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INVESTIGATION ON THE LUMINESCENCE PROPERTIES OF BARE AND RHODAMINE B FUNCTIONALIZED Zr-MOF-808

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Metal organic frameworks (MOFs) are materials well known for their high surface and catalytic properties as well as because they are relatively easy to synthesize and, in some cases, extremely flexible.^[1] Recently, there has been also a growing interest in the optical properties of these materials, particularly in luminescence, which has potential applications in various fields, such as sensors, LEDs, scintillators, and bioimaging agents. One very promising route to obtain luminescent MOFs is to load them with organic luminescent dyes. This approach is both highly versatile and straightforward, as a vast array of dyes with diverse optical properties are readily available. As a result, it is feasible to cover the entire visible spectrum and even the near-infrared region in terms of emission. So, it is possible to tailor the optical properties of a material by properly combining MOFs and dyes.^[2] Nevertheless, for this approach to be viable, it is essential to utilize MOFs that can withstand post-synthetic loading and possess adequately sized cages to effectively accommodate the typically large dye molecules. From this perspective zirconium MOF-808 is a valid candidate for loading organic dyes because it is well known to be chemical and thermally stable. In addition, it possesses high surface area (~2000 m²/g) and cages with diameter of 18 Å, that is comparable to the size of many organic dyes.^[3]

Here we present a pioneering study on the luminescent properties of bare zirconium-based MOF-808 and on the same MOF loaded with Rhodamine B organic luminescent dye (MOF-808@RhB). In this work MOF-808 was synthesized by room temperature approach and later loaded with Rhodamine B by a post-synthetic soaking. The structural and morphological characterizations were performed by XRD, FTIR-ATR, TGA, SEM, and by estimation of the specific surface with the BET method, while luminescence properties were studied by time resolved photoluminescence (TRPL), both for dry powders and for powders dissolved in distilled water. Our results show that upon laser excitation at a wavelength of 280 nm, bare MOF-808 exhibits a wide luminescent band peaked at 425 nm which decays in the nanosecond temporal range. Regarding MOF-808@RhB, we were able to observe both the luminescence bands of the bare MOF-808 and of the embedded Rhodamine B, with the latter redshifted compared to free Rhodamine in water. Surprisingly, we have found that the two bands observed for MOF-808@RhB share the same decay lifetime which, interestingly, is different from the one pertaining to MOF-808 and Rhodamine B taken alone.

The reported study has permitted us to obtain for the first time a comprehensive description of the luminescence properties of bare MOF-808 and of MOF-808@RhB interaction. Furthermore, our data points out that the luminescence properties of Rhodamine B are significantly modified by the interaction between the luminescent molecule and the hosting matrix. These results have strong impact on fundamental research focused on luminescent MOFs, shedding new lights on the effects of the host-guest interaction, and making possible prediction for analogue systems.

References

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