Supplementary Information (SI) for Physical Chemistry Chemical Physics.

Unveiling MOF-808 Photocycle and its Interaction with Luminescent Guests

G. Ficarra[1,*], A. Sciortino[1,*], L.G. Barbata[1], R. Ettlinger[2,4], V. De Michele[3], E. Marin[3], M. Cannas[1], R.E. Morris[2], and G.Buscarino[1,*]

[1]Department of Physics and Chemistry "Emilio Segrè", University of Palermo, Via Archirafi 36, 90123, Palermo, Italy
[2]EastChem School of Chemistry, University of St Andrews, North Haugh, St Andrews, UK
[3]Université Jean Monnet, CNRS, IOGS, Laboratoire Hubert Curien UMR 5516, 42000 Saint-Etienne, France
[4]TUM School of Natural Sciences Technical University of Munich Lichtenbergstr.4; 85748 Garching b. München, Germany
[*]giuseppe.ficarra02@unipa.it, alice.sciortino02@unipa.it, gianpiero.buscarino@unipa.it

MOF-808 particle's size

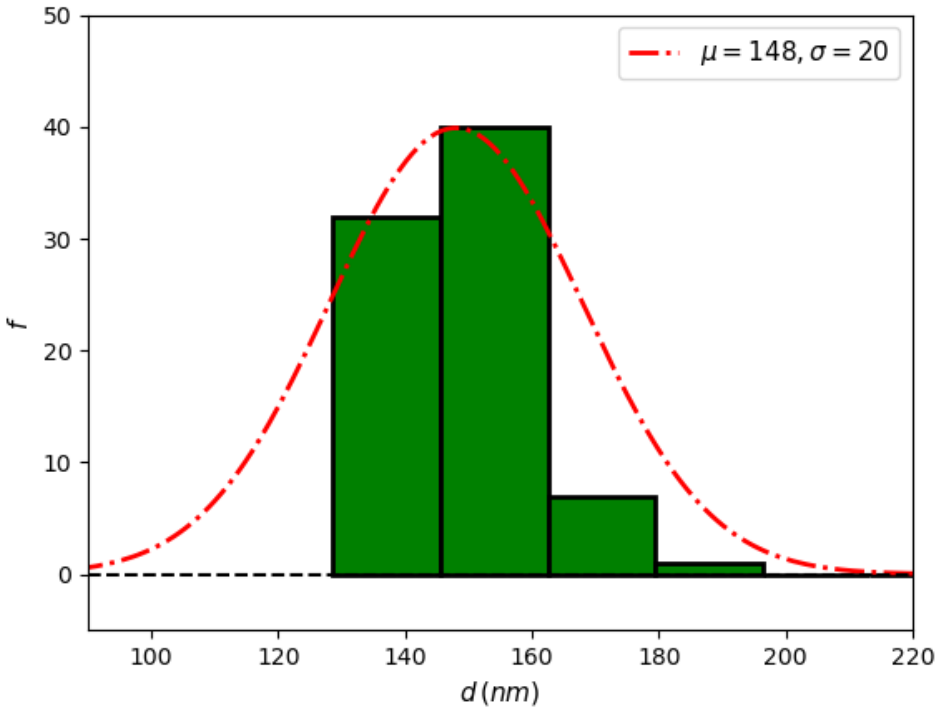


Figure S1. The green histogram represents the particle's size distribution for MOF-808 obtained by collecting SEM images, while the dashodotted red line is an overlapping Gaussian function with 148 nm mean value and 20 nm variance.

MOF-808 H_2O

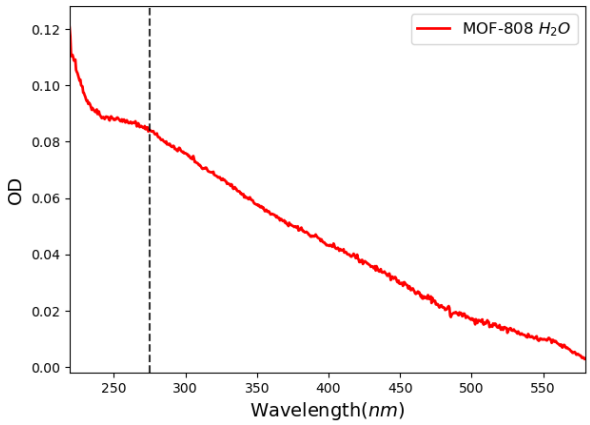


Figure S2. Optical absorption of MOF-808 in H_2O in red, the dashed line indicating the absorption peak.

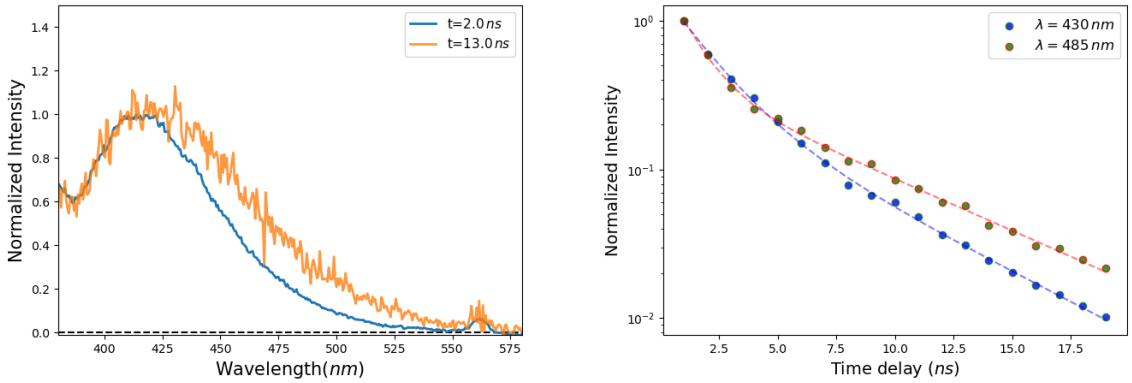


Figure S3. **(a)**The emission band of MOF-808 in water at $2.0\,ns$ is reported in blue, in orange the band at $13.0\,ns$ from the photoexcitation; **(b)** Blue dots are the kinetic decay taken at $430\,nm$: there are two components of lifetime resulting from a double exponential fitting: $1.8\,ns$ and $5.3\,ns$. Green dots are relative to the $485\,nm$ kinetic from which result $1.6\,ns$ and $6.2\,ns$ components.

MOF-808 powder

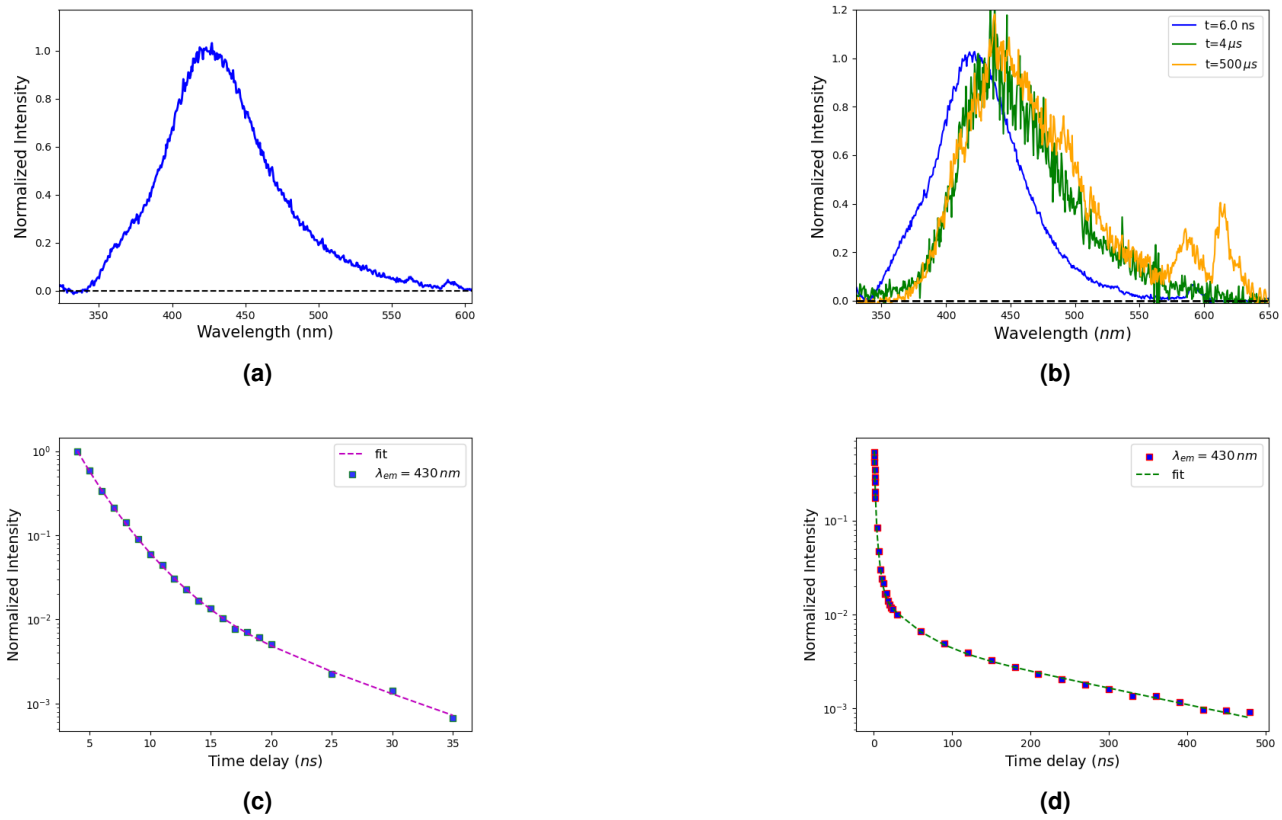


Figure S4. **(a)** PL spectrum of MOF-808 in powder with a peak centered at 425 nm; **(b)** PL spectra collected at different time from the photoexcitation: 6 *ns* in blue, 4 μs in green and 500 μs, the last spectrum is centered at 450 nm. **(c)** The kinetic decay of MOF-808 up to 35 ns is reported with blue squares while the purple line represents the double exponential fitting; **(d)** The kinetic decay of MOF-808 from 2 to 500 μs is reported with blue squares while the dashed green line represents the best curve fit.

TA kinetics fitting

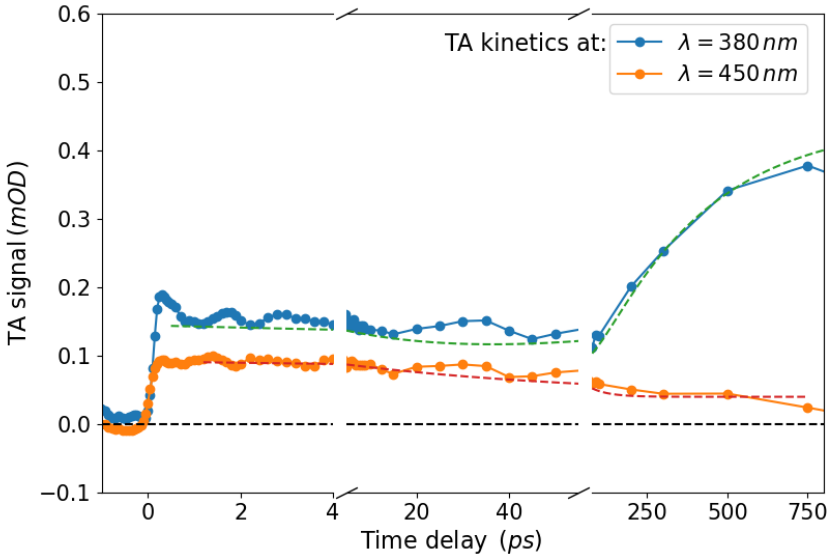


Figure S5. TA kinetic traces at 380 and 450 nm with respective best curve fit.

N_2 adsorption RhB@MOF-808

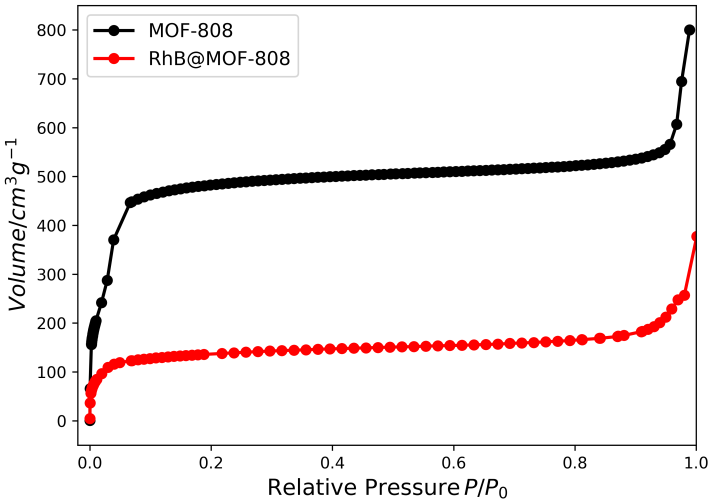


Figure S6. N_2 adsporbtion of RhB@MOF-808 (red curve) and bare MOF-808 (black curve) also reported in the main paper. The estimated internal surface area is $577\,m^2g^{-1}$ for the MOF-808 loaded with Rhodamine B.

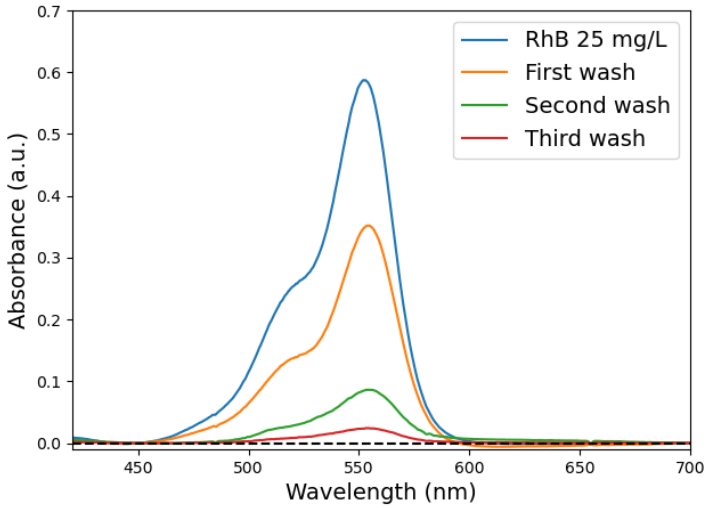
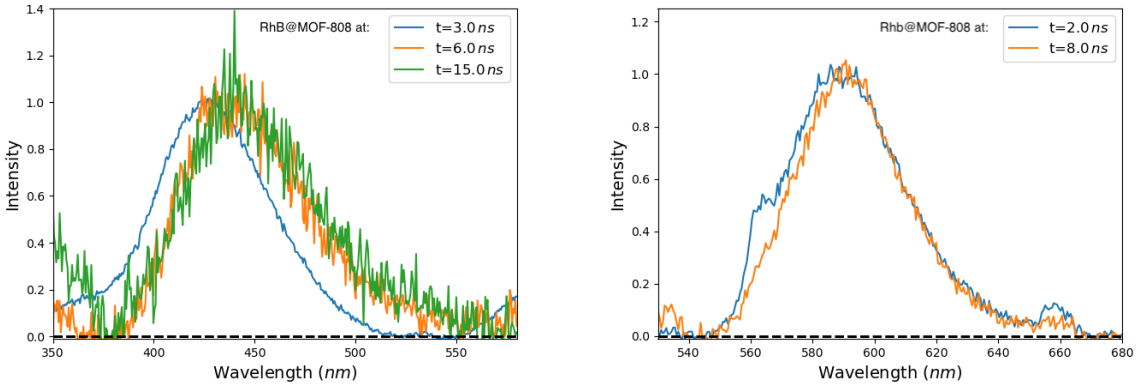


Figure S7. Absorbance spectra of Rhodamine B mother solution (25 mg/L) and of the supernatant solutions obtained after subsequent washing steps.

Rhb@MOF-808 in H_2O



(a) **(b)**

Figure S8. **(a)**The blue band of RhB@MOF-808 in water which is centered at 430 nm and undergoes a redshit with time up to 450 nm; **(b)** Red emission band of RhB@MOF-808 which maintains its position unchanged with respect to time delay.

RhB@MOF-808

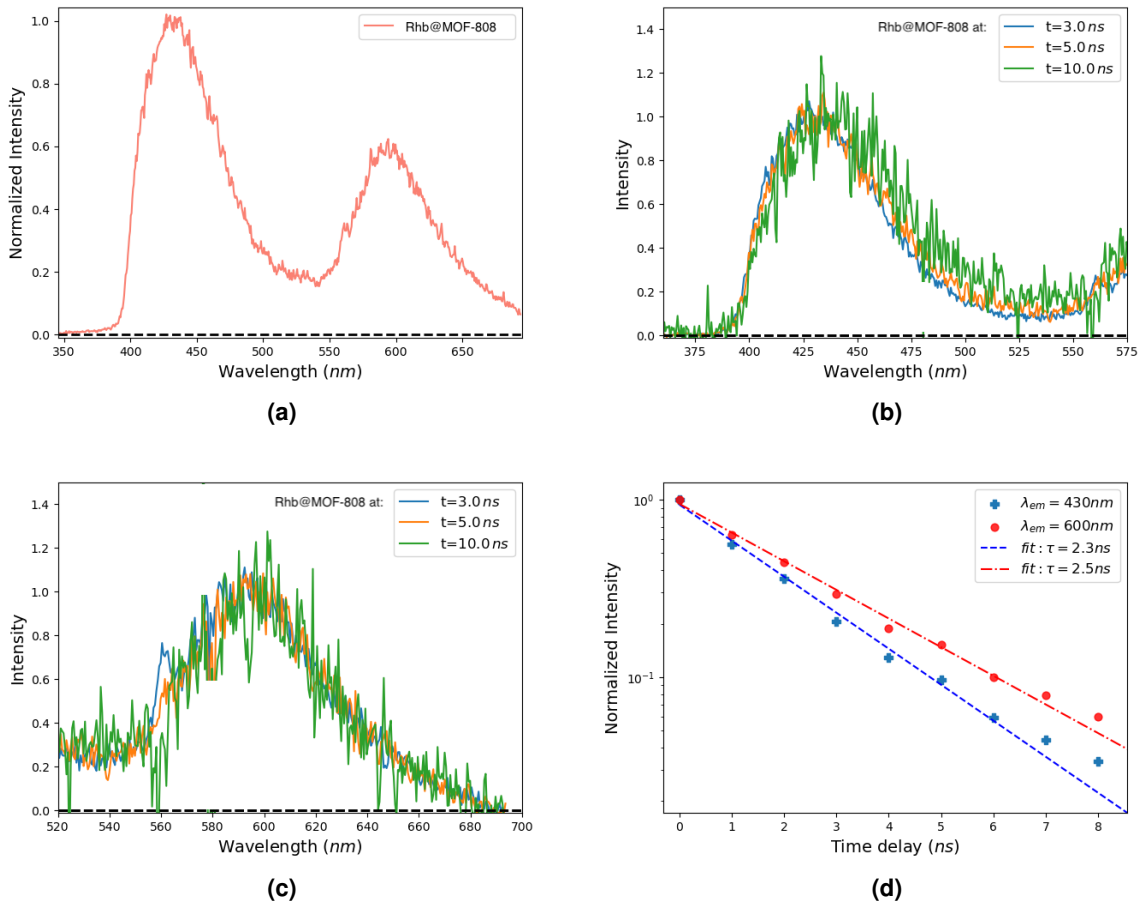


Figure S9. (**a**) PL spectra of RhB@MOF-808 in powder, the abrupt cut in the blue spectral region is due to a 400 nm filter;(**b**)Emission band related to the MOF-808 itself reported at different time delays;(**c**)Emission band related the encapsulated Rhodamine B reported with different time delays;(**d**) Blue markers are the kinetic decay of the blue band ($\lambda_{em} = 430nm$), while the red dots correspond to the kinetic of the band centered at $\lambda_{em} = 590nm$. The red and blue dashed lines are the respective monoexponetial fitted curves.

Photobleaching

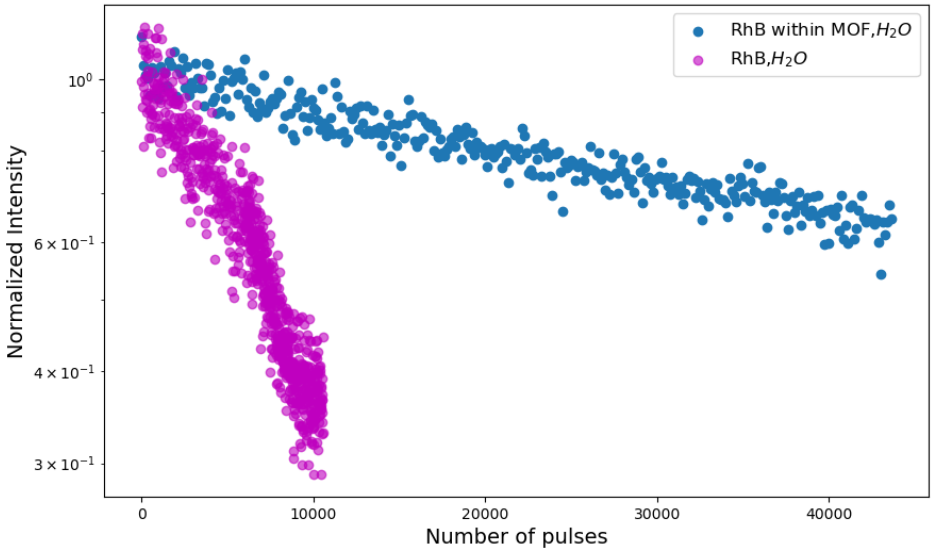


Figure S10. Photobleaching kinetics of bare Rhodamine B (pink dots) and Rhodamine encpsulated within the MOF cavities (blue dots).

PL of BTC and Metal oxocluster

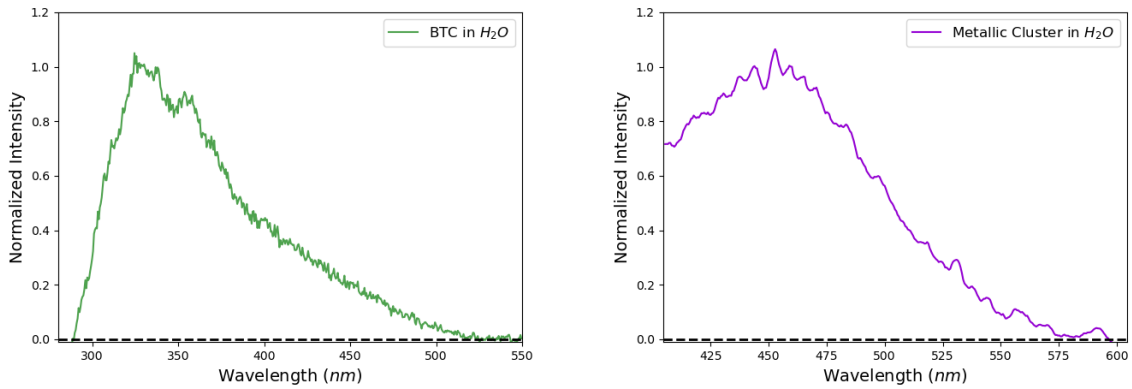


Figure S11. **(a)** The green emission band is the PL showed by the organic ligand when in water, the principal activity is centered at 330 nm; **(b)** The violet broad band is the emission of the metallic cluster in water and it is centered at 450 nm.

Photocycle of RhB@MOF-808

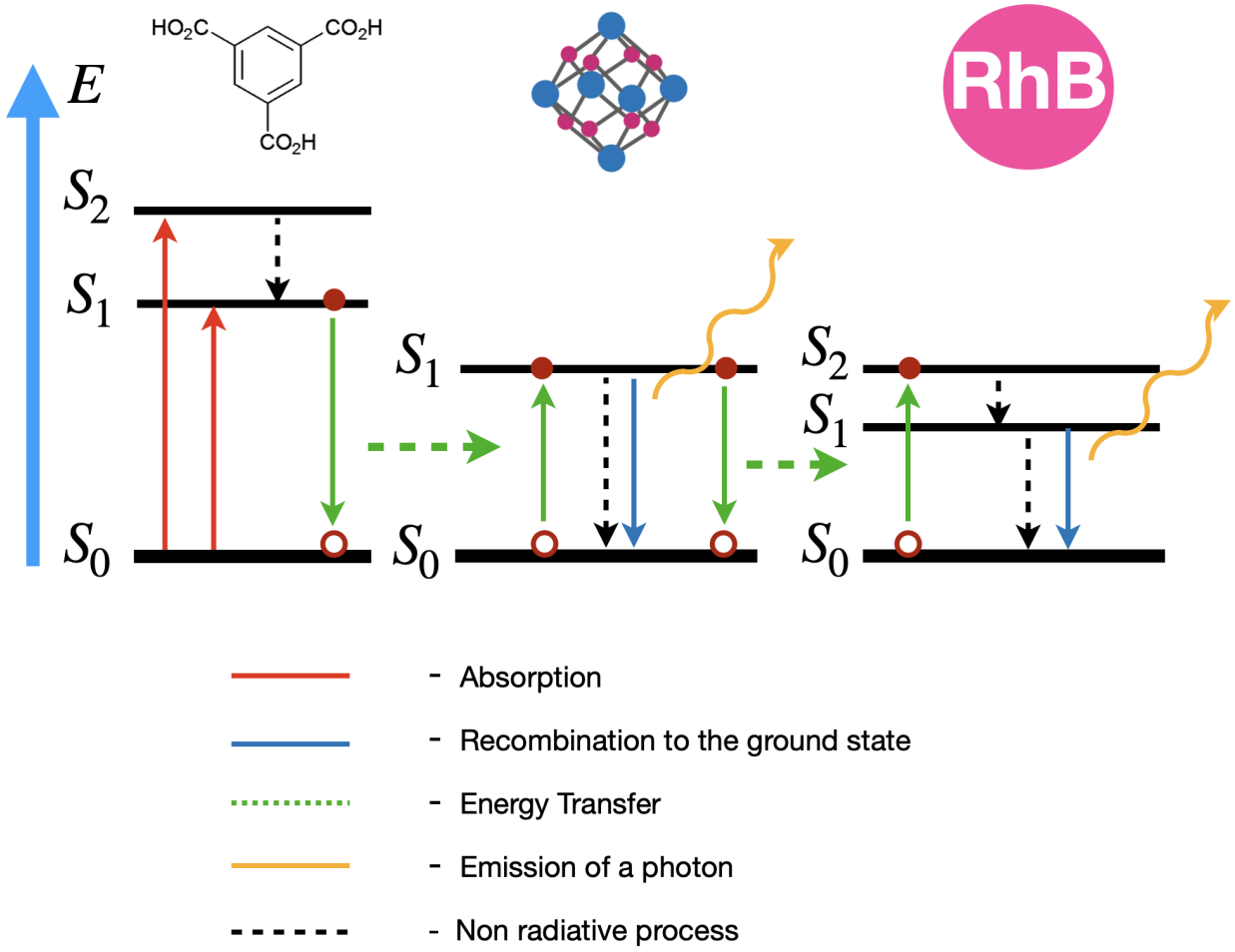


Figure S12. Photocycle of the dual-emitting system RhB@MOF-808.From the left to the right are depited the ligand BTC, the metal oxocluster and finally the guest dye Rhodamine B. On the bottom there is a legend where all the involved processes are summarized.