

Doping Light Emitters into Metal–Organic Frameworks**

Paolo Falcaro and Shuhei Furukawa*

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Cubic Space Division, the lithograph by Dutch painter M. C. Escher (1898–1972), illustrates the concept of a cubic framework partitioning three-dimensional space into smaller compartments. This concept portends the recent development of metal–organic frameworks (MOFs). Indeed, the chemical realization of the cubic framework at the nanoscale, $[\text{Zn}_4\text{O}(\text{bdc})_3]_n$, known as MOF-5,^[1] boosted the expansion of the research field owing to its potential applications using the nanosized compartments or pores for gas storage, gas separation, catalysis, and sensing.^[2]

Besides the intrinsic porous properties of MOFs, research in the field is currently expanding towards new technological challenges in which the functional electronic properties of the frameworks are pivotal. Solid-state luminescence is particularly targeted owing to the advantages of the designability that allows the fine-tuning of the luminescent properties. In particular, MOFs offer the advantages of the rational choice of light-emissive building blocks for both the metal clusters as nodes and the functional organic ligands as spokes; furthermore, the spatial regularity of these building blocks prevents the preferential aggregation that causes self-quenching.^[3] In pure inorganic luminescent materials, doping other elements into the main material body is a classic approach to tune the electronic properties and to induce or improve the emissive performance. However, this approach cannot be simply translated to MOFs, because the framework construction totally relies on the self-assembly process from a solution; any additional component often perturbs the delicate coordination equilibrium preventing the porous crystal formation or resulting in a different framework with respect to the original or expected structure.

Two remarkable examples of successful doping with another metal element into the inorganic nodes are presented

herein. This approach produces novel luminescent properties while maintaining the original framework topologies. In both cases, the lanthanide metal ion, europium(III), was used as a dopant owing to its intrinsic red emission.

The first report, by Chen et al., suggested a new application of MOFs as a luminescent thermometer using temperature-dependent luminescence.^[4] The advantages of using luminescence over other conventional thermometers are fast response, high sensitivity, noninvasive operation, and inertness to strong electric and magnetic fields. To date, most luminescence-based thermometers rely on a single emission. The authors overcame this issue by doping the framework scaffold with another luminophore element. First, the authors synthesized novel MOFs based on Tb^{3+} or Eu^{3+} and dmbdc (2,5-dimethoxy-1,4-benzenedicarboxylate), leading to isostructural frameworks, $[\text{Tb}_2(\text{dmbdc})_3]_n$ or $[\text{Eu}_2(\text{dmbdc})_3]_n$. The organic ligand of dmbdc efficiently worked as a sensitizer, because upon excitation at 381 nm, attributed to the π – π^* electron transition of the ligand, the frameworks exhibited the luminescence from lanthanide metal centers: green emission based on the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4$ and 3) transitions of Tb^{3+} , and red emission based on the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 1, 2, 3$ and 4) transition of Eu^{3+} . By increasing the temperature from 10 K to 300 K, the emission intensities gradually decreased owing to the thermal activation of nonradiative decay.

The doping of the Tb framework with Eu^{3+} ions was successfully achieved by simply adding an Eu^{3+} metal source into the reaction solution of the Tb framework (one-pot approach), leading to the $[(\text{Eu}_{0.0069}\text{Tb}_{0.9931})_2(\text{dmbdc})_3]_n$ formation. Remarkably, the mixed Tb/Eu metal framework demonstrated an interesting temperature-dependent luminescence; although the main emission bands of 613 (Eu^{3+}) and 545 (Tb^{3+}) nm were comparable at 10 K, the emission of Eu^{3+} almost dominates the whole spectrum at 300 K (Figure 1). This is most likely attributed to the temperature-dependent energy-transfer probability. Thus, at high-temperatures, an efficient energy transfer from Tb^{3+} to Eu^{3+} was achieved by the phonon-assisted Förster transfer mechanism, as evidenced by luminescent lifetime measurements. Such a two-color Tb/Eu MOF featuring temperature-dependent luminescence enables itself to be an excellent candidate for self-referencing luminescent thermometers as no further calibration of luminescence intensity is required.

[*] Prof. Dr. S. Furukawa
Institute for Integrated Cell-Material Sciences (WPI-iCeMS)
Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501 (Japan)
E-mail: shuhei.furukawa@icems.kyoto-u.ac.jp

Dr. P. Falcaro
Division of Materials Science and Engineering, CSIRO
Private Bag 33, Clayton South MDC, Victoria 3169 (Australia)

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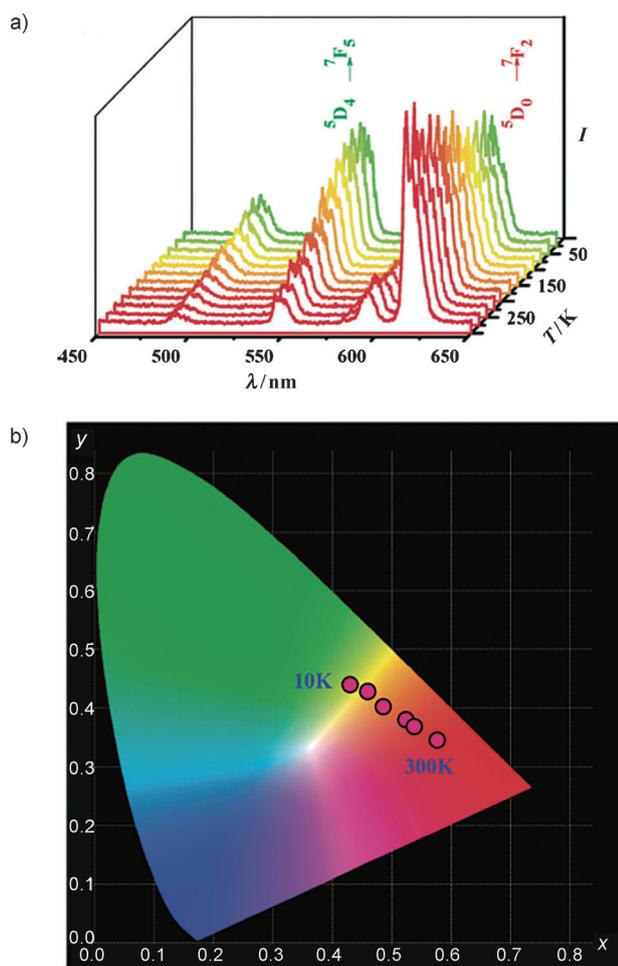


Figure 1. a) Temperature-dependent luminescent spectra of the mixed Tb/Eu framework between 10 to 300 K and b) the corresponding CIE chromaticity diagram showing the change of luminescent color by increasing the temperature. (Reprinted from Ref. [4]. Copyright 2012 American Chemical Society.)

The second example of a doped Eu^{3+} framework was reported by Nenoff et al.^[5] The authors aimed to fabricate a solid-state white-light emitter taking advantage of the designability of MOFs. First, the authors synthesized a novel MOF based on indium ions, btb, and oa (btb = 1,3,5-tris(4-carboxyphenyl)benzene, oa = oxalic acid), leading to the indium framework formation (namely $[\text{In}_3(\text{btb})_2(\text{oa})_3]_n$). Interestingly, the material already emitted a white light owing to the broad-band emission over the entire visible light region. The explanation sits on a ligand–metal charge transfer (LMCT) transition mechanism. Then, the authors obtained an extra red emission narrow band by introducing the Eu^{3+} dopant ion into the indium framework. The aim of this approach was to further improve the color properties such as color rendering index (CRI), correlated color temperature (CCT), and chromaticity to approach the requirements for solid-state lighting (SSL). Similar to the first report, the simple mixing of Eu^{3+} metal source into the reaction solution of the indium framework successfully led to the formation of a mixed-metal framework. After the optimization of the Eu^{3+}

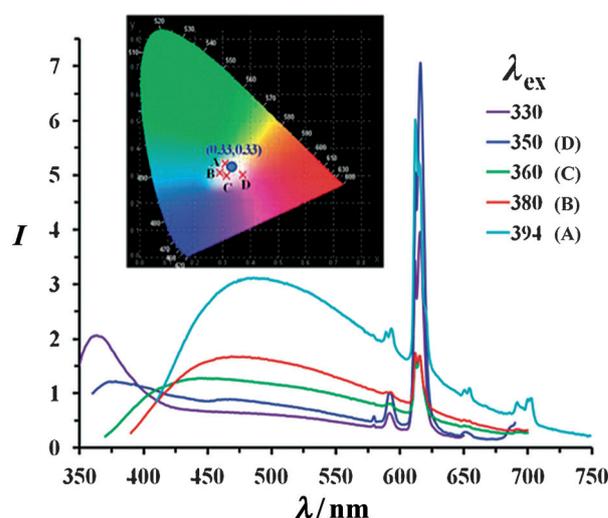


Figure 2. Emission spectra of the mixed In/Eu framework when excited between 330 and 380 nm; inset CIE chromaticity diagram highlighting corresponding chromaticity coordinates (A–D) approaching targeted values of (0.33, 0.33). (Reprinted from Ref. [5]. Copyright 2012 American Chemical Society.)

doping quantities, the best performance was detected by $[(\text{Eu}_{0.09}\text{In}_{0.91})_3(\text{btb})_2(\text{oa})_3]_n$ with 9% Eu^{3+} doping, which has white-light chromaticity coordinates very close to the target (0.33, 0.33) established by the Commission Internationale de l'Éclairage (CIE), as shown in Figure 2.

These studies clearly demonstrate that doping the framework with other elements allows the preparation of a new generation of functional MOFs. In particular, a fine-tuning of the color property emission can be easily achieved. It is worth noting that europium-doped MOFs have been previously investigated by Lin et al.^[6] for biomedical application. Such MOFs, with crystal size in the nanoscale (NMOFs), are promising materials if used as contrast agents, controlled releasing medium, and luminescent sensors.

Although a better understanding of the potential for the fabrication of novel emitting MOFs is needed, device fabrication based on novel luminescent properties appears to be a very promising research stream. Furthermore, the ability to control the luminescent properties in combination with the intrinsic framework porous properties would offer an efficient strategy for the fabrication of multifunctional materials.

In this context, a previous study by Kitagawa et al.^[7] demonstrated how luminescent properties can be combined with the adaptive dynamic response of two chemically non-interconnected frameworks; the presence of aromatic compounds induced a particular displacement resulting in a strong luminescent emission with a color dependent on the chemical functionality of the aromatic compound. While the displacement has been efficiently used for molecular decoding purposes, white-light emission can be possibly obtained by simply tuning the combination and concentration of guest molecules. A different strategy for the preparation of emitting materials based on MOFs has been presented by Buso et al.,^[8] who embedded a class of highly efficient emitting nanoparticles (quantum dots) within MOF-5 porous crystals. The

luminescent QD@MOF-5 composites were shown to maintain the emitting properties of the luminescent nanoparticles, and this framework composite has shown interesting capability as a molecular sensor that can discriminate molecules on the basis of their size. The last two examples show how the luminescent properties have been actively combined with the porous framework properties (that is, displacement and molecular sieve).

In summary, different pioneering methods for the synthesis and application of luminescent MOFs are emerging. The potential of these novel emitting frameworks is promising as efficient light emitters, transducers, and sensors. New devices for microelectronics (for example, LEDs and electrochromics), energy production (up- and down- conversions), and sensing (thermochromics and chemosensors) could possibly take advantage of emitting MOFs. However, device fabrication requires the ability to control the MOF position and further progress in this field is also needed.^[9]

Interestingly, the recent implementation of MOFs with novel luminescent properties has the potential to be used for other unconventional applications, such as biology and medical screening. In fact, the precise measurement of the local temperature based on a change of luminescent spectra can provide important information on cell functions,^[10] the recognition of specific biomolecules by measuring an emission shift could be used for the early detection of particular diseases,^[11] and the preparation of novel luminescent labeling probes could overcome limitations related to the dyes^[12] for biolabeling (for example, microarray data strongly rely on dye properties^[13]).

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