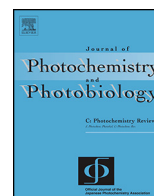




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Evolution of 2, 3'-bipyridine class of cyclometalating ligands as efficient phosphorescent iridium(III) emitters for applications in organic light emitting diodes

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Abbreviations: MLCT, metal–to–ligand charge transfer; LC, ligand centered; MC, metal centered; ILET, intramolecular inter–ligand energy transfer; SOC, spin–orbit coupling; ξ_{ir} , spin–orbit coupling constant; ISC, intersystem crossing; LEECs, light emitting electrochemical cells; OLEDs, organic light emitting diodes; PhOLEDs, phosphorescent organic light emitting diodes; PDT, photodynamic therapy; DNA, deoxyribonucleic acid; CN, cyclometalating ligand; LX, ancillary ligand; DFT, density functional theory; HOMO, highest occupied molecular orbital; LUMO, lowest unoccupied molecular orbital; LFSE, ligand field stabilization energy; MOs, molecular orbitals; CIE, Commission Internationale de L'Eclairage; EL, Electroluminescence; PL, Photoluminescence; λ_{max} , wavelength at emission maximum; Φ_{PL} , photoluminescence quantum yield; τ , phosphorescence lifetime; k_{isc} , intersystem crossing rate constant; k_{nr} , non–radiative decay rate constant; η_p , power efficiency; η_c , current efficiency; L_{max} , maximum brightness; EQE, external quantum efficiency; ppy, 2–phenylpyridine; dfppy, 2,6–difluoro–2,3–bipyridine; dfppy, 2–(4,6–difluorophenyl)pyridine; dpm, Dipivaloylmethanate; dtBubpy, 4,4'–di–tert–butyl–2,2'–bipyridine; NHC, N–heterocyclic carbenes; Ph₂P=O, diphenyl phosphoryl; Htpip, tetraphenylimidodiphosphinic acid; dipcca, 9H–(carbazol–9–yl)(diisopropyl)amidate; mppy, 5–methyl–2–phenylpyridine; CBP, 4,4'–bis(N–carbazolyl)–1,10–biphenyl; ITO, indium–tin oxide; PEDOT:PSS, poly(3,4–ethylenedioxythiophene):poly(styrenesulfonate); TAPC, 4,4'–cyclohexylidenebis[N,N–bis(4–methylphenyl)aniline]; mCP, 1,3–bis(N–carbazolyl)benzene; TSP01, diphenylphosphine oxide–4–(triphenylsilyl)phenyl; B3PyPB, 1,3–bis(3,5–dipyrid–3–ylphenyl)benzene; PPO21, 3–diphenylphenyl–9–(4–diphenylphosphinylphenyl)carbazole; TmPyPB, 1,3,5–tri(m–pyridin–3–ylphenyl)benzene; mCPPO1, 9–(3–(9H–carbazol–9–yl)phenyl)–9Hcarbazol–3–yl)diphenylphosphine oxide; HAT–CN, 4,5,8,9,11–hexaazatriphenylene–hexacarbonitrile; DTAF, 9,9–di[4–(di–p–tolyl)aminophenyl]fluorene; CaSi, diphenylbis[4–(9–carbazolyl)phenyl]silane; POCz3, 3,3'–phosphoryl tris(9–phenyl–9H–carbazole); 3TPYMB, tris–[3–(3–pyridyl)mesityl]borane; *fac*, facial; *mer*, meridional; Ir(dfppy)₃, tris(2,6–difluoro–2,3–bipyridinato–N,C4')iridium(III); Ir(ppy)₃, tris[2–(phenyl)pyridinato–N, C2] iridium(III); Flrpic, bis[2–(4,6–difluorophenyl)pyridinato–N, C2] iridium(III) (picolinate); Ir1, *fac*–tris(2,6–difluoro–2,3–bipyridinato–N,C4')iridium(III); Ir2, *mer*–tris(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III); Ir3, bis(2,6–difluoro–4–formyl–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir4, bis(2,6–difluoro–4–trifluoromethyl–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir5, bis(2,6–difluoro–4–cyano–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir6, bis(2,6–difluoro–4–methoxy–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir7, bis(2,6–difluoro–4–N,N–dimethylamine–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir8, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir9, bis(2,6–difluoro–4–methyl–2,3–bipyridinato–N,C4') iridium(III) (dipivaloylmethanoate); Ir10, bis(2,6–difluoro–4–methoxy–2,3–bipyridinato–N,C4') iridium(III) (dipivaloylmethanoate); Ir11, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (dipivaloylmethanoate); Ir12, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (3–trifluoromethyl–5–(2–pyridyl) pyrazolate); Ir13, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (3–(trifluoromethyl)–5–(4–t–butylpyridyl)pyrazolate); Ir14, bis(2,6–difluoro–4–tert–butyl–2,3–bipyridinato–N,C4') iridium(III) (3–trifluoromethyl–5–(2–pyridyl) pyrazolate); Ir15, bis(2,6–difluoro–4–tert–butyl –2,3–bipyridinato–N,C4') iridium(III) (3–(trifluoromethyl)–5–(4–t–butylpyridyl)pyrazolate); Ir16, bis(2,6–difluoro–4–tert–butyl–2,3–bipyridinato–N,C4') iridium(III) (1,10–Dimethyl–3,3'–methylenediimidazole); Ir17, bis(2,6–difluoro–4–tert–butyl–2,3–bipyridinato–N,C4') iridium(III) (acetylacetonate); Ir18, bis(2,6–trifluoromethyl–2,3–bipyridinato–N,C4') iridium(III) (tetraphenylimidodiphosphinate); Ir19, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (tetraphenylimidodiphosphinate); Ir20, bis(2,6–bis(2–methoxyethoxy)–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir21, bis(2,6–dimethoxy–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir22, bis(6–methoxy–2'–methyl–2,3–bipyridinato–N,C4') iridium(III) (acetylacetonate); Ir23, bis(6'–methoxy–2'–methyl–2,3–bipyridinato–N,C4') iridium(III) (picolinate); Ir24, bis(2,6–dimethoxy–4–methyl–2,3–bipyridinato–N,C4') iridium(III) (acetylacetonate); Ir25, bis(2,6–dimethoxy–4–methyl–2,3–bipyridinato–N,C4') iridium(III) (acetylacetonate); Ir26, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (acetylacetonate); Ir27, bis(6'–methoxy–2'–methyl–4–methyl–2,3–bipyridinato–N,C4') iridium(III) (4,4'–di–tert–butyl–2,2'–bipyridine) hexafluorophosphate; Ir28, bis(2,6–dimethoxy–4–methyl–2,3–bipyridinato–N,C4') iridium(III) (4,4'–di–tert–butyl–2,2'–bipyridine) hexafluorophosphate; Ir29, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (4,4'–di–tert–butyl–2,2'–bipyridine) hexafluorophosphate; Ir30, bis(5,6–Dimethyl–2,3–bipyridinato–N,C4') iridium(III) (4,4'–di–tert–butyl–2,2'–bipyridine) hexafluorophosphate; Ir31, bis(1–methyl–3–(2'–pyridyl)pyridinium –N,C4') iridium(III) (2,2'–bipyridine) tris–hexafluorophosphate; Ir32, bis(1–methyl–3–(2'–pyridyl)pyridinium –N,C4') iridium(III) (4,4'–di–tert–butyl–2,2'–bipyridine) tris–hexafluorophosphate; Ir33, bis(1–methyl–3–(2'–pyridyl)pyridinium –N,C4') iridium(III) (4,4'–di–tert–butyl–2,2'–bipyridine) tris–hexafluorophosphate; Ir36, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) 3–methyl–1–(4–methyl–2–pyridyl)benzimidazolium hexafluorophosphate; Ir37, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) 3–methyl–1–(4–trifluoromethyl–2–pyridyl)benzimidazolium hexafluorophosphate; Ir38, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) 3–(4–(pyridin–2–yl)–1H–1,2,3–triazol–1–yl)propane–1–sulfonate; Ir39, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) trifluoro((4–(pyridin–2–yl)–1H–1,2,3–triazol–1–yl)methyl)–borate; Ir40, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) tris(pyrazolyl)–methanesulfonates; Ir41, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (4–fluorophenyl)imidodiphosphinate; Ir42, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (9H–carbazol–9–yl)(diisopropyl)amidate; Ir43, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (pyrazinate); Ir44, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (isoquinolate); Ir45, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) (quinaldinate); Ir46, bis(2,6–bis(2–methoxyethoxy)–2,3–bipyridinato–N,C4') iridium(III) (pyrazinate); Ir47, bis(2,6–bis(2–methoxyethoxy)–2,3–bipyridinato–N,C4') iridium(III) (isoquinolate); Ir48, bis(2,6–bis(2–methoxyethoxy)–2,3–bipyridinato–N,C4') iridium(III) (quinaldinate); Ir49, bis(2,6–difluoro–2,3–bipyridinato–N,C4') iridium(III) 5–methyl–2–phenylpyridinato; BTPBA, bis(2–(2–benzothiazolyl–N3)phenyl–C) iridium(III) (phenyl)(N,N–diisopropylbenzimidamide); BTIPG, bis(2–(2–benzothiazolyl–N3)phenyl–C) iridium(III) (9H–carbazol–9–yl)(1,1,2,3–tetraisopropylguanidinate).

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ABSTRACT

Nowadays, the design and development of novel phosphorescent iridium(III) complexes for various optoelectronic applications is a well-recognized area of research. The fascinating photophysical properties of iridium(III) compounds are strongly influenced by the spin-orbit coupling exerted by the iridium(III) core, usually resulting in intense emissions with short excited-state lifetimes, which can be precisely controlled with the aid of molecular engineering of the chelating ligand. This review focuses on the recent developments and state of the art knowledge on phosphorescent iridium(III) compounds, especially on heteroleptic complexes derived from 2,3'-bipyridine class of cyclometalating and ancillary ligands, highlighting the excited state phenomenon behind their emission behavior.

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1. Introduction and scope

There has been an upsurge of interest in phosphorescent iridium(III) compounds due to their fascinating photophysical properties such as promising phosphorescence quantum yields, relatively shorter excited-state lifetimes, large cross-section for the exciton formation and facile tuning of emission colors through molecular engineering [1–21]. The efficient phosphorescent emission is essentially ascribed to the strong SOC-induced by the 5d orbitals of Ir^{3+} ion ($\xi_{\text{Ir}} = 4430 \text{ cm}^{-1}$) [22–24], which facilitates efficient ISC of the singlet excited state to the triplet manifold ($k_{\text{ISC}} < 1 \text{ ps}$) [25,26]. Thus, mixing of the singlet and triplet

excited states allows the radiative relaxation of the triplet state, which is known as spin-forbidden [14,27]. The emission from phosphorescent iridium(III) complexes mainly arises from triplet metal-to-ligand charge transfer ($^3\text{MLCT}$) or the mixture of $^3\text{MLCT}$ and ligand-centered (^3LC) transitions [25]. Further, in some of the iridium(III) complexes, intramolecular inter-ligand energy transfer (ILET), ligand-to-ligand charge transfer (LLCT) and other processes [28–34] are also known (Fig. 1).

The lowest excited state energy can be controlled in a more desirable way by tuning the energy of the ligand orbitals via substituent effects in the cyclometalating or ancillary ligand systems, which can generate a diverse range of emission colors from iridium(III) complexes. Consequently, phosphorescent iridium(III) compounds have been extensively explored for many potential applications (Fig. 2) including OLEDs [35–43], light-emitting electrochemical cells (LEECs) [44–46], biological labelling [47–52], photodynamic therapy (PDT) [53–56], photosensitizers for photo-driven water splitting [57–59], nonlinear optics [60–62], chemosensors [51,63–66], metallo-pharmaceuticals [67,68], photocatalyst for organic synthesis and CO_2 reduction [69,70], luminescent sensitizers for charge-transfer reactions in DNA [71,72], singlet oxygen sensitizers [73,74], dye-sensitized solar cells [75,76] and electro-generated chemiluminescence [77]. The cyclometalated iridium(III) complexes are recognized as excellent phosphorescent emitters and have been widely investigated because of their ability to achieve maximum internal quantum efficiency, nearly 100%, as well as high external quantum efficiencies in OLEDs [37]. A simplified working principle of an OLED motif can be seen from Fig. 3.

In quest of developing novel iridium(III) compounds with high quantum yields for use in organic light emitting diodes, many heteroleptic complexes having the general formula $[\text{Ir}(\text{C}^-\text{N})_2(\text{L}^-\text{X})]$ were designed during the last decade, where C^-N is a monoanionic cyclometalating chelate and L^-X is an ancillary ligand

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