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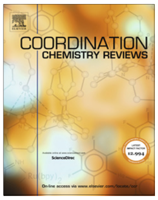

Review

Heteroleptic diimine–diphosphine Cu(I) complexes as an alternative towards noble-metal based photosensitizers: Design strategies, photophysical properties and perspective applications

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ABSTRACT

Photoactive Cu(I) complexes are considered as a promising alternative to traditional noble-metal complexes that are mainly based on Ru(II) and Ir(III). Therefore, in recent years heteroleptic Cu(I) complexes of the type $[Cu(N\text{^}N)(P\text{^}P)]^+$ have been developed exhibiting impressive performance, e.g., long-lived excited-states, high emission quantum yields with tunable emission spectra as well as largely adjustable redox properties. These favorable features render heteroleptic Cu(I) complexes as suitable non-noble metal photosensitizers. Due to the exploding number of examples reported in literature, this review aims at systematically comparing the fundamental features of various cationic and neutral diimine–diphosphine Cu(I) complexes regarding to their geometrical, optical as well as electrochemical properties. In particular, this review focuses on the ability to tune the optoelectronic properties and excited-state dynamics by the design and the choice of the underlying N^N and P^P chelate ligands. Finally, this review briefly indicates some application scenarios of these novel class of complexes, e.g., in the fields of photocatalytic hydrogen evolution and light-emitting devices. As a result this review likes to contribute to a detailed understanding of structure–function relationships and to the rational design of heteroleptic diimine–diphosphine Cu(I) complexes for specific photophysical applications in the future.

Contents

Abbreviations: ACN, acetonitrile; ATRA, atom transfer radical addition; bpy, 2,2′-bipyridine; CDC, cross-dehydrogenative coupling; DCM, dichloromethane; DFT, density functional theory; DHA, dihedral angle; DMF, dimethylformamide; DSSC, dye sensitized solar cell; FC, Franck-Condon; Fc^+/Fc, ferrocenium/ferrocene redox couple; HER, hydrogen evolution reaction; HOMO, highest occupied molecular orbital; IC, internal conversion; ILCT, intraligand charge transfer; ISC, intersystem crossing; LC, ligand centered; LEC, light-emitting electrochemical cell; LLCT, ligand-to-ligand charge transfer; LUMO, lowest unoccupied molecular orbital; MC, metal-centered; mCP, 1,3-bis(carbazol-9-yl)benzene; MeOH, methanol; 2-MeTHF, 2-methyltetrahydrofuran; MLCT, metal-to-ligand charge transfer; OLED, organic light-emitting diode; PHE, photocatalytic hydrogen evolution; phen, 1,10-phenanthroline; PJT, pseudo-Jahn–Teller; PLQY, photoluminescence quantum yield; PMMA, poly(methyl methacrylate); PPAAm, plasma-polymerized allylamine; PS, photosensitizer; RR, resonance Raman (spectroscopy); SOC, spin orbit coupling; SR, sacrificial reductant; TA, transient absorption; TADF, thermally activated delayed fluorescence; TCSPC, time-correlated single photon counting; TDDFT, time-dependent DFT; TEA, triethylamine; THF, tetrahydrofuran; TOF, turnover frequency; TON, turnover number; UV, ultraviolet; UV–Vis, ultravioletvisible (spectroscopy); WRC, water reduction catalyst; XAS, X-ray absorption spectroscopy.

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1. Introduction

Coordination compounds composed of transition metals and polypyridine ligands, such as Ru(II) polypyridine and cyclometalated Ir(III) complexes, are of utmost importance in artificial photosynthetic assemblies, i.e., as light-harvesting units or as primary electron donors [1–6]. In order to bring such photochemical molecular devices to work on a larger scale, e.g., to contribute to the fields of solar energy conversion and of light generation by electroluminescence, it is indispensable to replace noble metals by more abundant and less expensive ones [7–11]. In this respect particularly complexes based on Cu(I) have attracted considerable attention during the last decades [7,12–19]. They have been reported to exhibit great potential, i.e., they display favorable and largely tunable redox and luminescence properties. In a large number of examples the applicability of such Cu(I) complexes could be demonstrated, e.g., as photosensitizers (PSs) in hydrogen evolution reaction (HER) schemes [17–22] and dye sensitized solar cells (DSSCs) [23–27], or as emitters in organic light-emitting diodes (OLEDs) and light-emitting electrochemical cells (LECs) [28–36], or as sensors for oxygen [37] as well as photoredoxcatalysts in various organic reactions [16,38,39]. Significant improvements in the design of homoleptic bis-diimine complexes $[Cu(N^\wedge N)_2]^+$ and heteroleptic diimine–diphosphine Cu(I) complexes of the type $[Cu(N^\wedge N)(P^\wedge P)]^+$, where N^N and P^P indicate chelating diimine and diphosphine ligand respectively, resulted in promising photophysical properties, e.g., in highly luminescent Cu(I) complexes with long-lived excited-states [7,10,14,17,28,40–45]. Homoleptic Cu(I) complexes $[Cu(N^\wedge N)_2]^+$ and the tuning of the underlying diimine ligands have been extensively studied in the past [12,46–53]. These compounds generally exhibit a strong absorption in the visible range, however, further enhancement of the luminescence quantum efficiency is challenging, sometimes even at the expense of thermodynamic stability [52,53]. In recent years the impressive performance of the heteroleptic $[Cu(N^\wedge N)(P^\wedge P)]^+$ counterparts have drawn increasing attention as they exhibit a greatly enhanced emission efficiency, much longer excited state lifetimes and a broader tuning range than the $[Cu(N^\wedge N)_2]^+$ systems [14,31,54–59]. Therefore, this review will focus on the tunable optical and electrochemical properties of heteroleptic $[Cu(N^\wedge N)(P^\wedge P)]^+$ complexes and their variations of the underlying N^N and P^P chelate ligands. Besides this, a summary of advances in the design of diimine–diphosphine Cu(I) compounds towards extraordinary photophysical properties is presented. Moreover, the consequences of these properties for the light-induced excited state processes as well as for potential applications of this emerging class of photoactive non-noble metal complexes are discussed. This review is meant to introduce relevant structure–function relationships for a rational design of heteroleptic diimine–diphosphine Cu(I) complexes for specific photophysical applications in the future.

2. General considerations – some background on Cu(I) complexes

The first systematic investigations of Cu(I) complexes were started in the 1970s mostly concerned with $[Cu(phen)_2]^+$ and derivatives [46,48,60,61] thereof as well as with $[Cu(N^\wedge N)(PPh_3)_2]^+$ (PPh_3 = triphenylphosphine) [60,62–64]. Many of these studies dealt with the relationships between geometry, type of substituents, substitution pattern and photophysical features and have been in the focus of research until now [7,12,17,40,46,48,60,65–67]. These studies benefited from the rapid developments in photophysical and theoretical methods over the last two decades and led to detailed insights into the (ultrafast) light-induced processes and their geometrical implications [12,41,68–79]. Consequently, general insights into the present geometries of Cu(I) complexes that impact the photophysical and optical properties have been obtained and are sketched in Fig. 1. Some diimine ligands utilized for Cu(I) complexes are shown in Fig. 2.

In the ground state Cu(I) complexes possess a closed shell d^{10} electronic configuration with a preferred pseudotetrahedral D_{2d} geometry (Fig. 1) [12,41,71,80]. The completely filled external electronic shell implies the absence of metal-centered (MC) states (also called d–d states). A deviation from the ideal tetrahedral geometry ($D_{2d} \rightarrow D_2$) of the ground state structure is caused by structural distortion via steric and electronic interligand interactions, or torsional motions [22,72,78]. Usually, in the solid state homoleptic $[Cu(N^\wedge N)_2]^+$ complexes prefer to adopt a D_2 structure due to the intermolecular stacking interactions among the heteroaromatic ligands [46], and the dihedral angle (DHA) between the two ligands planes is largely affected by the counterions [81,82]. For example, the DHA of $[Cu(dmp)_2]^+$ varies in the range from 73° to 85° strongly depending on the respective anion (i.e., NO_3^-, Br^- or ClO_4^-) [81]. The same effect can be observed for $[Cu(dmbpy)_2]^+$, where the DHA diverges to 74–81° in dependence of the counterions (PF_6^-, BF_4^- and ClO_4^-) [82]. In contrast, in solution the DHA between the two ligands planes is typically near 90° (88±2°) in the ground state of homoleptic $[Cu(N^\wedge N)_2]^+$ complexes [17,46,72,80]. Exceptions from that can be observed for some 1,10-phenanthrolines with bulky aryl substituents in 2,9-position, such as $[Cu(dpp)_2]^+$, $[Cu(tpp)_2]^+$ or $[Cu(dpdmp)_2]^+$ (see Fig. 2) [7]. For these complexes, π-stacking interactions between the phenyl groups of one ligand and the phenanthroline moiety of the other ligand, in conjunction with steric hindrance, lead to a 10–20° distortion from the ideal tetrahedral DHA [7,17,67]. However, this distortion can be inhibited in highly congested structures, such as in $[Cu(dptmp)_2]^+$ complexes [67].

Typical homoleptic $[Cu(N^\wedge N)_2]^+$ complexes, such as $[Cu(phen)_2]^+$, $[Cu(bpy)_2]^+$ and their analogs, absorb in the UV region by intense ligand-centered (LC) transitions, which are accompanied by moderately intense absorptions in the visible range [7]. The visible