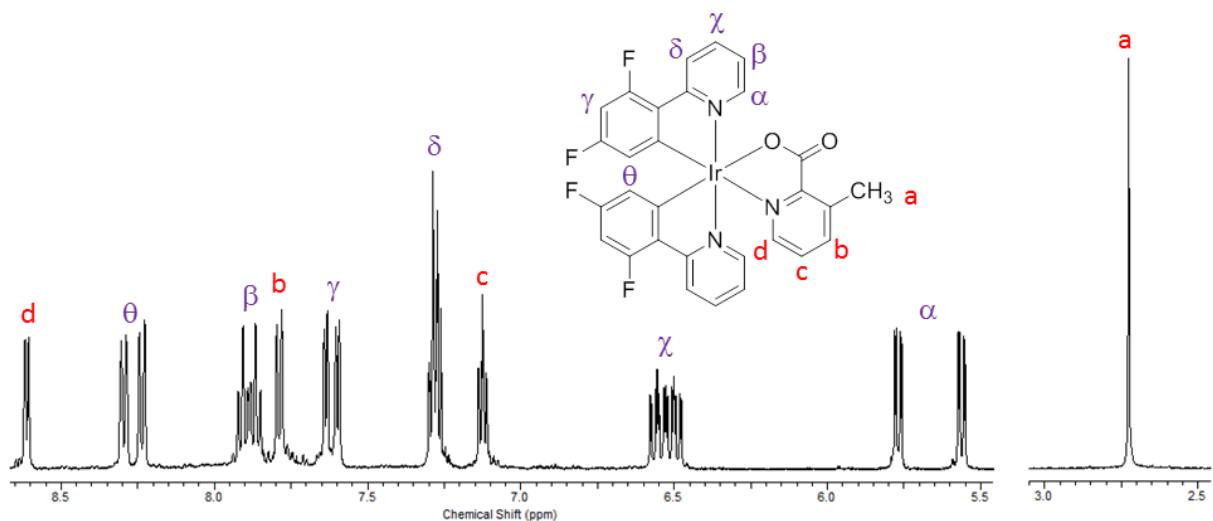


## Supporting Information

### MOLECULAR-ENGINEERED [Ir(*Fppy*)<sub>2</sub>(*Mepic*)] TOWARDS EFFICIENT BLUE EMISSION

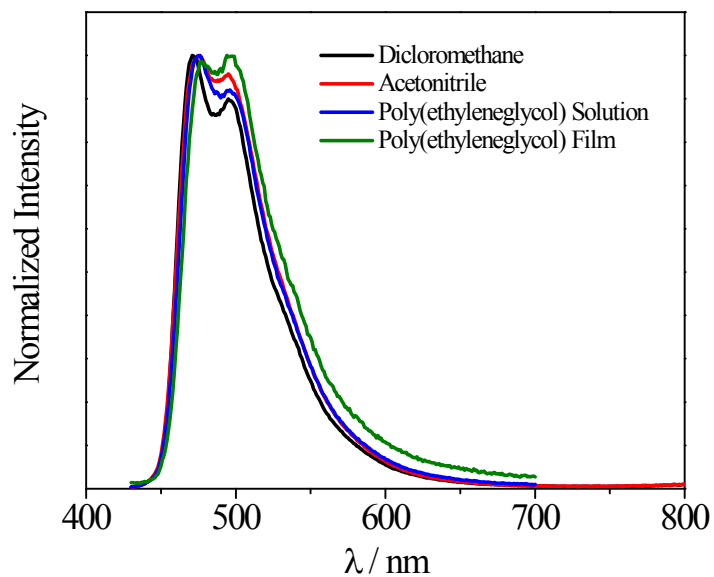
*Kassio P.S. Zanoni, Akitaka Ito and Neyde Y. Murakami Iha*



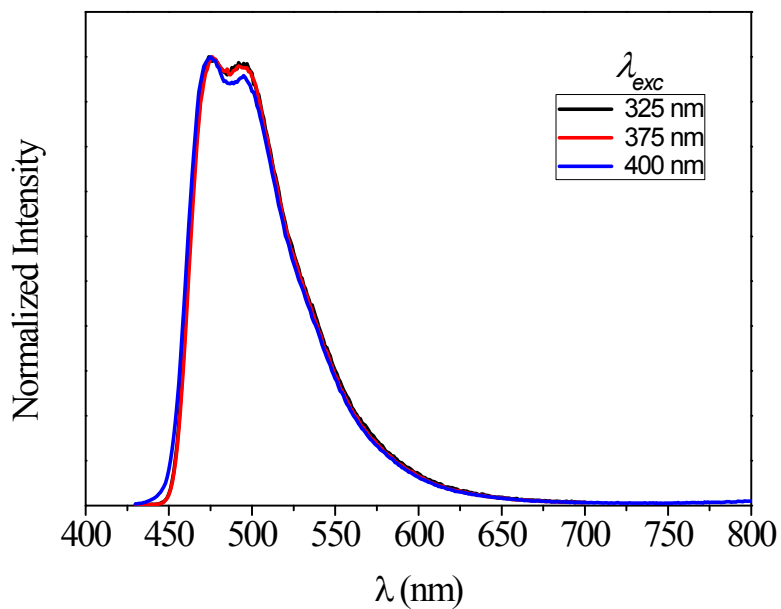
**Figure S1.** <sup>1</sup>H NMR spectrum in CD<sub>3</sub>CN and chemical structure of **FIrMepic** (500 MHz, *T* = 298 K).

**Table S1.** <sup>1</sup>H NMR assignment for **FIrMepic** (shown in Figure 1).

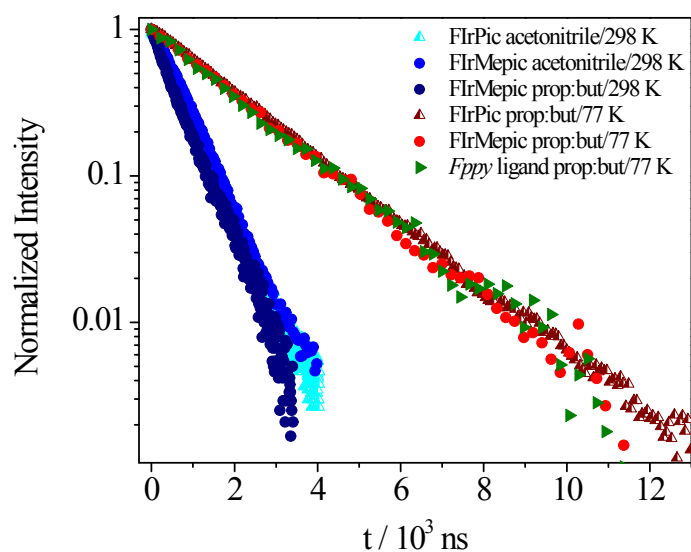
| Proton         | $\delta$ / ppm               | <i>J</i> / Hz |
|----------------|------------------------------|---------------|
| H <sub>a</sub> | 2.72 (s, 3H)                 |               |
| H <sub>b</sub> | 7.78 (d, 1H)                 | 7.6           |
| H <sub>c</sub> | 7.12 (t, 1H)                 | 5.8           |
| H <sub>d</sub> | 8.61 (d, 1H)                 | 5.8           |
| H <sub>α</sub> | 5.55 (dd, 1H); 5.76 (dd, 1H) | 8.9; 2.4      |
| H <sub>β</sub> | 7.86 (t, 1H); 7.91 (t, 1H)   | 7.6           |
| H <sub>χ</sub> | 6.52 (m, 2H)                 |               |
| H <sub>δ</sub> | 7.27 (m, 2H)                 |               |
| H <sub>γ</sub> | 7.60 (d, 1H); 7.63 (d, 1H)   | 5.8           |
| H <sub>θ</sub> | 8.22 (d, 1H); 8.30 (d, 1H)   | 8.5           |



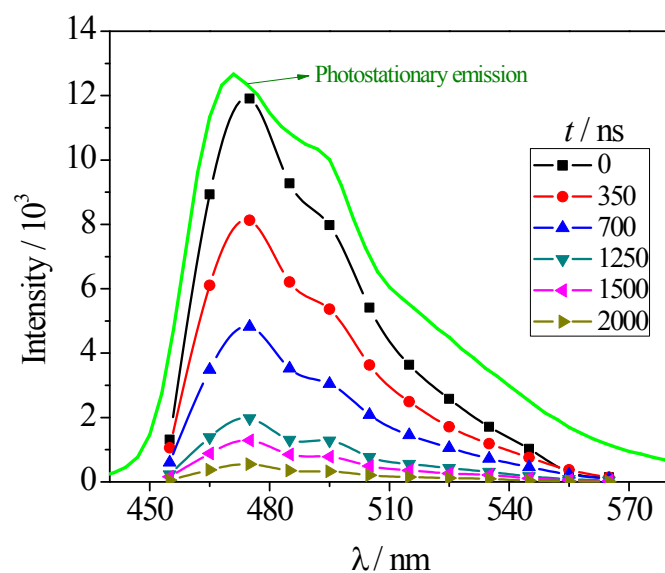
**Figure S2.** Emission spectra at 298 K for **FIrMepic** in different media ( $\lambda_{exc} = 365$  nm, with a 389 nm long pass filter).



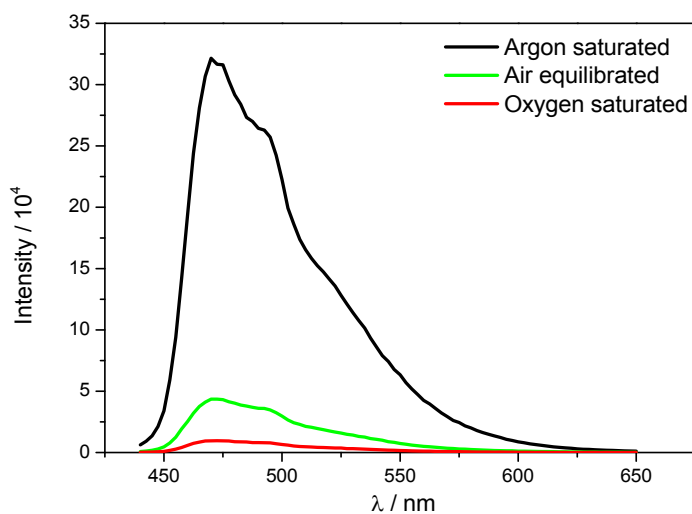
**Figure S3.** Emission spectra at 298 K for **FIrMepic** in acetonitrile varying excitation wavelengths.



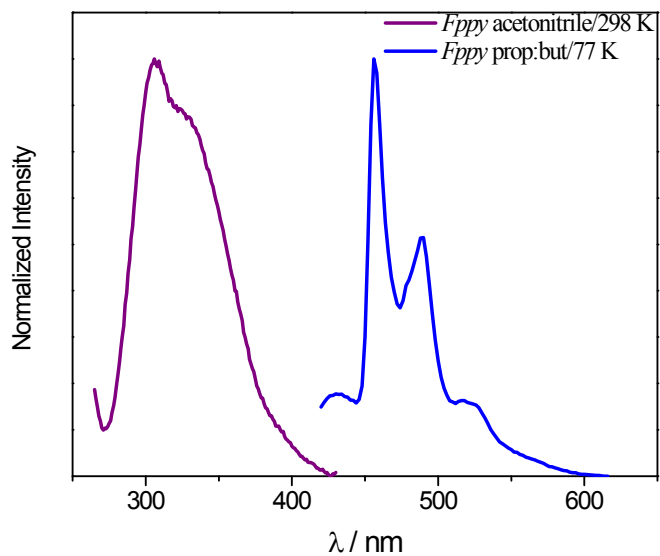
**Figure S4.** Emission decays of **FIrMepic**, **FIrpic** and *Fppy* in different media and temperatures ( $\lambda_{exc} = 378$  nm,  $\lambda_{em} = 480$  nm).



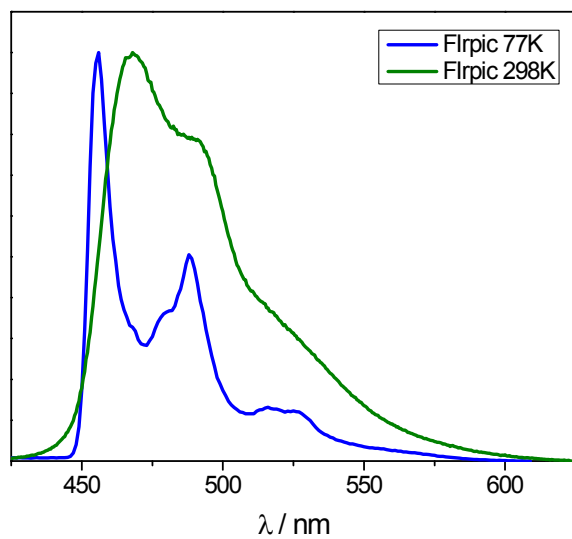
**Figure S5.** Time resolved spectrum of **FIrMepic** in acetonitrile at 298 K in different times after the laser pulse ( $\lambda_{exc} = 378$  nm).



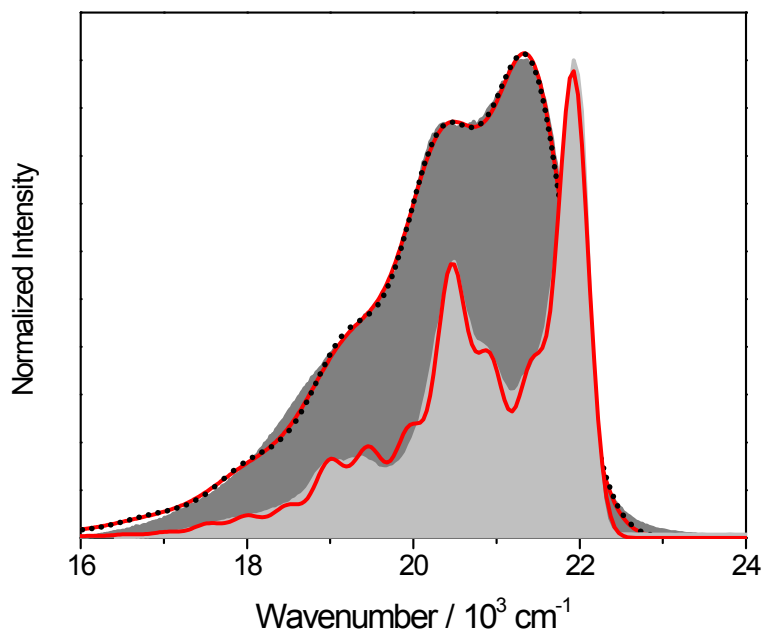
**Figure S6.** Comparison between emission spectra of argon saturated, oxygen saturated and air equilibrated samples of **FIrMepic** in acetonitrile at 298 K.



**Figure S7.** Emission spectra for the free *Fppy* ligand in acetonitrile at 298 K ( $\lambda_{exc} = 230$  nm) or prop:but at 77 K ( $\lambda_{exc} = 365$  nm, with a 389 nm long pass filter).



**Figure S8.** Emission spectra for **FIrpic** in acetonitrile at 298 K or prop:but at 77 K ( $\lambda_{exc} = 365$  nm, with a 389 nm long pass filter).



**Figure S9.** Experimental (solid areas; dark grey – 298 K, light grey – 77 K) and fitted emission spectra for **FIrpic** by using Equations 2 (•••) or 3 (—) and parameters summarized in Table 4.

**Table S2.** Contributions of individual orbitals in excited states of **FIrMepic** and their relative energies.

| Excited State | Transition             | Energy (Wavelength)      | Oscillator Strength |
|---------------|------------------------|--------------------------|---------------------|
| S01           | HOMO-0 → LUMO+0 (61 %) | 3.1561 eV<br>(392.84 nm) | 0.0534              |
|               | HOMO-0 → LUMO+1 (39 %) |                          |                     |
| S02           | HOMO-0 → LUMO+1 (80 %) | 3.2243 eV<br>(384.52 nm) | 0.0009              |
|               | HOMO-0 → LUMO+2 (20 %) |                          |                     |
| S03           | HOMO-0 → LUMO+0 (18 %) | 3.2707 eV<br>(379.08 nm) | 0.0009              |
|               | HOMO-0 → LUMO+2 (82 %) |                          |                     |
| S04           | HOMO-1 → LUMO+0 (40 %) | 3.6322 eV<br>(341.34 nm) | 0.0064              |
|               | HOMO-1 → LUMO+1 (36 %) |                          |                     |
|               | HOMO-1 → LUMO+2 (24 %) |                          |                     |
| S05           | HOMO-2 → LUMO+1 (19 %) | 3.6805 eV<br>(336.87 nm) | 0.0426              |
|               | HOMO-1 → LUMO+0 (81 %) |                          |                     |
| S06           | HOMO-1 → LUMO+2 (56 %) | 3.7682 eV<br>(329.02 nm) | 0.0240              |
|               | HOMO-0 → LUMO+3 (44 %) |                          |                     |
| S07           | HOMO-1 → LUMO+1 (19 %) | 3.7903 eV<br>(327.11 nm) | 0.0412              |
|               | HOMO-0 → LUMO+3 (81 %) |                          |                     |
| S08           | HOMO-4 → LUMO+0 (24 %) | 3.8721 eV<br>(320.20 nm) | 0.0284              |
|               | HOMO-3 → LUMO+0 (23 %) |                          |                     |
|               | HOMO-2 → LUMO+0 (40 %) |                          |                     |
|               | HOMO-2 → LUMO+1 (13 %) |                          |                     |
| S09           | HOMO-0 → LUMO+4 (00 %) | 3.9426 eV<br>(314.47 nm) | 0.0156              |
| S10           | HOMO-4 → LUMO+0 (09 %) | 3.9600 eV<br>(313.09 nm) | 0.0542              |
|               | HOMO-4 → LUMO+2 (13 %) |                          |                     |
|               | HOMO-3 → LUMO+0 (10 %) |                          |                     |
|               | HOMO-3 → LUMO+2 (11 %) |                          |                     |
|               | HOMO-2 → LUMO+0 (18 %) |                          |                     |
|               | HOMO-2 → LUMO+2 (20 %) |                          |                     |
|               | HOMO-0 → LUMO+4 (19 %) |                          |                     |
| T01           | HOMO-3 → LUMO+2 (13 %) | 2.8304 eV<br>(438.04 nm) | --                  |
|               | HOMO-0 → LUMO+0 (53 %) |                          |                     |
|               | HOMO-0 → LUMO+1 (34 %) |                          |                     |
| T02           | HOMO-3 → LUMO+0 (12 %) | 2.8731 eV<br>(431.53 nm) | --                  |
|               | HOMO-1 → LUMO+2 (13 %) |                          |                     |
|               | HOMO-0 → LUMO+1 (19 %) |                          |                     |
|               | HOMO-0 → LUMO+2 (56 %) |                          |                     |
| T03           | HOMO-2 → LUMO+0 (16 %) | 3.1847 eV<br>(389.31 nm) | --                  |
|               | HOMO-0 → LUMO+1 (84 %) |                          |                     |
| T04           | HOMO-3 → LUMO+2 (10 %) | 3.1884 eV<br>(388.86 nm) | --                  |
|               | HOMO-3 → LUMO+4 (11 %) |                          |                     |
|               | HOMO-1 → LUMO+0 (29 %) |                          |                     |

|     |                        |                          |    |
|-----|------------------------|--------------------------|----|
|     | HOMO-1 → LUMO+1 (13 %) |                          |    |
|     | HOMO-0 → LUMO+2 (37 %) |                          |    |
| T05 | HOMO-3 → LUMO+0 (08 %) | 3.2301 eV<br>(383.84 nm) | -- |
|     | HOMO-3 → LUMO+1 (08 %) |                          |    |
|     | HOMO-2 → LUMO+0 (12 %) |                          |    |
|     | HOMO-2 → LUMO+1 (14 %) |                          |    |
|     | HOMO-2 → LUMO+2 (13 %) |                          |    |
|     | HOMO-1 → LUMO+2 (06 %) |                          |    |
|     | HOMO-0 → LUMO+0 (22 %) |                          |    |
|     | HOMO-0 → LUMO+2 (17 %) |                          |    |

**Table S3.** Contributions of individual orbitals in excited states of **Flrpic** and their relative energies.

| Excited State | Transition                                                                                                                                               | Energy (Wavelength)      | Oscillator Strength |
|---------------|----------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|---------------------|
| S01           | HOMO-0 → LUMO+1 (00 %)                                                                                                                                   | 3.1715 eV<br>(390.93 nm) | 0.0540              |
| S02           | HOMO-0 → LUMO+0 (51 %)<br>HOMO-0 → LUMO+1 (49 %)                                                                                                         | 3.2104 eV<br>(386.20 nm) | 0.0010              |
| S03           | HOMO-0 → LUMO+2 (00 %)                                                                                                                                   | 3.2787 eV<br>(378.15 nm) | 0.0008              |
| S04           | HOMO-1 → LUMO+1 (62 %)<br>HOMO-1 → LUMO+2 (38 %)                                                                                                         | 3.6677 eV<br>(338.04 nm) | 0.0081              |
| S05           | HOMO-3 → LUMO+0 (09 %)<br>HOMO-1 → LUMO+0 (50 %)<br>HOMO-1 → LUMO+1 (26 %)<br>HOMO-1 → LUMO+2 (15 %)                                                     | 3.6890 eV<br>(336.09 nm) | 0.0309              |
| S06           | HOMO-1 → LUMO+2 (15 %)<br>HOMO-0 → LUMO+3 (85 %)                                                                                                         | 3.7518 eV<br>(330.47 nm) | 0.0045              |
| S07           | HOMO-3 → LUMO+2 (14 %)<br>HOMO-2 → LUMO+0 (16 %)<br>HOMO-1 → LUMO+2 (70 %)                                                                               | 3.8010 eV<br>(326.18 nm) | 0.0659              |
| S08           | HOMO-4 → LUMO+0 (19 %)<br>HOMO-4 → LUMO+2 (12 %)<br>HOMO-3 → LUMO+0 (16 %)<br>HOMO-3 → LUMO+2 (08 %)<br>HOMO-2 → LUMO+0 (29 %)<br>HOMO-2 → LUMO+2 (16 %) | 3.8845 eV<br>(319.18 nm) | 0.0324              |
| S09           | HOMO-4 → LUMO+2 (33 %)<br>HOMO-3 → LUMO+2 (21 %)<br>HOMO-2 → LUMO+2 (46 %)                                                                               | 3.9488 eV<br>(313.98 nm) | 0.0446              |
| S10           | HOMO-0 → LUMO+4 (00 %)                                                                                                                                   | 3.9613 eV<br>(312.99 nm) | 0.0177              |
| T01           | HOMO-3 → LUMO+2 (20 %)<br>HOMO-0 → LUMO+1 (80 %)                                                                                                         | 2.8352 eV<br>(437.31 nm) | --                  |
| T02           | HOMO-2 → LUMO+0 (14 %)<br>HOMO-1 → LUMO+0 (15 %)<br>HOMO-1 → LUMO+2 (10 %)<br>HOMO-0 → LUMO+1 (12 %)<br>HOMO-0 → LUMO+2 (49 %)                           | 2.8759 eV<br>(431.12 nm) | --                  |
| T03           | HOMO-0 → LUMO+0 (53 %)<br>HOMO-0 → LUMO+1 (47 %)                                                                                                         | 3.1726 eV<br>(390.80 nm) | --                  |
| T04           | HOMO-3 → LUMO+4 (13 %)<br>HOMO-1 → LUMO+1 (27 %)<br>HOMO-0 → LUMO+0 (18 %)                                                                               | 3.2028 eV<br>(387.11 nm) | --                  |

|     |                        |                          |    |
|-----|------------------------|--------------------------|----|
|     | HOMO-0 → LUMO+2 (42 %) |                          |    |
| T05 | HOMO-3 → LUMO+1 (13 %) | 3.2392 eV<br>(382.76 nm) | -- |
|     | HOMO-3 → LUMO+2 (08 %) |                          |    |
|     | HOMO-2 → LUMO+1 (20 %) |                          |    |
|     | HOMO-2 → LUMO+2 (17 %) |                          |    |
|     | HOMO-1 → LUMO+2 (09 %) |                          |    |
|     | HOMO-0 → LUMO+1 (13 %) |                          |    |
|     | HOMO-0 → LUMO+2 (20 %) |                          |    |

**Table S4.** Contributions of individual orbitals in excited states of *mer*-[Ir(*Fppy*)<sub>2</sub>(*dmb*)]<sup>+</sup> and their relative energies.

| Excited State | Transition                                                                                                                     | Energy (Wavelength)      | Oscillator Strength |
|---------------|--------------------------------------------------------------------------------------------------------------------------------|--------------------------|---------------------|
| S01           | HOMO-0 → LUMO+0 (00 %)                                                                                                         | 2.8627 eV<br>(433.10 nm) | 0.0002              |
| S02           | HOMO-0 → LUMO+1 (00 %)                                                                                                         | 3.3357 eV<br>(371.68 nm) | 0.0543              |
| S03           | HOMO-0 → LUMO+2 (00 %)                                                                                                         | 3.4364 eV<br>(360.80 nm) | 0.0071              |
| S04           | HOMO-3 → LUMO+0 (47 %)<br>HOMO-2 → LUMO+0 (53 %)                                                                               | 3.4484 eV<br>(359.55 nm) | 0.0002              |
| S05           | HOMO-4 → LUMO+0 (12 %)<br>HOMO-1 → LUMO+0 (56 %)<br>HOMO-0 → LUMO+2 (32 %)                                                     | 3.4683 eV<br>(357.48 nm) | 0.0296              |
| S06           | HOMO-3 → LUMO+0 (00 %)                                                                                                         | 3.6782 eV<br>(337.08 nm) | 0.0005              |
| S07           | HOMO-4 → LUMO+0 (00 %)                                                                                                         | 3.6824 eV<br>(336.70 nm) | 0.0801              |
| S08           | HOMO-0 → LUMO+3 (00 %)                                                                                                         | 3.8103 eV<br>(325.39 nm) | 0.0041              |
| S09           | HOMO-4 → LUMO+2 (16 %)<br>HOMO-3 → LUMO+1 (29 %)<br>HOMO-2 → LUMO+1 (35 %)<br>HOMO-1 → LUMO+2 (20 %)                           | 3.9455 eV<br>(314.25 nm) | 0.0227              |
| S10           | HOMO-5 → LUMO+1 (08 %)<br>HOMO-4 → LUMO+1 (22 %)<br>HOMO-3 → LUMO+2 (11 %)<br>HOMO-2 → LUMO+2 (13 %)<br>HOMO-1 → LUMO+1 (46 %) | 3.9527 eV<br>(313.67 nm) | 0.0235              |
| T01           | HOMO-6 → LUMO+0 (15 %)<br>HOMO-0 → LUMO+0 (85 %)                                                                               | 2.8259 eV<br>(438.75 nm) | --                  |
| T02           | HOMO-1 → LUMO+2 (36 %)<br>HOMO-1 → LUMO+6 (12 %)<br>HOMO-0 → LUMO+1 (52 %)                                                     | 2.8936 eV<br>(428.48 nm) | --                  |
| T03           | HOMO-1 → LUMO+1 (48 %)<br>HOMO-0 → LUMO+2 (52 %)                                                                               | 2.9213 eV<br>(424.41 nm) | --                  |
| T04           | HOMO-6 → LUMO+0 (78 %)<br>HOMO-6 → LUMO+3 (22 %)                                                                               | 3.0263 eV<br>(409.69 nm) | --                  |
| T05           | HOMO-5 → LUMO+0 (14 %)<br>HOMO-4 → LUMO+0 (46 %)<br>HOMO-1 → LUMO+0 (40 %)                                                     | 3.2646 eV<br>(379.79 nm) | --                  |

**Table S5.** Electron density populations for **FIrpic** and  $[\text{Ir}(\text{Fppy})_2(\text{dmb})]^+$  in  $\text{CH}_3\text{CN}$ .

|         |        | $[\text{Ir}(\text{Fppy})_2(\text{dmb})]^+$ |             |            | <b>FIrpic</b> |             |            |
|---------|--------|--------------------------------------------|-------------|------------|---------------|-------------|------------|
|         |        | Iridium                                    | <i>Fppy</i> | <i>dmb</i> | Iridium       | <i>Fppy</i> | <i>pic</i> |
| triplet | LUMO+7 | 07.50                                      | 07.89       | 84.61      | 13.02         | 83.33       | 03.65      |
|         | LUMO+6 | 19.29                                      | 76.03       | 04.68      | 14.06         | 76.46       | 09.48      |
|         | LUMO+5 | 09.99                                      | 79.07       | 10.94      | 03.63         | 94.62       | 01.75      |
|         | LUMO+4 | 03.17                                      | 95.98       | 00.85      | 04.12         | 79.33       | 16.55      |
|         | LUMO+3 | 03.66                                      | 91.14       | 05.20      | 02.83         | 18.62       | 78.55      |
|         | LUMO+2 | 04.91                                      | 93.09       | 02.00      | 02.46         | 04.30       | 93.24      |
|         | LUMO+1 | 04.66                                      | 91.52       | 03.82      | 05.12         | 91.64       | 03.24      |
|         | LUMO+0 | 03.41                                      | 02.98       | 93.61      | 06.00         | 90.06       | 03.94      |
| singlet | LUMO+7 | 08.66                                      | 79.73       | 11.61      | 11.80         | 84.99       | 03.21      |
|         | LUMO+6 | 03.94                                      | 93.07       | 02.99      | 07.74         | 85.05       | 07.21      |
|         | LUMO+5 | 04.69                                      | 72.89       | 22.42      | 02.95         | 54.45       | 42.60      |
|         | LUMO+4 | 00.60                                      | 03.94       | 95.46      | 03.58         | 95.46       | 00.96      |
|         | LUMO+3 | 04.26                                      | 24.03       | 71.71      | 02.93         | 44.18       | 52.89      |
|         | LUMO+2 | 05.80                                      | 91.57       | 02.63      | 05.29         | 91.21       | 03.50      |
|         | LUMO+1 | 05.14                                      | 91.76       | 03.10      | 05.85         | 62.64       | 31.51      |
|         | LUMO+0 | 03.29                                      | 02.26       | 94.45      | 02.03         | 34.05       | 63.92      |
|         | HOMO-0 | 46.09                                      | 50.71       | 03.20      | 49.86         | 44.43       | 05.71      |
|         | HOMO-1 | 11.06                                      | 87.48       | 01.46      | 54.31         | 31.90       | 13.79      |
|         | HOMO-2 | 22.58                                      | 75.16       | 02.26      | 30.56         | 64.94       | 04.50      |
|         | HOMO-3 | 62.46                                      | 29.80       | 07.74      | 23.75         | 68.86       | 07.39      |
|         | HOMO-4 | 60.58                                      | 30.32       | 09.10      | 49.08         | 46.34       | 04.58      |
|         | HOMO-5 | 11.70                                      | 84.30       | 04.00      | 06.29         | 66.88       | 26.83      |
|         | HOMO-6 | 02.26                                      | 01.72       | 96.02      | 02.01         | 23.92       | 74.07      |
|         | HOMO-7 | 08.95                                      | 60.30       | 30.75      | 05.49         | 29.09       | 65.42      |

**Table S6.** Electron density populations and orbital energies for optimized geometry in the ground state of **FIrMepic** in CH<sub>3</sub>CN.

|         | Molecular<br>Orbital | Energy /<br>Hartree <sup>a</sup> | Contribution / % |             |                |
|---------|----------------------|----------------------------------|------------------|-------------|----------------|
|         |                      |                                  | iridium          | <i>Fppy</i> | <i>3-Mepic</i> |
| triplet | 149 (LUMO+7)         | −0.01126                         | 12.08            | 84.50       | 03.42          |
|         | 148 (LUMO+6)         | −0.01817                         | 13.43            | 76.97       | 09.60          |
|         | 147 (LUMO+5)         | −0.03069                         | 03.34            | 90.60       | 06.06          |
|         | 146 (LUMO+4)         | −0.03273                         | 04.06            | 69.24       | 26.70          |
|         | 145 (LUMO+3)         | −0.04232                         | 02.62            | 31.18       | 66.20          |
|         | 144 (LUMO+2)         | −0.06621                         | 02.43            | 03.89       | 93.68          |
|         | 143 (LUMO+1)         | −0.07048                         | 05.10            | 91.93       | 02.97          |
|         | 142 (LUMO+0)         | −0.09353                         | 05.97            | 90.39       | 03.64          |
| singlet | 149 (LUMO+7)         | −0.00344                         | 11.19            | 85.81       | 03.00          |
|         | 148 (LUMO+6)         | −0.00434                         | 07.37            | 85.48       | 07.15          |
|         | 147 (LUMO+5)         | −0.03122                         | 02.58            | 32.68       | 64.74          |
|         | 146 (LUMO+4)         | −0.03504                         | 03.55            | 95.37       | 01.08          |
|         | 145 (LUMO+3)         | −0.04158                         | 02.78            | 64.11       | 33.11          |
|         | 144 (LUMO+2)         | −0.0583                          | 05.19            | 88.27       | 06.54          |
|         | 143 (LUMO+1)         | −0.05977                         | 05.29            | 35.27       | 59.44          |
|         | 142 (LUMO+0)         | −0.06159                         | 02.71            | 65.09       | 32.20          |
|         | 141 (HOMO−0)         | −0.20551                         | 50.22            | 43.59       | 06.19          |
|         | 140 (HOMO−1)         | −0.22423                         | 56.66            | 27.18       | 16.16          |
|         | 139 (HOMO−2)         | −0.23084                         | 29.73            | 65.83       | 04.44          |
|         | 138 (HOMO−3)         | −0.23390                         | 23.09            | 68.61       | 08.30          |
|         | 137 (HOMO−4)         | −0.23849                         | 44.77            | 50.31       | 04.92          |
|         | 136 (HOMO−5)         | −0.24428                         | 06.75            | 46.04       | 47.21          |
|         | 135 (HOMO−6)         | −0.25154                         | 02.45            | 44.08       | 53.47          |
|         | 134 (HOMO−7)         | −0.26956                         | 00.96            | 04.44       | 94.60          |

<sup>a</sup>1 Hartree = 27.2116 eV.

**Table S7.** Electron density populations for optimized geometry in the T<sub>1</sub> state of **FIrMepic** in CH<sub>3</sub>CN.

|         | Molecular<br>Orbital | Eigenvalues<br>/ Hartree <sup>a</sup> | Contribution / % |             |              |
|---------|----------------------|---------------------------------------|------------------|-------------|--------------|
|         |                      |                                       | Iridium          | <i>Fppy</i> | <i>Mepic</i> |
| triplet | 144 (LUMO+2)         | −0.06224                              | 02.57            | 05.24       | 92.19        |
|         | 143 (LUMO+1)         | −0.06459                              | 04.79            | 91.24       | 03.97        |
|         | 142 (LUMO+0)         | −0.11422                              | 05.78            | 91.15       | 03.07        |
| singlet | 145 (LUMO+3)         | −0.04012                              | 02.48            | 62.31       | 35.21        |
|         | 144 (LUMO+2)         | −0.05900                              | 04.83            | 67.23       | 27.94        |
|         | 143 (LUMO+1)         | −0.06006                              | 03.18            | 28.60       | 68.22        |
|         | 142 (LUMO+0)         | −0.07084                              | 05.77            | 90.93       | 03.30        |
|         | 141 (HOMO−0)         | −0.20181                              | 45.15            | 48.45       | 06.40        |
|         | 140 (HOMO−1)         | −0.22375                              | 38.07            | 52.77       | 09.16        |
|         | 139 (HOMO−2)         | −0.22766                              | 45.67            | 41.18       | 13.15        |
|         | 138 (HOMO−3)         | −0.23487                              | 19.09            | 73.53       | 07.38        |

<sup>a</sup>1 Hartree = 27.2116 eV.

**Table S8.** Electron density populations and orbital energies for *mer*-[Ir(*Fppy*)<sub>2</sub>(4-*Mepic*)] in CH<sub>3</sub>CN.

|         | Molecular<br>Orbital | Energy /<br>Hartree <sup>a</sup> | Contribution / % |             |                 |
|---------|----------------------|----------------------------------|------------------|-------------|-----------------|
|         |                      |                                  | Iridium          | <i>Fppy</i> | 4- <i>Mepic</i> |
| triplet | 149 (LUMO+7)         | −0.01163                         | 12.81            | 83.60       | 03.59           |
|         | 148 (LUMO+6)         | −0.01855                         | 13.83            | 76.85       | 09.32           |
|         | 147 (LUMO+5)         | −0.03103                         | 03.48            | 92.55       | 03.97           |
|         | 146 (LUMO+4)         | −0.03291                         | 04.13            | 70.13       | 25.74           |
|         | 145 (LUMO+3)         | −0.04253                         | 03.42            | 28.81       | 67.77           |
|         | 144 (LUMO+2)         | −0.06499                         | 02.23            | 03.29       | 94.48           |
|         | 143 (LUMO+1)         | −0.07068                         | 05.07            | 92.73       | 02.20           |
|         | 142 (LUMO+0)         | −0.09364                         | 05.96            | 90.25       | 03.79           |
| singlet | 149 (LUMO+7)         | +0.00324                         | 11.70            | 85.16       | 03.14           |
|         | 148 (LUMO+6)         | −0.00462                         | 07.54            | 85.46       | 07.00           |
|         | 147 (LUMO+5)         | −0.03179                         | 03.29            | 35.05       | 61.66           |
|         | 146 (LUMO+4)         | −0.03509                         | 03.53            | 95.59       | 00.88           |
|         | 145 (LUMO+3)         | −0.04165                         | 03.20            | 61.65       | 35.15           |
|         | 144 (LUMO+2)         | −0.05847                         | 04.67            | 72.08       | 23.25           |
|         | 143 (LUMO+1)         | −0.05898                         | 04.90            | 39.04       | 56.06           |
|         | 142 (LUMO+0)         | −0.06148                         | 03.28            | 76.85       | 19.87           |
|         | 141 (HOMO−0)         | −0.20585                         | 50.03            | 44.20       | 05.77           |
|         | 140 (HOMO−1)         | −0.22516                         | 55.20            | 30.66       | 14.14           |
|         | 139 (HOMO−2)         | −0.23101                         | 35.47            | 59.56       | 04.97           |
|         | 138 (HOMO−3)         | −0.23419                         | 24.89            | 67.12       | 07.99           |
|         | 137 (HOMO−4)         | −0.23825                         | 41.78            | 53.17       | 05.05           |
|         | 136 (HOMO−5)         | −0.24593                         | 05.43            | 64.72       | 29.85           |
|         | 135 (HOMO−6)         | −0.25419                         | 01.99            | 25.54       | 72.47           |
|         | 134 (HOMO−7)         | −0.27225                         | 05.01            | 25.21       | 69.78           |

<sup>a</sup>1 Hartree = 27.2116 eV.

**Table S9.** Electron density populations and orbital energies for *mer*-[Ir(*Fppy*)<sub>2</sub>(5-*Mepic*)] in CH<sub>3</sub>CN.

|         | Molecular<br>Orbital | Energy /<br>Hartree <sup>a</sup> | Contribution / % |             |                 |
|---------|----------------------|----------------------------------|------------------|-------------|-----------------|
|         |                      |                                  | Iridium          | <i>Fppy</i> | 5- <i>Mepic</i> |
| triplet | 149 (LUMO+7)         | −0.01174                         | 12.89            | 83.49       | 03.62           |
|         | 148 (LUMO+6)         | −0.01863                         | 13.77            | 76.79       | 09.44           |
|         | 147 (LUMO+5)         | −0.03118                         | 03.48            | 92.52       | 04.00           |
|         | 146 (LUMO+4)         | −0.03289                         | 04.17            | 70.43       | 25.40           |
|         | 145 (LUMO+3)         | −0.04303                         | 03.33            | 29.16       | 67.51           |
|         | 144 (LUMO+2)         | −0.06594                         | 02.39            | 03.56       | 94.05           |
|         | 143 (LUMO+1)         | −0.07084                         | 05.11            | 92.18       | 02.71           |
|         | 142 (LUMO+0)         | −0.09375                         | 05.97            | 90.22       | 03.81           |
| singlet | 149 (LUMO+7)         | +0.00311                         | 11.78            | 85.03       | 03.19           |
|         | 148 (LUMO+6)         | −0.00470                         | 07.52            | 85.34       | 07.14           |
|         | 147 (LUMO+5)         | −0.03189                         | 03.18            | 36.78       | 60.04           |
|         | 146 (LUMO+4)         | −0.03520                         | 03.56            | 95.56       | 00.88           |
|         | 145 (LUMO+3)         | −0.04211                         | 03.21            | 60.83       | 35.96           |
|         | 144 (LUMO+2)         | −0.05860                         | 05.02            | 84.05       | 10.93           |
|         | 143 (LUMO+1)         | −0.05967                         | 05.26            | 37.21       | 57.53           |
|         | 142 (LUMO+0)         | −0.06176                         | 02.79            | 66.06       | 31.15           |
|         | 141 (HOMO−0)         | −0.20612                         | 49.97            | 44.24       | 05.79           |
|         | 140 (HOMO−1)         | −0.22527                         | 55.33            | 30.23       | 14.44           |
|         | 139 (HOMO−2)         | −0.23122                         | 31.64            | 63.86       | 04.50           |
|         | 138 (HOMO−3)         | −0.23439                         | 24.11            | 68.21       | 07.68           |
|         | 137 (HOMO−4)         | −0.23870                         | 45.70            | 49.39       | 04.91           |
|         | 136 (HOMO−5)         | −0.24592                         | 05.98            | 62.77       | 31.25           |
|         | 135 (HOMO−6)         | −0.25398                         | 02.01            | 26.96       | 71.03           |
|         | 134 (HOMO−7)         | −0.26873                         | 02.72            | 05.31       | 91.97           |

<sup>a</sup>1 Hartree = 27.2116 eV.

**Table S10.** Contributions of individual orbitals in excited states of *mer*-[Ir(*Fppy*)<sub>2</sub>(4-*Mepic*)] and their relative energies.

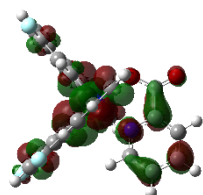
| Excited State | Transition             | Energy (Wavelength)      | Oscillator Strength |
|---------------|------------------------|--------------------------|---------------------|
| S01           | HOMO-0 → LUMO+0 (74 %) | 3.1645 eV<br>(391.79 nm) | 0.0535              |
|               | HOMO-0 → LUMO+1 (26 %) |                          |                     |
| S02           | HOMO-0 → LUMO+1 (66 %) | 3.2574 eV<br>(380.62 nm) | 0.0005              |
|               | HOMO-0 → LUMO+2 (34 %) |                          |                     |
| S03           | HOMO-0 → LUMO+0 (27 %) | 3.2880 eV<br>(377.08 nm) | 0.0016              |
|               | HOMO-0 → LUMO+2 (73 %) |                          |                     |
| S04           | HOMO-1 → LUMO+0 (48 %) | 3.6599 eV<br>(338.77 nm) | 0.0070              |
|               | HOMO-1 → LUMO+1 (34 %) |                          |                     |
|               | HOMO-1 → LUMO+2 (18 %) |                          |                     |
| S05           | HOMO-1 → LUMO+1 (75 %) | 3.7345 eV<br>(332.00 nm) | 0.0548              |
|               | HOMO-1 → LUMO+2 (25 %) |                          |                     |
| T01           | HOMO-3 → LUMO+2 (15 %) | 2.8322 eV<br>(437.76 nm) | --                  |
|               | HOMO-0 → LUMO+0 (62 %) |                          |                     |
|               | HOMO-0 → LUMO+1 (23 %) |                          |                     |

**Table S11.** Contributions of individual orbitals in excited states of *mer*-[Ir(*Fppy*)<sub>2</sub>(5-*Mepic*)] and their relative energies.

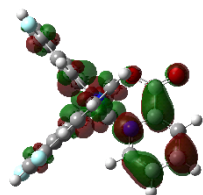
| Excited State | Transition             | Energy (Wavelength)      | Oscillator Strength |
|---------------|------------------------|--------------------------|---------------------|
| S01           | HOMO-0 → LUMO+0 (86 %) | 3.1688 eV<br>(391.26 nm) | 0.0530              |
|               | HOMO-0 → LUMO+2 (16 %) |                          |                     |
| S02           | HOMO-0 → LUMO+0 (28 %) | 3.2430 eV<br>(382.31 nm) | 0.0007              |
|               | HOMO-0 → LUMO+1 (56 %) |                          |                     |
|               | HOMO-0 → LUMO+2 (16 %) |                          |                     |
| S03           | HOMO-0 → LUMO+2 (00 %) | 3.2822 eV<br>(377.74 nm) | 0.0012              |
| S04           | HOMO-2 → LUMO+1 (20 %) | 3.6594 eV<br>(338.81 nm) | 0.0069              |
|               | HOMO-1 → LUMO+0 (80 %) |                          |                     |
| S05           | HOMO-1 → LUMO+1 (45 %) | 3.7127 eV<br>(333.94 nm) | 0.0435              |
|               | HOMO-1 → LUMO+1 (41 %) |                          |                     |
|               | HOMO-1 → LUMO+2 (14 %) |                          |                     |
| T01           | HOMO-2 → LUMO+1 (13 %) | 2.8342 eV<br>(437.46 nm) | --                  |
|               | HOMO-2 → LUMO+2 (18 %) |                          |                     |
|               | HOMO-1 → LUMO+2 (20 %) |                          |                     |
|               | HOMO-0 → LUMO+0 (49 %) |                          |                     |

*singlet MOs*

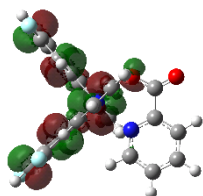
*triplet MOs*



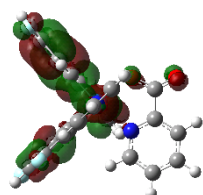
LUMO+1



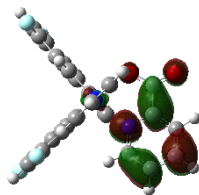
LUMO



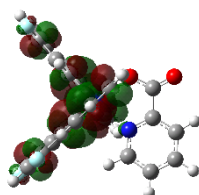
HOMO



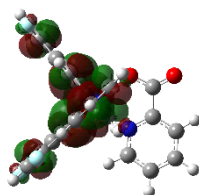
HOMO-3



LUMO+2



LUMO+1

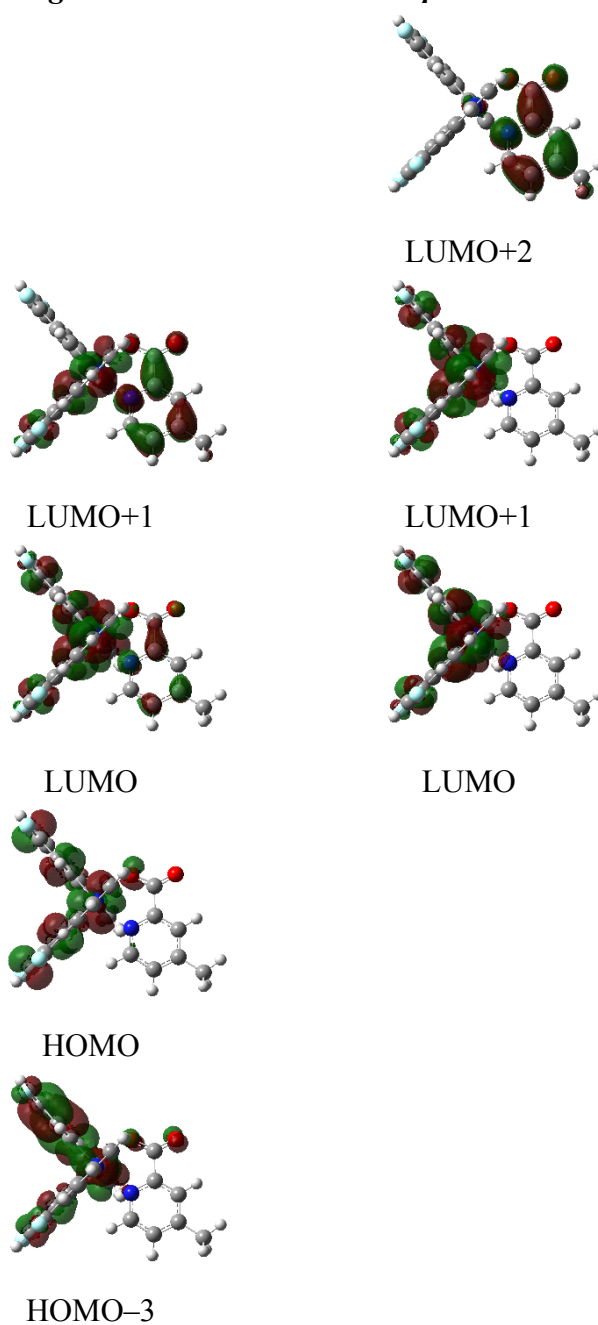


LUMO

**Figure S10.** Molecular-orbital electron contours ( $0.03 \text{ e}\text{\AA}^{-3}$ ) for **FIrpic**.

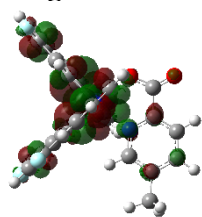
*singlet MOs*

*triplet MOs*

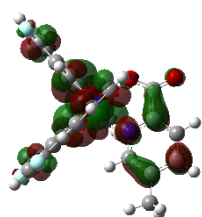


**Figure S11.** Molecular-orbital electron contours ( $0.03 \text{ e}\text{\AA}^{-3}$ ) for  $[\text{Ir}(\text{Fppy})_2(4\text{-Mepic})]$ .

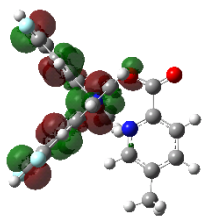
*singlet MOs*



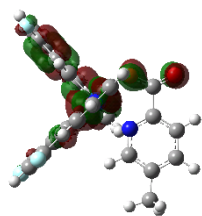
LUMO+2



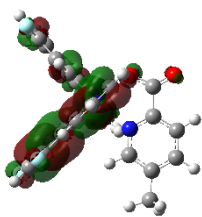
LUMO



HOMO

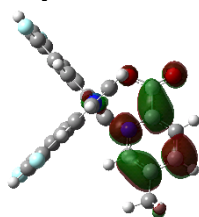


HOMO-1

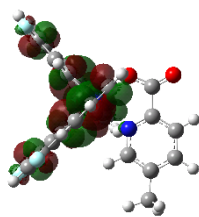


HOMO-2

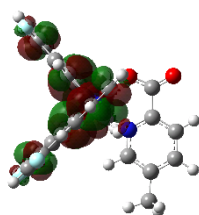
*triplet MOs*



LUMO+2



LUMO+1



LUMO

**Figure S12.** Molecular-orbital electron contours ( $0.03 \text{ e}\text{\AA}^{-3}$ ) for  $[\text{Ir}(\text{Fppy})_2(5\text{-Mepic})]$ .