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COMMUNICATION

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

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The photodynamic properties of a series of Fe(III)-MOFs have been examined via redox reactions with *N,N,N',N'*-tetramethyl-*p*-phenylenediamine as electron donor and methyl viologen as electron acceptor. Furthermore, photogeneration of long-lived species in MIL-88B(Fe) has been proven via transient absorption spectroscopy.

Metal-organic frameworks (MOFs) are porous, crystalline inorganic/organic solids that are built up from metal oxide clusters interconnected by organic linkers, resulting in a 3D network.¹ MOFs contain chromophores that can interact with light and upon photo-excitation undergo photochemical processes which make them interesting as possible photocatalysts.^{2,3} Recently, the photocatalytic behavior of certain MOFs has been investigated demonstrating the use of MOFs as potential photocatalysts. For instance, the group of Garcia has investigated the photocatalytic properties of the well-known MOF-5.² Moreover, the photocatalytic activity of MIL-125(Ti) and an Eu-based MOF have been studied for the degradation of organic compounds.^{4,5} Furthermore, Silva et al. have demonstrated that UiO-66(Zr) can act as a photocatalyst for H₂ generation and blue light response has been shown via the use of amino-substituted ligands.^{3,6} Recently, our research group has discovered the possibility of using certain Fe(III)-MOFs, which contain Fe₃-μ₃-oxo clusters, as visible light photocatalysts for water purification.⁷ From these results, it was concluded that decreasing the size of Fe₂O₃ into trimeric iron-oxo clusters, interconnected by aromatic carboxylates, has a favorable effect on the photocatalytic properties of Fe(III)-based materials. In fact, bulk Fe₂O₃ nanoparticles did not show any activity in the testing conditions used, due to the high rate of recombination of the photogenerated charge separated state, which occurs on a nanosecond timescale.⁸ Decreasing the size of Fe₂O₃ into Fe₃-μ₃-oxo clusters will decrease the rate of non-geminate recombination and increase the surface to volume ratio, resulting in a higher probability that reactive

photogenerated electrons and holes reach adsorbed reactants before recombination can take place, leading to an enhanced photocatalytic activity. Furthermore, hole transfer from the clusters to the organic carboxylates could trap the photogenerated holes at the aromatic linkers and thus reduce the rate of electron/hole pair recombination.

In the present study, we provide spectroscopic evidence supporting the photocatalytic properties of these Fe(III)-MOFs. Moreover, upon pulsed illumination, we spectroscopically detected long-lived species (on a microsecond time scale) indicating that electron/hole pair recombination is significantly delayed in these materials. This study focuses on Fe(III)-MOFs that contain Fe₃-μ₃-oxo clusters, such as MIL-88B(Fe), MIL-100(Fe), Basolite F300 and the amino-substituted materials MIL-101(Fe)-NH₂ and MIL-88B(Fe)-NH₂ (SI, Table 1). The results for MIL-88B(Fe) are presented in the main text as this MOF displayed the highest photocatalytic activity in our previous work.⁷ The results of the other Fe(III)-MOFs are in line with those for MIL-88B(Fe) and are presented in the supporting information. The crystal structure of MIL-88B(Fe) can be considered as a periodic repetition of Fe₃-μ₃-oxo clusters in which each iron atom is coordinated by the oxygen atoms of the linker carboxylate groups (terephthalic acid; abbrev. BDC). A detailed description of the experimental procedure for the photocatalytic degradation of *N,N,N',N'*-tetramethyl-*p*-phenylene-diamine (TMPD) and methyl viologen (MV²⁺) dichloride can be found in the SI (section 2 and 3). Detection of the radical cation of TMPD and the radical monocation of MV²⁺ was performed with UV-Vis spectroscopy. For the time-resolved measurements, an argon purged MOF suspension in DMF with an optical density of about 0.2 in the region 350 – 450 nm was prepared. The first set of time-resolved luminescence experiments was carried out with the third harmonic (UV light: 355 nm) of a Nd/YAG laser at the Instituto de Tecnología Química in Valencia (Spain); the second set used a home-built set-up at the department of chemistry, KU Leuven (Belgium) that provided excitation pulses of visible light (450 nm) generated by an OPO pumped by a YAG laser (see SI for details).

The photocatalytic behavior of the Fe(III)-MOFs was investigated via both photo-induced oxidation and reduction reactions. First, *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) was added to a deaerated MOF suspension in acetonitrile and illuminated with a solar simulator for about 15 min. TMPD is a good electron donor ($E_0 = +0.27$ V vs. SHE) and generates, upon electron transfer, the corresponding blue colored radical cation.⁵ The amine radical cation remains in solution and appears to be a long-lived species. The formation of the blue TMPD radical cation is shown in the inset of Figure 1. Moreover, the presence of the TMPD radical cation was also determined via UV-Vis spectroscopy; the absorption spectrum shows two clear peaks at 560 and 615 nm (Figure 1), characteristic of this species.⁵

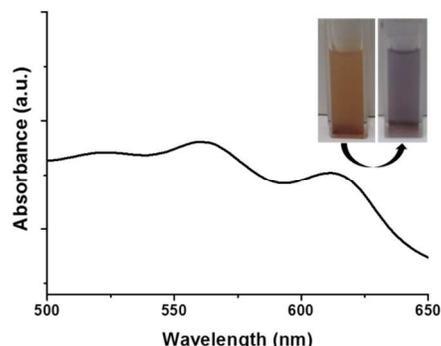


Fig 1 Photo-induced charge transfer process of TMPD with MIL-88B(Fe): the absorption spectrum of the TMPD radical; inset: photographs before and after illumination, illustrating the formation of the blue colored TMPD radical.

This observation supports the formation of the radical cation by an electron transfer from the HOMO of TMPD (donor) to the hole on MIL-88B(Fe), which acts as an electron acceptor. Similarly, one could expect that upon addition of a strong electron acceptor the photogenerated electrons in the Fe(III)-MOF can be captured. We tested this hypothesis by adding methyl viologen (MV^{2+}) to a suspension of MIL-88B(Fe). MV^{2+} has been widely used in photochemistry to trap electrons mainly because the corresponding monoradical cation can easily be identified by its typical blue colour and characteristic optical spectrum.⁹ Upon irradiation of a deaerated suspension of the MOF in DMF containing $MVCl_2$, by the third harmonic (355 nm) of a Nd/YAG laser for about 15 min, a blue color became visible (see inset Figure 2). The absorption spectrum obtained by UV/Vis spectroscopy (Figure 2) clearly showed absorption bands with maxima around 400 nm and 625 nm, characteristic for MV^{2+} -monocations.

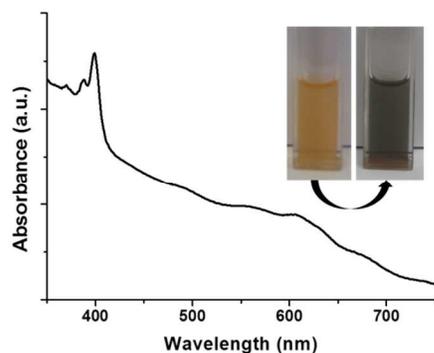


Fig 2 Photo-induced charge transfer process of MV^{2+} with MIL-88B(Fe): the absorption spectrum of the MV^{2+} radical; inset: photographs before and after illumination, illustrating the formation of the blue colored MV^{2+} radical.

These data show that it is possible to capture the photogenerated holes and electrons and that they are both accessible at the surface of MIL-88B(Fe) where they remain available to oxidize TMPD or reduce MV^{2+} . These experiments were also performed with the other Fe(III)-MOFs under study (MIL-100(Fe), Basolite F300 and amino-substituted MIL-88B(Fe) and MIL-101(Fe)) leading to similar results, which are listed in the SI (section 3 & 4). In contrast, reaction of TMPD or MV^{2+} with pure Fe_2O_3 nanoparticles did not lead to any color change.

Steady-state absorption and reflection spectra were taken to characterize the spectroscopic properties of MIL-88B(Fe). The absorption spectrum of a MIL-88B(Fe) suspension in DMF consists of a broad band with an onset at 750 nm and a shoulder around 550 and 375 nm, analogous to the diffuse reflectance absorption spectrum of the solid MIL-88B(Fe) (SI, section 1.2). A solution of the pure terephthalate linker is characterized by a band peaking at 285 nm and a shoulder at 300 nm, which can be attributed to a π - π^* transition (SI, section 2). By analogy with the spectra of other Fe(III)-complexes the broad long wavelength band of the Fe(III)-MOF can be attributed to a LMCT transition.¹⁰ The long wavelength *d-d* transitions of Fe(III)-complexes have a small oscillator strength as they are Laporte and possibly also spin forbidden.

The excited LMCT state of the $Fe_3-\mu_3$ -oxo cluster can be considered as a cluster containing one Fe(II)-ion, two Fe(III)-ions and a hole which is possibly delocalized towards the linker. The similarity of the diffuse reflectance absorption spectra of the $Fe_3-\mu_3$ -oxo clusters and the Fe(III)-MOF suggests that in the latter the LMCT transition also populates an excited state where the hole is situated on the linker while the electron still remains with an iron in the +II state.

In order to obtain a better insight into the photochemical processes taking place upon excitation of MIL-88B(Fe), the transient absorption spectra of a model system consisting of a mixture of the $Fe(NO_3)_3$ and the linker BDC dissolved in DMF were recorded. This mixture shows besides the absorption of the linker a broad tail with onset at 580 nm which can be attributed to the LMCT transition (SI, section 2.3). This suggests that the terephthalate anions can coordinate to the Fe(III)-ion forming a metal-carboxylate complex with a structure related to the local coordination sphere of Fe(III) in MIL-88B(Fe). Upon excitation of a solution of only $Fe(NO_3)_3$ or the BDC linker in DMF no transient absorption signal is recorded 0.4 μ s after excitation with 355 nm light (Figure 3A, black curve). However, when adding Fe(III)-ions to the linker solution, a clear broad and positive transient absorption band is observed indicating the formation of an intermediate species that can be related to an interaction between the terephthalate moiety and Fe(III)-ions (Figure 3A, orange curve). In order to obtain more information about the nature of the species responsible for the transient spectrum, quenchers were added to the solution. While upon the addition of the electron donor triethylamine the intensity of the transient spectrum clearly drops, a slight increase was observed when oxygen, which could act as electron acceptor, was added. This suggests that the observed transient absorption is due to the hole generated on the linkers by exciting the LMCT transition of the complex of linkers and Fe(III)-ions. The long lifetime of this hole (approx. 2 μ s) indicates that part of the generated holes move away from the position where they are generated and become trapped at a linker connected to the cluster. The absence of a clear absorption signal of the Fe(II)-ion is no surprise as the long wavelength *d-d* transitions of this ion are Laporte forbidden and as Fe(II)-complexes have no MLCT absorption band in the visible.

Similar experiments were also performed with Fe(III) and on the one hand trimesic acid (BTC), representing the interaction in MIL-

100(Fe) and Basolite F300, and on the other hand amino-substituted terephthalic acid ($\text{NH}_2\text{-BDC}$), representing amino-substituted

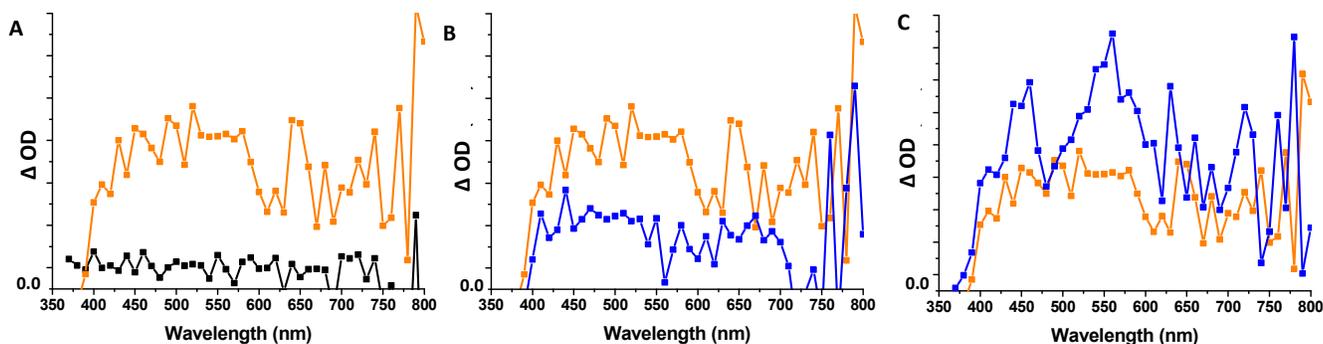


Fig 3 Transient absorption spectra (recorded 0.4 μs after 355 nm laser excitation) of BDC in DMF: [A] black: pure BDC solution, orange: BDC + Fe^{3+} -ions after stirring for 4 h; (B) orange: BDC + Fe^{3+} -ions after stirring (similar to orange curve in (A)), blue: after addition of electron donor, TEA; (C) orange: BDC + Fe^{3+} -ions after stirring (similar to orange curve in (A)), blue: after addition of electron acceptor O_2 .

MIL-88B(Fe) and MIL-101(Fe). The results obtained for both series, which can be found in the SI (section 5) resulted in analogous conclusions.

Further, time-resolved measurements of MIL-88B(Fe) in DMF suspension were performed to identify the photocatalytic mechanism in this Fe(III)-MOF. Firstly, when this MOF suspension in DMF was excited with a pump pulse of 355 nm, a transient absorption with features similar to that of the mixture of Fe(III) and the linker was observed (see SI, section 5) which decayed within 2 μs . In analogy to the signal observed for the mixture of $\text{Fe}(\text{NO}_3)_3$ and BDC, we can also attribute this signal to the radical cation of the carboxylate ligand. The fast decay of this signal can be due to the creation of a large number of electron/hole pairs in MIL-88B(Fe) which undergo non-geminate recombination. In this context, during the photocatalytic experiments it was observed that a too high irradiation flux indeed results in a negative effect on the photocatalytic activity possibly due to an increased non-geminate recombination.

However, upon using a pump pulse of 450 nm a more slowly decaying negative transient (Figure 4) is observed with onset at 800 nm and minima at 525 and 675 nm. This could be attributed to the depletion of the ground state of the MOF reducing the absorption by the LMCT transition. This strong negative depletion signal could possibly cancel out any weak positive absorption bands indicative of an intermediate metal-ligand charge transfer species.

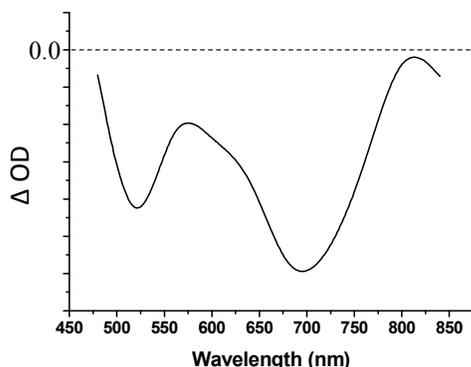


Fig 4 Transient absorption spectrum (recorded 1 μs after 450 nm laser excitation) of MIL-88B(Fe) suspension in DMF.

Figure 5 shows the decay traces which could be well fitted via global analysis with three different time constants of 40 ns, 5 μs and 33 μs . Since no positive signal is directly observed, no excited

species could be straightforwardly evidenced. However, the presence of the slowly decaying components (5 μs and 33 μs) that are indicative of additional delay in the ground state recovery suggests that the holes are captured in traps from which recombination with electrons on the Fe(II) is slowed down significantly. These data suggest that upon excitation at 450 nm the hole is not residing on the carboxylate ligand but remains on the $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ clusters. While excitation at 355 nm generates hot holes for which hole transfer to the carboxylate ligands can compete with vibrational relaxation and trapping on the $\text{Fe}_3\text{-}\mu_3\text{-oxo}$ clusters, this is no longer the case upon excitation at longer wavelengths creating less energetic holes. This assignment is supported by the fact that the depletion signal at 720 nm, i.e. in the red tail of the LMCT transition, decays clearly more slowly than the signal at 640 nm. The transition at 720 nm corresponds to an LMCT transition in which the hole goes to a higher lying (more stabilized) level from which escape and recombination with the electron on the Fe(II)-ion are slower.

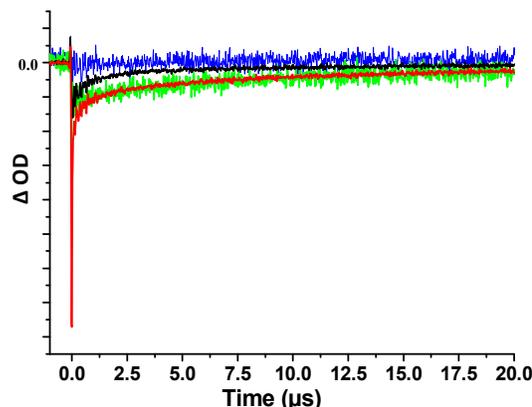


Fig 5 The decay profiles of the transient spectrum monitored at 520 (red), 640 (black), 720 (green) and at 800 nm (blue).

The slowed down recovery of the negative signal points to a multi-step charge recombination process most likely involving several linker units. The occurrence of long-lived species confirms that the different clusters in the MIL-88B(Fe) are electronically connected to each other enabling the charge carriers to transfer across these clusters to the surface and thus delaying charge carrier recombination.

Conclusions

In this study, the photocatalytic properties of a series of Fe(III)-MOFs are confirmed through redox reactions with on the one hand *N,N,N',N'*-tetramethyl-*p*-phenylene-diamine as electron donor and on the other hand methyl viologen dichloride as electron acceptor. Furthermore, via transient absorption spectroscopy, the generation of long-lived species is proven indicating that the charge carrier recombination in these Fe(III)-MOFs is actually delayed. Due to the complexity of the electron transfer processes occurring in the Fe(III)-MOFs, further investigation of the generated species and intermediates is required for a better understanding of the mechanism and hence the development of such materials for their application as visible light photocatalysts.

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Notes and references

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/c000000x/

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