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Semiconductor Behavior of a Metal-Organic Framework (MOF)

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Abstract: Upon light excitation MOF-5 behaves as a semiconductor and undergoes charge separation (electrons and holes) decaying in the microsecond time scale. The actual conduction band energy value was estimated to be 0.2 V versus NHE with a band gap of 3.4 eV. Photoinduced electron transfer processes to viologen generates the corresponding viologen radical cation, while holes of MOF-5 oxidizes *N*,*N*,*N*′,*N*′-tetramethyl-*p*-phenylenediamine. One application investigated for MOF-5 as a semiconductor has been the shape-selective photocatalyzed degradation of phenol in aqueous solutions.

Keywords: charge separation · electron transfer · metal-organic frameworks · photocatalysis · semiconductors

Introduction

Metal-organic frameworks (MOFs) are crystalline hybrid inorganic/organic solids with structures which are composed of clusters of a few metallic atoms held in a three-dimensional structure by organic linkers.[1–4] The remarkable crystallinity of MOF structures defining pores and cavities in the nanometric scale and the accessibility to guests of the high internal volume of these materials make MOFs analogous in many respects to zeolites. MOFs are attracting considerable attention as gas adsorber (H_2, CH_4, CO_2 etc.),[5–7] and application of MOFs in catalysis is a topic of current interest.[3,8–11] One of the most common materials, denoted as MOF-5,[12] contains clusters of Zn_4O located at the corners of the structure that are connected orthogonally to six units of terephthalate.

Zeolites are the most important solid catalysts.[13] The chemical and thermal robustness of their aluminosilicate framework and the ease in which acid sites can be formed are the main reasons for the wide catalytic use of zeolites in petrochemistry and fine chemicals industry.[13–16] In sharp contrast, the promising potential of zeolites and related crystalline microporous materials as advanced functional materials has been hampered by the inertness of the aluminosilicate structure and the difficulty to excite this framework to obtain measurable responses.

In contrast to zeolites, MOFs contain an organic component forming part of the solid structure. The presence of this organic component may make MOFs more versatile than zeolites for developing intelligent materials that can exhibit a response due to external stimuli. For example, while pure zeolites and aluminosilicates in general do not absorb UV radiations of wavelengths longer than 220 nm, MOF-5 has an absorption spectrum with an onset at 450 nm. In this context, this material can undergo photochemical processes upon photoexcitation of the organic linker. Thus, Zecchina and co-workers[17] have reported recently the observation of photoluminescence from MOF-5 upon excitation of the terephthalate units. In contrast to this, the lack of light absorption precludes observation of any emission from pristine zeolites.

The present work provides experimental evidence supporting the behavior of MOF-5 as semiconductor. By comparison with the photochemistry of aqueous terephthalate solutions, we have observed the photochemical generation of a charge-separated state with the photoejection of electrons from excited terephthalates. The charge-separated state decays in the microsecond time scale and can be useful for the development of photocatalytic applications of MOF-5.

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Results and Discussion

Photoluminescence spectroscopy: Excitation and emission spectra of MOF-5 powder purged with dry N_2 are shown in Figure 1. Upon excitation at 350 nm, an emission is recorded with a maximum at λ_{em} 540 nm. The excitation spectrum recorded monitoring at the maximum emission wavelength shows a band at 350 nm, which coincides reasonably well with the UV/Vis absorption spectrum. The curve fitting of the temporal profile of the emission gives a half life of 600 ns.

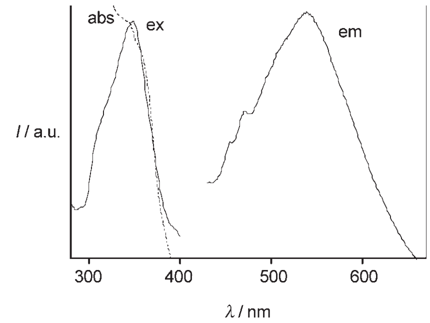


Figure 1. Emission (EM, λ_{exc} = 350 nm), excitation (ex, λ_{em} = 540 nm) and diffuse reflectance (abs) spectra recorded for a N_2-purged MOF-5 sample.

In order to rule out any possible photodegradation/photodecomposition (decarboxylation, structure collapse, etc.) of the solid during irradiation, photostability of MOF-5 was checked before performing the laser flash photolysis study. Aimed at this purpose, MOF-5 was submitted to irradiation with a 1000 W mercury lamp through Pyrex for 5 h without observing any significant change in the X-ray diffractogram of the sample after irradiation. The X-ray diffractogram of the MOF-5 after irradiation is exactly the same that before irradiation, as no new peaks can be observed. This fact allows us to rule out the occurrence of photodegradation in a significant extent. Given the resolution of our XRD instrument a maximum of 10% of crystallinity loss can be estimated.

Laser flash photolysis: The transient absorption spectrum in the microsecond timescale of MOF-5 recorded after 355 nm laser excitation is shown in Figure 2. The transient spectrum is dominated by a continuous absorption peaking at about 780 nm. An additional sharp negative absorption at 370 nm is also observed, corresponding to the bleaching of the MOF-5 ground state absorption. The temporal profiles of the signal monitored at 370 and 780 nm are shown in the inset of Figure 2. All the signals recorded at different wavelengths from 500 to 840 nm have the same temporal profile, which indicates that the continuous absorption from 500 to 840 has an homogeneous distribution of transient species (most probably two as deduced from the temporal fitting of the signals vide infra). The recovery of the signal at 370 nm can be adjusted to a monoexponential growth, with a lifetime of 5 μs. The best fit of the signal at 780 nm was obtained with two exponential decays with lifetimes of 5 and 30 μs, which indicates that this band has contributions of (at least) two species, one shorter and other longer lived. The short-lived species absorbing at 780 nm and the recovery of the ground state absorption at 370 nm have the same kinetic behavior indicating that the transient responsible for the short-lived (5 μs) absorption at 780 nm decays to the MOF-5 ground state.

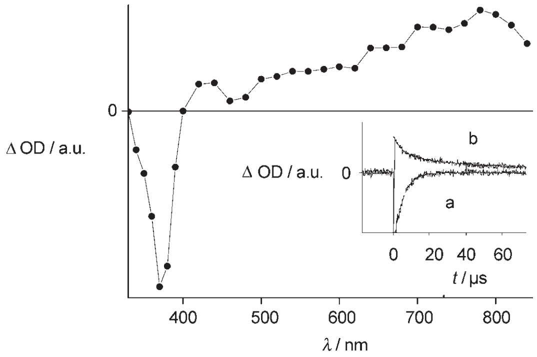


Figure 2. Time-resolved diffuse reflectance UV/Vis spectrum of a N_2-purged sample of MOF-5 recorded 3 μs after 355 nm laser excitation. The inset shows the temporal profiles of the transient spectrum monitored at a) 370 and b) 780 nm.

To get evidence about the nature of the species responsible for the transient spectrum, we monitored the signal temporal profile purging the solid sample with O_2 and N_2O. O_2 did not cause any effect on the signal compared with that recorded under N_2. However, the transient signal monitored at 780 nm was quenched by N_2O purging of the MOF-5 sample. N_2O is a well known electron quencher.[18] Thus, observation of the effect of N_2O in the temporal profile of the 780 nm signal supports the assignment of the transient species as being due to electrons. The broadness and λ_{max} of the signal is also in agreement with reported spectra of the hydrated electron in zeolites and other porous oxides.[19]

To better understand the photochemical processes taking place in the MOF-5, we have studied the photochemistry of an aqueous solution of sodium terephthalate which is the organic moiety forming part of the structure of the material. Laser excitation of an aqueous solution of sodium terephthalate at 355 nm does not lead to the observation of any transient. In contrast, 266 nm excitation allowed us to record the transient absorption spectrum shown in Figure 3. This transient exhibits maxima at 300, 400 and >800 nm. The two bands peaking at 300 and 400 nm are quenched by oxygen, indicating that they correspond to a triplet species (see Supporting Information). The lifetime of terephthalate triplet excited state obtained from the monoexponential fit of the decay monitored at 400 nm is $\tau = 47$ μs. The band with maximum wavelength beyond 800 nm is characteristic of the solvated electron in water[19] and indicates that terephthalate is able to undergo photoinduced electron ejection to the

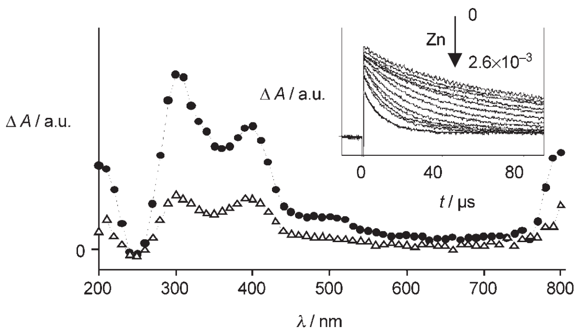


Figure 3. UV/Vis transient absorption spectra of a N_2-purged aqueous solution of sodium terephthalate (1.1×10^{-4} M) recorded 4 µs after 266 nm laser excitation before (●) and after (△) the addition of an aqueous solution of Zn^{2+} (2.6×10^{-3} M). The inset shows the temporal profile of the signal monitored at 400 nm recorded for a N_2-purged aqueous solution of sodium terephthalate upon addition of increasing amounts of Zn^{2+} from 0 to 2.6×10^{-3} M.

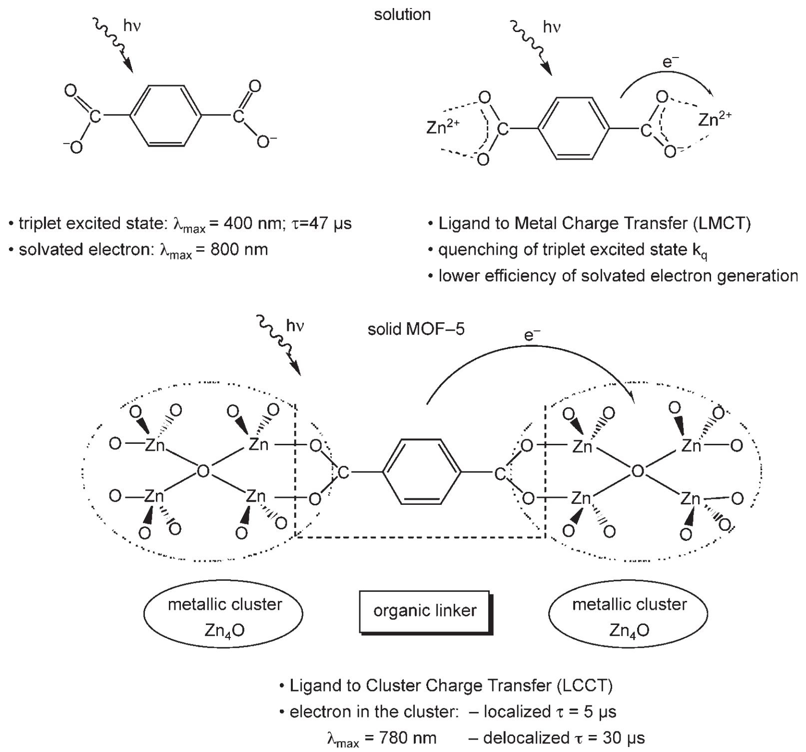
medium. This electron photoejection has been frequently observed for other carboxylate anions in water.[18]

The addition of Zn^{2+} to an aqueous solution of terephthalate causes a decrease of the maximum initial intensity of the signals corresponding to terephthalate triplet excited state accompanied by a faster decay. These features can be explained by the occurrence of a combination of a static and dynamic quenching of terephthalate triplet excited state by Zn^{2+}. Static quenching would arise from those terephthalate molecules having preassociated Zn^{2+}. These observations upon addition of increasing Zn^{2+} concentration proves the interaction between the terephthalate moiety and the Zn^{2+} (see inset of Figure 3). The rate constant k_q for the triplet quenching by Zn^{2+} was $k_q = 3.9\times10^{7}\,\text{M}^{-1}\,\text{s}^{-1}$ and as a result of Zn^{2+} quenching the photogenerated species formed in solution could correspond to a geminate pair of Zn^{+} and terephthalate radical monoanion, the latter having a half life of 9 µs. Also the signal at $\lambda_{max} > 800$ nm decreases intensity in the presence of Zn^{2+}, indicating that less solvated electrons are being generated as consequence to the transfer to the Zn^{2+}. Taking into account the electron donor capability of the terephtalate dianions upon photoexcitation in water, the quenching by Zn^{2+} can be considered as an electron transfer from the terephtalate excited state to the Zn^{2+}. In concentrated aqueous solutions, some of the terephthalate anions can coordinate to the Zn^{2+} cation forming a metal–carboxylate complex with a structure related to that occurring in the MOF-5. Then, the interaction between the terephthalate unit and the Zn^{2+} can be defined as a ligand-to-metal charge transfer (LMCT).

The laser flash photolysis study in aqueous solution is relevant to propose a rationalization to the observed photochemistry of MOF-5. The crystal structure of MOF-5 can be considered as a periodic repetition of Zn_4O clusters in which each Zn cation is coordinated to the oxygen atoms of the terephthalate carboxylate groups. The solid framework is therefore maintained by the metal–carboxylate interaction that in solution leads to photoinduced electron transfer from terephthalate in its excited state to Zn^{2+}. In a related precedent, Zecchina and co-workers[17] have proposed that this photoinduced electron transfer from the terephthalate antenna to the Zn_4O cluster is the origin of the photoluminescence spectrum. We propose that the emissive species is the singlet excited state corresponding to a state of charge separation formed upon excitation of the complex. Emission will arise from the collapse of this singlet excited state to the ground state by back electron transfer with a half life of 600 ns. Alternatively, long distance charge separation will produce longer lived transients that are the species being actually detected by laser flash photolysis. The transient absorption spectrum obtained upon laser excitation of MOF-5 showed the presence of photoejected electrons. The maximum wavelength of this absorption band is 780 nm which differs from that of the solvated electron in aqueous solution ($\lambda_{max} > 800$ nm) because the environment of the electron in the solid material is different, electrons being located at the Zn_4O^{6+} clusters or in the intracrystalline void space of the material maybe solvated by residual solvent molecules. The decay of this absorption corresponding to photoejected electrons fits well to a suite of two consecutive monoexponential decays with two different lifetimes. The first one, 5 µs, could correspond to electrons localized closest to the terephthalate units in MOF-5. The second type of photoejected electrons having a half life of 30 µs could be assigned to more delocalized electrons, probably populating states corresponding to the conducting band of the global structure of the MOF-5. The occurrence of long-lived species would confirm that the different clusters of the MOF-5 are electronically connected to each other.

The geminated radical ion pair species detected in solution photochemistry of terephthalate in the presence of zinc ($\lambda_{max} = 400$ nm; $\tau = 9$ µs) has not been observed in the transient absorption spectrum of the solid MOF-5 due to the crystal structure and spatial ordering of the solid compared with solution. In solution the electron is transferred to an individual metal ion while in the solid state the electron is transferred to a metallic Zn_4O cluster or even to the conduction band of the solid, thus behaving as a semiconductor. Scheme 1 summarizes the similarities and differences between the photochemistry taking place in solution and in the solid material.

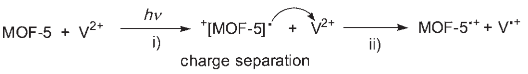
Trapping of electrons and holes: Based on the above rationalization of MOF-5 photochemistry, we wanted to provide examples in which the semiconductor behavior of MOF-5 can be revealed. For this purpose, we submitted to visible light irradiation using a solar simulator a suspension of MOF-5 in an aqueous solution containing methyl viologen (V^{2+}) dichloride. Viologens are well known electron acceptors and the corresponding radical cations ($V^{\bullet+}$) can be safely characterized by its corresponding optical spectrum. In some cases in which the radical cation is sufficiently stable (lifetime longer than seconds), they can even be observed visually by the development of blue color. For this reason, viologens are widely used as photochromic compounds.



Scheme 1. Photophysical processes that occur after the irradiation of the MOF-5 solid material and an aqueous solution containing the terephthalate unit and Zn^{2+}.

Given the microporosity of MOF-5, it was assumed that V^{2+} will diffuse from the solution through the internal voids of MOF-5. Upon solar light irradiation of the suspension, the appearance of the blue color characteristic of the photogeneration of $V^{\cdot+}$ was observed. Figure 4a shows some selected photographs of the visual changes occurring upon illumination. Noticeable was that the solution remained colorless and that the blue color was only observed on the MOF-5 powder. Control experiments exposing to illumination under the same conditions aqueous solutions of V^{2+} or an aqueous suspension of V^{2+} and silica did not lead to observation of any color change. In contrast to these blank controls, analogous experiments using titanium dioxide as semiconductor exhibited the same behavior as MOF-5.

These observations can be easily rationalized assuming that V^{2+} ions from the solution diffuse through the MOF-5 micropores becoming partly adsorbed. Absorption of solar irradiation (from 350 to 400 nm) by the MOF-5 framework will produce charge separation and the generation of photoejected electrons. These electrons will reduce V^{2+} to $V^{\cdot+}$. Equation (1) summarizes our proposal. This sequence of events parallels those occurring in TiO_2.



$$\text{MOF-5} + V^{2+} \xrightarrow[\text{i)}]{h\nu} \underbrace{{}^{+}[\text{MOF-5}]^{\cdot} + V^{2+}}_{\text{charge separation}} \xrightarrow[\text{ii)}]{} \text{MOF-5}^{\cdot+} + V^{\cdot+} \qquad (1)$$

i) photoinduced charge separation
ii) electron transfer

Following with the purpose of showing the semiconductor behavior of MOF-5, a suspension of MOF-5 in a deaerated acetonitrile solution of *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine was irradiated with Pyrex filtered light (Figure 4b). The sample became intense blue after irradiation. The blue color remains in the solution even one week after irradiation. A reasonable explanation for this fact is that upon irradiation of MOF and charge separation, an electron-transfer process takes place from the amine, which acts as an electron donor, to the hole of the MOF-5, which acts as an electron acceptor. As a result, the formation of the phenylenediamine radical, responsible of the blue color, is observed. The amine radical remains in solution and it is very long-lived (more than one week). Analogous behavior has been observed using TiO_2 which is in agreement with the semiconductor behavior of both solids. A control irradiating a solution of the amine does not change color upon irradiation under the same conditions; this observation indi-

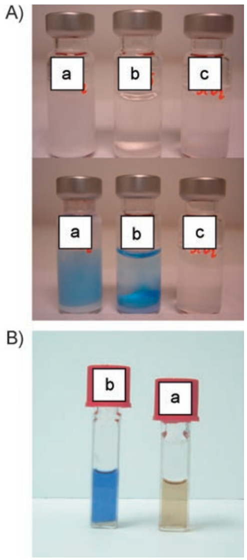


Figure 4. A) Photographs showing a) TiO_2 (P-25), b) MOF-5, c) and SiO_2 (Aerosil) solid samples in contact with aqueous solutions of V^{2+} dichloride, before (top) and after (bottom) irradiating with a solar simulator (525 W) through an AM1.5 filter for 10 min. B) Photograph showing a deaerated solution of *N*,*N*,*N′*,*N′*-tetramethyl-*p*-phenylenediamine in a) the absence and b) the presence of MOF-5 upon 355 nm laser irradiation.

cates that the aromatic amine in the absence of solid does not generate the radical. Another control experiment was performed irradiating a deaerated solution of the phenylenediamine in the presence of amorphous silica. Although in this case the suspension turned slightly blue, the solution turned colorless shortly after irradiation (2 min), in sharp contrast to the behavior observed for MOF-5 and TiO_2 (weeks).

The band gap of MOF-5 as a semiconductor was simply calculated from the plot of the reflectance versus the radiation energy giving a value of 3.4 eV. Determination of the energy value of the conduction band or valence band in contact with the neutral aqueous solution could not be obtained by electrochemical measurements due to the limitation of the available potential window in water. In order to get an estimation of these energy values we proceeded to construct a photovoltaic cell using MOF-5 as a semiconductor. The position of the conduction band was determined by comparison of the open circuit voltage obtained for a photovoltaic cell constructed with I_2/I^- as electrolyte and TiO_2 or MOF-5 as the photoactive semiconductor. The conduction band position for TiO_2 (−0.1 eV) has been reported in the literature.[20] The conduction band energy of MOF-5, 0.2 V versus NHE, has been estimated taking into account that the photovoltaic cell with MOF-5 gives a value of open current voltage that is 0.3 V lower than the one obtained for a solar cell with TiO_2. This estimation is based on the assumption of identical internal resistance for TiO_2 and MOF-5 photovoltaic cells. Figure 5 shows the estimated energy values for conduction and valence bands of MOF-5. With respect to these values in comparison to TiO_2 standard, the similarity of the band gap is remarkable which allows excitation of MOF-5 in similar UV spectral window as TiO_2. In the case of MOF-5 the conduction and valence band is shifted to more positive potentials than TiO_2. In other words, the charge-separated state of MOF-5 has a less-reducing conduction band electron and somewhat more oxidizing valence band hole than TiO_2.

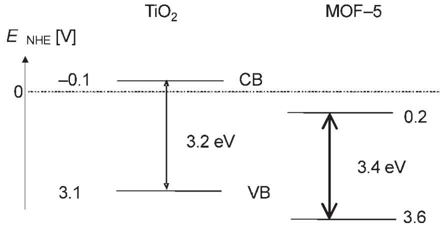


Figure 5. Calculated values of the band gap and position of the conduction and valence bands for MOF-5 in comparison with those of TiO_2.

Photocatalytic activity of MOF-5: A preparative experiment to demonstrate the behavior of MOF-5 as a microporous semiconductor was performed by carrying out a preliminary study of the photocatalytic degradation of phenol in aqueous solutions. One well established application of semiconductors is their use as photocatalysts to effect the degradation of organic pollutants in aqueous phase. In order to establish a valid comparison of the photocatalytic activity for different materials, the IUPAC has proposed the degradation of phenol in aqueous medium through Pyrex as a test to rank the photocatalytic efficiency of different materials with respect the degradation of aromatic compounds.[21,22] When performing this test, however, caution should be taken using fresh phenol solutions to avoid self-polymerization of stock solutions. Also, a blank without photocatalyst has to be performed to ensure that not direct photochemical degradation occurs.

Thus, we proceeded to determine the percentage of phenol degradation upon irradiation through Pyrex in identical aqueous suspensions of phenol containing MOF-5, standard P-25 TiO_2 and ZnO. We have selected ZnO for comparison because in case the MOF-5 would undergo structural damage in a small percentage, ZnO will be formed. Figure 6 shows the time conversion plots of phenol disappearance plotted per metal atom or per gram in the presence of these three photocatalysts. Each data point of the plot was obtained analyzing not only the liquid phase but also the possible adsorbed phenol, so that it represents the photodegraded phenol.

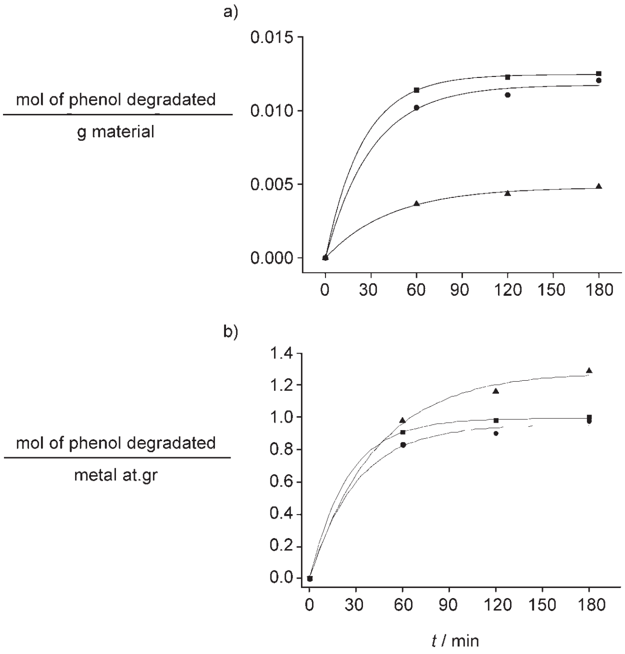
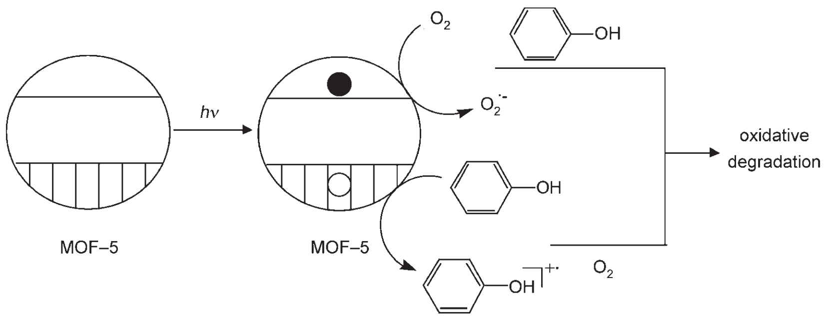


Figure 6. Time conversion plots of phenol disappearance a) per mass unit and b) per metal atom in the presence of MOF-5 (▲), TiO_2 (■) and ZnO (●).

As it can be seen in Figure 6, MOF-5 exhibits a remarkable photocatalytic activity in line with the data obtained by laser flash photolysis of charge separation. Since the composition and structure of MOF-5, having terephthalate units structurally necessary but photocatalytically inactive, the comparison between these materials is not straightforward. Comparison between the performance of MOF-5 and other photocatalysts can be made either per mass unit (plot a) or per metal atom (plot b). In any case, the remarkable photocatalytic activity of MOF-5 compared with that of ZnO rules out that it derives from minor adventitious ZnO clusters that could have been formed during the photocatalytic test.

As in the case of titanium dioxide, we assume that photodegradation of phenol may occur through a network of reactions including initial formation of radical cation by electron transfer from phenol to MOF-5 hole or generation of oxygen active species by reaction of the photoejected electrons with oxygen. Scheme 2 summarizes a possible mechanistic proposal. It can be easily anticipated that the relative photocatalytic activity of MOF-5 with respect to the other photocatalysts will most probably vary depending on the light source. In particular, visible irradiation using filtered light (cut-off filter $\lambda >$ 380 nm) would strongly disfavor the activity of TiO_2 and ZnO due to their lack of absorption at wavelength $>$350 nm while MOF-5 absorbs above 350 nm.



Scheme 2.

Conclusion

MOF-5 behaves in many respects as a microporous semiconductor that is stable to light exposure, giving rise to charge-separated states. Thus, upon light absorption on the ligand-to-metal charge transfer band, charge separation occurs. Delocalized electrons living in the microsecond time scale, and most probably occupying conduction bands, have been detected by laser flash photolysis. These photogenerated electrons are able to reduce electron acceptors. Holes, on the other hand, are able to oxidize *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine to its corresponding radical cation. The actual conduction band value is 0.2 V versus NHE with a band gap of 3.4 eV. The charge-separation state with electrons in the conduction band and holes in the valence band makes MOF-5 behaves as a semiconductor that exhibits photocatalytic activity for the degradation of phenol comparable to that of P-25 titanium dioxide standard. All the above findings are in total contrast with the characteristics of zeolites that are photochemically inert and exemplify the novel opportunities offered by MOFs as semiconductor hybrid organic–inorganic materials.

Experimental Section

MOF-5 was synthesized according to the procedure reported by Huang et al.[23] by precipitating a mixture of two DMF solutions with triethylamine at room temperature, one of them containing $Zn(NO_3)_2{\cdot}6H_2O$ and the other consisting of a solution of terephthalic acid. The mixture was allowed to stand for 2 h at room temperature and the resulting solid was filtered and washed exhaustively with CH_3Cl to remove DMF before drying under vacuum. Washing with CH3Cl is important to increase the photostability of MOF-5. The structure of the solid was confirmed by X-ray diffraction using a Philips X'Pert diffractometer. The diffuse reflectance UV-Visible spectrum of MOF-5 was recorded using a Varian Cary 5G spectrophotometer having an integrating sphere. The optical spectrum showed an intense absorption band with maximum at 350 nm and a tail extending down to 450 nm, which is in agreement with other spectra reported in literature.[17]

Photoluminescence and laser-flash experiments were performed placing the solid powdered sample inside Suprasil quartz cuvettes (7×3 mm^2) capped with septa. The samples were thoroughly purged with dry N_2 or the appropriate gas stream for at least 15 min before recording the spectra. Steady-state emission spectra were recorded with an Edinburgh FS900 instrument using a 75 W Hg/Xe lamp as excitation source and a Cerzny–Turner monochromator.

Laser flash photolysis measurements were performed using the third harmonic (355 nm) frequency of a Surelite Nd/YAG laser as the excitation source. Signals from the photomultiplier tube were captured and digitalized by a Tektronix 2440 transient digitizer and transferred to a PC programmed in the LabView enviroment. Details of similar time-resolved diffuse reflectance systems have been described elsewhere.[24]

Experiments with methyl viologen were carried out by addition of a saturated aqueous solution of methyl viologen dichloride (2 mL) to the solid samples (100 mg of MOF-5, Aerosil silica and Degussa P-25 TiO_2) inside a quartz cuvette and purging the suspension with dry N_2 before irradiation with a solar simulator (525 W) through an AM1.5 filter.

Experiments with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine were carried out by the addition of a saturated acetonitrile solution of the amine to the solid samples (MOF-5, Aerosil silica and Degussa P-25 TiO_2) under the same conditions described before for the viologen but the irradiation was carried out with the third harmonic (355 nm) of a Nd/YAG laser.

The photovoltaic cell has been prepared following standard procedures[20] using ITO and Pt as the electrodes. A detailed description of the cell prepared with MOF-5 as the active phase is given in ref. [25].

Photocatalytic tests of phenol degradation were carried out stirring at open air and at room temperature an air-saturated aqueous suspension (20 mL) of phenol (40 ppm) in the presence of the photocatalyst (80 mg). The suspension was stirred for at last 10 min in the dark before irradiation. The samples were placed in a series of independent Pyrex test tubes (25 mL capacity), each of them provided with a magnetic stirring bar. The test tubes were placed in a thermostated water bath around a water-refrigerated Pyrex well containing a 125 W medium pressure Hg lamp. The course of the irradiation was followed by taking each test tube at the required reaction time and analyzing the supernatant aqueous solution as well as the products retained in the solid. To recover the products from the solids, they were extracted by sonication of the powder after redispersing it in fresh water (3 mL). The combined extracts (supernatant plus products recovered from the solid) were analyzed by reversed-phase HPLC (Suprasil column, diode array detector monitoring at 254 nm).

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[1] M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319.
[2] S. L. James, *Chem. Soc. Rev.* **2003**, *32*, 276.
[3] J. L. C. Rowsell, O. M. Yaghi, *Microporous Mesoporous Mater.* **2004**, *73*, 3.
[4] N. W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2005**, *38*, 176.
[5] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127.
[6] J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670.
[7] G. Férey, C. Mellot-Draznieks, C. Serrer, F. Millange, J. Dutour, S. Surbli, J. Margiolaki, *Science* **2005**, *309*, 2040.
[8] M. Eddaoudi, J. Kim, N. L. Rosi, D. T. Vodak, J. Wachter, M. O'Keeffe, O. Yaghi, *Science* **2002**, *295*, 469.
[9] B. Gómez-Lor, E. Guttiérez-Puebla, M. Iglesias, M. Monge, C. Ruiz-Valero, N. Snejko, *Chem. Mater.* **2005**, *17*, 2568.
[10] K. Schlichte, T. Kratzke, S. Kaskel, *Microporous Mesoporous Mater.* **2004**, *73*, 81.
[11] C. Wu, A. Hu, L. Zhang, W. Lin, *J. Am. Chem. Soc.* **2005**, *127*, 8940.
[12] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276.
[13] A. Corma, *Chem. Rev.* **1995**, *95*, 559.
[14] D. R. C. Huybrechts, R. F. Parton, P. A. Jacobs, *Stud. Surf. Sci. Catal.* **1991**, *60*, 225.
[15] B. W. Wojciechowski, A. Corma, *Catalytic Cracking: Catalysts, Chemistry, and Kinetics*, Marcel Dekker, NY **1990**.
[16] H. van Bekkum, E. M. Flanigen, J. C. Jansen, *Introduction to Zeolite Science and Practice*, Elsevier, Amsterdam, **1991**.
[17] S. Bordiga, C. Lamberti, G. Ricchiardi, L. Regli, F. Bonino, A. Damin, K. P. Lillerud, M. Bjorgen, A. Zecchina, *Chem. Commun.* **2004**, 2300.
[18] J. C. Scaiano, H. Garcia, *Acc. Chem. Res.* **1999**, *32*, 783.
[19] S. L. Murov, *Handbook of Photochemistry*, **1973**.
[20] M. Grätzel, A. Hagfeldt, *Chem. Rev.* **1995**, *95*, 49.
[21] A. Salinaro, A. V. Emeline, J. C. Zhao, H. Hidaka, V. K. Ryabchuk, N. Serpone, *Pure Appl. Chem.* **1999**, *71*, 321.
[22] N. Serpone, A. Salinaro, *Pure Appl. Chem.* **1999**, *71*, 303.
[23] L. M. Huang, H. T. Wang, J. X. Chen, Z. B. Wang, J. Y. Sun, D. Y. Zhao, Y. S. Yan, *Microporous Mesoporous Mater.* **2003**, *58*, 105.
[24] F. Wilkinson, G. Kelly in *Handbook of Organic Photochemistry, Vol. 1* (Ed.: J. C. Scaiano), CRC Press, Boca Raton, FL, **1989**, p. 293.
[25] F. X. Llabrés i Xamena, A. Corma, H. Garcia, *J. Phys. Chem. C* **2007**, *111*, 80.

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