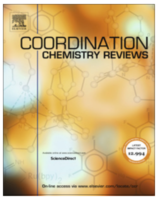
Coordination Chemistry Reviews 373 (2018) 116–147

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr



Review

Luminescent metal–organic frameworks and coordination polymers as alternative phosphors for energy efficient lighting devices

William P. Lustig, Jing Li *

Department of Chemistry, Rutgers University, 610 Taylor Road, Piscataway, NJ 08854, USA

ARTICLE INFO

Article history:
Received 20 July 2017
Received in revised form 12 September 2017
Accepted 17 September 2017
Available online 5 October 2017

ABSTRACT

The development of lower cost and higher performance phosphor materials for energy efficient lighting and other optoelectronic applications is both necessary and feasible. Luminescent metal–organic frameworks and coordination polymers (LMOFs and LCPs, respectively) are a class of materials that hold great promise for this application. Their luminescence is eminently tunable, and a myriad of structures with incredibly diverse properties have been reported, with emission wavelengths covering the entire visible spectrum, white light emission from a variety of mechanisms, and quantum yields approaching unity. This review will briefly describe the luminescence mechanisms commonly observed in these materials, discuss strategies for the rational design of LMOF/LCP phosphors, and present a number of representative examples of each mechanism and/or design strategy.

Contents

Abbreviations: 3,5-dsb, 3,5-disulfobenzoate; Ac, acetone; ad, adenine; AF, acriflavine; bdc, 1,4-benzenedicarboxylate; bp4mo, *N*-oxide-4,4′-bipyridine; bpdc, 4,4′-biphenyldicarboxylate; bpe, 4,4′-bis(4-pyridyl)ethane; bpee, 4,4′-bipyridyl-ethylene; bpp, 1,3-bis(4-pyridyl)propane; bpy, 4,4′-biphenyl; btb, 1,3,5-tris(4-carboxyphenyl)-benzene; btc, 1,3,5-benzenetricarboxylate; btec, benzene-1,2,4,5-tetracarboxylate; btpca, 1,1′,1″-(benzene-1,3,5- triyl)tripiperidine-4-carboxylate; DEF, diethylformamide; DMA, dimethylacetamide; DMA$^+$, dimethylammonium; DMF, dimethylformamide; dppy, 4-pyridyldiphenylphosphane oxide; ettc, 4′, 4‴, 4‴″, 4‴‴′-(ethene-1,1,2,2-tetrayl) tetrakis(([1,1′-biphenyl]-4-carboxylate)); glu, glutarate; H_2dcbppy, 2,2′-bipyridine-4,4′-dicarboxylic acid; H_2ida, iminodiacetic acid; H_2idpa, 5-(1-oxoisoindolin-2-yl)isophthalic acid; H_3ttaa, *N*,*N*′,*N*″-1,3,5-triazine-2,4,6-triyltris(4-aminomethylbenzoic acid); H_4L^6, 2-hydroxy-trimesic acid; H_6tatpt, 2,4,6-tris(2,5-dicarboxylphenylamino)-1,3,5-triazine; hfa, hexafluoroacetylacetonate; HL^1, 2-(2-sulfophenyl)-imidazo(4,5-*f*)(1,10)-phenanthroline; Hppy, 2-phenylpyridine; Htzib, 1-tetrazole-4-imidazole-benzene; im, imidazolate; imdc, 4,5-imidazoledicarboxylate; ina, isonicotinate; ip, isophthalate; L^2, 3,5-bis(3-carboxyphenyl)-1,2,4-triazole; L^3, *p*-terphenyl-2,2″,2‴,5,5″,5‴-hexacarboxylate; L^4, *p*-terphenyl-3,2″,3″,5,5″,5‴-hexacarboxylate; L^5, cyanobenzoate; m-bdc, 1,3-benzenetricarboxylate; ndc, 2,6-naphthalenedicarboxylate; oda, oxydiacetate; phda, phenylenediacetate; phen, 1,10-phenanthroline; ppmc, 2-phenylpyrimidine-4-carboxylate; py, pyridine; Q^1, bis-8-hydroxyquinoline; sdc, (*E*)-4,4′-(ethene-1,2-diyl)dibenzoate; TBA$^+$, tetrabutylammonium; tbapy, (1,3,6,8-tetrakis(*p*-benzoate)pyrene; tcbb, 1,3,5-tris(4′-carboxy[1,1′-biphenyl]-4-yl)benzene; tcbpe-F, 4′,4‴,4‴″,4‴‴′-(ethene-1,1,2,2-tetrayl) tetrakis(3-fluoro-[1,1′-biphenyl]-4-carboxylate); tf-bdc, tetrafluorobenenedicarboxylate; thca, *p*-ter-phenyl-3,3′,3″,5,5′,5″-hexacarboxylate; tib, 1,3,5-tris(imidazolyl) benzene; tppa, tri(4-pyridylphenyl)amine; tppe, 1,1,2,2-tetrakis(4-(pyridin-4-yl)phenyl)ethane; ttb, 4,4′,4″-s-triazine-2,4,6-triyl-tribenzoate; ttca, triphenylene-2,6,10-tricarboxylate.

* Corresponding author.

E-mail address: jingli@rutgers.edu (J. Li).

https://doi.org/10.1016/j.ccr.2017.09.017
0010-8545/

---

1. Introduction

1.1. General lighting devices and solid state lighting technologies

Global efforts to improve energy efficiency are important for reducing energy cost and consumption, decreasing carbon dioxide emission and slowing down global warming. A significant portion of global energy is directed toward infrastructure – transportation of goods and people, lighting, and heating/cooling are responsible for the bulk of energy use [1,2]. Improving the energy efficiency of these processes will lead to significant payoffs in global energy usage. Lighting is an especially attractive target, as it accounts for a significant portion of energy use. Developing more efficient lighting technologies has already begun, and addressing its energy efficiency requires less alteration of global infrastructure. Currently, three main types of general lighting technologies exist. Conventional incandescent bulbs generate white light by heating a filament to incandescence. Fluorescent bulbs function by ionizing mercury vapor through the use of an electric current, which produces UV radiation. This UV radiation excites a phosphor material on the interior surface of the bulb, which emits white light. Solid-state lighting based on light-emitting diodes (LEDs) uses an electroluminescent diode to produce narrow emission peaks, which can be converted into white light in a variety of ways. In multi-chip LEDs, white light is produced by mixing emission from red, green, and blue LED chips. However, using three LED chips drastically increases the cost of these bulbs. In phosphor-converted white LEDs (pc-WLEDs), phosphors excited by a single-chip LED produce white light, either directly or by combining the emission of the selected chip. There are three main varieties of pc-WLEDs. In the first, a UV-emitting LED chip is used to excite a mix of red, green, and blue phosphor materials to produce white light. The second is similar, with the UV-emitting LED chip exciting a phosphor which directly produces white light. The third common variety is a blue chip based pc-WLED, in which a blue-emitting LED chip is used to excite a yellow phosphor or multicomponent phosphors. The combined emissions from the blue chip and phosphor(s) give the white light.

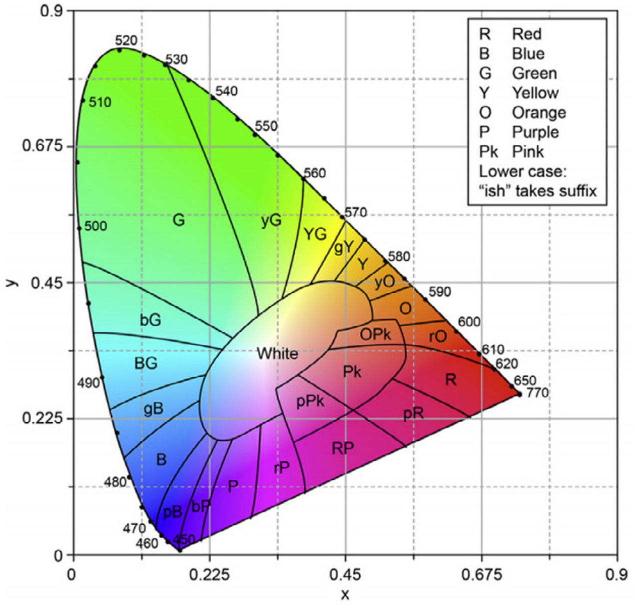


Fig. 1. CIE chromatography plot, showing the colors corresponding to each region of the plot. Reproduced with permission from Ref. [4]. Copyright 2016, Elsevier B. V.

When qualifying the light produced by a lighting device, two important characterization metrics are the color temperature and chromaticity. The color temperature of an emissive material relates the color of light produced to the temperature at which an ideal black body radiator would produce light of the same color. As such, it is only of use when describing light colors produced by black body radiators, from red, through orange and yellow, and into white light. It is most commonly used to indicate whether a bulb produces "cold" blue-white light (higher color temperatures) or "warm" yellow-white light (lower color temperatures) and is provided for most commercial light bulbs. Chromaticity describes the color of light more completely. The international standard method of plotting chromaticity was developed by the International Commission on Illumination (CIE) in 1931, which uses a coordinate system to indicate a specific color (Fig. 1) [3]. The CIE coordinates of a given light source may be calculated using its spectral power distribution and three color matching functions, allowing the hue of light perceived by the human eye to be determined from spectral data. For pure white light, the CIE coordinates are (0.333, 0.333).

While LED bulbs are the most energy efficient and longer-lasting general lighting technology, their highest initial cost has slowed their adoption. This is unfortunate, as the US Dept. of Energy has estimated that if the United States switched to entirely LED lighting, over 300 TWh of energy would be saved annually, which is nearly double the amount expected to be generated by wind and solar power generation plants by 2030 [5]. As the phosphor materials currently used in WLEDs rely on rare-earth elements (REEs), which contribute significantly to their high cost, developing new, more efficient phosphors materials that have little or no dependence on REEs could reduce the cost of these devices, resulting in faster adoption of the technology and major global energy savings.

1.2. Luminescent metal–organic frameworks

Metal-organic frameworks (MOFs) or coordination polymers (CPs) are crystalline solids composed of single metal ions (primary building units, PBUs) or metal ion clusters (secondary building units, SBUs) linked together by organic ligands with multiple binding sites to form extended network structures. As MOFs and CPs are crystalline materials, diffraction techniques can provide precise information about their structure, while their chemical and