Unravelling the mechanism of excited state interligand energy transfer and the engineering of dual-emission in $[Ir(C^\wedge N)_2(N^\wedge N)]^+$ complexes

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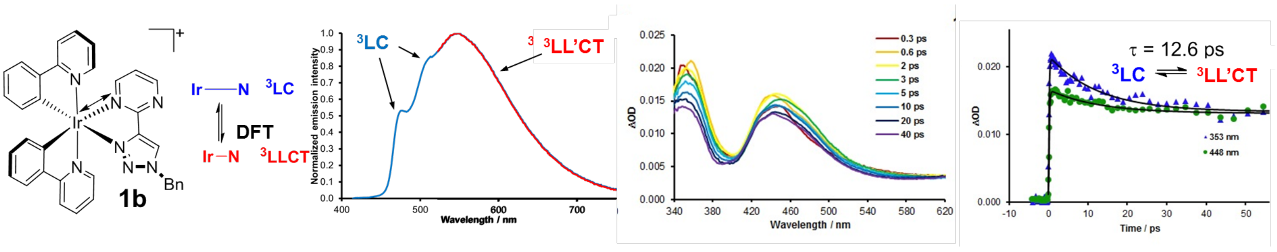
Heteroleptic bis-cyclometalated iridium complexes of the form $[Ir(C^\wedge N)_2(N^\wedge N)]^+$ form one of the corner stones of modern photophysics with application in light-emitting electrochemical cells, luminescent confocal imaging microscopy and solar catalysis. Complexes of this family typically emit from either a ^{3}MLCT/^{3}LC state where the excited electron resides on the cyclometalated ligand or a ^{3}MLCT/^{3}LL'CT state where charge transfer occurs to the neutral ancillary ligand. Structural variation of the cyclometalated and ancillary ligands and thus tuning of the energies of the ^{3}MLCT/^{3}LC and ^{3}MLCT/^{3}LL'CT states then determines which state ultimately emits.[1,2] Dependent on the ligand set present complexes can display switching of emission of these states between fluid solutions and cryogenic glass samples, but the exact nature switching mechanism is not clear.

In a thorough survey of complexes $[Ir(C^\wedge N)_2(N^\wedge N)]^+$ bearing a asymmetric ancillary ligand (**1a-c** (C^N = 2-phenylpyridine) & **2a-c** (C^N = 2-(2,4-difluorophenyl)pyridine); N^N = 2-(1-benzyl-1,2,3-triazol-4-yl)pyridine (**a**), 2-(1-benzyl-1,2,3-triazol-4-yl)pyrimidine (**b**), 2-(1-benzyl-1,2,3-triazol-4-yl)pyrazine (**c**)) we tune the relative energies of both 3MLCT/3LC and 3MLCT/3LL'CT states.[3] Complexes **1a**, **2a** & **2b** exhibit exclusively ^{3}MLCT/^{3}LC-based emission at both 77 K and room temperature whereas **1c** exhibits exclusively 3MLCT/3LL'CT-based emission. Complex **2c** exhibits switching from ^{3}MLCT/^{3}LC to ^{3}MLCT/^{3}LL'CT-based emission between frozen and fluid solutions. Significantly we are able to show that the energies of these two states can be tuned such that they are nearly isoenergetic in **1b** resulting in rare dual emission from both ^{3}MLCT/^{3}LC and ^{3}MLCT/^{3}LL'CT states over a broad range of solvents and temperatures. Computational DFT calculations have enabled us to optimise geometries for both ^{3}LC- and ^{3}LL'CT-admixed ^{3}MLCT states and to compute minimum energy paths connecting the various triplet states. This data reveal for the first time the key structural changes and key vibrations involved in the population transfer and highlight the mechanism by which these states interconvert. Furthermore, the theoretical data fully rationalises the observed photophysical behaviour. This work therefore provides significant new insights into this important class of transition metal phosphor.



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