Luminescent Metal-Organic Frameworks for White LEDs

Matthew Gole Literature Seminar November 9, 2017

Approximately 19% of global electricity is consumed by lighting.[1] The U.S. Department of Energy estimates that this could be reduced by one-third by 2025 through widespread implementation of light emitting diode (LED)-based solid-state lighting.[2] LED light bulbs have higher lumens per watt values than incandescent or compact fluorescent bulbs, as well as a 25,000 hour life span. In addition, LED visible light communication is becoming an increasingly attractive option for simultaneous illumination and high speed data transfer that is immune to electromagnetic interference.[3]

The current standard devices for these applications are based on white LEDs composed of yellow-emitting cerium doped yttrium aluminum garnet (YAG:Ce) coated on an InGaN blue LED. This was first patented in 1999 and has become a commercial success due to its simplicity and requirement of only one LED chip per device.[4,5] Their high performance compared to other light sources is due in part to >90% quantum yield for the phosphor, which is obtained by suspending monodisperse spherical phosphor particles in silicone resin to reduce scattering.[6] However, there are several weaknesses in these devices. As seen in figure 1, the emission spectrum of the device is strong in the blue to yellow region, but weak at the red end of the spectrum, resulting in an unpleasant blue tint.[7] A common solution to this is to add an additional red-emitting rare earth doped phosphor to the device. The phosphor also has a long emission lifetime of 200 ns, limiting the intrinsic frequency modulation for visible light data transfer to under 0.8 MHz.[8] This is overcome with pricey signal detection and amplification techniques.[8] There is also the issue of chromatic aberration as a result of differences in degradation rate between the LED and phosphor. Single phase broad spectrum white emitters excited by ultraviolet LEDs are seeing increasing interest to avoid this problem. Within these materials there is additionally a push to find alternatives to rare earth activators to avoid issues with supply risk and volatile prices for rare earth oxides.

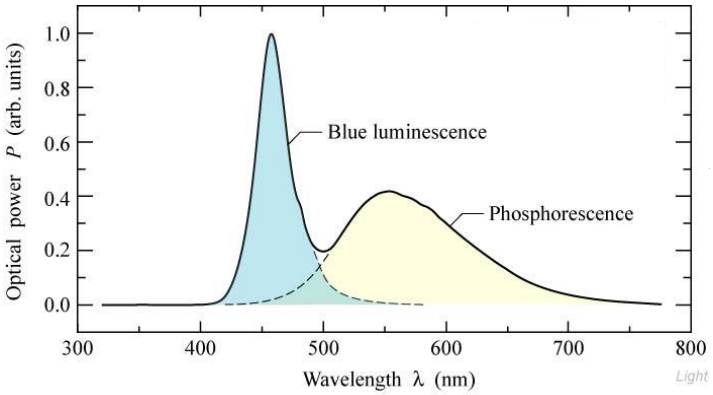

Figure 1. Emission spectrum of YAG:Ce-based white LED[7]

An area that shows promise for alternative high performance white LED materials are systems based on luminescent metal-organic frameworks (MOFs). Interest in MOFs has exploded over the past several decades due to the variety of possible structures, ease of synthesis, extremely high surface areas, and ability to adsorb a large quantity of guest molecules.[9] Additionally, BASF recently demonstrated the ability for MOFs to be manufactured on a one-ton scale, suggesting eventual commercial viability.[10] There are numerous ways to introduce luminescence into a MOF, including organic linker based luminescence (either through ligand localized emission or metal-ligand charge transfers), metal centered emission, or through luminescent adsorbates.[11] Many early reports of luminescent MOFs involve rare-earth doping,[12] but innovative alternatives have emerged.

Most recent work makes use of the fact that confining a fluorescent organic molecule's motion through incorporation into a rigid framework increases the quantum yield by decreasing the potential for non-radiative decay.[13] Qian and coworkers applied this strategy to an anionic indium based MOF with intrinsic blue fluorescence from 4,4',4''-benzene-1,3,5-triyl-tri-benzate linkers.[14] Red-emitting 4-(*p*-dimethylaminostyryl)-1-methylpyridinium (DSM) and green-emitting acriflavine dyes were loaded into the MOF by exchanging dimethylammonium cations in the negatively charged framework. Powder XRD data confirmed the crystal structure was undisturbed by the cation exchange process. They additionally showed the quantum yield of DSM in 0.02 wt% DSM doped ZJU-28 is 60.72%, compared to 6.93% in DMF solution, strengthening claims of molecular confinement reducing the amount of aggregation induced quenching. A pure white-emitting MOF was then produced by introducing 0.02 wt% DSM and 0.06 wt% acriflavine into ZJU-28. Excitation at 365 nm produced broad spectrum emission superior to that of YAG:Ce based LEDs, with a color rendering index of 91% and an external quantum yield of 17.4%. The quantum yield is a significant decrease from that of a single dye within the MOF, a fact which is not addressed by the authors.

Another effective strategy has emerged that combines a blue emitting MOF with red-, green-, and blue-emitting dyes. Adding a blue dye introduces the ability to tune the emission of all three primary colors, instead of being limited to tuning red and green dyes to match the intensity of the blue emission of the MOF framework. In this study, novel MOF HSB-W1 was synthesized by diffusion of a terephthalate solution into a mixture of hydrogenated Schiff base 1,2-Bis(4'-pyridylmethylamino)ethane (L) and $Zn(NO_3)$ over the course of one month.[15] The combination of L and Zn(II) formed planar layers with rhombic windows, with terephthalate coordinating to the Zn(II) to create 3D pillars. Linear dyes DCM (red), C6 (green) and CBS-127 (blue) were loaded into the narrow channels. By fine tuning the amounts of dye, broad spectrum white light with a color rendering index of 87% and a quantum yield of 24% was obtained. This is the most efficient white-emitting MOF to date.

While broad spectrum white light emission has been attained, little work has been done to assess the viability of MOF-based white LEDs for visible light communication. Recent work by Lin and coworkers has investigated a new MOF, Al-DBA, for this application.[8] This blue-emitting MOF was synthesized by solvothermal reaction of fluorescent 9,10-bis(*p*-benzoic acid)anthracene (H_2DBA), acetic acid, and $AlCl_3$. Rectangular nanocrystals of 100-200 nm were recovered, then loaded with Rhodamine-B dye (RhB) by soaking in an ethanolic solution. Molecular dynamics simulations were used to determine that the dye most stably conforms in defect sites with a missing H_2DBA linker. The most optimal white light was achieved for a 0.019 wt% dye loaded MOF, with an emission quantum yield of 12%. A prototype LED lamp was then assembled by coating a quartz plate with the RhB@Al-DBA, then placing over a LED chip emitting at 395 nm. Frequency response of this device in visible light communication was measured by driving the LED chip with an arbitrary waveform generator, and collecting the white light with an avalanche photodiode before transforming back to an electric signal. The LED was measured as having an intrinsic modulation frequency of 3.6 MHz, 6 times greater than a commercial white LED. The maximum bit rate of transmission was then measured at 3.6 megabytes per second for the MOF based device, compared to 1.2 megabytes per second for the commercial LED.

Significant progress has been made towards improving the efficiency of white-emitting MOFs through the introduction of fluorescent linkers and dyes. These potentially provide a platform for single-phase white LEDs compatible with commercial ultraviolet LEDs. However, the quantum yields of these materials still fall far below those of commercial YAG:Ce devices.

Since the high quantum yield of commercial phosphors for LEDs is based on distributing monodisperse particles in a silicone resin, the effects of particle size and matrix dispersion should be tested for dye-loaded MOFs. There also must be more data on how these MOF based devices degrade over time. As of now there is no information on how the quality of the luminescence changes over the 25,000 hour lifetime of an LED chip. Additionally, there should be increased rationality in MOF design and fluorophore selection beyond what has been seen in the literature to this point. Addressing these issues could inform future design and modification for increased practicality of these materials.

References

1. Humphreys, C. J. *MRS Bull.* **2008**, *33* (4), 459–470.
2. Bardsley, N.; Bland, S.; Pattison, L.; Pattison, M.; Stober, K.; Walsh, F.; Yamada, M. *Solid-State Lighting Research and Development: Multi-Year Program Plan*; U.S. Department of Energy, 2014.
3. Khan, L. U. *Digit. Commun. Netw.* **2017**, *3* (2), 78–88.
4. Shimizu, Y.; Sakano, K.; Noguchi, Y.; Moriguchi, T. US Patent 5,998,925 A, 1999.
5. Cho, J.; Park, J. H.; Kim, J. K.; Schubert, E. F. *Laser Photonics Rev.* **2017**, *11* (2), 1600147.
6. Gorrotxategi, P.; Consonni, M.; Gasse, A. *J. Solid State Light.* **2015**, *2* (1).
7. Emission spectrum of a phosphor-based white LED https://www.ecse.rpi.edu/~schubert/Light-Emitting-Diodes-dot-org/chap21/chap21.htm (accessed Nov 1, 2017).
8. Wang, Z.; Wang, Z.; Lin, B.; Hu, X.; Wei, Y.; Zhang, C.; An, B.; Wang, C.; Lin, W. *ACS Appl. Mater. Interfaces* **2017**, *9* (40), 35253–35259.
9. D. Allendorf, M.; Stavila, V. *CrystEngComm* **2015**, *17* (2), 229–246.
10. Gaab, M.; Trukhan, N.; Maurer, S.; Gummaraju, R.; Müller, U. *Microporous Mesoporous Mater.* **2012**, *157*, 131–136.
11. D. Allendorf, M.; A. Bauer, C.; K. Bhakta, R.; T. Houk, R. J. *Chem. Soc. Rev.* **2009**, *38* (5), 1330–1352.
12. E. Barry, D.; F. Caffrey, D.; Gunnlaugsson, T. *Chem. Soc. Rev.* **2016**, *45* (11), 3244–3274.
13. Wei, Z.; Gu, Z.-Y.; Arvapally, R. K.; Chen, Y.-P.; McDougald, R. N.; Ivy, J. F.; Yakovenko, A. A.; Feng, D.; Omary, M. A.; Zhou, H.-C. *J. Am. Chem. Soc.* **2014**, *136* (23), 8269–8276.
14. Cui, Y.; Song, T.; Yu, J.; Yang, Y.; Wang, Z.; Qian, G. *Adv. Funct. Mater.* **2015**, *25* (30), 4796–4802.
15. Wen, Y.; Sheng, T.; Zhu, X.; Zhuo, C.; Su, S.; Li, H.; Hu, S.; Zhu, Q.-L.; Wu, X. Adv. Mater. **2017**, 29 (37), 1700778.