Observation of two distinct luminescence bands for open- and closed-pore structures in MIL-53(Al)

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Metal-organic frameworks (MOF) are very promising materials, as they exhibit many exciting properties inspiring many outstanding applications. One very intriguing property of a class of MOF consists in their ability to *breath*, i.e. to undergo a crystalline-to-crystalline structural change, usually induced by modifying the temperature, applying external pressure or by adsorbing of specific gases [1]. Such structural changes in turn affect many properties of the material, further increasing the potential applications of these materials. The advantages of the breathing process in sensing applications, for example, are obvious. One of the most interesting breathing MOF is MIL-53(Al) [2]. It has strong potentialities in many fields, as adsorption, separation and storage of gases, catalysis, drug delivery, sensing [3,4]. Since its first report, MIL-53(Al) has gained the role of prototype system, giving the opportunity to unveil many properties pertaining to such outstanding class of highly reactive (breathing) MOF materials.

Here we report on the result of our recent research on MIL-53 (Al) proving for the first time that two well distinguishable luminescence bands pertain to the different structures induced in MIL-53(Al) by the breathing process, the open- and closed-pore structures. We have fully characterized such bands by state-of-the-art time-resolved luminescence spectroscopy clearly indicating that both spectroscopic properties and time response to the exciting laser pulse of the luminescence bands are strongly correlated with the structure of the material. In particular, we have proved that the luminescence band associated to the open-pore structure of MIL-53(Al) is characterized by an asymmetric band peaked at 420 nm with lifetime about 3 ns, whereas that pertaining to the closed-pore structure is symmetric and peaked at 340 nm with lifetime about 2 ns. In Figure 1 the emission spectrum of a sample in powder form in which both open- and closed-pore structures coexist is reported. As shown, the two related emission bands are well distinguishable. To obtain a comprehensive characterization of the material under study, XRD, TGA, Raman, AFM measurements were also performed, as well as surface estimation by BET method.

Our results have strong impact in the field of fundamental research focused on the fascinating world of breathing MOF, as they give an outstanding example of the indirect effects induced by such structural process on other relevant properties of the material, as the optical one. Furthermore, since the optical properties of MOFs and the breathing process are key features in many potential applications, our results give also new relevant insights also in the applicative field of MOFs.

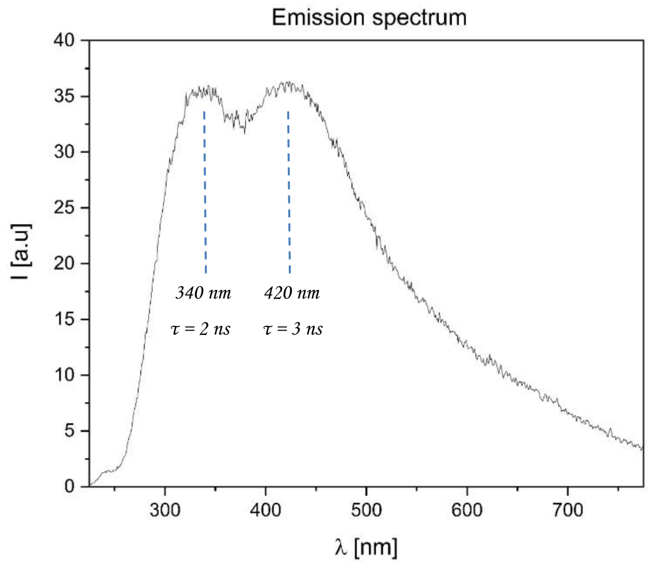

Figure 1. Emission spectrum excited at 305 nm of a sample of MIL-53(Al) in powder form in which both open- and closed-pore structures coexist. The spectrum has been acquired just after the decay of the exciting laser pulse.

References

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