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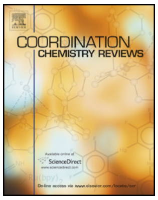

Review

Metal complexes with pyridyl azolates: Design, preparation and applications

Yun Chi[a,*], Bihai Tong[a,b], Pi-Tai Chou[c,*]

[a] Department of Chemistry and Low Carbon Energy Research Center, National Tsing Hua University, Hsinchu 30013, Taiwan
[b] College of Metallurgy and Resources, Institute of Molecular Engineering and Applied Chemistry, Anhui University of Technology, Ma'anshan 243002, Anhui, China
[c] Department of Chemistry and Center for Emerging Material and Advanced Devices, National Taiwan University, Taipei 10617, Taiwan

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* Corresponding authors at: Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan. Tel.: +886 3 5712956.
E-mail addresses: ychi@mx.nthu.edu.tw (Y. Chi), chop@ntu.edu.tw (P.-T. Chou).

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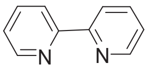
ABSTRACT

This review is aimed at updating the current advance of metal complexes bearing pyridyl azolates or relevant functionality. Of particular emphasis is the emerging metal complexes, which show bright prospect in the energy relevant issues such as organic light emitting diodes (OLEDs) and dye sensitized solar cells (DSCs). Our motive lies in the development of OLED phosphors as well as the realization of superior sensitizers in DSCs. It covers a great extension of azolates based derivatives as well as a large variety of core metal ions spanning from Re(I), Ru(II), Os(II), Ir(III), Pt(II) and to Cu(I). Their synthetic strategy, chemical/physical and photophysical properties and electroluminescence as a function of chelate or metal characteristics are systematically discussed. The potential applications are far-reaching in the wake of the previously unrecognized feature on harnessing the highly excited states, which are then realized by several new designs endowed with this unique property. Also, the interplay of the ligand design, i.e, the sameness and difference, between lighting and photovoltaic oriented metal complexes is highlighted.

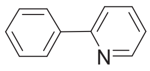
1. Introduction

Ever since the first report by Tang and VanSlyke [1], organic light emitting diodes (OLEDs) have attracted intensive attention in both academic and industrial sectors. This technology has been considered as one of the most important breakthrough during the past three decades because of its features for enhancing display qualities, thin and light weight, fast optical and electrical response, and high contrast. In reality, OLEDs have already penetrated in many modern products such as smartphones and notepads. The advantages of OLEDs are expected to be revolutionary to the visual products that are currently dominated by the liquid crystal displays (LCDs).

Undisputedly, transition metal complexes play an important role in the development of OLED technology [2–4]. For acquiring luminescent metal complexes, tactically, it is important to select chelates with appropriate frontier molecular orbitals and suitable central metal core. The assembly allows efficient electronic transitions occurring between different energy states associated with both metal atom and chelating ligands, and hence the formation of the emissive materials showing all three RGB colors. The desired metal phosphors should possess (i) the stronger metal–ligand bonding that would increase the energy level of dd excited states and afford less radiationless quenching due to the suppressed population to this higher lying state with repulsive potential energy surface, and (ii) effective mixing of ligand-centered $\pi\pi^*$ excited state and metal-to-ligand charge transfer (MLCT) states that allows facile tuning of emission wavelength. Two prototypical aromatic chelates that are suitable for making the luminescent transition-metal complexes are 2,2′-bipyridine (bpy) [5–7] and 2-phenyl pyridine (ppy) [8–10]. The associated research studies were motivated by the interests in their basic photophysical properties as well as the great versatility for further derivatization.



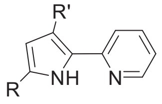
2,2'-bipyridine



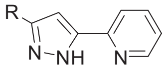
2-phenyl pyridine

In principle, on the one hand, the bpy chelates are a prime choice for assembling the ionic luminescent metal complexes. This is mainly attributed to the stronger chelate-to-metal dative interaction induced by the two nitrogen atoms. On the other hand, the class of 2-phenyl pyridine based chelates seems to be even more suitable for assembling the charge–neutral metal phosphors versus its bpy counterparts. Their differences are manifested by the fact that the phenyl (or functionalized aromatics) substituent undergoes the so-called cyclometalation reaction. The resulting metal–carbon covalent bonding is much stronger (cf. the dative bond) and is critical for providing the more stable and rigidified coordination environment and, in turn, destabilizing the metal-centered dd excited state. The net effect is to minimize the non-radiative deactivation process at RT. Furthermore, cyclometalation also creates the anionic chromophoric chelates that can partially balance the positive charge at the central metal atom. The formation of charge–neutral complexes increases their relative volatility, such that the as-synthesized metal complexes are suitable for forming layered thin film or doped thin film using thermal vacuum deposition, which is the readily accessible technology for fabrication of OLEDs in the current commercial markets.

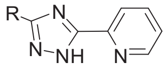
Based on the promising technological future of OLEDs, much attention has recently been paid to metal complexes with more stable and efficient luminescent properties. In this approach, we are quite fortunate to recognize that the C-linked 2-pyridyl azoles (i.e. pyrrole, pyrazole, triazole and tetrazole) are akin to both 2,2′-bipyridine and 2-phenyl pyridine, and all are capable of using two adjacent nitrogen atoms to form a stable chelate interaction [11–15].



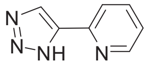
2-pyridyl pyrroles, **L1H**



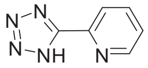
pyrazoles, **L2H**



1,2,4-triazoles, **L3H**



1,2,3-triazoles, **L4H**



tetrazoles, **L5H**

Moreover, azolate-based ligands are ideal motifs for attaining the desired metal complexes [16]. The strong σ-donor property of the azolate (i.e. in the deprotonated state), together with the π-accepting ability of the associated pyridyl fragment [17], provides a synergism of the electron delocalization via a highly stable, five-membered metal–chelate interaction. Alternatively, the azolic N—H fragment would allow a greater reactivity toward the relatively inert transition-metal elements, such that these azole chelates can serve as the replacement for the 2-phenyl pyridine type of ligands; the latter has been well known for its capability in forming the emissive Ir(III) and Pt(II) complexes [9,18]. but failed to react properly with the less reactive Ru(II) and Os(II) reagents, unless it were stabilized by the greater rigidity and activated by attachment of the electron withdrawing substituent [19,20]. Exploiting proper synthetic skill, both azole or azolate chelates would open the possibility to design transition metal complexes having potentials in a number of cutting-edge optoelectronic applications.