

# Supporting Information

## Spectral and Dynamical Properties of a Zr- Based MOF

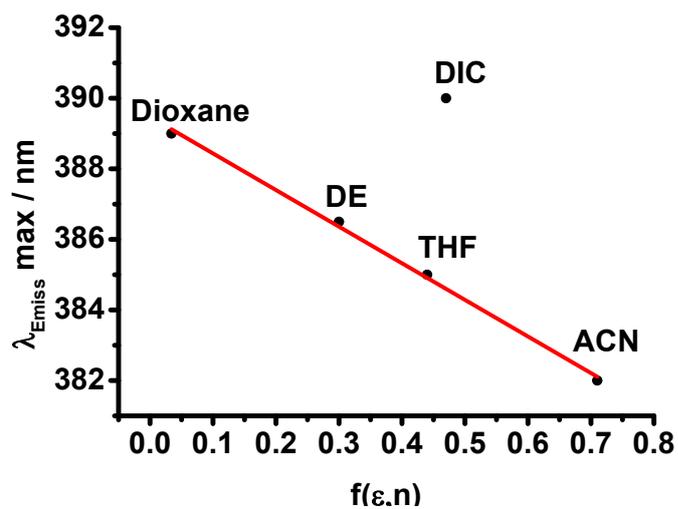
Mario Gutiérrez,<sup>1</sup> Félix Sánchez<sup>2</sup> and Abderrazzak Douhal<sup>1\*</sup>

<sup>1</sup>Departamento de Química Física, Facultad de Ciencias Ambientales y Bioquímica, and INAMOL, Universidad de Castilla-La Mancha, Avenida Carlos III, S.N., 45071 Toledo, Spain.

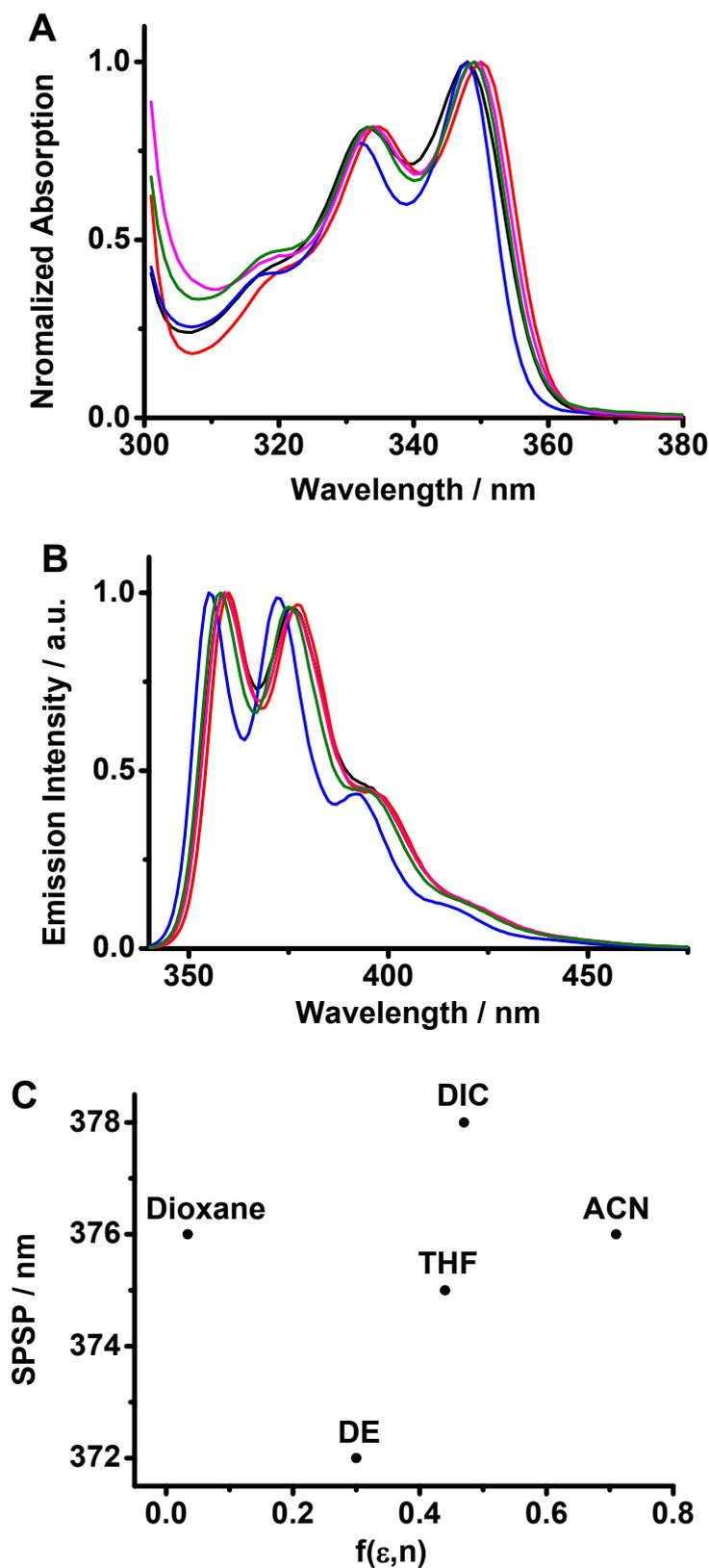
<sup>2</sup> Instituto de Química Orgánica, CSIC, Juan de la Cierva, 3, 28006 Madrid, Spain.

\*Corresponding author at Universidad de Castilla-La Mancha.

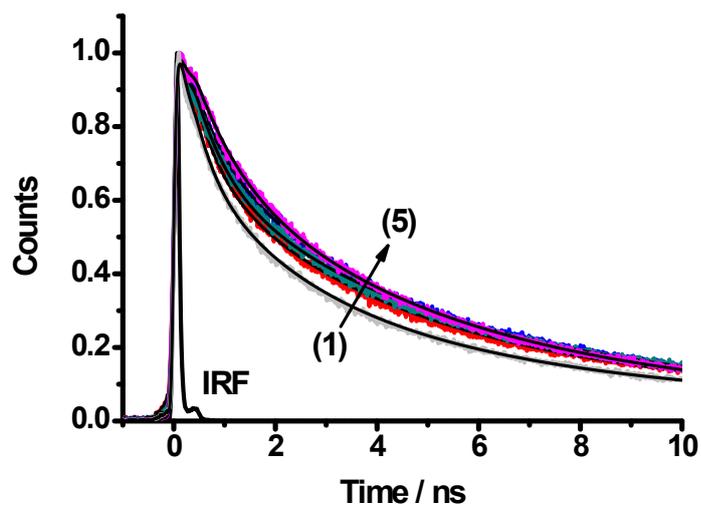
Tel.: +34 925 265 717; E-mail address: [abderrazzak.douhal@uclm.es](mailto:abderrazzak.douhal@uclm.es)



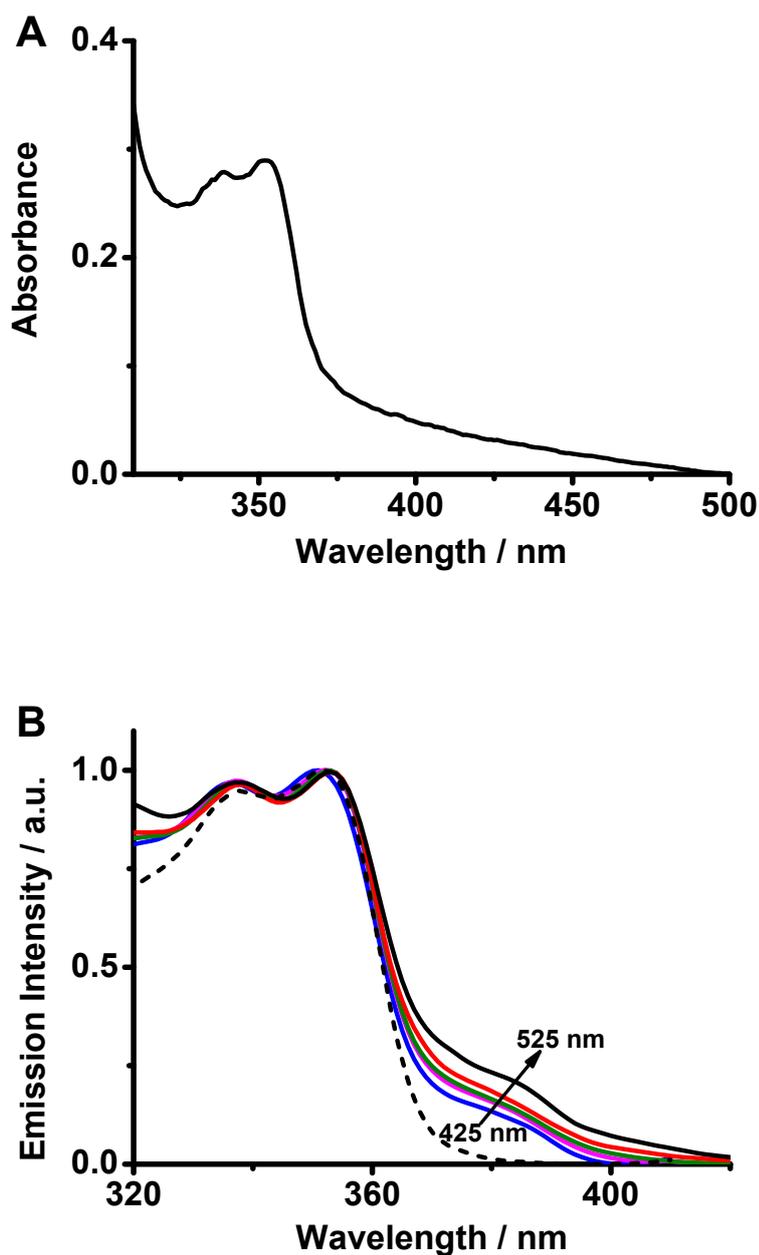
**Figure S1.** Change of the wavelength of the emission intensity maximum of Zr-NDC with  $f(\epsilon, n)$ , where  $\epsilon$  and  $n$  are the dielectric constant and the refractive index, respectively.



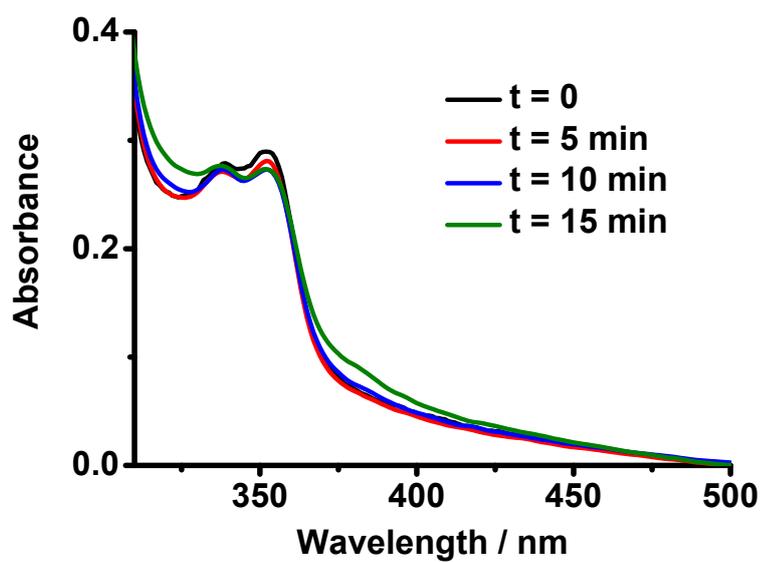
**Figure S2.** Normalized UV-visible (A) absorption and (B) emission spectra of 2,6-NDC in DE (blue line), ACN (black line), THF (green line), DO (pink line) and DIC (red line) solutions. (C) Change of the emission Second Peak Spectral Position (SPSP) of 2,6-NDC with the  $f(\epsilon, n)$ , where  $\epsilon$  and  $n$  are the dielectric constant and the refraction index, respectively.



**Figure S3.** Emission decays of Zr-NDC in (1) DE (grey line), (2) ACN (red line), (3) THF (green line), (4) DO (blue line) and (5) DIC (pink line) suspensions. The observation wavelength was 405 nm and the samples were excited at 371 nm. The solid lines are from the best-fit using a multiexponential function and the IRF is the instrumental response function.



**Figure S4.** (A) UV-visible absorption spectrum (without normalize) of a high concentrated Zr-NDC THF suspension (B) Normalized to the maximum intensity UV-visible excitation spectra of Zr-NDC in a diluted (black dashed line) and concentrated (solid lines) Zr-NDC THF suspensions. The excitation spectra of the diluted sample are independently of the observation wavelength. The observation wavelengths of the concentrated sample range from 425 to 525 nm, to see the aggregation effect.



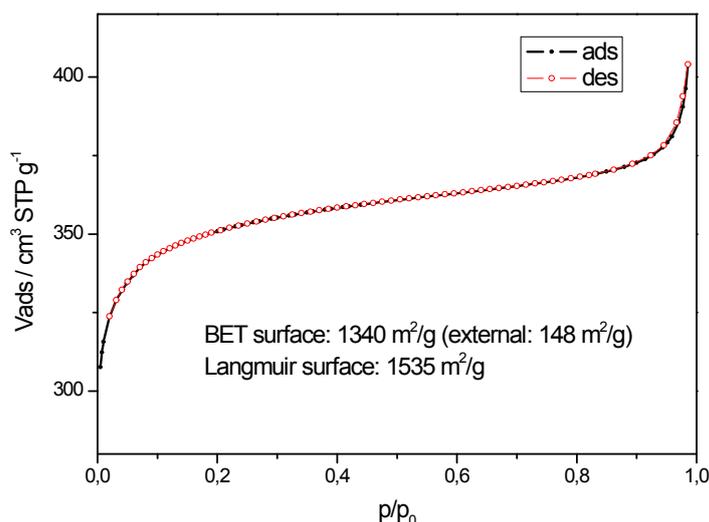
**Figure S5.** UV-visible absorption spectra of a concentrated Zr-NDC THF suspension upon different irradiation times with a 350 nm fs-pulse laser beam. The irradiation times are indicated as inset.

### Synthesis of Zr-NDC MOF

The synthesis of Zr-based metal organic framework was performed in a 250 mL round bottom flask using a procedure similar to that previously described for UiO66.<sup>1</sup> ZrCl<sub>4</sub> (0.4 g, 1.7 mmol) in dimethylformamide (DMF) (75 mL) was dispersed by ultrasound at 50-60 °C, acetic acid (2.85 mL, 850 mmol) was added. A DMF solution (25 mL) of the linker 2,6-naphthalene dicarboxylic acid (368 mg, 1.7 mmol) was added to the above solution in an equimolar ratio with regard to ZrCl<sub>4</sub>. Finally, water (0.125 mL, 0.007 mmol) was added to the solution. The tightly capped flask was sonicated at 60 °C and kept in a bath at 120 °C under static conditions duringr 24 h. After 24 h, the solutions were cooled to room temperature and the precipitate was isolated by centrifugation. The solid washed with DMF (10 mL). After standing at room temperature for 2 h, the suspension was centrifuged and the solvent was decanted off. The obtained particles were washed several times with ethanol. Finally, the solid was dried under reduced pressure (80 °C, 3 h).

### Analytical data:

The textural properties were analyzed by N<sub>2</sub> adsorption/desorption experiments performed at -196 °C using a static volumetric apparatus, Micromeritics ASAP 2010 analyzer. The samples (200–250 mg) were outgassed, previous to the analysis, for 12 h at 100 °C, or till the outgassing pressure reached less than 5 mm Hg. For the analysis at low relative pressure range, up to  $P/P_0 = 0.05$ , successive doses of nitrogen of 4 cm<sup>3</sup> STP/g were added, equilibrating for at least 2 h. The adsorption branch of the isotherm was obtained following a standard 40-points  $P/P_0$  table, and the desorption branch following a fixed to 20-points  $P/P_0$  table. The specific total surface area was calculated using the Brunauer–Emmett–Teller (BET) method<sup>2</sup>, selecting the adsorption data respective to the  $P/P_0$  between 0.05 and 0.2, considering a nitrogen molecule cross-section area value of 0.162 nm<sup>2</sup>.<sup>3</sup> The external surface area and micropore volume was obtained by means of the t-plot according to De Boer's method.<sup>4</sup>

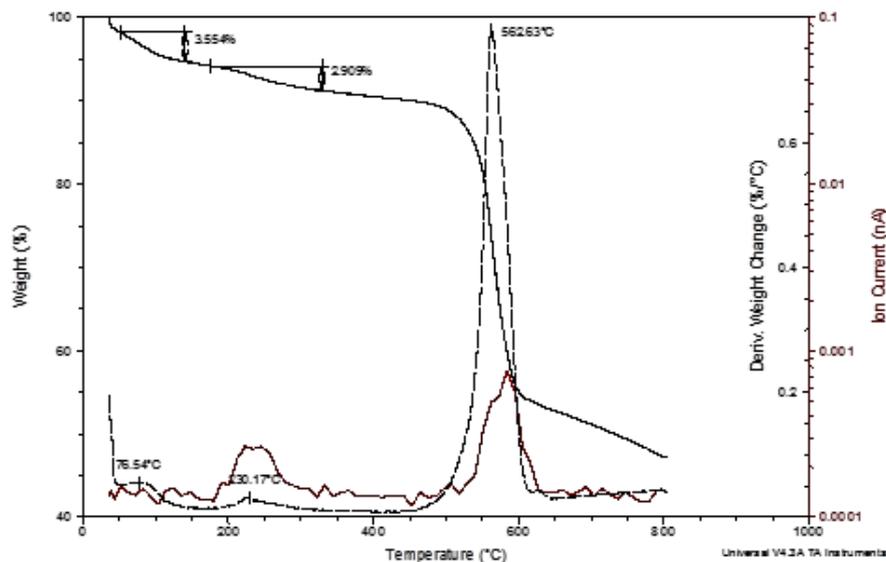


The N<sub>2</sub> adsorption-desorption isotherms (77K) of Zr-NDC MOF

The N<sub>2</sub> adsorption-desorption isotherms at 77K shown in the figure exhibit a classic microporous type I isotherm without any hysteresis. The framework showed a BET surface area of 1340 m<sup>2</sup>/g (micropore area of 1141 m<sup>2</sup>/g and 148 m<sup>2</sup>/g of external surface) and calculated Langmuir surface area of 1535 m<sup>2</sup>/g.

### Thermal gravimetric analysis

Thermogravimetric and differential thermal analyses (TGA-DTA) were conducted in an TA Universal Instrument. The samples were heated under an air stream from 40 °C to 800 °C with a heating rate of 10 °C/min. TGA results showed that Zr-NDC MOF was stable till 500°C. We can distinguish two steps which can be assigned to the loss of acetic acid during heating, at 230°C, and to the decomposition of the linkers, above 575°C. The residue (up to 35%) can be due to the thermally formed monoclinic ZrO<sub>2</sub>. Taking into account that acetic acid was not removed from the powder after heating at vacuum and 120°C, it is probably chemically bounded on the crystal surface.



TGA-Mass spectroscopy for Zr-NDC MOF ( $m/z = 70-130$ )

### References:

1. Schaate, A.; Roy, P.; Godt, A.; Lippke, J.; Waltz, F.; Wiebcke, M.; Behrens, P., Modulated Synthesis of Zr-Based Metal–Organic Frameworks: From Nano to Single Crystals. *Chemistry – A European Journal* **2011**, *17* (24), 6643-6651.
2. S. Brunauer, P.H. Emmett, E. Teller, *J. Am. Chem. Soc.* **60** (1938) 309–319.
3. F. Rouquerol, J. Rouquerol, K.S.W. Sing, *Adsorption by powders and porous solids, Principles, Methodology and Applications*, Academic Press, London, 1999.
4. B.C. Lippens, J.H. De Boer, *J. Catal.* **4** (1965) 319–323.

### Acknowledgments

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