

MOF PHOTOLUMINESCENCE VIA METAL-LIGAND TUNABILITY

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Introduction

Solid-state lighting (SSL) is anticipated to be the next generation of efficient lighting to replace traditional incandescent or fluorescent lamps.¹ SSL devices are primarily based on inorganic light emitting diodes (LEDs), with ongoing development in organic LEDs (OLEDs).² A challenge is to improve the color quality of such devices. Currently, commercial LEDs produce white light by exciting yellow-emitting YAG:Ce phosphors with blue InGaN LEDs, resulting in bluish white light having a poor color rendering index that is not suitable for general illumination. Higher quality devices add a red-emitting inorganic phosphor, such as Eu²⁺-doped nitridosilicates,³ to produce light that can realistically render orange and red objects; yet, they have a broad emission that extends to the near IR, producing unseen illumination. Increasing the lumens of red light per watt of light emitted (high luminous efficacy of radiation) requires strong emission at ~615 nm, which can be achieved with Eu³⁺-doped phosphors. Eu³⁺-doped inorganic phosphors have quantum yields (QYs) as high as 88%,⁴ extremely low thermal quenching, and tremendous thermal and chemical stability. Unfortunately, they have drawbacks including high annealing temperatures (900°C or higher), and low blue absorbance (which limits their use in SSL devices that are based on blue InGaN LED excitation).

Metal-organic frameworks (MOFs) are crystalline, periodic systems that are a unique alternative to inorganic phosphors.⁵ MOFs have many advantages over phosphors as they: (i) are inherently more tunable due to their inorganic-organic hybrid structure; (ii) have a homogeneous composition and limited defect sites; (iii) allow the controlled spatial distribution of metal ions into the framework, eliminating agglomeration; (iv) are produced at much lower temperatures; and (v) can be processed as films.⁶ High QY, thermal stability, and low thermal quenching are among the criteria that MOFs must satisfy for SSL applications.

We demonstrate for the first time that Eu³⁺-based metal-organic frameworks (MOFs) can produce the characteristic narrowband red emission of Eu³⁺, with QYs as high as 50% under UV excitation at room temperature, which is among the highest QYs reported for MOFs.⁷ Thermal quenching in this material is reversible, maintaining a high QY of 48% at 150°C. This is the highest QY measured at high temperatures (150°C) reported for this class of materials. These findings reveal the potential of Eu-based MOFs to be developed as energy-efficient emitters for inorganic LEDs and possibly OLEDs for SSL that can operate at elevated temperatures.

Experimental

Structure-property relationships were determined by a combined effort of solvo-thermal synthesis of crystalline MOF phases, powder X-ray diffraction, thermal analyses, photoluminescence measurements, quantum yield and thermal quenching measurements.

Results and Discussion

The compounds in this family are comprised of In, In-Eu, or Eu metal centers and organic ligand chromophores. Systematic variations in the metal and organic components resulted in materials with emissions ranging from white to red. The single component white-light emitter material is made of In, 4,4',4''-s-triazine-2,4,6-triyl-tribenzoic acid (TTB) and oxalic acid. Red-emitting MOFs

comprised of Eu metal centers and TTB ligands have a room temperature quantum yield (QY) of 50%, and a 48% QY at 150°C due to reversible thermal quenching. This is the highest quantum yield measured at elevated temperatures reported for this class of materials. The materials are thermally stable, retaining their high QY after heating at 150°C for several hours.

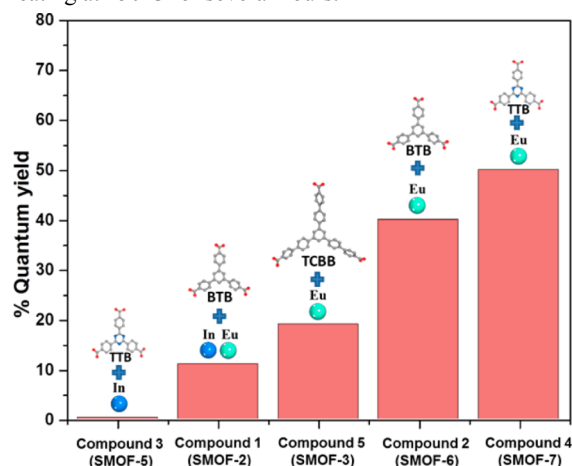


Figure 1. Percent quantum yield for MOF phases with tunable PL.

Conclusions

The reported materials are structurally related, tuned for white and red emissions by choice of metal and/or ligand, and importantly by the charge transfer between the two components. Eu-based compounds **2** and **4** have the highest quantum yields (40 and 50%, respectively) after thermal treating at 150°C. These findings represent the highest quantum yields reported for MOFs at high temperatures. It was found that the coordination environment of the metal center plays a significant role in the emission quenching, in conjunction with the electronic configuration of the organic linker.

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References

- (1) DOE; Solid-State Lighting http://www1.eere.energy.gov/buildings/ssl/sslbasics_ledbasics.html
- (2) DOE; Solid-State Lighting http://www1.eere.energy.gov/buildings/ssl/sslbasics_oledbasics.html
- (3) (a) Mueller-Mach, R.; Mueller, G.; Krames, M.R.; Hoppe, H.A.; Stadler, F.; Schnick, W.; Jüstel, T.; Schmidt, P. *Phys. Stat. Sol. A* **2005**, *202*, 1727-1732; (b) Xie, R.-J.; Hirotsaki, N.; Suehiro, T.; Xu, F.-F.; Mitomo, M. *Chem. Mater.* **2006**, *18*, 5578-5583.
- (4) Nyman, M.; Rodriguez, M.A.; Rohwer, L.E.S.; Martin, J.E.; Waller, M.; Osterloh, F. *Chem. Mater.* **2009**, *21*, 4731-4737.
- (5) (a) Sava, D. F.; Rohwer, L. E. S.; Rodriguez, M. A.; Nenoff, T. M. *J. Am. Chem. Soc.* **2012**, *134*, 3983-3986. (b) Sava Gallis, D.F.; Rohwer, E.S.; Rodriguez, M.A.; Nenoff, T.M. *Chem. Mater.* **2014**, *26*(9), 2943-2951.
- (6) Bétard A.; Fischer, R. A. *Chem. Rev.* **2012**, *112*, 1055-1083.
- (7) (a) Zurawski, A.; Mai, M.; Baumann, D.; Feldmann, C.; Müller-Buschbaum, K. *Chem. Commun.* **2011**, *47*, 496-498. (b) Harbuzaru, B. V.; Corma, A.; Rey, F.; Jord, J. L.; Ananias, D.; Carlos, L. D.; Rocha, J. *Angew. Chem., Int. Ed.* **2009**, *48*, 6476-6479. (c) Miyata, K.; Konno, Y.; Nakanishi, T.; Kobayashi, A.; Kato, M.; Fushimi, K.; Hasegawa, Y. *Angew. Chem., Int. Ed.* **2013**, *52*, 6413-6416.