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Review

Sustainable metal complexes for organic light-emitting diodes (OLEDs)

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ABSTRACT

Organic light-emitting diodes (OLEDs) produced from metal complexes play an important role in modern electroluminescent devices. While OLEDs are being used in display various applications such as TVs, smartphones and wearables already, a drastic increase in the production volume in the next years is being expected as soon as OLED lighting applications and printed OLEDs hit the market. Given that thus far, phosphorescent iridium compounds are required to make these products, sustainability issues are imminent. To review viable alternatives, we highlight the current status of sustainable metal complexes with a special focus on copper and zinc complexes. Ligand structures and complex preparation were highlighted. We also briefly address features like cooperativity, chirality, and printing.

Contents

Abbreviations: ^{3}MLCT, triplet metal–ligand charge transfer; 4MTPD, *N,N*′-diphenyl-*N,N*′-(3-methyl)-1,1′-biphenyl-4,4′-diamine; acac, acetylacetonate; AIEE, aggregation induced enhanced emission; An, (*ortho*)-anisyl; BAlq, bis(2-methyl-8-quninolinato)-4-phenylphenolate; BCP, 2,9-dimethyl-4,7 diphenyl-1,10-phenanthroline (bathocuproine); BINAP, (2,2′-bis(diphenylphosphino)-1,1′-binaphthyl); bpy, 2,2′-bipyridine; btz, 2-(2-hydroxyphenyl)benzothiazole; CBP, 4,4′-bis(*N*-carbazolyl)-1,1′-biphenyl; lCFx, fluorohydrocarbon; CIE, Commission internationale de l'éclairage; Coumarin 6, 3-(2-benzothiazolyl)-7-(diethylamino)coumarin; CPPyC, 3-(carbazol-9-yl)-5-((3-carbazol-9-yl)phenyl)pyridine; CPzPC, (9-(3-(6-(carbazol-9-yl)pyrazin-2-yl)-phenyl)-carbazole); CPzPyC, (9-(5-(6-(carbazol-9′-yl)pyrazin-2″-yl)-pyridin-3‴-yl)-carbazole); CuPc, copper phthalocyanine; CoTPP, cobalt trinitrophthalocyanine; Cz, *N*-carbazolyl; Cy, cyclohexyl; DAlq, dinuclear aluminium 8-hydroxyquinoline complex; DDQ, dichlorodicyanobenzoquinone; DPEPO, bis[2-(diphenylphosphino)phenyl]ether oxide; DPEPhos, bis(2-(diphenylphosphanyl)phenyl)ether; DPIQ, 1-isoquinolinyldiphenylphosphine; dppm, 1,1-bis(diphenylphosphino)methane; EIL, electron injection layer; EL, electron-blocking layer; EML, emissive layer; EQE, external quantum efficiency (yield); ETL, electron transport layer; FWHM, full width at half maximum; Go-CoTPP, graphene oxide–cobalt trinitrophthalocyanine; HBL, hole blocking layer; HIL, hole injection layer; HTL, hole transporting layer; IL, intraligand; ISC, intersystem crossing; ITO, indium tin oxide; LEC, light-emitting electrochemical cell; LLCT, ligand to ligand charge transfer; LMCT, ligand metal charge transfer; M^{3}D, mask-less mesoscale materials deposition; MC, metal centered; mCP, *N,N*′-dicarbazolyl-3,5-benzene; mCPy, (3,5-bis(carbazol-9-yl)pyridine); MDDW, micro-dispensing deposition write; MLCT, metal to ligand charge transfer; MO, molecular orbital; n.a., not applicable; NDP, *N,N*′-di(1-naphthyl)-*N,N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine (also NPB); NEXAFS, Near-Edge X-ray Absorption Fine Structure; NHC, *N*-heterocyclic carbene; NIR, near infra-red; NLO, nonlinear optics; NPB, *N,N*′-di(1-naphthyl)-*N,N*′-diphenyl-(1,1′-biphenyl)-4,4′-diamine(also NDP); OPV, organic photovoltaics; paz, 2-(pyridin-2-yl)-1H-pyrrolo[2,3-b]pyridine; PBD, 2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole; pbim, 2-(2′-pyridyl)benzimidazole; pbo, 2-(2′-pyridyl)benzoxazole; pbt, 2,2′-pyridyl)benzothiazole; PEDOT:PSS, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate; PGM, platinum group metals; Phen, 1,10-phenanthroline; PHOLED, phosphorescent organic light-emitting diode; PLQY, photo luminescence quantum yield; PNNA, 9,9-dimethyl-10-(6-(3-phenyl-1H-pyrazol-1-yl)pyridin-3-yl)-9,10-dihydroacridine; POLED, polymer organic light-emitting diodes; poly-TPD, poly(*N,N*′-bis-4-butylphenyl-*N,N*′-bisphenyl)benzidine; PVK, (poly(9-vinylcarbazole)); PYD2, 2,6-dicarbazolo-1,5-pyridine; q, hydroxyquinoline; R2R, roll-to-roll; RASI, rotationally accessed spin-state inversion; RISC, reverse intersystem crossing; sal, salene; SAlq, triphenylsilyloxy aluminium 8-hydroxyquinoline complex; sat, sitting atop; SOLED, stacked organic light-emitting diode; TAPC, 1,1-bis[(di-4-tolylamino)phenyl]cyclohexane; TAZ, 3-(biphenyl-4-yl)-5-(4-tert-butylphenyl); TCIQ, (4-[3,6-di(carbazol-9-yl)carbazol-9-yl]isoquinoline); TPBi, 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole); TPD, *N,N*′-bis(3-methylphenyl)-*N,N*′-diphenylbenzidine; TNATA, 4,4,4-tris(2-naphthyl-phenyl-amino)triphenylamine; TPP, tetraphenylporphyrin; XANES, X-ray Absorption Near-Edge Structure; XantPhos, 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene); XAS, X-ray absorption spectroscopy; XLCT, halide-to-ligand charge transfer; XMCT, halide to metal charge transfer; η_c, current efficiency; η_P, power efficiency; λ_{el}, emission wavelength peak of electroluminescence; λ_{max}, peak emission wavelength.

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1. Introduction

Organic light-emitting diodes (OLEDs) are booming right now: after the launch of commercial OLED displays based on phosphorescent iridium complexes, OLEDs are on their way to replace LCD technology. There is one major issue limiting the growth of the OLED market: the availability of rare metals, especially iridium.

As shown in Fig. 1, iridium is an extremely scarce resource: In the last years, the annual production of iridium was about 3 t, according to the U.S. Geological Survey [1]. With an abundance of only 0.0007 ppm in the earth's crust, it is in fact one of the rarest elements on the planet.

Looking at potential supply bottlenecks as a result of the incorporation of rare metals, we concluded in an earlier study [2] that the growth of the market share of OLED technology for flat screen displays will not be hindered due to the low amount of material incorporated per device and the comparably low sales numbers. However, we pointed out that future industrial mass-market applications such as lighting panels and especially the hypothetical use as smart labels could not be possible without finding alternatives for elements, such as iridium, which is being used in PHOLED displays now [3–7]. The replacement of phosphorescent materials based on iridium with novel metal complex materials using alternative emission pathways such as the recently emerged TADF process (*vide infra*) could solve this problem.

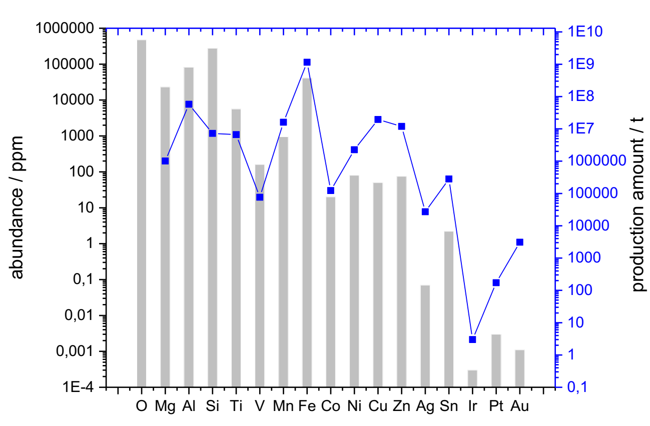

Fig. 1. Abundance and production amount of various metals, compared with O, Al and Si as rock-forming elements [9].

However, sustainability goes beyond avoiding supply bottlenecks: the key idea of the concept of 'elemental sustainability' is to ensure that all extant elements in the periodic table are kept available for future generations [8]. Apart from iridium, the rare element indium, which is being used in indium-tin-oxide (ITO) could also be critical here.

1.1. Availability issues

In 2009, 29% of computer displays, 17% of TVs and 8% of mobile devices ready for end-of-life management were collected for recycling in the U.S., according to a study of the U.S. Environmental Protection Agency. The majority of devices in all of the three product categories were disposed, primarily in landfills [10]. Estimations on reserves for platinum group metals (PGM), such as iridium, indicate that there are only between 91,000 and 338,000 t remaining [11].

Models for the future development of the annual production of PGMs predict that the annual production could grow until the second half of this century [11]. After that point we might start to run out of PGMs depending on the further exploration of new resources and the establishment of more extensive recycling methods. A striking approach, which could open up new resources for PGMs, is space mining. The abundance of iridium in certain asteroids is about five orders of magnitude higher than in the earth's crust [12]. If the exploitation of these deposits was realized, a continuous supply of PGMs would be secured in the future [13]. Nevertheless, from a conservative point of view, scientists and engineers should not rely heavily on this possibility. Besides optoelectronics, PGMs are required for a variety of other industrial applications. For platinum, the largest share is required for catalytic converters, whereas iridium is mainly used in alloys. Both iridium and platinum are used as heterogeneous catalysts in the chemical industry [14]. Of course, the most feasible way is not to rely on space mining, but