Luminescence tuning behavior by adjusting the Eu^{3+} doping concentrations into Zn-MOF prepared by hydrothermal method assisted by microwave

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Metal-Organic Frameworks (MOFs) are high crystalline supramolecular solids with strong bonding providing robustness, geometrically well-defined structure and linking units that are available for synthetic modification.[1] These materials exhibits a wide range of emissive phenomena, as linker, metal or adsorbate-based luminescence and *antennae* effect.[2] This work demonstrate the synthesis, characterization and photoluminescence properties of the $[Zn_3(BTC)_2 \cdot 12H_2O]$ (BTC: 1,3,5-benzenetricarboxylate) MOF, doped in situ with 0,1; 0,5; 1,0; 1,5; 2,0; 2,5; 3,0; 4,0 and 5,0 mol% of Eu^{3+} ions. The materials were synthesized by the hydrothermal method assisted by microwave at 160 °C, during 25 minutes by aqueous solution of the $[Zn(Ac)_2 \cdot 2H_2O]$, $[EuCl_3 \cdot 6H_2O]$ and H_3BTC precursors. The doped-MOFs were characterized by elemental analysis (CHN), X-ray powder diffraction (XRPD), infrared absorption spectroscopy (FTIR), thermal analysis (TGA), inductively coupled plasma optical emission spectrometry (ICP-OES) and scanning electron microscopy (SEM). The synthesized materials present isomorphic crystalline character, same coordination modes, decomposition profile and morphology, with increasing doping concentration. The photoluminescent properties of the materials were investigated using the excitation and emission spectra of the MOFs, as well the determination of the lifetime of the emitting level $^5D_0$ (τ), quantum efficiency (η), experimental intensities parameters ($\Omega\lambda$), spontaneous emission coefficients (A_{ij}) and monochromatic character by the color coordinates (CIE). The emission spectra of the Eu^{3+}-doped MOFs (Fig. 1 - left) exhibit the emission band of the ligand in ~ 500 nm, even in higher doping mol%, which permits a luminescent tuning[3] from blue to red with the increase of the Eu^{3+} ions amount, as shown in the CIE chromaticity diagram (Fig. 1 - right). The lifetime values of the $^5D_0$ emitter level of Eu^{3+} ions (τ) shown a biexponential behavior, indicating more than one symmetry site around of the dopant. These MOFs present quantum efficiency values (η) in the range of 40 to 48%, making these materials promising for luminescent applications.

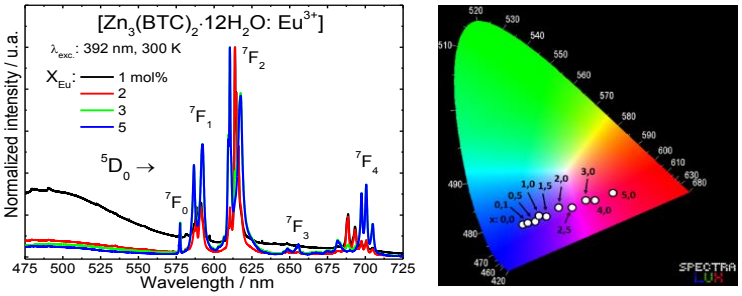

Fig. 1. Emission spectra (left) and CIE chromaticity diagram (right) of $[Zn_3(BTC)_2 \cdot 12H_2O: Eu^{3+}$ (x mol%)].

References

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