**Supplementary Information:**

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| MO | Energy | Contribution (%) | | | | Assignment |
|  |  | Ir | | NHC | ADC |  |
| L+10 | 1.23 | 5 | | 5 | 90 | π\*(ADC) |
| L+9 | 0.81 | 4 | | 95 | 1 | π\*(NHC) |
| L+8 | 0.67 | 4 | | 94 | 2 | π\*(NHC) |
| L+7 | 0.58 | 2 | | 95 | 3 | π\*(NHC) |
| L+6 | 0.48 | 4 | | 63 | 33 | π\*(NHC+ADC) |
| L+5 | 0.41 | 3 | | 37 | 60 | π\*(NHC+ADC) |
| L+4 | 0.01 | 1 | | 95 | 4 | π\*(NHC) |
| L+3 | -0.11 | 1 | | 99 | 0 | π\*(NHC) |
| L+2 | -0.24 | 3 | | 8 | 89 | π\*(ADC) |
| L+1 | -0.49 | 4 | | 94 | 2 | π\*(NHC) |
| L | -0.58 | 4 | | 94 | 2 | π\*(NHC) |
| HOMO–LUMO energy gap ( 4.67 eV ) | | | | | | |
| H | -5.25 | 36 | | 58 | 6 | d(Ir)+π(NHC) |
| H-1 | -5.65 | 29 | | 31 | 40 | d(Ir)+π(NHC+ADC) |
| H-2 | -5.91 | 8 | | 73 | 19 | π(NHC+ADC) |
| H-3 | -6.06 | 6 | | 71 | 23 | π(NHC+ADC) |
| H-4 | -6.23 | 18 | | 64 | 18 | d(Ir)+π(NHC+ADC) |
| H-5 | -6.38 | 11 | | 36 | 53 | d(Ir)+π(NHC+ADC) |
| H-6 | -6.46 | 17 | | 75 | 8 | d(Ir)+π(NHC) |
| H-7 | -6.67 | 2 | | 71 | 27 | π(NHC+ADC) |
| H-8 | -6.9 | 4 | | 61 | 35 | π(NHC+ADC) |
| H-9 | -6.99 | 18 | | 58 | 24 | d(Ir)+π(NHC+ADC) |
| H-10 | -7.22 | 4 | | 95 | 1 | π(NHC) |
|  | |

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| MO | Energy | Contribution (%) | | | | Contribution (%) |
|  |  | Ir | | NHC | ADC |
| L+10 | 1.18 | 4 | | 8 | 88 | π\*(ADC) |
| L+9 | 0.77 | 3 | | 95 | 2 | π\*(NHC) |
| L+8 | 0.72 | 3 | | 96 | 1 | π\*(NHC) |
| L+7 | 0.57 | 2 | | 94 | 4 | π\*(NHC) |
| L+6 | 0.55 | 4 | | 90 | 6 | π\*(NHC) |
| L+5 | 0.45 | 4 | | 9 | 87 | π\*(ADC) |
| L+4 | 0.02 | 1 | | 95 | 4 | π\*(NHC) |
| L+3 | -0.09 | 1 | | 97 | 2 | π\*(NHC) |
| L+2 | -0.28 | 4 | | 10 | 86 | π\*(ADC) |
| L+1 | -0.50 | 5 | | 92 | 3 | π\*(NHC) |
| L | -0.55 | 3 | | 95 | 2 | π\*(NHC) |
| HOMO–LUMO energy gap ( 4.76 eV ) | | | | | | |
| H | -5.31 | 39 | | 52 | 9 | d(Ir)+π(NHC) |
| H-1 | -5.63 | 26 | | 72 | 46 | d(Ir)+π(NHC+ADC) |
| H-2 | -5.79 | 5 | | 81 | 14 | π(NHC+ADC) |
| H-3 | -6.06 | 18 | | 65 | 17 | d(Ir)+π(NHC+ADC) |
| H-4 | -6.11 | 5 | | 62 | 33 | π(NHC+ADC) |
| H-5 | -6.32 | 19 | | 32 | 49 | d(Ir)+π(NHC+ADC) |
| H-6 | -6.37 | 20 | | 72 | 8 | d(Ir)+π(NHC) |
| H-7 | -6.57 | 2 | | 89 | 9 | π(NHC) |
| H-8 | -6.81 | 4 | | 55 | 41 | π(NHC+ADC) |
| H-9 | -7.13 | 21 | | 57 | 22 | d(Ir)+π(NHC+ADC) |
| H-10 | -7.20 | 2 | | 95 | 3 | π(NHC) |
|  | |

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| MO | Energy | Contribution (%) | | | | Assignment |
|  |  | Ir | | NHC | ADC |  |
| L+10 | 0.66 | 3 | | 96 | 1 | π\*(NHC) |
| L+9 | 0.56 | 2 | | 94 | 4 | π\*(NHC) |
| L+8 | 0.48 | 3 | | 65 | 32 | π\*(NHC+ADC) |
| L+7 | 0.38 | 3 | | 35 | 62 | π\*(NHC+ADC) |
| L+6 | 0.05 | 1 | | 27 | 72 | π\*(NHC+ADC) |
| L+5 | -0.04 | 1 | | 74 | 25 | π\*(NHC+ADC) |
| L+4 | -0.12 | 1 | | 98 | 1 | π\*(NHC) |
| L+3 | -0.34 | 0 | | 0 | 100 | π\*(ADC) |
| L+2 | -0.51 | 5 | | 91 | 4 | π\*(NHC) |
| L+1 | -0.60 | 5 | | 96 | 1 | π\*(NHC) |
| L | -0.71 | 3 | | 6 | 91 | π\*(ADC) |
| HOMO–LUMO energy gap ( 4.59 eV ) | | | | | | |
| H | -5.30 | 35 | | 58 | 7 | d(Ir)+π(NHC) |
| H-1 | -5.69 | 27 | | 31 | 42 | d(Ir)+ π(NHC+ADC) |
| H-2 | -5.93 | 7 | | 72 | 21 | π(NHC+ADC) |
| H-3 | -6.08 | 6 | | 71 | 23 | π(NHC+ADC) |
| H-4 | -6.28 | 17 | | 65 | 18 | d(Ir)+π(NHC+ADC) |
| H-5 | -6.37 | 12 | | 34 | 54 | d(Ir)+π(NHC+ADC) |
| H-6 | -6.48 | 17 | | 73 | 10 | d(Ir)+π(NHC) |
| H-7 | -6.68 | 1 | | 74 | 25 | π(NHC+ADC) |
| H-8 | -6.93 | 3 | | 62 | 35 | π(NHC+ADC) |
| H-9 | -6.99 | 14 | | 50 | 36 | d(Ir)+π(NHC+ADC) |
| H-10 | -7.23 | 4 | | 54 | 42 | π(NHC+ADC) |
|  | |

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| MO | Energy | Contribution (%) | | | | Assignment |
|  |  | Ir | | NHC | ADC |  |
| L+10 | 1.47 | 85 | | 5 | 10 | d\*(Ir) |
| L+9 | 0.85 | 4 | | 95 | 1 | π\*(NHC) |
| L+8 | 0.73 | 4 | | 30 | 66 | π\*(NHC+ADC) |
| L+7 | 0.69 | 5 | | 73 | 22 | π\*(NHC+ADC) |
| L+6 | 0.62 | 2 | | 94 | 4 | π\*(NHC) |
| L+5 | 0.49 | 2 | | 92 | 6 | π\*(NHC) |
| L+4 | 0.21 | 4 | | 9 | 87 | π\*(ADC) |
| L+3 | 0.02 | 1 | | 95 | 4 | π\*(NHC) |
| L+2 | -0.08 | 1 | | 99 | 0 | π\*(NHC) |
| L+1 | -0.45 | 4 | | 95 | 1 | π\*(NHC) |
| L | -0.54 | 4 | | 95 | 1 | π\*(NHC) |
| HOMO–LUMO energy gap ( 4.63 eV ) | | | | | | |
| H | -5.17 | 36 | | 54 | 10 | d(Ir)+π(NHC) |
| H-1 | -5.46 | 24 | | 18 | 58 | d(Ir)+π(NHC+ADC) |
| H-2 | -5.82 | 8 | | 74 | 18 | π(NHC+ADC) |
| H-3 | -5.95 | 8 | | 68 | 24 | π(NHC+ADC) |
| H-4 | -6.12 | 17 | | 50 | 33 | d(Ir)+π(NHC+ADC) |
| H-5 | -6.21 | 12 | | 46 | 42 | d(Ir)+π(NHC+ADC) |
| H-6 | -6.40 | 18 | | 76 | 6 | d(Ir)+π(NHC) |
| H-7 | -6.57 | 2 | | 78 | 20 | π(NHC+ADC) |
| H-8 | -6.78 | 7 | | 64 | 29 | π(NHC+ADC) |
| H-9 | -6.91 | 16 | | 61 | 23 | d(Ir)+π(NHC+ADC) |
| H-10 | -7.19 | 4 | | 95 | 1 | π(NHC) |
|  | |

**Table S5** Frontier molecular orbital energies (eV) and compositions (%) in the ground state for complex **5**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| MO | Energy | Contribution (%) | | | | Assignment |
|  |  | Ir | | NHC | ADC |  |
| L+10 | 1.48 | 86 | | 5 | 9 | d\*(Ir) |
| L+9 | 0.86 | 4 | | 95 | 1 | π\*(NHC) |
| L+8 | 0.72 | 4 | | 71 | 25 | π\*(NHC+ADC) |
| L+7 | 0.68 | 6 | | 35 | 59 | π\*(NHC+ADC) |
| L+6 | 0.63 | 2 | | 91 | 7 | π\*(NHC) |
| L+5 | 0.49 | 2 | | 87 | 11 | π\*(NHC+ADC) |
| L+4 | 0.36 | 4 | | 9 | 87 | π\*(ADC) |
| L+3 | 0.03 | 1 | | 97 | 2 | π\*(NHC) |
| L+2 | -0.07 | 1 | | 99 | 0 | π\*(NHC) |
| L+1 | -0.44 | 4 | | 95 | 1 | π\*(NHC) |
| L | -0.53 | 4 | | 95 | 1 | π\*(NHC) |
| HOMO–LUMO energy gap ( 4.61 eV ) | | | | | | |
| H | -5.14 | 31 | | 40 | 29 | d(Ir)+π(NHC+ADC) |
| H-1 | -5.28 | 14 | | 20 | 66 | d(Ir)+π(NHC+ADC) |
| H-2 | -5.69 | 23 | | 52 | 25 | d(Ir)+π(NHC+ADC) |
| H-3 | -5.91 | 14 | | 68 | 18 | d(Ir)+π(NHC+ADC) |
| H-4 | -6.03 | 9 | | 63 | 28 | π(NHC+ADC) |
| H-5 | -6.17 | 17 | | 61 | 22 | d(Ir)+π(NHC+ADC) |
| H-6 | -6.39 | 17 | | 76 | 7 | d(Ir)+π(NHC) |
| H-7 | -6.56 | 2 | | 82 | 16 | π(NHC+ADC) |
| H-8 | -6.78 | 7 | | 64 | 29 | π(NHC+ADC) |
| H-9 | -6.90 | 16 | | 61 | 23 | d(Ir)+π(NHC+ADC) |
| H-10 | -7.18 | 4 | | 95 | 1 | π(NHC) |
|  | |

**Table S6** Selected calculated wavelength (nm) /energies (eV), oscillator strength (ƒ), major contribution and transition characters for **1-5** in CH2Cl2 media from TDDFT. (H and L indicate HOMO and LUMO, respectively.)

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
|  | State | λ/E | ƒ | Configuration | Assignment | Nature | Exptla |
| **1** | S1 | 327/3.78 | 0.0103 | H→L (93%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT | 302 |
|  | S5 | 287/4.30 | 0.1629 | H-1→L+1 (81%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S7 | 278/4.45 | 0.1481 | H→L+4 (67%)  H-2→L (12%) | d(Ir)+π(NHC)→π\*(NHC)  π(NHC+ADC)→π\*(NHC) | MLCT/ILCT  LLCT/ILCT |  |
|  | S12 | 262/4.72 | 0.1098 | H-4→L (58%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S15 | 257/4.82 | 0.1481 | H-2→L+2 (27%) | π(NHC+ADC)→π\*(ADC) | LLCT/ILCT |  |
|  |  |  |  | H→L+6 (20%) | d(Ir)+π(NHC)→π\*(NHC+ADC) | MLCT/LLCT/ILCT |  |
|  | S26 | 241/5.12 | 0.1130 | H→L+8 (40%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S31 | 236/5.23 | 0.1823 | H-2→L+4 (27%) | π(NHC+ADC)→π\*(NHC) | LLCT/ILCT |  |
|  |  |  |  | H-6→L+1 (21%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S36 | 230/5.37 | 0.2223 | H-3→L+4 (31%) | π(NHC+ADC)→π\*(NHC) | LLCT/ILCT |  |
|  |  |  |  | H-5→L+2 (25%) | d(Ir)+π(NHC+ADC)→π\*(ADC) | MLCT/LLCT/ILCT |  |
|  | S39 | 227/5.44 | 0.1986 | H-7→L+1 (15%) | π(NHC+ADC)→π\*(NHC) | LLCT/ILCT |  |
|  | S43 | 224/5.51 | 0.1055 | H-4→L+4 (12%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
| **2** | S1 | 322/3.84 | 0.0038 | H→L (89%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S5 | 288/4.29 | 0.1062 | H-1→L+1 (83%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S11 | 267/4.64 | 0.1303 | H-3→L (63%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S13 | 261/4.73 | 0.1071 | H-3→L+1 (43%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  |  |  |  | H-2→L+2 (21%) | π(NHC+ADC)→π\*(ADC) | LLCT/ILCT |  |
|  | S23 | 247/5.00 | 0.1258 | H→L+7 (28%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  |  |  |  | H→L+6 (22%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S28 | 242/5.10 | 0.1986 | H-2→L+4 (27%) | π(NHC+ADC)→π\*(NHC) | LLCT/ILCT |  |
|  |  |  |  | H-6→L (18%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S32 | 237/5.21 | 0.1747 | H→L+8 (51%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S39 | 230/5.38 | 0.1047 | H-1→L+6 (15%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
| **3** | S1 | 333/3.71 | 0.0023 | H→L (89%) | d(Ir)+π(NHC)→π\*(ADC) | MLCT/LLCT |  |
|  | S4 | 300/4.12 | 0.1976 | H-1→L (89%) | d(Ir)+ π(NHC+ADC)→π\*(ADC) | MLCT/LLCT/ILCT |  |
|  | S9 | 277/4.46 | 0.1717 | H-2→L (44%) | π(NHC+ADC)→π\*(ADC) | LLCT/ILCT |  |
|  |  |  |  | H→L+5 (14%) | d(Ir)+π(NHC)→π\*(NHC+ADC) | MLCT/LLCT/ILCT |  |
|  | S28 | 247/5.01 | 0.1621 | H-6→L (47%) | d(Ir)+π(NHC)→π\*(ADC) | MLCT/LLCT |  |
|  | S33 | 241/5.13 | 0.1261 | H-2→L+4 (32%) | π(NHC+ADC)→π\*(NHC) | LLCT/ILCT |  |
|  |  |  |  | H-6→L+1 (27%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/LLCT |  |
|  | S39 | 237/5.23 | 0.1288 | H-6→L+2 (40%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  |  |  |  | H-2→L+5 (32%) | π(NHC+ADC)→π\*(NHC+ADC) | LLCT/ILCT |  |
| **4** | S1 | 332/3.73 | 0.0092 | H→L (93%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S4 | 295/4.20 | 0.1441 | H-1→L+1 (88%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S7 | 281/4.41 | 0.1099 | H→L+3 (56%)  H→L+4 (21%) | d(Ir)+π(NHC)→π\*(NHC)  d(Ir)+π(NHC)→π\*(ADC) | MLCT/LLCT/ILCT  MLCT/LLCT |  |
|  | S16 | 258/4.80 | 0.2182 | H→L+5 (50%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S23 | 244/5.07 | 0.1266 | H→L+8 (24%) | d(Ir)+π(NHC)→π\*(NHC+ADC) | MLCT/LLCT/ILCT |  |
|  |  |  |  | H-6→L (19%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  | S30 | 238/5.19 | 0.1136 | H-6→L+1 (30%) | d(Ir)+π(NHC)→π\*(NHC) | MLCT/ILCT |  |
|  |  |  |  | H-2→L+3 (25%) | π(NHC+ADC)→π\*(NHC) | LLCT/ILCT |  |
|  | S42 | 227/5.46 | 0.1217 | H-5→L+4 (11%) | d(Ir)+π(NHC+ADC)→π\*(ADC) | MLCT/LLCT/ILCT |  |
| **5** | S1 | 332/3.72 | 0.0077 | H→L (87%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S6 | 284/4.35 | 0.1318 | H-2→L (56%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  |  |  |  | H→L+2 (13%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S13 | 265/4.67 | 0.1327 | H-3→L+1 (72%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S15 | 262/4.72 | 0.1603 | H-1→L+4 (44%) | d(Ir)+π(NHC+ADC)→π\*(ADC) | MLCT/LLCT/ILCT |  |
|  |  |  |  | H→L+5 (12%) | d(Ir)+π(NHC+ADC)→π\*(NHC+ADC) | MLCT/LLCT/ILCT |  |
|  | S29 | 240/5.15 | 0.1196 | H→L+9 (50%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  | S33 | 236/5.23 | 0.1061 | H-1→L+6 (24%) | d(Ir)+π(NHC+ADC)→π\*(NHC) | MLCT/LLCT/ILCT |  |
|  |  |  |  | H-2→L+4 (21%) | d(Ir)+π(NHC+ADC)→π\*(ADC) | MLCT/LLCT/ILCT |  |
|  | S40 | 230/5.38 | 0.2524 | H-4→L+3 (47%) | π(NHC+ADC)→π\*(NHC) | LLCT/ILCT |  |
|  |  |  |  | H-7→L+1 (11%) | π(NHC+ADC)→π\*(NHC) | LLCT/ILCT |  |

a Ref. 19

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

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | MO | Energy/eV | Composition (%) | | | Assignment |
|  |  |  | Ir | NHC | ADC |  |
| **1** | L | -1.14 | 7 | 91 | 2 | π\*(NHC) |
|  | H | -4.83 | 34 | 55 | 11 | d\*(Ir)+π\*(NHC+ADC) |
| **2** | L | -0.71 | 5 | 90 | 5 | π\*(NHC) |
|  | H | -5.08 | 27 | 69 | 4 | d\*(Ir)+π\*(NHC) |
| **3** | L | -1.58 | 7 | 7 | 86 | π\*(ADC) |
|  | H | -4.84 | 33 | 55 | 12 | d\*(Ir)+π\*(NHC+ADC) |
| **4** | L | -1.08 | 7 | 92 | 1 | π\*(NHC) |
|  | H | -4.72 | 35 | 51 | 14 | d\*(Ir)+π\*(NHC+ADC) |
| **5** | L | -1.06 | 7 | 92 | 1 | π\*(NHC) |
|  | H | -4.73 | 35 | 52 | 13 | d\*(Ir)+π\*(NHC+ADC) |