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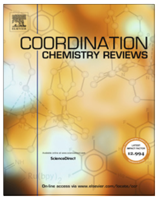

Review

Rational design of phosphorescent iridium(III) complexes for emission color tunability and their applications in OLEDs

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ABSTRACT

This review is an update on recent developments in emissive iridium(III) phosphorescent complexes and their applications in organic light-emitting diodes (OLEDs). The emphasis is focused on complexes with emission colors spanning the whole visible spectral region, which is extremely important for applications of OLEDs in display and white-light luminance. In each color section, materials are classified according to their coordination configuration, including homoleptic, heteroleptic and tridentate, trying to clarify the relationship between the molecular structure and the photophysical properties. Since the emission color, photoluminescence efficiency and carrier mobility of the phosphors are critical for device performances, we endeavor to dig out these values along with the measuring methods from the publications, and rational chemical modifications aiming for high efficiency and carrier mobility with different colors are also discussed.

Contents

Abbreviations: 26DCzPPy, 2,6-bis(3-(9*H*-carbazol-9-yl)phenyl)pyridine; 3TPYMB, tris-[3-(3-pyridyl)mesityl]borane; Alq$_3$, tris(8-hydroxyquinolinato) aluminium; B3PYMPM, 4,6-bis(3,5-di(pyridin-3-yl)phenyl)-2-methylpyrimidine; B3PyPB, bis-1,2-(3,5-di-3-pyridylphenyl)benzene; BAlq, bis(2-methyl-8-quinolinolate)-4-(phenylphenolato)aluminium; BCP, bathocuproine; Bphen, bathophenanthroline; BCPO, bis-4-(*N*-carbazolyl)phenyl)phenylphosphine oxide; BmPyPB, 1,3-bis(3,5-dipyrid-3-yl-phenyl)benzene; BP4mPy, 3,3′,5,5′-tetra[(*m*-pyridyl)-phen-3-yl]biphenyl; (bt$_2$Ir(acac), bis(2-benzo[*b*]thiophen-2-ylpyridine)(acetylacetonate)iridium(III); CaSi, diphenylbis[4-(9-carbazoyl)phenyl]silane; CBP, 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl; DIC-TRZ, 11-(4,6-di(biphenyl-4-yl)-1,3,5-triazin-2-yl)-12-phenyl-11,12-dihydroindolo[2,3-*a*]carbazole; DTAF, 9,9-di[4-(di-*p*-tolyl)aminophenyl]fluorine; DPEPO, bis[2-(diphenylphosphino)phenyl]ether oxide; FIr6, bis(2,4-difluorophenylpyridinato)-tetrakis(1-pyrazolyl)borate iridium(III); FIrpic, bis[2-(4,6-difluorophenyl)pyridinato-C^2,*N*](picolinato)iridium(III); HAT-CN, 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile; ITO, indium tin oxide; Liq, 8-hydroxyquinolinato lithium; mB-4CZ, 3,300,5,500-tetra(9*H*-carbazol-9-yl)-1,10:30,100-terphenyl; mCBP, 3,3′-di(9*H*-carbazol-9-yl)-1,1′-biphenyl; mCP, 1,3-bis(*N*-carbazolyl)benzene; mCPCN, 9-(3-(9*H*-carbazol-9-yl)phenyl)-9*H*-carbazole-3-carbonitrile; mCPPO1, 9-(3-(9*H*-carbazol-9-yl)phenyl)-3-(diphenylphosphoryl)-9*H*-carbazole; m-MTDATA, 4,4′,4″-tris[phenyl(*m*-tolyl)amino]triphenylamine; NPB, *N*,*N*′-di(1-naphthyl)-*N*,*N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine; OTPD, N^4,$N^{4\prime}$-bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyl)phenyl)-N^4,$N^{4\prime}$-diphenylbiphenyl-4,4′-diamine; OXD-7, 1,3-bis[2-(4-*tert*-butylphenyl)-1,3,4-oxadiazo-5-yl]benzene; PBD, 2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole; PC, polycarbonate; PEDOT:PSS, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate); PO9, 3,6-bis(diphenylphosphoryl)-9-phenylcarbazole; POAPF, 2,7-bis(diphenylphosphoryl)-9-[4-(*N*,*N*-diphenylamino)phenyl]-9-phenylfluorene; POCz3, 3,3′,3″-phosphinylidyne tris[9-phenyl-9*H*-carbazole; PPO21, 3-(diphenylphosphoryl)-9-(4-(diphenyl phosphoryl)phenyl)-9*H*-carbazole; PVE, polyvinyl ether; PVK, poly(*N*-vinylcarbazole); (piq)$_2$Ir(acac), bis[2-(1-isoquinolinyl-*N*)phenyl-C](2,4-pentanedionato-O^2,O^4)iridium(III); QUPD, N^4,$N^{4\prime}$-bis(4-(6-((3-ethyloxetan-3-yl)methoxy)hexyloxy)phenyl)-*N4*,*N4*′-bis(4-methoxyphenyl)biphenyl-4,4′-diamine; SimCP2, 3,5-di(9*H*-carbazol-9-yl)tetraphenylsilane; Spiro-2CBP, 2,7-bis(carbazol-9-yl)-9,9-spirobifluorene); TAPC, 4,4′-cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)benzenamine]; TAZ, 3-(biphenyl-4-yl)-5-(4-*tert*-butylphenyl)-4-phenyl-4*H*-1,2,4-triazole; *t*-BuCPO, (3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)diphenylphosphine oxide; TCTA, tris(4-carbazoyl-9-ylphenyl)amine; TmPyPB, 1,3,5-tris(3-pyridyl-3-phenyl)benzene; TPD, *N*,*N*′-bis(3-methylphenyl)-*N*,*N*′-diphenylbenzidine; TPBi, 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-*H*-benzimidazole); TSPO1, diphenyl-4-triphenylsilylphenylphosphine oxide; UGH2, 1,4-bis(triphenyl silyl)benzene.

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1. Introduction

As our society enters the Information Age, a tremendous amount of display screens and lighting sources are demanded. Nowadays, these markets are occupied by well-established liquid crystal display (LCD) technology and light emitting diodes (LED). Organic light emitting diode (OLED) technology, which was first demonstrated by Tang and Van Slyke in 1987, attracts broad interest due to the capability of flexible devices, extremely thin and light screens and surface light sources [1]. Since the recombination of electrons and holes provide 25% singlet excitons and 75% triplet excitons, the device efficiency is limited to 25% when fluorescence materials are employed. Only singlet excitons can be harvested to excite such materials up to their emissive singlet excited state and decay back to the ground state via a radiative route. The energy of the triplet excitons is exhausted as heat via non-radiative decay. The most important breakthrough in the development of highly efficient OLEDs was the discovery of electrophosphorescence in 1998 by Forrest and Ma [2,3]. Unlike fluorescent materials, phosphorescent complexes with a heavy metal center (such as Ru (ruthenium), Rh (rhodium), Os (osmium), Ir (iridium), Pt (platinum) and Au (gold)) are able to harvest both singlet and triplet excitons due to the fast intersystem crossing between the emissive triplet excited state to the singlet ground state, enabled by the strong spin-orbital coupling (SOC) effect or heavy metal effect, and the theoretical internal efficiency can consequently reaches 100%.

Among all these phosphors, iridium(III) complexes are the most promising candidates, with facile chemical modifications, tunable photophysical properties and good stability. Much research is aimed at developing novel Ir(III) phosphorescent complexes with a high luminescent quantum efficiency, good manufacturing capability and excellent electronic properties. Moreover, for different applications, distinct properties are required. For example, high color purity of the three primary colors (red, green and blue) are needed for full color displays, while broad emission spectra and yellow and/or orange emitters are favorable for white lighting to cover a wide spectral region [4]. With the exploration of Ir(III) phosphors for additional applications, near infrared (NIR) emitters have become more and more important in the field of chemical sensors, bio-imaging and telecommunication. Most of these properties can be realized by rational chemical design of the coordinating organometallic ligand. There are two main series of Ir(III) phosphors, namely neutral and cationic complexes. Since most OLEDs were fabricated using neutral Ir(III) complexes, this review will mainly focus on these materials. Only two examples of cationic complexes that can be sublimed are discussed. For further knowledge on cationic phosphorescent Ir(III) compounds, there are several previous reviews as references [5–8].

Normally, phosphorescent Ir(III) complexes adopt a disordered octahedral geometry with six coordination bonds. In order to balance the trivalent Ir(III) cation center as neutral compounds, different types of organometallic ligands and coordination structures are introduced, shown as **A**–**E** in Scheme 1. For complexes with structures **A**–**C**, three monovalent bidentate ligands are used to form a homoleptic complex (**A**) with same organometallic ligands and heteroleptic complexes (**B** and **C**) with different types of ligands. For complexes with structures **D** and **E**, tridentate ligands are employed. In molecule **D**, two tridentate ligands, one monovalent and the other divalent, are required, while monovalent tridentate and bidentate ligands and a balance monovalent atom are needed to construct the coordinating structure in molecule **E**. Since the emitting properties of the Ir(III) phosphors are mainly determined by the triplet metal-to-ligand charge transfer state (^{3}MLCT) and/or triplet ligand centered charge transfer state (^{3}LC), the energy levels and the ligand field strengths of the organometallic ligands are essential for the emission color, band width, decay time and quantum yields, etc. There are several aspects that should be considered during the design of Ir(III) phosphors: (1) a desired ligand should establish strong metal-ligand bonding that can lift the metal centered (MC) d-d* excited state. Consequently, the quantum yield can be improved by suppressing the population of this high-lying non-radiative state; (2) sufficient mixing of the ^{3}LC π-π^* excited state with the ^{3}MLCT state is required to accelerate the radiative decay rate and enhance the quantum yield by depressing the non-radiative decay; (3) chemical modifications on the ligands are able to tune not only the energy levels of the complexes but also the injection and/or transportation of the free charge carriers. Thus, the emission color and electronic properties of the emitters can be modified. For example, moieties with electron withdrawing/donating properties, such as —F, —CF$_3$, —OMe, —^{t}Bu, are usually introduced into the conjugation system of the ligand to influence the HOMO/LUMO bandgap. Moieties with main-group elements, such as B, N, O, P and S, are employed to optimize the electronic features of the emitters [9].

The general device structure of OLEDs is shown in Fig. 1 along with the energy level diagram of the different functional layers. Normally, the lifetime of the emissive excited state in a phosphorescent Ir(III) complex is relatively long, on the scale of a microsecond. They are usually doped in host materials at low concentrations to form an emission layer (EML), aiming to avoid efficiency loss caused by triplet-triplet annihilation (TTA). However, there are also publications on self-host phosphorescent Ir (III) complexes bearing ligands with a large steric hindrance. Other functional layers are induced to facilitate the injection, transporting and confinement of charge carriers, including an electron/hole injection layer (EIL/HIL), electron/hole transporting layer (ETL/HTL) and hole blocking layer (HBL). The electrons and holes are injected