

Femtosecond Pump – Probe Spectroscopy Reveals the Photo-excited State and Charge Transfer of a Photocatalytic Metal-Organic Framework.

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Abstract: Metal-organic frameworks are nanoporous materials recently shown capable of photocatalysis. To optimize them as photocatalysts we need to understand the charge transfer to species included in the pores. We measured for the first time with femtosecond pump-probe spectroscopy the metal-organic framework NH₂-MIL-125. We found that after photo-excitation the hole resides on –NH₂. Charge transfer from the MOF to an occluded molecule capable to shuttle single charges to a reaction centre is extremely fast (< 200 fs) while charge recombination only occurs on the ns-μs time scale.

Introduction

Photocatalysis can be used to harvest solar energy and to enable visible-light driven organic synthesis. The use of metal-organic frameworks (MOFs) for this purpose is receiving more and more attention [1,2]. Metal-organic frameworks consist of metal ions linked together into a 3-D structure by ligands that bind to several metal ions. The resulting structure has crystalline pores smaller than 4 nm. Recently several metal-organic frameworks have been shown to be able to reduce CO₂, evolve H₂ and perform organic transformations photocatalytically [1,2]. In metal-organic frameworks the possibilities are virtually endless due to variation of organic ligands and inorganic nodes in the frameworks, and the inclusion of additional catalytic activity by embedded well-defined catalytic centres [3]. A fundamental understanding of the photocatalytic process has the potential to move this field forward greatly.

Vital to the performance of a MOF as photocatalyst is the transfer of photo-excited charges to species occluded in the pores. These can either directly be the reactants or well-defined catalytic centres trapped in the pore cavities. As such efficient charge transfer is at the core of efficient photocatalytic conversions of these materials. The most heavily studied photocatalytic metal-organic framework is MIL-125 which consists Ti₈OH₄O₄ clusters linked into a porous 3-D framework by terephthalic acid derivatives [2]. Here we report the charge transfer processes associated with NH₂-MIL-125 (scheme 1a,b). Our aim is to elucidate the pathway and life times of the photo-excited electron and hole to formulate strategies for improved MOF-based photocatalysts. To this end we used femtosecond visible pump – mid-IR probe and visible pump – visible probe spectroscopy. We found that the photo-excited hole resides on amino group of NH₂-MIL-125. We also included a molecule inside the pores that mimics a pair of tyrosine and histidine. This pair of amino acids provides the last shuttle of single charges to the oxygen evolution centre in natural photosynthesis [4]. Indeed, we found that charge transfer to this phenolic molecule was very fast (< 200 fs).

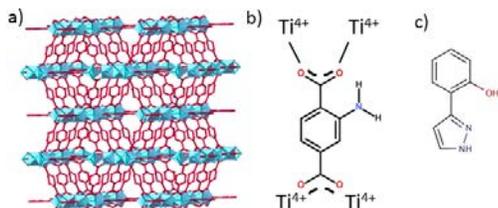
Experimental

For the visible pump- visible probe spectroscopy measurements, samples were excited with 400 nm pump pulses from an OPA (Light Conversion ORPHEUS) after a regenerative amplifier (Light Conversion PHAROS). Transient absorption spectra were recorded with an Ultrafast Systems HELIOS spectrometer using broadband probe pulses from a sapphire or CaF₂ crystal pumped by 1030 nm. In the visible pump – mid IR probe experiments, laser pulses (800 nm, 50 fs) from a regenerative amplifier (Spectra-Physics, Spitfire ace amplifier) are converted to mid infrared pulses with a home-build optical parametric amplifier (OPA). As pump pulse the second-harmonic (400 nm, via a BBO crystal) of the output of the Spitfire amplifier is used. A probe and reference beam are spectrally dispersed onto a mercury cadmium-telluride array detector. In both set-ups a variable delay between probe and pump pulses was introduced to yield difference absorption spectra, as a function of pump – probe delay and probe energy.

Results

To understand the nature of the photo-excited MOF we also used a mid-IR probe, and probed the region from 1250 – 3550 cm⁻¹ both in tetrachloroethane and D₂O. It has been shown before that the photoexcited electron reside on Ti⁴⁺ leading to Ti³⁺ [5]. The vibrations of the bonds with the N-atom (C-N stretch, and N-H stretch vibrations) of

the amino group lead to the largest changes in the transient absorption spectra. For example, in figure 1, the ground state bleach/stimulated emission of the ground state of the symmetric and asymmetric N-H stretch vibrations can be seen by the negative ΔOD at 3365 and 3485 cm^{-1} . The excited state absorption corresponds to positive red shifted ΔOD at 3340 cm^{-1} , an a broad increase of absorption in the 3000 -3600 cm^{-1} range. This means that one N-H bond has significantly weakened. We conclude that the hole reside on the aminogroup. From these results it could be postulated that water with its ability to stabilize protons would enhance the charge separated state. Nonetheless, we found that we found that for both tetrachloroethane and D_2O a tri-exponential decay of the excited state occurred in the 1230-2000 cm^{-1} range with the same life times, namely 10 ps, 1,2 ns and ~ 200 ns.



Scheme 1 a) MIL-125, b) amino-terephthalate c) 2-(1H-Pyrazol-3-yl)phenol (HPP)

In those regions, the spectral features were, apart from solvatochromic shifts, also the same for both solvents.

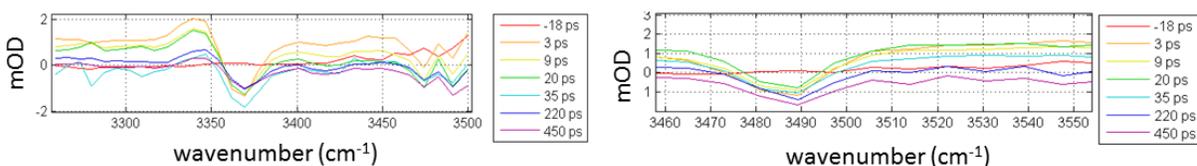


Figure 1. transient mid-IR spectra of NH2-MIL-125 in tetrachloroethane from 3250-3550 cm^{-1} .

As mentioned, Ti^{4+} is reduced to Ti^{3+} after photo-excitation, and NH2-MIL-125 containing Ti^{3+} shows a broad increase in absorbance in the visible range [5]. Our transient absorbance measurements confirm this, and the found life times of 10 ps, 1 ns and a significantly longer component, correspond well with the transient mid-infrared spectra (figure 2 left). The ultimate goal is to achieve fast charge transfer from the MOF to occluded species. Therefore we placed 2-(1H-Pyrazol-3-yl)phenol (HPP, see scheme 1c) in the pores. This molecule is capable to undergo a reversible one-electron oxidation on the phenolic part aided by proton transfer from the hydroxyl to the basic nitrogen in the vicinity. The transient absorbance (TA) spectra of NH2-MIL-125 (fig. 2 left) and HPP@NH2-MIL-125 (fig. 2 right) are very different: the HPP@NH2-MIL-125 spectra has higher ΔOD values and different wavelengths of maximum absorbance. The positive ΔOD in the HPP@NH2-MIL-125 spectra is due to the negatively charged MOF and/or positively charged HPP. The rise in absorbance by HPP@NH2-MIL-125 occurs before the time resolution of the set-up (~ 200 fs). Thus hole transfer from the MOF to HPP is thus extremely fast. The life time before recombination is significantly larger than the time limit of the measurement (3ns, fig. 2 right).

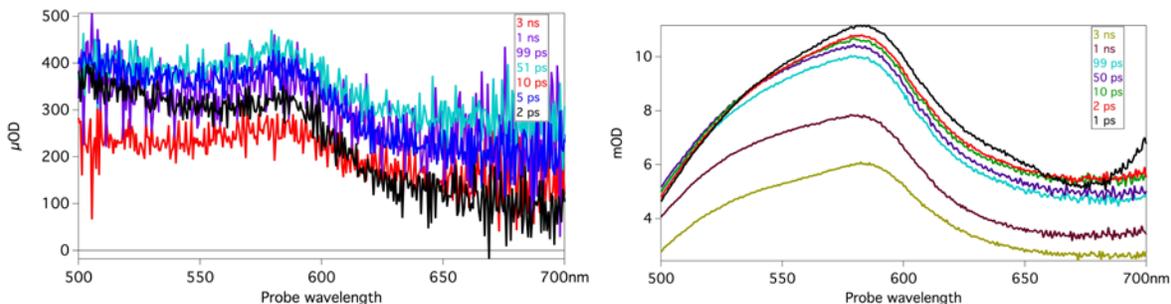


Figure 2. Transient absorption spectra for NH2-MIL-125(left) and HPP@NH2-MIL-125 (right) in DMF.

Conclusion

We measured for the first time with femtosecond pump-probe spectroscopy the photo-excited state and charge transfer of a metal-organic framework, namely the photocatalytically active NH2-MIL-125. We found that the after photo-excitation the hole resides on the amino group. The charge transfer to a molecule capable to shuttle single charges in a photosynthetic scheme was extremely fast (< 200 fs) while charge recombination is only complete on the nanosecond-microsecond time scale.

References

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