

Supplementary Information (ESI) for PCCP

Delayed electron/hole pair recombination in iron(III) oxide metal-organic frameworks

Katrien G.M. Laurier¹, Eduard Fron¹, Pedro Atienzar³, Koen Kennes¹, Hermenegildo Garcia³,
Mark Van der Auweraer¹, Dirk E. De Vos², Johan Hofkens¹, and Maarten B.J. Roeffaers^{1,2}

¹ *Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001, Heverlee, Belgium.*

² *Department of Microbial and Molecular Systems, KU Leuven, Kasteelpark Arenberg 23, B-3001, Heverlee, Belgium.*

³ *Instituto de Tecnología Química, Universidad Politécnica Valencia, Camino de Vera s/n, 46022 Valencia, Spain.*

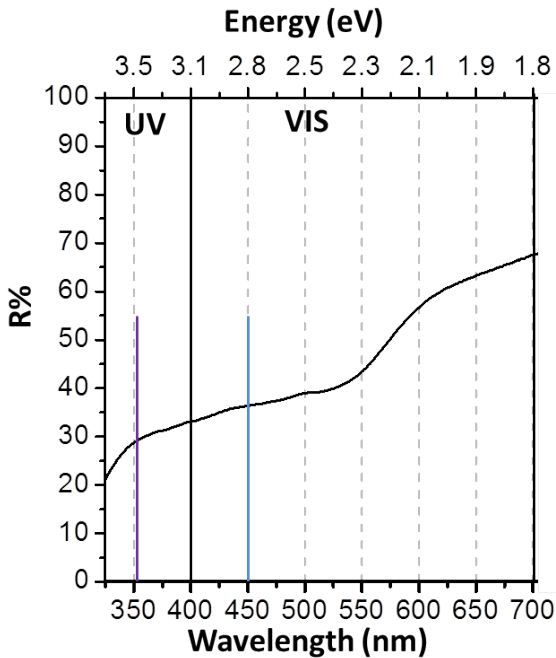
1. Properties of the photocatalytic materials

1.1. Chemical composition of the photocatalysts in this study

Photocatalyst	Chemical composition	Organic linker
MIL-100(Fe)	$\text{Fe}_3\text{O}(\text{H}_2\text{O})_2\text{F}[\text{C}_6\text{H}_3(\text{CO}_2)_3]_2$	BTC
Basolite F300	$\text{FeC}_9\text{H}_3\text{O}_6$	BTC
MIL-101(Fe)-NH ₂	$\text{Fe}_3\text{O}(\text{H}_2\text{O})_2\text{F}[\text{C}_6\text{H}_4(\text{CO}_2)_2\text{NH}_2]_3$	NH ₂ -BDC
MIL-88B(Fe)	$\text{Fe}_3\text{O}(\text{CH}_3\text{OH})_3[\text{C}_6\text{H}_3(\text{CO}_2)_2]_3 \cdot \text{CH}_3\text{CO}_2 \cdot (\text{CH}_3\text{OH})_{4.5}$	BDC
MIL-88B(Fe)-NH ₂	$\text{Fe}_3\text{O}(\text{CH}_3\text{OH})_3[\text{C}_6\text{H}_3(\text{CO}_2)_2\text{NH}_2]_3 \cdot \text{CH}_3\text{CO}_2 \cdot (\text{CH}_3\text{OH})_{4.5}$	NH ₂ -BDC

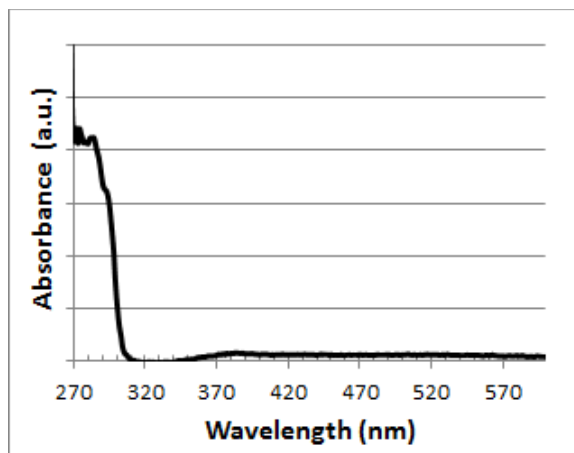
1.2. Diffuse Reflectance spectrum of MIL-88B(Fe)

The purple and blue line represent respectively the excitation at 355 nm and the excitation at 450 nm.

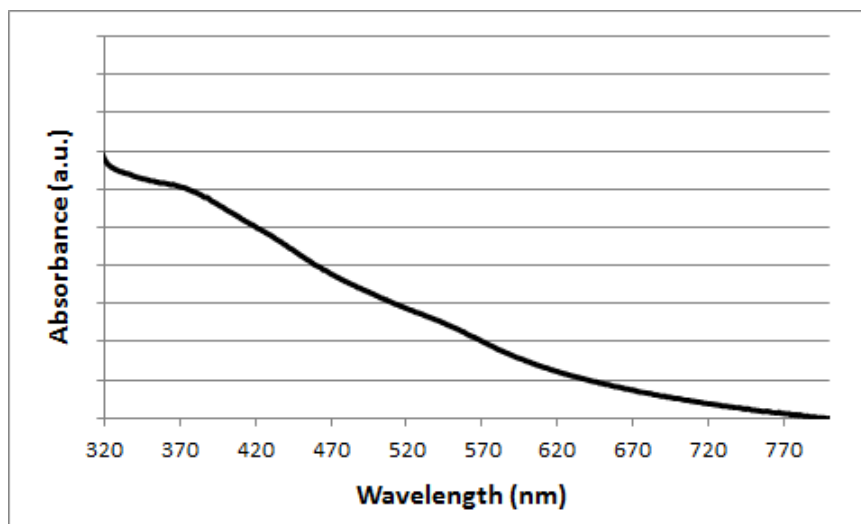


2. Steady-state absorption spectra

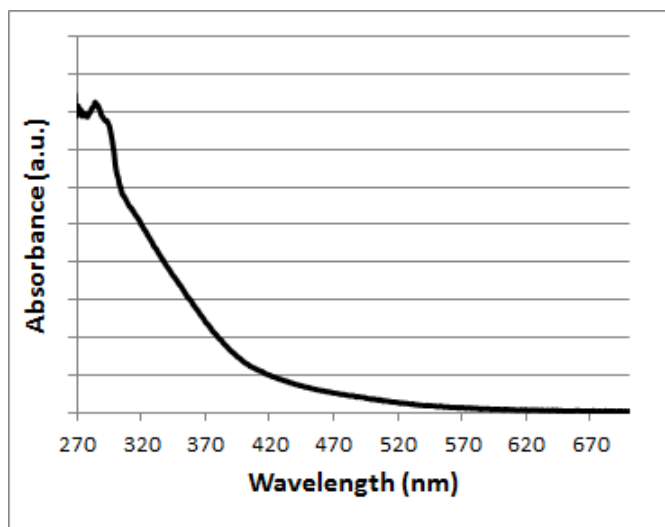
2.1. Solution of the BDC linker in DMF



2.2. Suspension of MIL-88B(Fe) in DMF



2.3. Mixture of the BDC linker and Fe(III)-ions in DMF

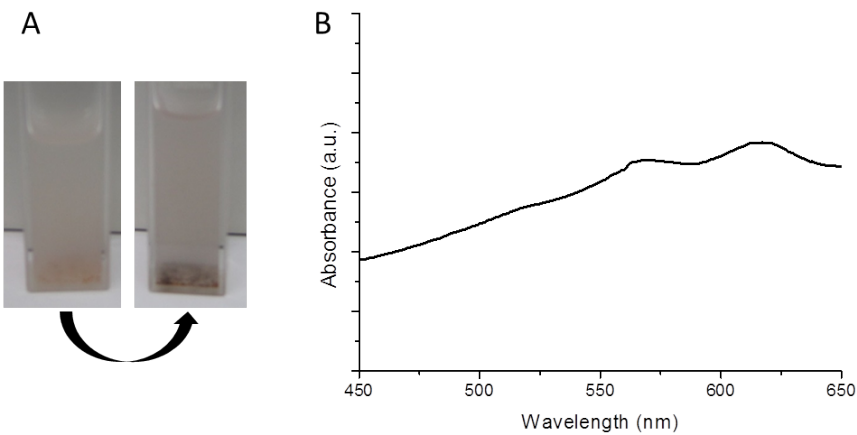


3. Photo-generated hole consumption with electron donor TMPD

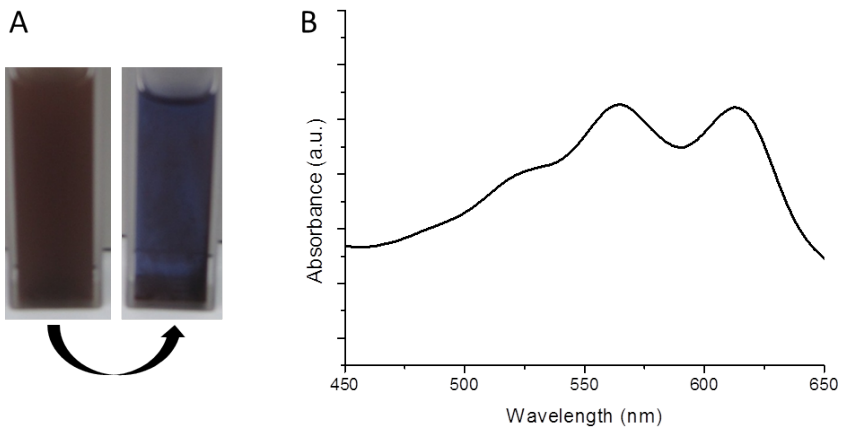
Experiments with N,N,N',N'-tetramethyl-p-phenylenediamine(TMPD) were carried out by the addition of a 2 mL acetonitrile solution of TMPD to the MOF samples (3 mg) inside a quartz cuvette. The suspension was purged with argon before illumination with a solar simulator (150 W) through an AM 1.5 filter for about 15 min. Detection of the radical cation of TMPD was performed on a Perkin Elmer UV/VIS spectrophotometer (Lambda 950).

Below the results of MIL-100(Fe), MIL-101(Fe)-NH₂, MIL-88B(Fe)-NH₂ and Basolite F300 are shown: (A) Photographs before and after illumination illustrating the formation of the blue colored TMPD radical, (B) The absorption spectrum of the suspensions with added TMPD after illumination showing the presence of the TMPD radical cation with maxima at 560 and 615 nm. Without illumination, no TMPD radical was detected.

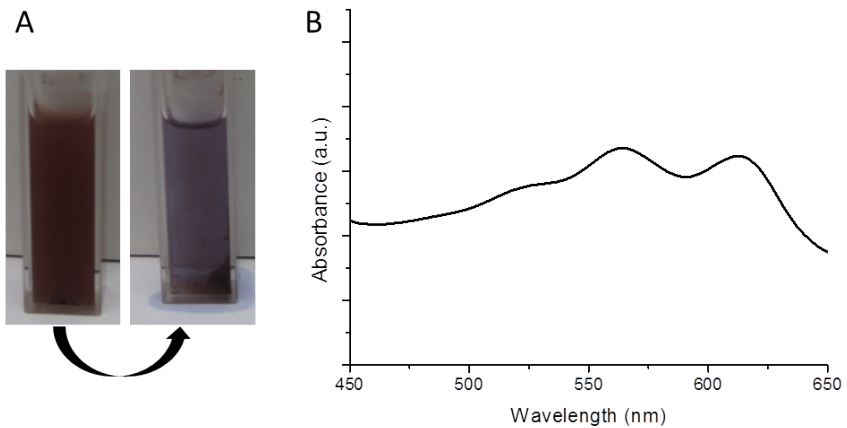
MIL-100(Fe)



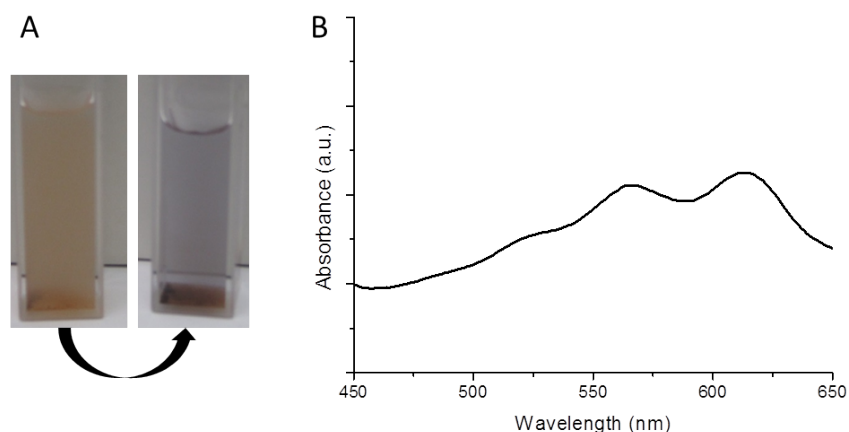
MIL-101(Fe)-NH₂



MIL-88B(Fe)-NH₂



Basolite F300

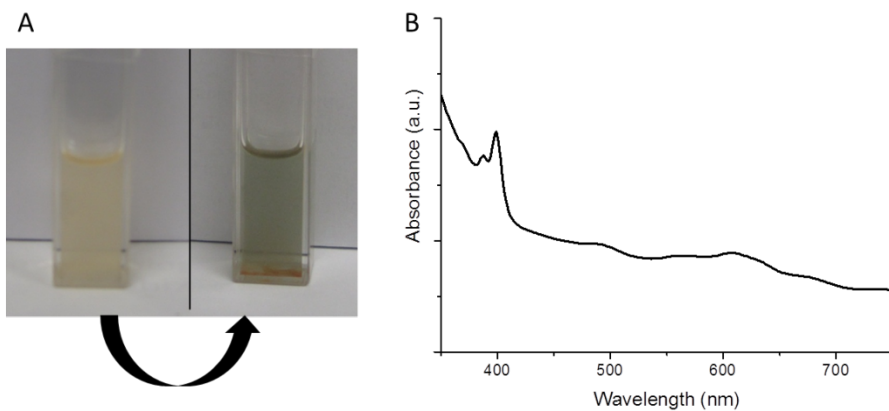


4. Photogenerated electron consumption with electron acceptor MV^{2+}

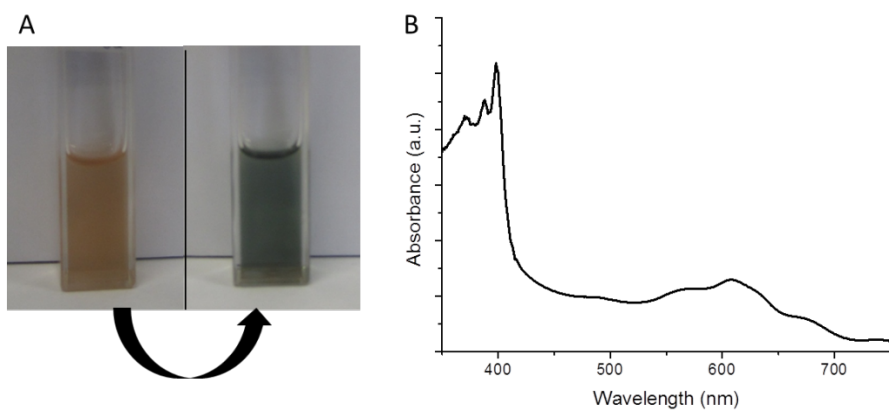
Experiments with methyl viologen were carried out by addition of a saturated solution of methyl viologen dichloride in DMF to a MOF suspension in a quartz cuvette. Illumination was carried out with the third harmonic (355 nm) of a ND/YAG laser (10 Hz, 30 mW) for about 15 min. The methyl viologen radical was detected with a Varian Cary 5G spectrophotometer.

Below the results of MIL-100(Fe), MIL-101(Fe)- NH_2 , MIL-88B(Fe)- NH_2 and Basolite F300 are shown: (A) Photographs before and after illumination illustrating the formation of the blue colored MV^{2+} radical, (B) The absorption spectrum of the suspensions with added MV^{2+} after illumination showing the presence of the MV^{2+} radical monocation with a sharp peak at 395 nm and a broader peak at 606 nm. Without illumination, no MV^{2+} radical was detected.

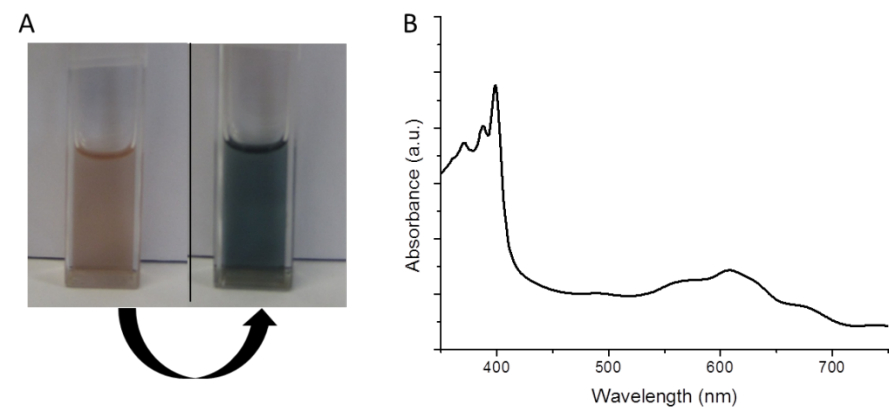
MIL-100(Fe)



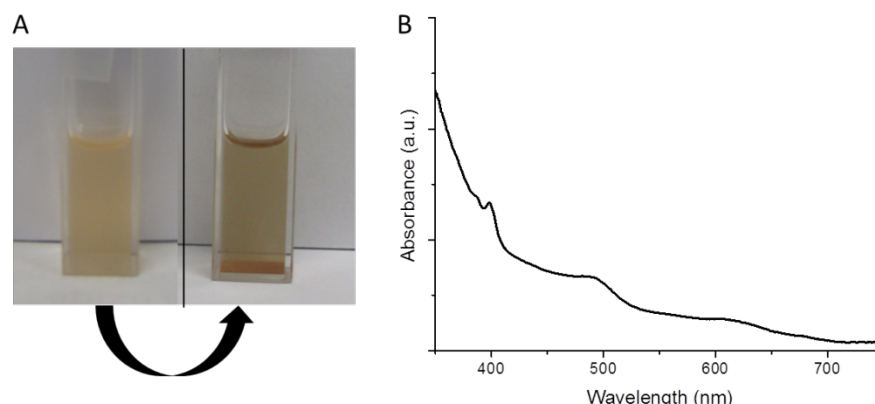
MIL-101(Fe)-NH₂



MIL-88B(Fe)-NH₂



Basolite F300



5. Transient absorption measurements on the combination of the linker (BDC, BTC, NH₂-BDC) and Fe³⁺-ions + quenching experiments with TEA as electron donor and O₂ as electron acceptor

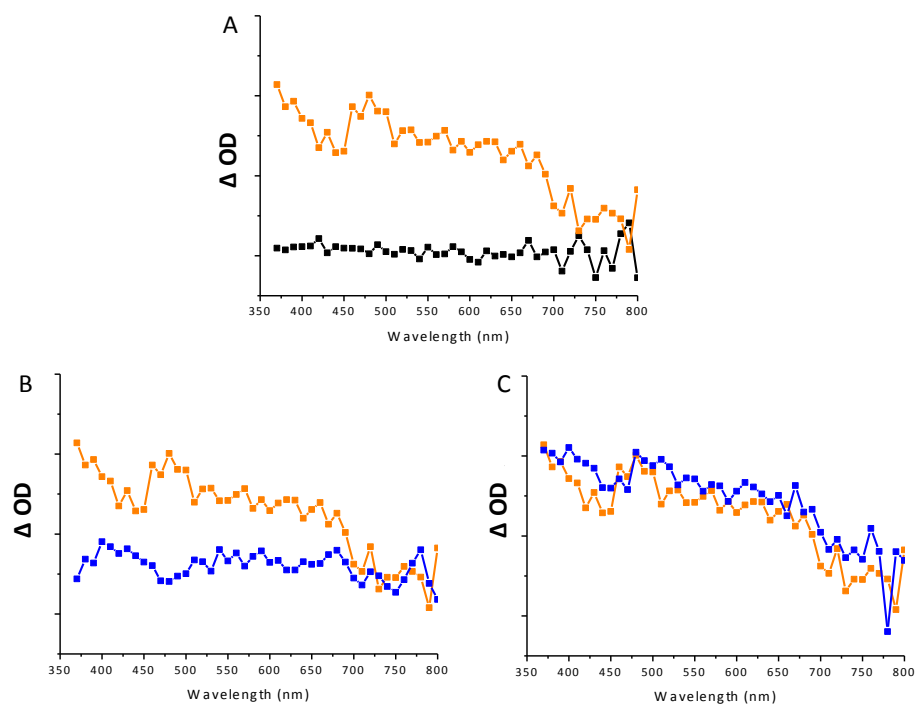
Linker solutions (10 mL) were made in DMF: 10⁻³ mol/L terephthalic acid (BDC)¹, 10⁻³ mol/L trimesic acid (BTC) and 10⁻⁴ mol/L amino-terephthalic acid (NH₂-BDC). To form the linker-metal complex, 2 mL of a 0.32 mmol/L Fe(NO₃)₃ solution in DMF was added to 10 mL of the linker solution. These mixtures were stirred before measurement.

Transient absorption measurements were performed using the third harmonic (355 nm) frequency of a Nd/YAG laser as the excitation source (10 Hz, 30 mW). A pulsed Xenon lamp was used as probe light. Signals from the photomultiplier tube were captured and digitalized by a Tektronix 2440 transient digitizer and transferred to a PC programmed in the LabView environment.

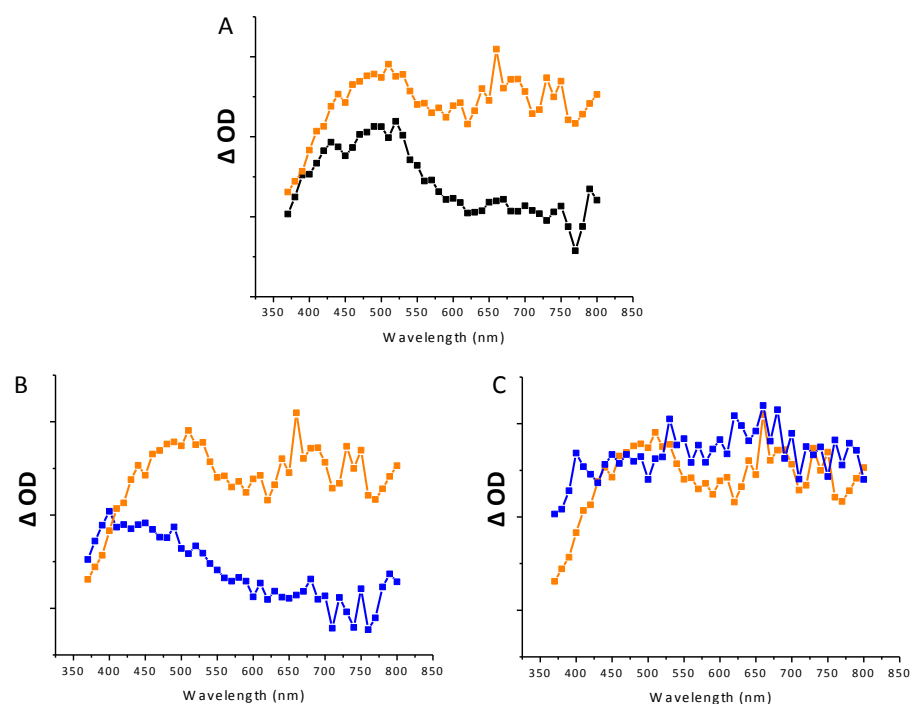
The transient absorption spectra (0.06 μs after laser pulse) are shown below: (A) *black*: pure linker solution (DMF), *orange*: linker + Fe³⁺-ions after stirring for 4 hours (BDC and BTC) or 2 hours (NH₂-BDC); (B) orange: linker + Fe³⁺-ions after stirring (similar to orange curve in (A)), blue: with the addition of the electron donor, TEA; (C) orange: linker + Fe³⁺-ions after stirring (similar to orange curve in (A)), blue: with the addition of electron acceptor, O₂.

¹The results of the experiments with BDC are shown in the main manuscript.

Trimesic acid (BTC) + Fe³⁺



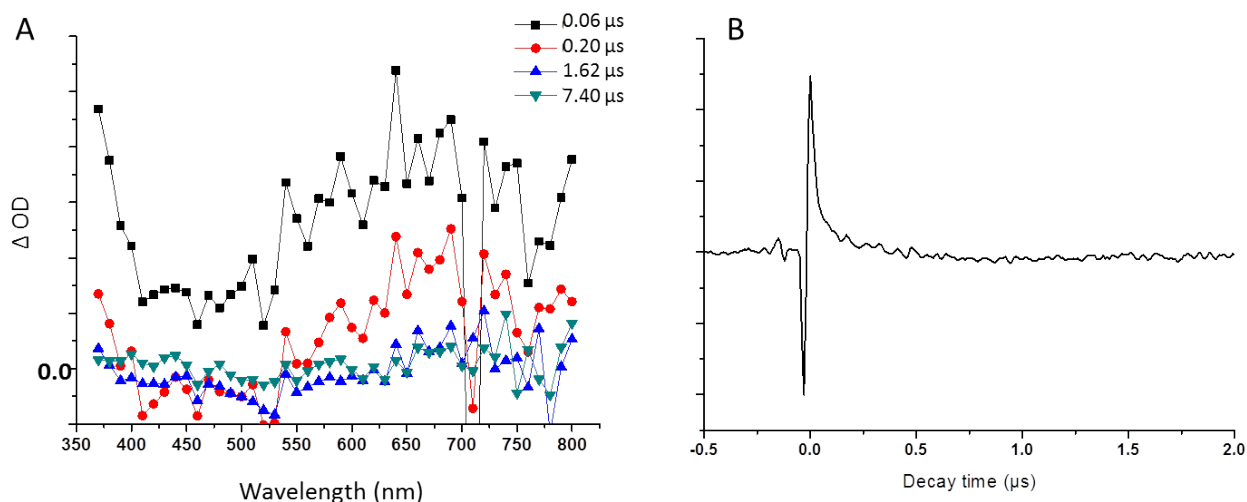
Amino-terephthalic acid + Fe³⁺



6. Transient absorption measurements on MIL-88B(Fe): UV illumination (355 nm)

Transient absorption measurements were performed using the third harmonic (355 nm) frequency of a Nd/YAG laser as the excitation source (10 Hz, 30 mW). A pulsed Xenon lamp in combination with band pass filters was used as probe light. Signals from the photomultiplier tube were captured and digitalized by a Tektronix 2440 transient digitizer and transferred to a PC programmed in the LabView environment.

Time-resolved experiment of MIL-88B(Fe) suspension in DMF with 355 nm excitation: (A) Transient absorption curves (0.06, 0.4, 1.6 and 7.4 μ s after laser pulse), (B) Decay trace at 610 nm detection.



7. Time-resolved transient absorption measurements: VIS illumination (450 nm)

The excitation pulses (450 nm) used to excite the sample were generated by a YAG laser (INDI, Spectra-Physics) equipped with an OPO system. The duration of the pump pulse which is the limiting factor for the time resolution of this setup was determined by measuring the scattered light and found to be 10 ns (FWHM). A broad spectral output of a pulsed Xenon lamp in

combination with band pass filters was used as probe light. The excitation light was focused and overlapped with the probe light beam on the sample by a 300-mm focal length lens. An almost collinear configuration between excitation and white light beams was used. The probe light was collimated, filtered and focused on the entrance slit of a 30 cm focal length computer controlled monochromator. The optical signal was converted to an electrical response by a photomultiplier tube (R928, Hamamatsu), amplified by a four channel amplifier (SR445A) and sent to a computer controlled digital oscilloscope (Agilent Technologies DSO3152A). The kinetic data recorded on the oscilloscope were transferred to the control computer, averaged to increase the signal-to-noise ratio and stored. A custom made Labview software was used to control the instruments, acquire and store the data.