



## Review

## Recent advances in copper complexes for electrical/light energy conversion

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## ABSTRACT

A great deal of research effort has been put in green energy applications in the past few decades based on organic optoelectronics. Compared with conventional inorganic semiconductors, organic counterparts offer a much simpler strategy for low-cost mass production and structural modification. Hence, continuous and intensive academic and industrial research works have been done in these areas. In terms of the materials used, transition-metal complexes with the unique features of the transition metal centers represent a large group of candidates, showing high performance in energy conversion technologies. However, the commonly used transition metals, like Pt(II), Ir(III) and Ru(II), are expensive and of relatively low abundance. Concerning elemental sustainability and marketability, some abundant and cheaper metals should be investigated and further developed to replace these precious metals. Cu(I) complexes have shown their potentiality in solar energy harvesting and light emitting applications, due to their well-studied photophysics and structural diversity. In addition, copper is one of the earth-

**Abbreviations:** Alq<sub>3</sub>, tris(8-hydroxyquinolinato) aluminum(III); BCP, bathocuproine; BHJSCs, bulk heterojunction solar cells; BALq-13, bis(2-methyl-quinolin-8-olato)(2,6-diphenylphenolato)aluminum(III); Bphen, bathophenanthroline; bpy, 2,2'-bipyridine; bq, 2,2'-biquinoline; CAAC, cyclic alkyl(amino)carbene; CBP, 4,4'-bis(carbazol-9-yl)biphenyl; CDCA, chenodeoxycholic acid; CE<sub>max</sub>, maximum current efficiency; CIE, Commission internationale de l'éclairage; CPPyC, 3-(carbazol-9-yl)-5-((3-carbazol-9-yl)phenyl)pyridine; CPy, 3-(carbazol-9-yl)pyridine; CPzPC, 9-(3-(6-(carbazol-9-yl)pyrazin-2-yl)phenyl)carbazole; CRI, color rendering index; CT, charge transfer; CuPc, copper(II)phthalocyanine; CzBPDCb, 5-(3'-(9H-carbazol-9-yl)-(1,1'-biphenyl)-3-yl)-5H-pyrido[3,2-b]indole; czpzpy, 2-(9H-carbazolyl)-6-(1H-pyrazolyl)pyridine; CzSi, 9-(4-tert-butylphenyl)-3,6-bis(triphenylsilyl)-9H-carbazole; DFT, density functional theory; dmp, 2,9-dimethyl-1,10-phenanthroline; dpbq, 4,4'-diphenyl-2,2'-biquinoline; DPEphos, bis[2-(diphenylphosphino)phenyl]ether; DPEPO, bis[2-(diphenylphosphino)phenyl]ether oxide; dppb, 1,2-bis(diphenylphosphino)benzene; dppm, bis(diphenylphosphino)methane; DPVBi, 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl; DSSCs, dye-sensitized solar cells; D-π-A, donor-π-acceptor; EBL, electron-blocking layer; EL, electroluminescent/electroluminescence; EQE<sub>max</sub>, maximum external quantum efficiency; FB9ox, 1-methyl-2-[2,4,6-tris(9-oxiranyl-nonyloxy)phenyl]fulleropyrrolidine; FF, fill factor; Flrpic, bis[2-(4,6-difluorophenyl)pyridinato-C<sup>2</sup>,N](picolinato)iridium(III); HETPHEN, heteroleptic phenanthroline; HAT-CN, dipyrzino[2,3-f:2',3'-h]quinoxaline-2,3,6,7,10,11-hexacarbonitrile; HLCT, hybridized local and charge transfer; HOMO, highest occupied molecular orbital; ILCT, intraligand charge transfer; Ir(ppy)<sub>3</sub>, tris[2-phenylpyridinato-C<sup>2</sup>,N]iridium(III); ISC, intersystem crossing; ITO, indium tin oxide; J<sub>sc</sub>, short-circuit photocurrent density; k<sub>nr</sub>, non-radiative decay rate constant; k<sub>r</sub>, radiative decay rate constant; LC, ligand-centered; LED, light emitting diode; Liq, 8-hydroxyquinolinato lithium; LLCT, interligand charge transfer; L<sub>max</sub>, maximum luminance; LMMCT, ligand-to-metal-to-metal charge transfer; LUMO, lowest unoccupied molecular orbital; MC, metal-centered; mCP, 1,3-bis(N-carbazolyl)benzene; mdpbq, 3,3'-methylene-4,4'-diphenyl-2,2'-biquinoline; MLCT, metal-to-ligand charge transfer; (M + X)LCT, (metal + halide)-to-ligand charge transfer; m-MTDATA, 4,4',4''-tris[phenyl(m-tolyl)amino]triphenylamine; NHC, N-heterocyclic carbene; NHetPHOS, N-heterocyclic phosphine; NIR, near-infrared; NPB, N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-benzidine-4,4'-diamine; N<sup>o</sup>N, diimine; OFETs, organic field-effect transistors; OLEDs, organic light emitting diodes; OPVs, organic photovoltaic cells; OXD7, 1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yl]benzene; Pc, phthalocyanine; PCE, power conversion efficiency; PCE<sub>ref</sub>, power conversion efficiency of standard dye; PC<sub>71</sub>BM, [6,6]-phenyl C<sub>71</sub> butyric acid methyl ester; PEDOT:PSS, poly(3,4-ethylenedioxythiophene):polystyrene sulfonate; PolyTPD, poly(4-butylphenyldiphenylamine); PE<sub>max</sub>, maximum power efficiency; phen, 1,10-phenanthroline; PPh<sub>3</sub>, triphenylphosphine; PL, photoluminescent/photoluminescence; PLQY, photoluminescence quantum yield; PMMA, poly(methyl methacrylate); PVK, poly(9-vinylcarbazole); PYD2, 2,6-dicarbazolo-1,5-pyridine; pz<sub>2</sub>Bph<sub>2</sub>, diphenyl-bis(pyrazol-1-yl)borate; P<sup>o</sup>P, diphosphine; p-6P, para-sexiphenyl; RISC, reverse intersystem crossing; SOC, spin-orbit coupling; SPP01, 2-(diphenylphosphoryl)spirofluorene; SQ2, 2,4-bis[4-(N,N-dibutylamino)-2,6-dihydroxyphenyl]squinaraine; SSL, solid-state lighting device; TADF, thermally-activated delayed fluorescence; TAPC, 4,4'-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine]; TAZ, 3-(biphenyl-4-yl)-5-(4-tert-butylphenyl)-4-phenyl-4H-1,2,4-triazole; TCCz, N-(4-(carbazol-9-yl)phenyl)-3,6-bis(carbazol-9-yl)carbazole; TC1Q, 4-[3,6-di(carbazol-9-yl)carbazol-9-yl]isoquinoline; TCO, transparent conductive oxide; TCPy, 3-[3,6-di(carbazol-9-yl)carbazol-9-yl]pyridine; TCTA, tris(4-carbazol-9-ylphenyl)amine; T<sub>d</sub>, decomposition temperature; TFB, poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl)diphenylamine)]; TmPyPb, 1,3,5-tri(m-pyridin-3-ylphenyl)benzene; TPBI, 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1H-benzimidazole); TPD, N,N'-bis(3-methylphenyl)-N,N'-diphenylbenzidine; TTA, triplet-triplet annihilation; V<sub>oc</sub>, open-circuit photovoltage; V<sub>ON</sub>, turn-on voltage; Xantphos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; XLCT, halide-to-ligand charge transfer; XMCT, halide-to-metal charge transfer; 26mCPy, 2,6-bis(N-carbazolyl)pyridine; 3TPYMB, tris(2,4,6-trimethyl-3-(pyridin-3-yl)phenyl)borane; 4ClQ, 4-(carbazol-9-yl)isoquinoline; ε, molar absorptivity; ΔE(S<sub>1</sub>-T<sub>1</sub>), band gap between the lowest singlet and triplet excited states; λ<sub>em</sub>, emission peak wavelength; λ<sub>max</sub>, maximum peak wavelength; λ<sub>EL</sub>, electroluminescent peak wavelength; λ<sub>EL,max</sub>, maximum electroluminescent peak wavelength; λ<sub>PL,max</sub>, maximum photoluminescent peak wavelength; η<sub>ext</sub>, device efficiency; τ, excited-state lifetime.

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abundant metals with less toxicity, which makes it competitive to precious transition metals. As a result, a series of rational molecular engineering has been developed to boost the device performance of copper complexes. In this review, the recent progress of copper complexes in the fields of organic light emitting devices (OLEDs), photovoltaic cells (dye-sensitized solar cells (DSSCs) and bulk heterojunction solar cells (BHJSCs)) in the past two decades will be presented. Representative examples are chosen for discussion.

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## 1. Introduction

Transition metal complexes have aroused tremendous attention for different energy-related applications due to the unique characters of the metal centers. One of the unique characteristics is the strong spin-orbit coupling (SOC) of organometallic complexes, which enables fast intersystem crossing (ISC) and long-lived phosphorescent decay, as compared with the pure organic compounds. As a result, most of the heavy transition-metal complexes show phosphorescence [1] and are of particular interest for use in organic light emitting devices. By excitation of the lowest triplet excited state, a strong phosphorescence is produced. In view of the molecular orbitals, the emission is largely determined by the metal-to-ligand charge transfer (MLCT) state between the *d* orbitals of the metal center and the  $\pi$  orbitals of the organic ligand. It turns out that the electronic transfer between different energy states (color tuning) can be carefully controlled by modifying the chelating ligands with appropriate frontier molecular orbitals [2]. As a result, organometallic complexes are being actively studied in order to boost the efficiency of optoelectronic devices.

A great deal of research effort has been paid to green energy applications using organic optoelectronics since the 1980s [3,4]. Compared to conventional inorganic semiconductors, organic small molecules and polymers can be synthesized and fabricated by utilizing different strategies to offer low-cost mass-production over a span of applications, including organic light emitting diodes (OLEDs), organic field-effect transistors (OFETs) and organic photovoltaic cells (OPVs). This triggered the fast-growing development of the field that involves the synthesis of new organometallic/organic materials and device performance engineering. Regarding light emitting devices, the materials used were dominated by the phosphorescent emitters, especially Pt(II) and Ir(III) organometallic complexes, due to their long-lived triplet excited states [5]. On the other hand, there is a growing trend to use less expensive Cu(I) complexes, due to their thermally-activated delayed fluorescent (TADF) nature to harvest both singlet and triplet excitons. These

new findings redefine the traditional views of Cu(I) complexes, which were originally regarded as poor candidates for OLED active materials.

In yet another important area of organic photovoltaic devices, Cu(I) complexes have attracted much attention as the active layer for the conversion of sunlight into electricity. This is because the intrinsic long-lived triplet excited state prolongs the exciton diffusion length in a solar cell and reduces the chance of charge recombination [6]. This benefits the transfer and migration of charge carriers and boosts the photocurrent within the device (Tables 1–4).

Herein, we summarize the recent progress made using Cu(I) complexes in light emitting and light harvesting applications. The photophysical and electrochemical features are discussed in Section 2, which allow the readers to gain a general background of Cu(I) materials. Subsequently, representative Cu(I) complexes used as emissive materials in OLEDs are reviewed together with their device performance in Section 3, followed by a survey of their light harvesting materials for use in dye-sensitized solar cells (DSSCs) and bulk heterojunction solar cells (BHJSCs) in Section 4. Of particular emphasis is the correlation between the structures and photophysical properties, which aims at improving the photoluminescence and photosensitization performance through precise structural modifications. Finally, a short summary of the design strategies will be given in the conclusion.

## 2. Fundamental properties of copper(I) complexes

In this section, both of the photophysical and electrochemical characters of Cu(I) complexes will be illustrated. The scientific interest in investigating the structure-property relationship of Cu(I) complexes has increased significantly since the discovery of the room temperature luminescence of [Cu(dmp)<sub>2</sub>]<sup>+</sup> (dmp = 2,9-dimethyl-1,10-phenanthroline) by Sauvage and McMillin [7–9]. However, the development of Cu(I) complexes was rather limited for light harvesting and light emitting applications in the 90s due

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