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The synthesis of brominated heteroleptic *tris*-cyclometallated Ir(III)-complexes as photoactive building blocks on polyaryl backbones.

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Abstract: Luminescent facial *tris*-cyclometallated iridium complexes of generic structure Ir(L)₂(dbppy) with one 2-(4-bromophenyl)-5-bromopyridyl (dbppy) ligand {where L represents the cyclometallating ligands [2-phenylpyridyl (ppy), 2-(4,6-difluorophenyl)pyridyl] (dfppy), [1-phenylpyrazole] (ppz) or [1-(4,6-difluorophenyl)pyrazole] (dfppz)} were synthesized. The bromine substituents allow the further incorporation of the iridium complexes into a polyaryl backbone. The route starts from μ -chloro-bridged dimers L₂Ir(μ Cl)₂IrL₂. Further reaction of these precursors with an excess of dbppyH at temperatures of 95–120 °C leads to the target complexes only in the case of the phenylpyridine based precursors (L = ppy and dfppy). All complexes were characterized via 1D- and 2D NMR spectroscopic methods. All the facial *tris*-cyclometallated complexes exhibited strong absorptions between 200 and 320 nm typical of a $\pi \rightarrow \pi^*$ transition together with weaker MLCT absorptions below 320 nm. The emission spectra of all these luminescent Ir(III)-complexes cover the region between approximately 500 to 700 nm. This strongly supports the hypothesis that the luminescent properties are controlled mainly by the dbppy ligand. The lifetimes of the complexes are quite different relative to each other and are much shorter than their homoleptic Ir(L)₃ counterparts.

Keywords: Iridium complex, Phosphorescence, Triplet emitting polymer, Copolymerization, OLED, triplet emitter

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