Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Electronic Supplementary Information (ESI)

Early instability of MIL-125-NH2 in aqueous solution and mediation of the visible photogeneration of NADH cofactor

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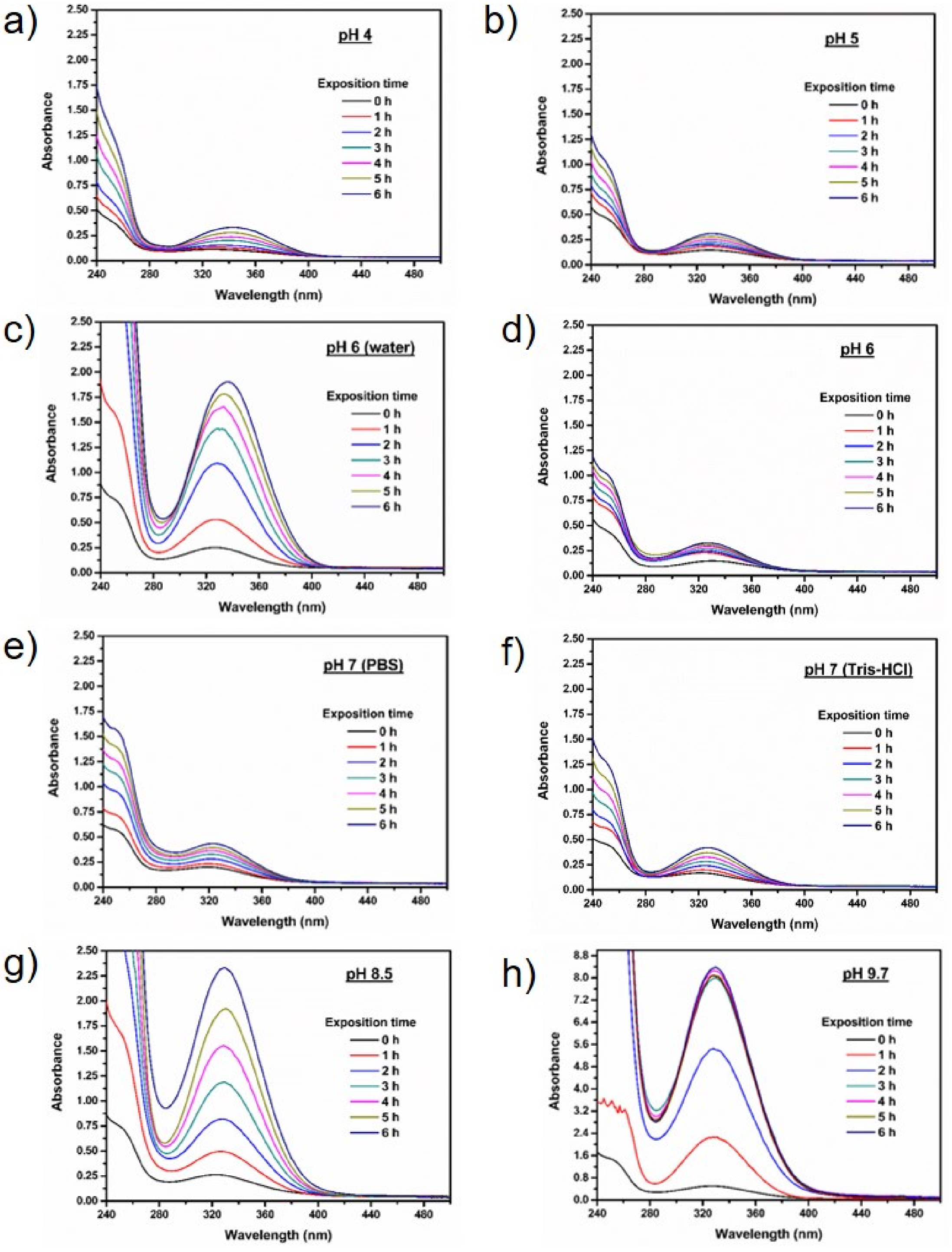

Figure S1. UV-Visible absorption spectra of the supernatant obtained after exposition for different times of MIL-125-NH_2 to aqueous unbuffered and pH-regulated media. Conditions: acetate buffer at pH 4 (a) and pH 5 (b), pure water at pH 6 (c), phosphate buffer (PBS) at pH 6 (d) and pH 7 (e), Tris-HCl buffer at pH 7 (f) and pH 8.5 (g) and ammonia buffer at pH 9.7 (h). In all the cases, the concentration of the buffer solutions was 0.05 mol L^{-1}.

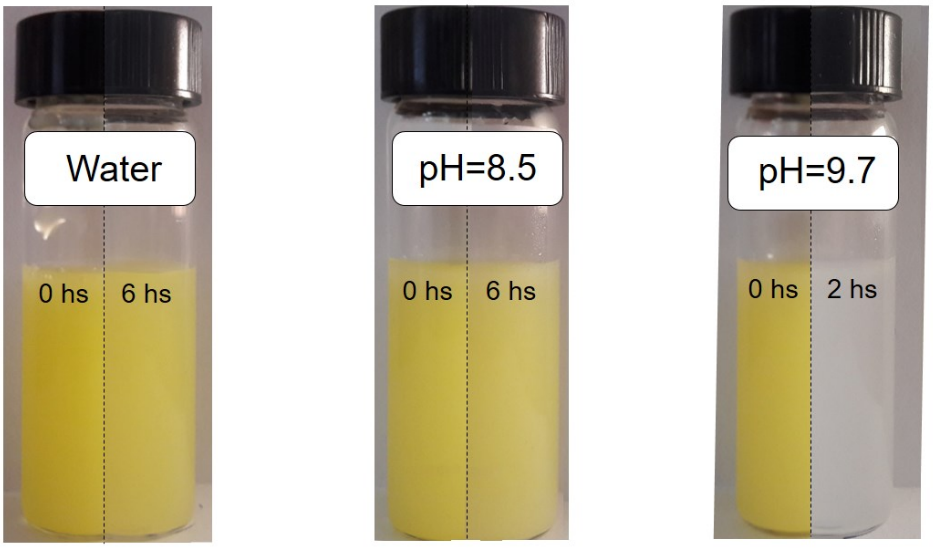

Figure S2. Comparison of the aspect of the suspensions of MIL-125-NH_2 in aqueous media before and after the time indicated on the pictures. The images were not digitally manipulated.

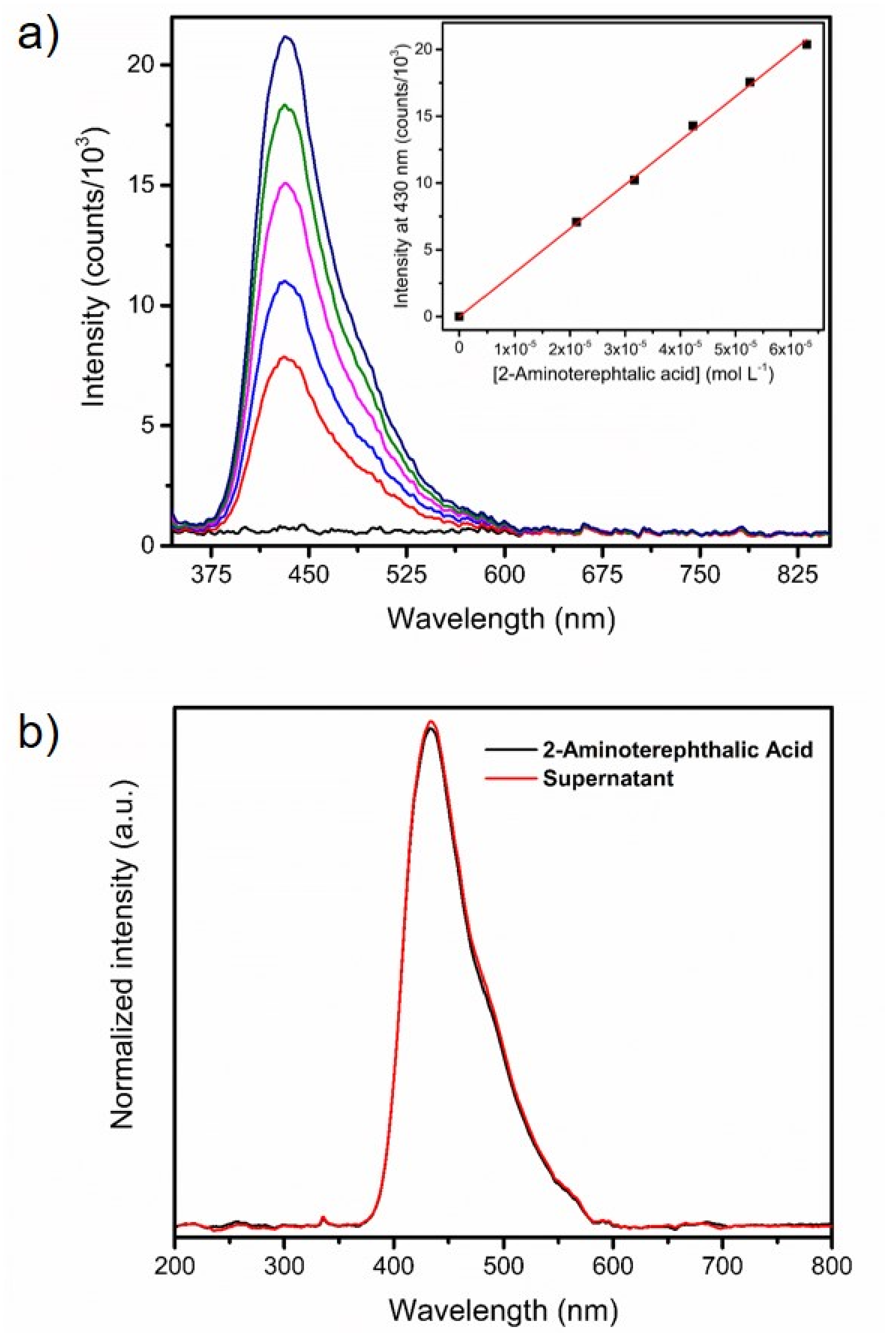

Figure S3. Emission spectra (λ_{Exc} = 330 nm) of standard solutions of 2-aminoterephthalic acid in 0.05 mol L^{-1} Tris-HCl buffer (pH = 8.5) with concentrations between 0 and 6.3 x 10^{-5} mol L^{-1}. Calibration curve and linear fit derived from the emission data at 430 nm ($y = 3.295*10^8 x + 2.664$), in inset (a). Emission spectra normalized by the absorbance at 330 nm of 3.35 x10^{-5} mol L^{-1} 2-aminoterephthalic acid in aqueous solution and of the supernatant obtained after the suspension of MIL-125-NH_2 in pure water for 6 hours (b).

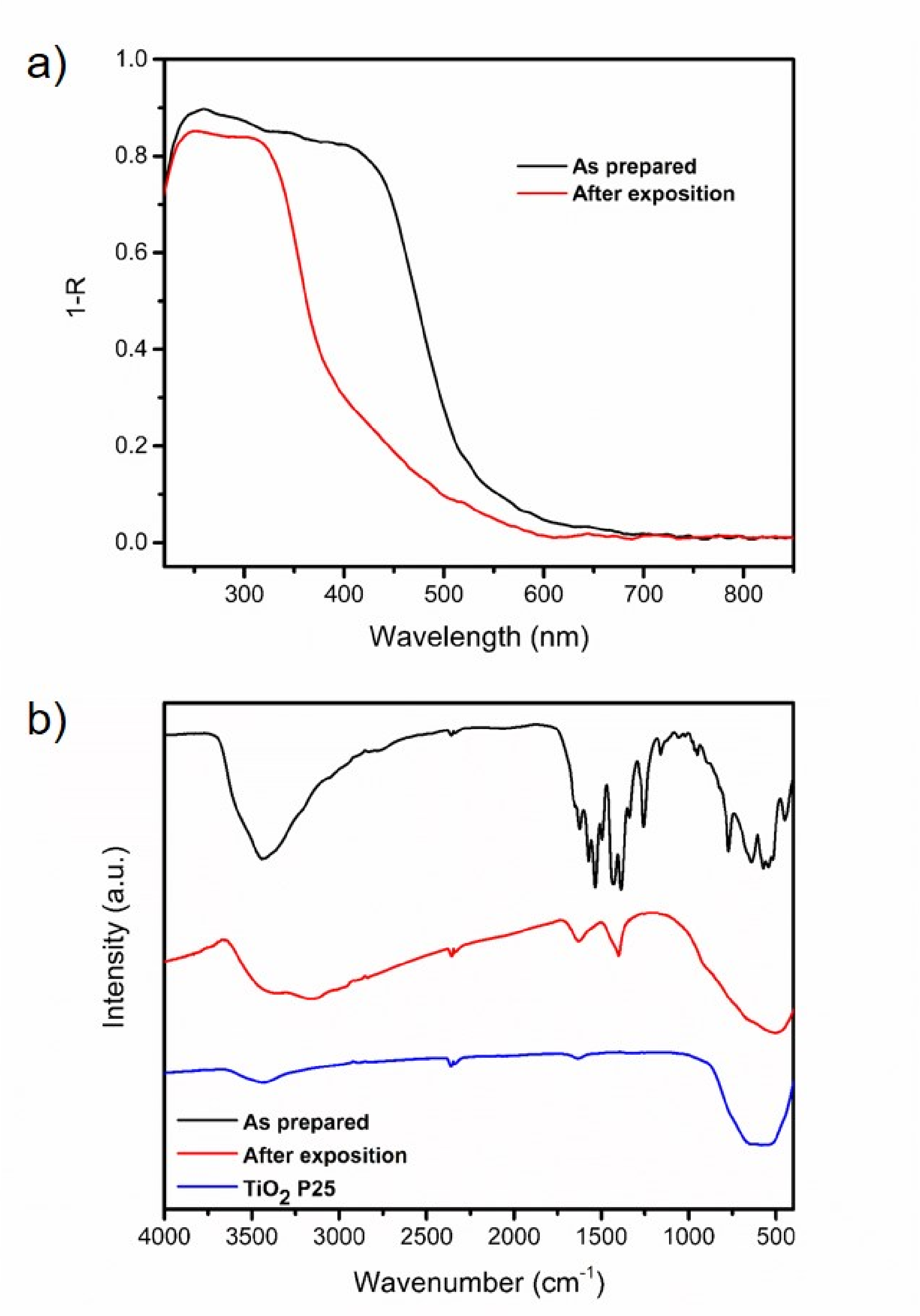

Figure S4. DRUV (a) and FTIR (b) spectra of as-prepared MIL-125-NH_2 and of the resultant white solid after 4 h of exposition of the framework to 0.05 mol L^{-1} ammonia buffer (pH 9.7). FTIR spectrum of TiO_2 P25 is shown for comparison in (b).

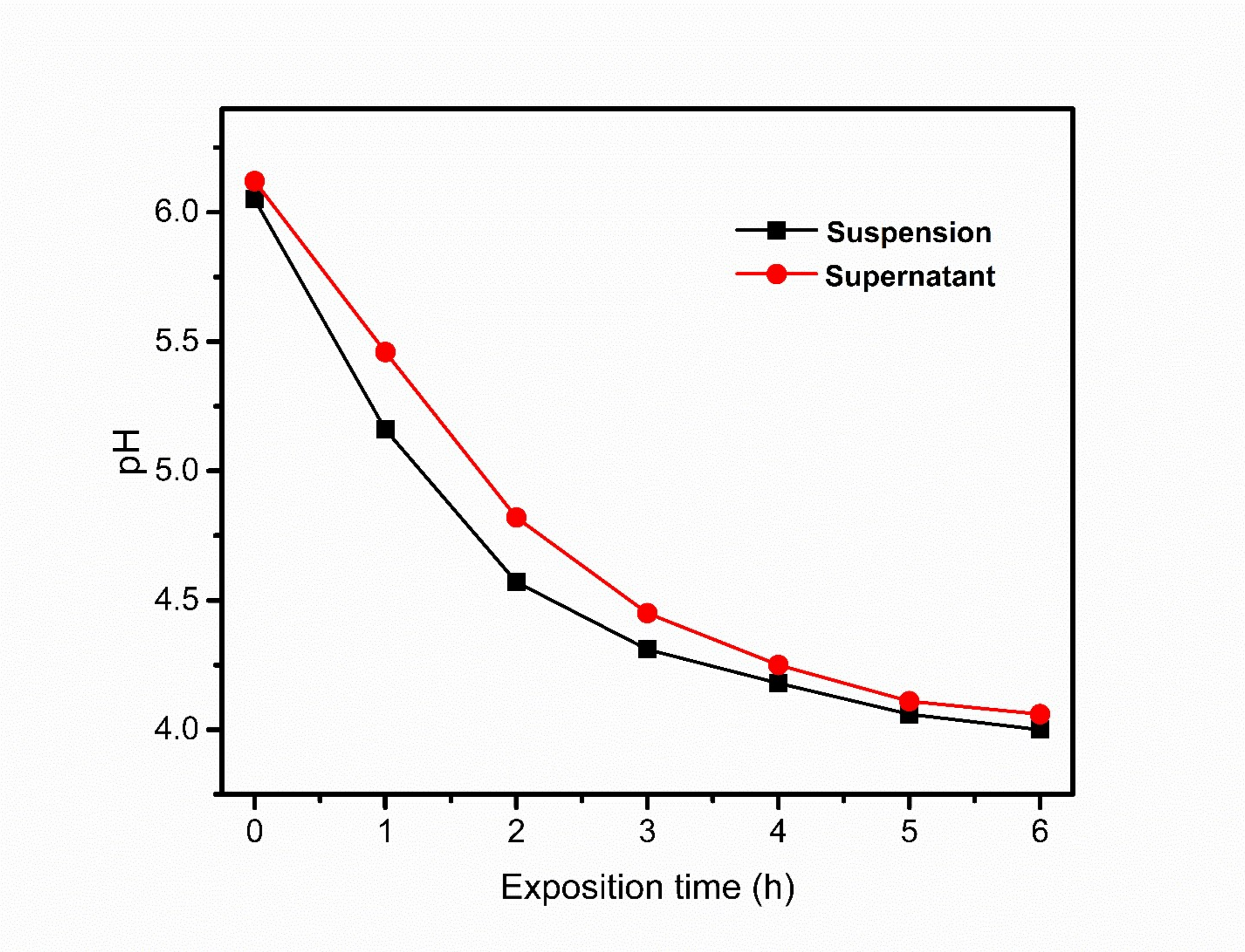

Figure S5. Temporal pH-evolution in a suspension obtained by dispersion of MIL-125-NH_2 (1 g L^{-1}) in pure water, initially at pH 6 (black), and in the supernatant solution obtained after centrifugation of the first one (red).

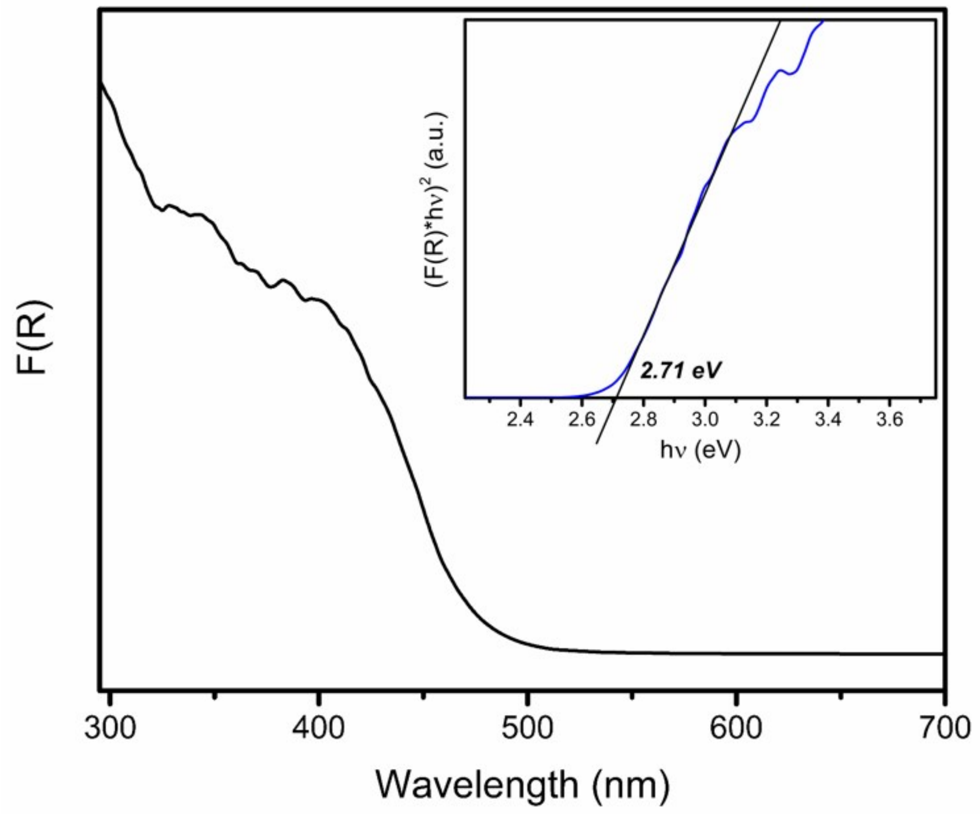

Figure S6. Kubelka-Munk representation derived from diffuse reflectance spectrum. Inset shows the Tauc plot for MIL-125-NH_2 treated as a direct semiconductor and the estimated optical bandgap [1].

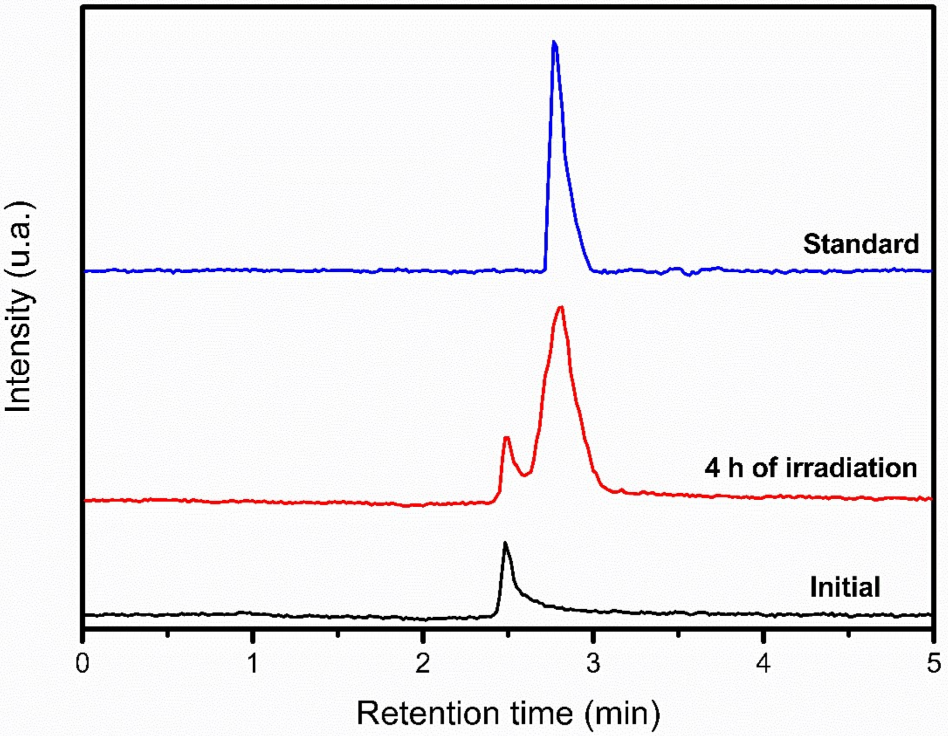

Figure S7. HPLC chromatograms of the supernatant from the reaction mixture (1:5 dilution) before (black) and after (red) 4 h of anaerobic visible irradiation, and 31.75 μmol L^{-1} aqueous 1,4-NADH standard solution (blue).

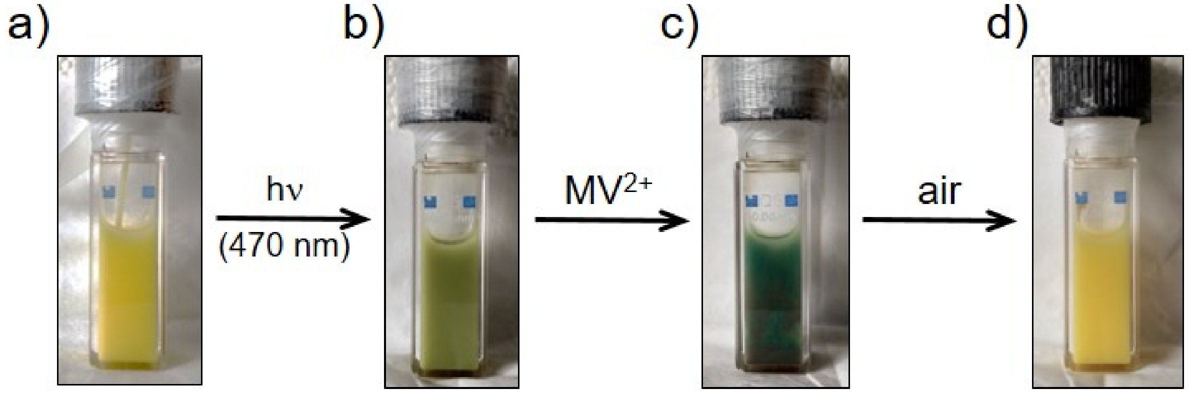

Figure S8. Sequential view of the anaerobic aqueous suspension of MIL-125-NH_2 at pH 7 in the presence of TEOA before irradiation (a), after 10 minutes visible irradiation (b), after addition of methylviologen to (b) in anaerobic conditions (c) after opening for air entrance followed by vigorous agitation (d).

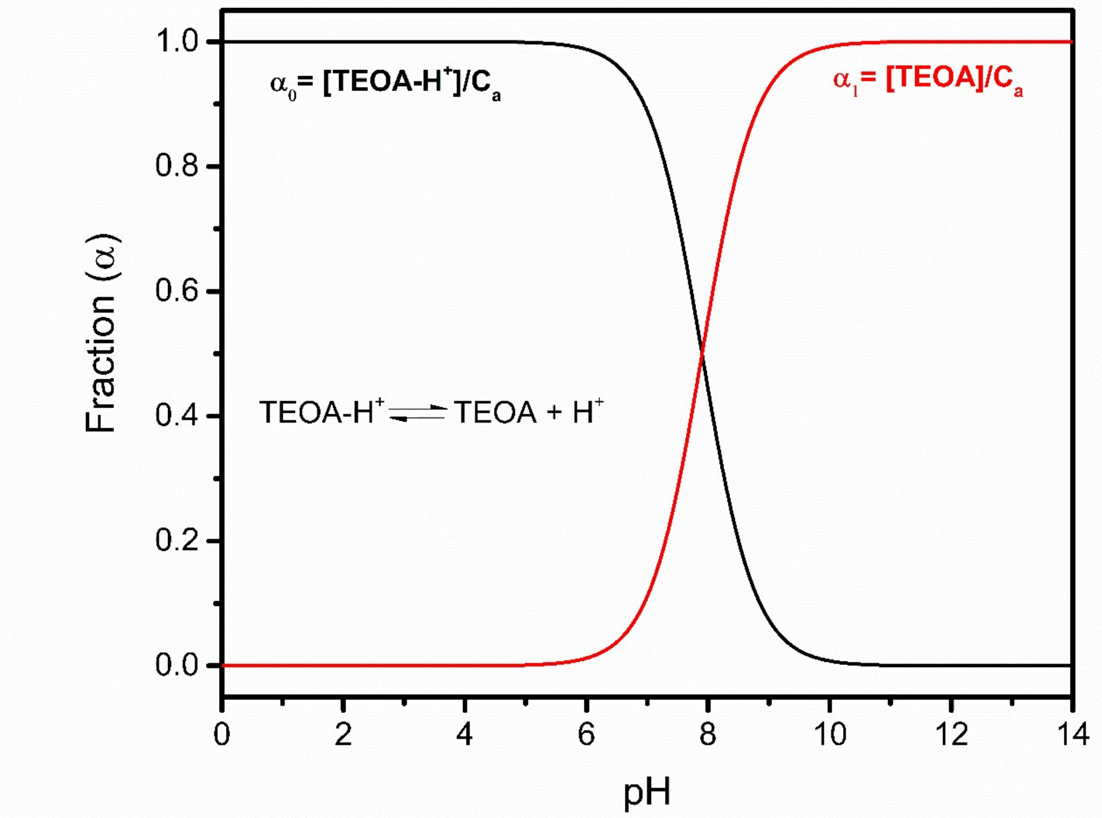

Figure S9. Relative concentration of TEOA species (α_0: protonated form, black line, α_1: neutral form, red line) in water as a function of pH, estimated for $pK_a = 7.9$ [2]. C_a denotes the analytical concentration of TEOA.

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1. M. A. Nasalevich, R. Becker, E. V. Ramos-Fernandez, S. Castellanos, S. L. Veber, M. V. Fedin, F. Kapteijn, J. N. H. Reek, J. I. van der Vlugt and J. Gascon, *Energy Environ. Sci.*, 2015, **8,** 364-375.

2. K. Kalyanasundaram, J. Kiwi and M. Grätzel, *Helv. Chim. Acta*, 1978, **61,** 2720–2730.