**Table S1** Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **1**. (Ir, ML and POXD denote the iridium atom, main ligand and N-(5-phenyl-1,3,4-oxadiazol-2-yl)-diphenylphosphinic amide ligand, respectively, in the complex.)

| MO | Energy | Compositions | | | Assignment |
|---|---|---|---|---|---|
| | | Ir | ML | POXD | |
| L+10 | 0.15 | 11 | 83 | 6 | d*(Ir)+π*(ML) |
| L+9 | 0.01 | 0 | 2 | 98 | π*(POXD) |
| L+8 | -0.07 | 0 | 0 | 100 | π*(POXD) |
| L+7 | -0.17 | 0 | 2 | 98 | π*(POXD) |
| L+6 | -0.28 | 0 | 1 | 98 | π*(POXD) |
| L+5 | -0.77 | 1 | 97 | 2 | π*(ML) |
| L+4 | -0.87 | 0 | 3 | 97 | π*(POXD) |
| L+3 | -0.88 | 0 | 95 | 5 | π*(ML) |
| L+2 | -1.16 | 0 | 5 | 94 | π*(POXD) |
| L+1 | -1.83 | 3 | 96 | 1 | π*(ML) |
| L | -1.91 | 3 | 96 | 2 | π*(ML) |
| HOMO–LUMO energy gap ( 3.57 eV ) | | | | | |
| H | -5.48 | 41 | 47 | 11 | d(Ir)+π(ML+POXD) |
| H-1 | -5.84 | 31 | 20 | 49 | d(Ir)+π(ML+POXD) |
| H-2 | -6.24 | 46 | 36 | 18 | d(Ir)+π(ML+POXD) |
| H-3 | -6.43 | 24 | 66 | 10 | d(Ir)+π(ML+POXD) |
| H-4 | -6.56 | 16 | 71 | 13 | d(Ir)+π(ML+POXD) |
| H-5 | -6.75 | 9 | 86 | 6 | π(ML) |
| H-6 | -6.88 | 3 | 94 | 4 | π(ML) |
| H-7 | -7.01 | 6 | 78 | 16 | π(ML+POXD) |
| H-8 | -7.12 | 22 | 62 | 15 | d(Ir)+π(ML+POXD) |
| H-9 | -7.34 | 2 | 6 | 92 | π(POXD) |
| H-10 | -7.43 | 1 | 6 | 93 | π(POXD) |

**Table S2** Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **2**. (Ir, ML and POXD denote the iridium atom, main ligand and N-(5-phenyl-1,3,4-oxadiazol-2-yl)-diphenylphosphinic amide ligand, respectively, in the complex.)

| MO | Energy | Compositions | | | Assignment |
|---|---|---|---|---|---|
| | | Ir | ML | POXD | |
| L+10 | -0.04 | 0 | 94 | 6 | π*(ML) |
| L+9 | -0.10 | 0 | 1 | 99 | π*(POXD) |
| L+8 | -0.14 | 0 | 4 | 95 | π*(POXD) |
| L+7 | -0.33 | 0 | 3 | 96 | π*(POXD) |
| L+6 | -0.37 | 0 | 1 | 99 | π*(POXD) |
| L+5 | -0.79 | 2 | 95 | 3 | π*(ML) |
| L+4 | -0.91 | 3 | 92 | 6 | π*(ML) |
| L+3 | -0.98 | 0 | 5 | 95 | π*(POXD) |
| L+2 | -1.24 | 0 | 6 | 93 | π*(POXD) |
| L+1 | -1.49 | 3 | 93 | 3 | π*(ML) |
| L | -1.59 | 3 | 94 | 2 | π*(ML) |
| HOMO–LUMO energy gap ( 3.90 eV ) | | | | | |
| H | -5.49 | 43 | 45 | 13 | d(Ir)+π(ML+POXD) |
| H-1 | -5.79 | 30 | 19 | 51 | d(Ir)+π(ML+POXD) |
| H-2 | -6.06 | 42 | 49 | 9 | d(Ir)+π(ML) |
| H-3 | -6.18 | 19 | 75 | 5 | d(Ir)+π(ML) |
| H-4 | -6.36 | 18 | 80 | 2 | d(Ir)+π(ML) |
| H-5 | -6.66 | 36 | 29 | 35 | d(Ir)+π(ML+POXD) |
| H-6 | -6.81 | 7 | 87 | 6 | π(ML) |
| H-7 | -7.25 | 0 | 100 | 0 | π(ML) |
| H-8 | -7.26 | 0 | 100 | 0 | π(ML) |
| H-9 | -7.38 | 3 | 53 | 44 | π(ML+POXD) |
| H-10 | -7.42 | 0 | 89 | 10 | π(ML+POXD) |

**Table S3** Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **3**. (Ir, ML and POXD denote the iridium atom, main ligand and N-(5-phenyl-1,3,4-oxadiazol-2-yl)-diphenylphosphinic amide ligand, respectively, in the complex.)

| MO | Energy | Compositions | | | Assignment |
|---|---|---|---|---|---|
| | | Ir | ML | POXD | |
| L+10 | -0.08 | 0 | 0 | 100 | π*(POXD) |
| L+9 | -0.20 | 1 | 4 | 95 | π*(POXD) |
| L+8 | -0.27 | 2 | 44 | 54 | π*(ML+POXD) |
| L+7 | -0.28 | 2 | 68 | 30 | π*(ML+POXD) |
| L+6 | -0.36 | 3 | 75 | 23 | π*(ML+POXD) |
| L+5 | -0.86 | 1 | 43 | 56 | π*(ML+POXD) |
| L+4 | -0.89 | 2 | 61 | 37 | π*(ML+POXD) |
| L+3 | -1.00 | 3 | 81 | 15 | π*(ML+POXD) |
| L+2 | -1.17 | 0 | 9 | 91 | π*(POXD) |
| L+1 | -1.57 | 2 | 97 | 1 | π*(ML) |
| L | -1.63 | 2 | 97 | 1 | π*(ML) |
| HOMO–LUMO energy gap ( 3.79 eV ) | | | | | |
| H | -5.42 | 37 | 59 | 3 | d(Ir)+π(ML) |
| H-1 | -5.81 | 30 | 15 | 55 | d(Ir)+π(ML+POXD) |
| H-2 | -5.97 | 9 | 85 | 6 | π(ML) |
| H-3 | -6.15 | 31 | 62 | 7 | d(Ir)+π(ML) |
| H-4 | -6.32 | 33 | 57 | 9 | d(Ir)+π(ML) |
| H-5 | -6.52 | 7 | 90 | 3 | π(ML) |
| H-6 | -6.73 | 43 | 24 | 33 | d(Ir)+π(ML+POXD) |
| H-7 | -7.34 | 4 | 9 | 87 | π(POXD) |
| H-8 | -7.39 | 11 | 35 | 54 | d(Ir)+π(ML+POXD) |
| H-9 | -7.44 | 0 | 1 | 98 | π(POXD) |
| H-10 | -7.48 | 0 | 0 | 100 | π(POXD) |

**Table S4** Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **4**. (Ir, ML and POXD denote the iridium atom, main ligand and N-(5-phenyl-1,3,4-oxadiazol-2-yl)-diphenylphosphinic amide ligand, respectively, in the complex.)

| MO | Energy | Compositions | | | Assignment |
|---|---|---|---|---|---|
| | | Ir | ML | POXD | |
| L+10 | -0.08 | 0 | 0 | 100 | π*(POXD) |
| L+9 | -0.17 | 0 | 46 | 53 | π*(ML+POXD) |
| L+8 | -0.22 | 1 | 84 | 16 | π*(ML+POXD) |
| L+7 | -0.27 | 1 | 51 | 49 | π*(ML+POXD) |
| L+6 | -0.3 | 1 | 19 | 81 | π*(ML+POXD) |
| L+5 | -0.83 | 2 | 85 | 13 | π*(ML+POXD) |
| L+4 | -0.87 | 2 | 55 | 43 | π*(ML+POXD) |
| L+3 | -0.9 | 1 | 52 | 46 | π*(ML+POXD) |
| L+2 | -1.17 | 0 | 4 | 96 | π*(POXD) |
| L+1 | -1.58 | 5 | 93 | 2 | π*(ML) |
| L | -1.65 | 4 | 94 | 2 | π*(ML) |
| HOMO–LUMO energy gap ( 3.76 eV ) | | | | | |
| H | -5.41 | 31 | 67 | 2 | d(Ir)+π(ML) |
| H-1 | -5.88 | 24 | 22 | 54 | d(Ir)+π(ML+POXD) |
| H-2 | -5.92 | 5 | 83 | 13 | π(ML+POXD) |
| H-3 | -6.27 | 61 | 29 | 10 | d(Ir)+π(ML+POXD) |
| H-4 | -6.39 | 23 | 75 | 2 | d(Ir)+π(ML) |
| H-5 | -6.69 | 31 | 42 | 27 | d(Ir)+π(ML+POXD) |
| H-6 | -6.82 | 14 | 75 | 11 | d(Ir)+π(ML+POXD) |
| H-7 | -7.35 | 1 | 2 | 97 | π(POXD) |
| H-8 | -7.44 | 1 | 6 | 94 | π(POXD) |
| H-9 | -7.48 | 3 | 32 | 64 | π(ML+POXD) |
| H-10 | -7.49 | 1 | 8 | 91 | π(POXD) |

**Table S5** Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **5**. (Ir, ML and POXD denote the iridium atom, main ligand and N-(5-phenyl-1,3,4-oxadiazol-2-yl)-diphenylphosphinic amide ligand, respectively, in the complex.)

| MO | Energy | Compositions | | | Assignment |
|---|---|---|---|---|---|
| | | Ir | ML | POXD | |
| L+10 | 0.00 | 1 | 73 | 26 | π*(ML+POXD) |
| L+9 | -0.02 | 1 | 36 | 64 | π*(ML+POXD) |
| L+8 | -0.07 | 0 | 0 | 100 | π*(POXD) |
| L+7 | -0.20 | 0 | 2 | 97 | π*(POXD) |
| L+6 | -0.29 | 0 | 2 | 98 | π*(POXD) |
| L+5 | -0.77 | 3 | 93 | 5 | π*(ML) |
| L+4 | -0.86 | 1 | 38 | 61 | π*(ML+POXD) |
| L+3 | -0.90 | 2 | 59 | 39 | π*(ML+POXD) |
| L+2 | -1.16 | 0 | 6 | 94 | π*(POXD) |
| L+1 | -1.48 | 3 | 95 | 2 | π*(ML) |
| L | -1.56 | 3 | 96 | 2 | π*(ML) |
| HOMO–LUMO energy gap ( 3.85 eV ) | | | | | |
| H | -5.41 | 38 | 58 | 4 | d(Ir)+π(ML) |
| H-1 | -5.80 | 29 | 18 | 53 | d(Ir)+π(ML+POXD) |
| H-2 | -5.94 | 7 | 84 | 9 | π(ML) |
| H-3 | -6.12 | 29 | 67 | 4 | d(Ir)+π(ML) |
| H-4 | -6.24 | 48 | 46 | 6 | d(Ir)+π(ML) |
| H-5 | -6.62 | 19 | 62 | 19 | d(Ir)+π(ML+POXD) |
| H-6 | -6.71 | 26 | 52 | 22 | d(Ir)+π(ML+POXD) |
| H-7 | -7.09 | 1 | 98 | 1 | π(ML) |
| H-8 | -7.13 | 0 | 99 | 0 | π(ML) |
| H-9 | -7.34 | 1 | 5 | 94 | π(POXD) |
| H-10 | -7.42 | 1 | 25 | 74 | π(ML+POXD) |

**Table S6** Selected calculated wavelength λ(nm), oscillator strength *f*, major contribution, transition characters, and the available experimental wavelengths (nm) for complexes **1**–**5**. (H and L indicate HOMO and LUMO, respectively.)

| | State | λ(nm)/E(eV) | *f* | Configuration | Assignment | Nature | Exp.[a] |
|---|---|---|---|---|---|---|---|
| **1** | $S_1$ | 461/2.688 | 0.0231 | H→L(90%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | 453 |
| | $S_{11}$ | 321/3.855 | 0.1624 | H-4→L(76%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| | $S_{14}$ | 311/3.986 | 0.1011 | H-4→L+1(41%) | d(Ir)+π(ML+POXD)→π*(ML)) | MLCT/LLCT/ILCT | |
| | | | | H-1→L+2(30%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT | |
| | $S_{17}$ | 298/4.159 | 0.1085 | H-5→L+1(47%) | π(ML)→π*(ML) | ILCT | |
| | | | | H-6→L(13%) | π(ML)→π*(ML) | ILCT | |
| | $S_{18}$ | 294/4.215 | 0.1020 | H-1→L+3(59%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| | | | | H-5→L(22%) | π(ML)→π*(ML) | ILCT | |
| | $S_{23}$ | 285/4.342 | 0.0804 | H-7→L(45%) | π(ML+POXD)→π*(ML) | LLCT/ILCT | |
| | | | | H-1→L+5(32%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| | $S_{39}$ | 258/4.801 | 0.1379 | H-4→L+2(36%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT | |
| | | | | H-3→L+3(23%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| **2** | $S_1$ | 418/2.965 | 0.0382 | H→L(94%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| | $S_5$ | 350/3.535 | 0.0838 | H-2→L(62%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT | |
| | | | | H-3→L(11%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT | |
| | $S_{10}$ | 321/3.851 | 0.2131 | H-1→L+2(67%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT | |
| | | | | H→L+5(12%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| | $S_{13}$ | 310/3.988 | 0.4552 | H-3→L+1(63%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT | |
| | | | | H-2→L+1(14%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT | |
| | $S_{15}$ | 305/4.063 | 0.1649 | H-1→L+4(74%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| | | | | H-4→L(13%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT | |
| | $S_{23}$ | 285/4.345 | 0.1828 | H-3→L+2(36%) | d(Ir)+π(ML)→π*(POXD) | MLCT/LLCT | |
| | | | | H-5→L+1(30%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| **3** | $S_1$ | 422/2.935 | 0.0225 | H→L(94%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT | |
| | $S_{12}$ | 317/3.908 | 0.1389 | H-1→L+2(63%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT | |
| | | | | H-1→L+3(18%) | d(Ir)+π(ML+POXD)→π*(ML+POXD) | MLCT/LLCT/ILCT | |
| | $S_{15}$ | 309/4.005 | 0.3245 | H-1→L+3(42%) | d(Ir)+π(ML+POXD)→π*(ML+POXD) | MLCT/LLCT/ILCT | |
| | | | | H-1→L+2(32%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT | |
| | $S_{24}$ | 287/4.315 | 0.1123 | H-2→L+3(28%) | π(ML)→π*(ML+POXD) | LLCT/ILCT | |
| | | | | H-3→L+2(22%) | d(Ir)+π(ML)→π*(POXD) | MLCT/LLCT | |
| | $S_{28}$ | 281/4.407 | 0.2549 | H-6→L+1(21%) | d(Ir)+π(ML+POXD)→π*(ML) | MLCT/LLCT/ILCT | |
| | | | | H-3→L+3(20%) | d(Ir)+π(ML)→π*(ML+POXD) | MLCT/LLCT/ILCT | |
| | $S_{41}$ | 258/4.792 | 0.1425 | H-5→L+2(17%) | π(ML)→π*(POXD) | LLCT | |
| | | | | H-2→L+6(14%) | π(ML)→π*(ML+POXD) | LLCT/ILCT | |
| **4** | $S_1$ | 426/2.906 | 0.0526 | H→L(92%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT | |
| | $S_{10}$ | 332/3.731 | 0.1269 | H-2→L+1(32%) | π(ML+POXD)→π*(ML) | LLCT/ILCT | |
| | | | | H→L+3(27%) | d(Ir)+π(ML)→π*(ML+POXD) | MLCT/LLCT/ILCT | |
| | $S_{14}$ | 310/3.995 | 0.3556 | H-1→L+2(71%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT | |
| | $S_{15}$ | 305/4.053 | 0.2103 | H-4→L+1(66%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT | |
| | | | | H-1→L+2(11%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT | |
| | $S_{21}$ | 288/4.304 | 0.0901 | H-1→L+5(48%) | d(Ir)+π(ML+POXD)→π*(ML+POXD) | MLCT/LLCT/ILCT | |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | | H-2→L+5(15%) | π(ML+POXD)→π*(ML+POXD) | LLCT/ILCT |
| | $S_{33}$ | 268/4.616 | 0.2617 | H→L+9(46%) | d(Ir)+π(ML)→π*(ML+POXD) | MLCT/LLCT/ILCT |
| | $S_{37}$ | 259/4.781 | 0.1167 | H-4→L+4(31%) | d(Ir)+π(ML)→π*(ML+POXD) | MLCT/LLCT/ILCT |
| | | | | H-4→L+3(23%) | d(Ir)+π(ML)→π*(ML+POXD) | MLCT/LLCT/ILCT |
| | $S_{40}$ | 256/4.841 | 0.1454 | H-5→L+2(61%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT |
| **5** | $S_1$ | 417/2.968 | 0.0681 | H→L(93%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT |
| | $S_6$ | 343/3.604 | 0.0924 | H-2→L(40%) | π(ML)→π*(ML) | ILCT |
| | | | | H-3→L(26%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT |
| | $S_{10}$ | 325/3.810 | 0.1326 | H→L+5(34%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT |
| | $S_{11}$ | 319/3.876 | 0.2846 | H-2→L+1(45%) | π(ML)→π*(ML) | ILCT |
| | | | | H-3→L+1(24%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT |
| | $S_{14}$ | 313/3.955 | 0.4721 | H-4→L(54%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT |
| | | | | H-3→L(29%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT |
| | $S_{25}$ | 281/4.402 | 0.1679 | H-2→L+5(32%) | π(ML)→π*(ML) | ILCT |
| | $S_{31}$ | 271/4.570 | 0.1160 | H-2→L+5(29%) | π(ML)→π*(ML) | ILCT |
| | | | | H-3→L+5(25%) | d(Ir)+π(ML)→π*(ML) | MLCT/ILCT |
| | $S_{33}$ | 268/4.620 | 0.1118 | H→L+10(28%) | d(Ir)+π(ML)→π*(ML+POXD) | MLCT/LLCT/ILCT |
| | | | | H→L+6(19%) | d(Ir)+π(ML)→π*(POXD) | MLCT/LLCT |
| | $S_{40}$ | 258/4.802 | 0.2203 | H-5→L+2(54%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT |
| | | | | H-6→L+2(25%) | d(Ir)+π(ML+POXD)→π*(POXD) | MLCT/LLCT/ILCT |

[a] Ref. 17

**Table S7** Partial frontier molecular orbital composition (%) of complexes **1**–**5** in the triplet excited states. (H and L indicate HOMO and LUMO, respectively)

| | MO | Energy/eV | Composition (%) | | | Assignment |
|---|---|---|---|---|---|---|
| | | | Ir | ML | POXD | |
| **1** | L | -2.10 | 4 | 95 | 1 | π*(ML) |
| | H | -5.35 | 40 | 40 | 20 | d(Ir)+π(ML) |
| | H-2 | -6.14 | 33 | 36 | 31 | d(Ir)+π(ML+POXD) |
| **2** | L+1 | -1.57 | 4 | 94 | 2 | π*(ML) |
| | L | -1.78 | 3 | 95 | 3 | π*(ML) |
| | H | -5.33 | 40 | 45 | 15 | d(Ir)+π(ML+POXD) |
| | H-2 | -6.02 | 23 | 65 | 11 | d(Ir)+π(ML+POXD) |
| **3** | L | -1.83 | 1 | 98 | 1 | π*(ML) |
| | H | -5.30 | 32 | 64 | 3 | d(Ir)+π(ML) |
| | H-1 | -5.69 | 29 | 31 | 40 | d(Ir)+π(ML+POXD) |
| **4** | L | -1.88 | 4 | 94 | 2 | π*(ML) |
| | H | -5.20 | 24 | 73 | 3 | d(Ir)+π(ML) |
| **5** | L | -1.76 | 3 | 96 | 1 | π*(ML) |
| | H | -5.24 | 34 | 58 | 8 | d(Ir)+π(ML) |
| | H-1 | -5.77 | 28 | 33 | 39 | d(Ir)+π(ML+POXD) |