1a** | 511/2.43 | H→L(95%) | IL | |
| **2a** | 470/2.64 | H→L(53%); H-1→L(36%) | MLCT/IL | 468 |
| **3a** | 471/2.63 | H-1→L(48%); H→L(33%) | MLCT/IL | |
| **4a** | 429/2.89 | H-3→L(44%); H-2→L(25%) | MLCT/IL | |
| **1a'** | 485/2.56 | H→L+1(34%); H→L(28%); H-1→L+1(22%) | LLCT/IL | |
| **2a'** | 478/2.59 | H→L(89%) | MLCT/IL | |
| **3a'** | 480/2.58 | H→L(89%) | MLCT/IL | |
| **4a'** | 447/2.77 | H-1→L(71%); H→L(20%) | MLCT/IL | |

[a] H = HOMO; L= LUMO. [b] Experimental data from Ref. 11.

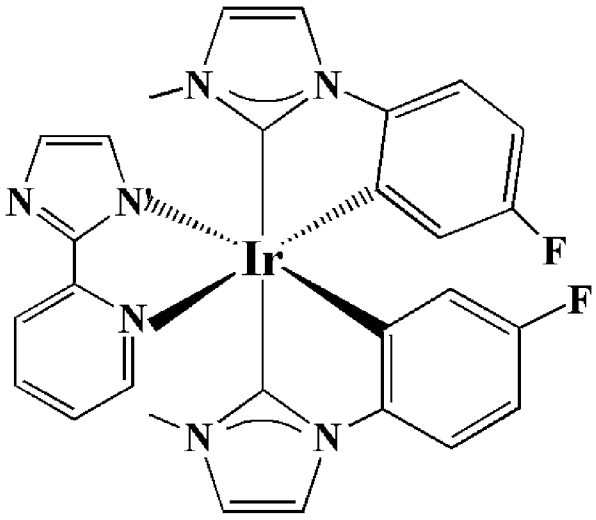
**Table S13**: Selected bond lengths (in Å) calculated for the studied complexes in the metal-centered ($^3$MC) triplet excited states

| | Ir-C1 | Ir-C2 | Ir-C3/Ir-N3 | Ir-C4/Ir-N4 | Ir-N1 | Ir-N2 |
|---|---|---|---|---|---|---|
| **1a** | 2.023 | 2.039 | 2.020 | 2.065 | 2.129 | 3.130 |
| **2a** | 2.019 | 2.041 | 2.022 | 2.058 | 2.120 | 3.232 |
| **3a** | 2.023 | 2.042 | 2.025 | 2.056 | 2.131 | 3.233 |
| **4a** | 2.025 | 2.040 | 2.028 | 2.053 | 2.140 | 3.294 |
| **1a'** | 2.045 | 2.059 | 2.063 | 2.479 | 2.014 | 2.477 |
| **2a'** | 2.021 | 2.027 | 2.103 | 2.473 | 2.045 | 2.458 |
| **3a'** | 2.014 | 2.011 | 2.124 | 2.512 | 2.058 | 2.448 |
| **4a'** | 2.008 | 1.998 | 2.144 | 2.526 | 2.074 | 2.427 |

**Table S14**: The xyz coordinates for the optimized structures for **2a** in the $S_0$ and $T_1$ states

| **2a** | **$S_0$** | | | **$T_1$** | | |
|---|---|---|---|---|---|---|
| Ir | 0.12837900 | -0.12331000 | 0.00747300 | 0.12436700 | -0.12616400 | -0.01779900 |
| C | 2.12127400 | -3.82735800 | -0.51539400 | 2.15065600 | -3.82118200 | -0.48749200 |
| H | 2.10743700 | -4.90193700 | -0.64970000 | 2.13216100 | -4.89747500 | -0.60908600 |
| C | 3.21591500 | -2.97154800 | -0.44519800 | 3.23665600 | -2.98405200 | -0.39133200 |
| H | 4.26664400 | -3.21933400 | -0.51067300 | 4.28606200 | -3.23818900 | -0.41680100 |
| C | 2.62482700 | -1.71429300 | -0.26143700 | 2.65453300 | -1.69430300 | -0.24020000 |
| C | 3.12840200 | -0.37474700 | -0.12306800 | 3.14876000 | -0.40174800 | -0.06565300 |
| C | 4.49027900 | -0.03605000 | -0.14733600 | 4.53046400 | -0.04791400 | -0.03486600 |
| H | 5.22641600 | -0.82347800 | -0.27213700 | 5.26330400 | -0.84903700 | -0.08961300 |
| C | 4.87060600 | 1.28689700 | -0.01675700 | 4.91911600 | 1.25550400 | 0.05761600 |
| H | 5.92274000 | 1.55799100 | -0.03517200 | 5.96713700 | 1.53359100 | 0.08492500 |
| C | 3.88731400 | 2.26754500 | 0.13414600 | 3.88944000 | 2.26042200 | 0.11188700 |
| H | 4.14013600 | 3.31773200 | 0.23339300 | 4.13539700 | 3.31514400 | 0.16954800 |
| C | 2.56033000 | 1.87067900 | 0.15201400 | 2.55179900 | 1.87448100 | 0.09368000 |
| H | 1.74970000 | 2.58425400 | 0.26879700 | 1.76109800 | 2.61910700 | 0.14890600 |
| C | -0.02010000 | 0.33568200 | -1.96302000 | -0.02521000 | 0.36926500 | -1.98397000 |
| C | -0.19179600 | 0.61649000 | -4.18710900 | -0.17310600 | 0.70770300 | -4.20246100 |
| H | -0.10588200 | 0.34124400 | -5.22710600 | -0.07352300 | 0.46080600 | -5.24832300 |
| C | -0.65187000 | 1.75347700 | -3.60728700 | -0.64390600 | 1.82689200 | -3.59786700 |
| H | -1.05233700 | 2.65305100 | -4.04653500 | -1.04153400 | 2.73690400 | -4.01763900 |
| C | 0.72176700 | -1.57426100 | -3.36786400 | 0.74564100 | -1.49647300 | -3.42830500 |
| H | 0.37839100 | -2.22829100 | -2.56489300 | 0.38184400 | -2.17620300 | -2.65675300 |

| | | | | | | |
|---|---|---|---|---|---|---|
| H | 1.81560100 | -1.55612500 | -3.36301700 | 1.83907300 | -1.47098600 | -3.39508400 |
| H | 0.36851000 | -1.95406400 | -4.32930800 | 0.42133800 | -1.84936300 | -4.40995800 |
| C | -0.71502800 | 1.72961300 | 0.10173100 | -0.74016500 | 1.71476800 | 0.10823500 |
| C | -0.91654600 | 2.36565500 | -1.14506900 | -0.93904700 | 2.37479200 | -1.12546000 |
| C | -1.42383800 | 3.64919600 | -1.28889600 | -1.46298200 | 3.65433000 | -1.24488300 |
| H | -1.55746100 | 4.09777500 | -2.27002000 | -1.59391400 | 4.12312500 | -2.21677400 |
| C | -1.76669500 | 4.37411600 | -0.14923100 | -1.82635600 | 4.34792200 | -0.09267000 |
| H | -2.16943400 | 5.37924900 | -0.21005700 | -2.24159600 | 5.34890000 | -0.13435000 |
| C | -1.58184400 | 3.77133600 | 1.08467600 | -1.64587600 | 3.71907000 | 1.12892900 |
| C | -1.07133500 | 2.48547500 | 1.22388600 | -1.11926700 | 2.43776600 | 1.24390900 |
| H | -0.96584700 | 2.08234500 | 2.22748500 | -1.01749700 | 2.01465800 | 2.23937900 |
| C | -0.08237400 | -0.53023700 | 1.99251500 | -0.06199300 | -0.52936600 | 1.96985300 |
| C | -1.29392900 | -1.40520700 | 3.69034100 | -1.26197600 | -1.37502300 | 3.68833100 |
| H | -2.13063500 | -1.88926000 | 4.16757500 | -2.08999400 | -1.86053600 | 4.17909900 |
| C | -0.13491200 | -0.93114100 | 4.20972700 | -0.10757300 | -0.87287800 | 4.19345300 |
| H | 0.23386500 | -0.92558500 | 5.22386900 | 0.26168800 | -0.83701200 | 5.20684400 |
| C | 1.91345300 | 0.17740500 | 3.28950000 | 1.90977300 | 0.27749100 | 3.24485000 |
| H | 2.66870700 | -0.49819500 | 2.87849200 | 2.63701900 | -0.22752500 | 2.60574700 |
| H | 2.12094700 | 0.34800600 | 4.34800000 | 2.23739100 | 0.21639000 | 4.28455100 |
| H | 1.95881500 | 1.12989300 | 2.75934200 | 1.84531200 | 1.32704500 | 2.94809200 |
| C | -1.70649100 | -0.98511500 | 0.03410800 | -1.70271500 | -1.01395600 | 0.02659000 |
| C | -2.57889200 | -1.22192200 | -1.03119600 | -2.58206700 | -1.26948100 | -1.02848300 |
| H | -2.32949900 | -0.92555700 | -2.04548400 | -2.34660000 | -0.97145600 | -2.04589200 |
| C | -3.79864000 | -1.85258000 | -0.82191300 | -3.78851800 | -1.92020300 | -0.80388700 |
| C | -4.22218900 | -2.27307100 | 0.42832200 | -4.19101200 | -2.34248000 | 0.45299700 |
| H | -5.18374700 | -2.76097000 | 0.54375600 | -5.14271200 | -2.84651200 | 0.58039100 |
| C | -3.37724800 | -2.04629900 | 1.51138900 | -3.33961800 | -2.09636100 | 1.52683000 |
| H | -3.68082700 | -2.36561100 | 2.50493900 | -3.62817800 | -2.41651700 | 2.52460300 |
| C | -2.15968200 | -1.41708900 | 1.29759900 | -2.13521100 | -1.44725100 | 1.29753700 |
| F | -1.90662800 | 4.46092800 | 2.19388800 | -1.99175400 | 4.37775000 | 2.25007600 |
| F | -4.60458100 | -2.06200800 | -1.87976500 | -4.60207600 | -2.14916800 | -1.85153100 |
| N | 1.27545300 | -1.88030900 | -0.23433700 | 1.25802600 | -1.87414000 | -0.27428600 |
| N | 0.95678100 | -3.15411700 | -0.38619200 | 0.95425200 | -3.14045500 | -0.41159400 |
| N | 2.18348800 | 0.59021300 | 0.03646000 | 2.14345900 | 0.61238100 | 0.03382000 |
| N | 0.18483600 | -0.24042100 | -3.16787000 | 0.19432600 | -0.17418900 | -3.20119100 |
| N | -0.53756900 | 1.56197900 | -2.24796900 | -0.54542800 | 1.59948200 | -2.24274600 |
| N | -1.24132200 | -1.14944900 | 2.33888900 | -1.21365500 | -1.15432300 | 2.33049400 |
| N | 0.59103800 | -0.39566800 | 3.15971600 | 0.61380500 | -0.36073700 | 3.12961200 |




**$(fpmi)_2Ir(pyim)$ (2b)**

**Fig. S1.** Schematic structures of $(fpmi)_2Ir(pyim)$ (**2b**).

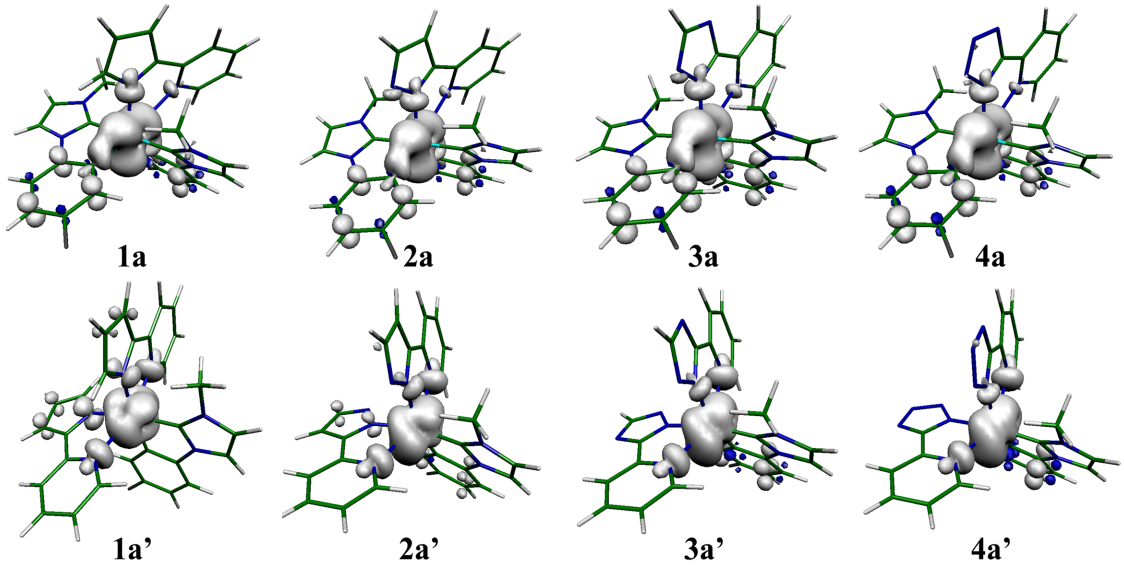



**Fig. S2.** The spin-density contours of the $^3$MC d-d state for the studied complexes.