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Transient absorption spectroscopy and photochemical reactivity of CAU-8

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CAU-8 is a metal organic framework with the composition [Al(OH)(BPDC)] (BPDC: 4,4′-benzophenone dicarboxylate) whose structure is constituted by chains of corner-sharing AlO_6 octahedra connected by BPDC linkers, giving rise to an array of non-intersecting channels. According to the well known photochemical behavior of benzophenone, in the present study we have been able to obtain spectroscopic evidence of the photochemical reactivity of CAU-8, including the generation of short-lived triplet excited states that react with either electron donors (triethylamine) or hydrogen donors (isopropanol) and lead to the corresponding radical anions or ketyl radicals, respectively. These two species have long half live times in CAU-8 and their decay is not complete hundreds of microseconds after the laser pulse. The photochemical activity of the BPDC linker in CAU-8 has been used to promote the radical-induced (co)polymerization of styrene and the coupling of BPDC and ethanol has been followed with IR spectroscopy.

Introduction

Since the early times of organic photochemistry, in which processes have been studied in solution and in media as homogenous as possible, a continuing tendency has been to explore photochemistry in confined media.[1–3] Due to the short life times of the species involved and their high energy, control of the behavior of the electronic excited states has proven to be difficult in solution. The most successful strategy to gain control of the selectivity of a photochemical reaction has been to confine the organic chromophore in a restricted reaction cavity.[4] Studies of heterogeneous photochemistry started with organic molecules deposited on the external surface of silica,[5–9] but, further control was gained by entrapping the molecules inside the cavities of porous solids.[10–12] Zeolites and mesoporous aluminosilicates have been among the preferred hosts to perform heterogeneous photochemical reactions, with the aim being to achieve a product selectivity higher than in the liquid phase.[4,12–15]

In this context, a more recent class of crystalline porous materials that have considerable possibilities in photochemistry are Metal Organic Frameworks (MOFs).[16–21] These solids are constituted by metal ions or clusters of metal ions at nodal positions held in place by rigid bi- or multipodal organic linkers, with aromatic polycarboxylates being the most widely used linkers. In contrast to zeolites that are photochemically inert due to their composition, MOFs containing organic linkers can have intrinsic photochemical properties derived from the presence of organic chromophores.[22,23] There are a large number of precedents showing that MOFs exhibit a photochemistry that can be different from that of the incorporated organic linkers in solution.[24–26] The main difference in the photochemical behavior between the MOF and the corresponding linker in solution typically derives from the presence of electron-accepting metallic nodes that can produce a highly efficient electron transfer, quenching the electronic excited state of the organic ligand.[27–30] In some cases, MOFs exhibit semiconducting properties with the occurrence of charge separation and mobile charge carriers.[24]

Organic photochemistry has developed to a large extent based on the understanding of the behavior of key probe molecules containing chromophores that illustrate general photochemical pathways common to many molecules having the same chromophores.[1,2] One of the particularly important probe molecules in photochemistry is benzophenone and its derivatives (Scheme 1).[31–35] It is known that upon excitation, the singlet excited state of benzophenone undergoes fast intersystem crossing to the first triplet excited state with a quantum efficiency of unity (Scheme 1). This triplet excited state has a $\pi^* \leftarrow n$ nature and behaves like a biradical centered on the oxygen and carbon atoms of the carbonyl group. Depending on the presence of quenchers, this triplet excited state can undergo hydrogen abstraction to form a ketyl radical or can be involved in single electron transfer processes forming the corresponding benzophenone radical anion. In the presence of strong electron acceptors, even benzophenone radical cations can be obtained.

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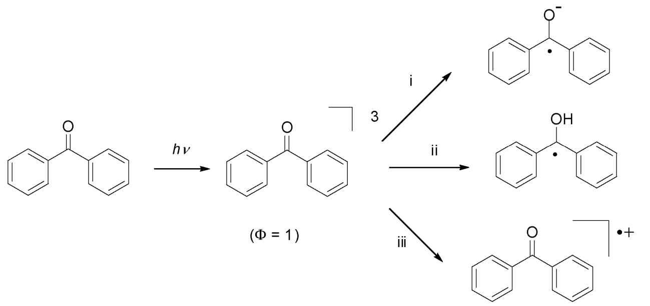


Scheme 1 Simplified overview of the photochemistry of benzophenone with the formation of a triplet excited state and the possibility to generate radical anions in the presence of electron donors (i), ketyl radicals by hydrogen abstraction (ii) or radical cations by quenching with electron acceptors (iii).

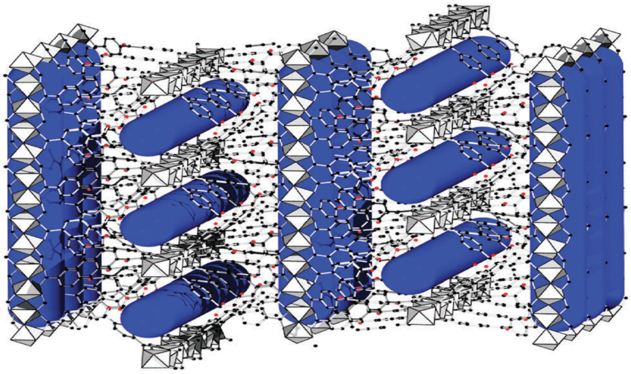


Fig. 1 Crystal structure of CAU-8 showing the octahedrally coordinated Al^{3+} ions, the BPDC linkers connecting the chains of corner-sharing AlO_6 polyhedra (grey) and the resulting pores (blue).

Considering the interest and the key role of benzophenone in photochemistry, it occurred to us that it would be of interest to study the photochemistry of this in a MOF. CAU-8 is an Al-based MOF with the composition [Al(OH)(BPDC)] (BPDC: 4,4′-benzophenone dicarboxylate), whose structure is formed by trans corner-sharing AlO_6 polyhedra.[36] The other four positions of the octahedrally coordinated Al^{3+} ions are occupied by the O-atoms of four different carboxylate groups from different BPDC linkers. This leads to the interconnection of adjacent chains. The network defines two non-intersecting channel systems running along the *a* and *z*-axes of the unit cell with a pore dimension of 0.8 nm. The keto groups point into the channels. Fig. 1 presents the structural components of CAU-8 and a view of the pores contained in the structure.

With these precedents in mind, the present article is aimed at the investigation of some photochemical properties of the BPDC chromophore in CAU-8. We will show that BPDC follows the general reactivity pattern expected for benzophenones and also that it is possible to photochemically modify the CAU-8 structure by irradiation in isopropanol.

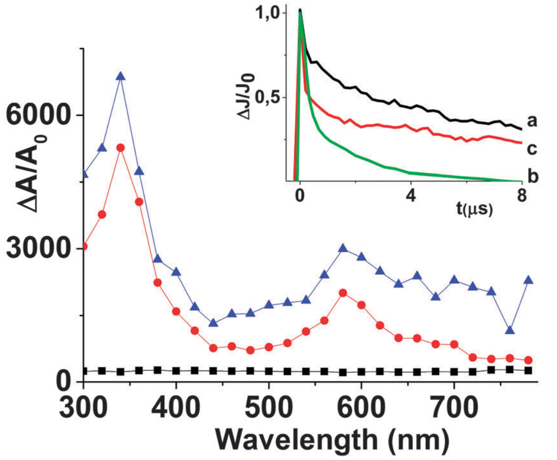


Fig. 2 Transient absorption spectra recorded for an Ar-purged acetonitrile suspension of CAU-8 recorded 0.1 (blue), 1 (red) and 10 (black) μs after the laser flash (355 nm, 7 ns fwhp, 30 mJ per pulse). The inset shows the temporal profile of the transient signal monitored at 350 (a), 390 (b) and 580 (c) nm.

Results and discussion

In the present study, CAU-8 powders were suspended in acetonitrile by sonication, resulting in a transparent dispersion. XRD analysis of the suspended CAU-8 after sonication indicated that the crystal structure was not altered upon sonication, although some broadening of the peaks was observed. The concentration of CAU-8 was adjusted to have an optical absorption at 355 nm of 0.3. Suspensions of CAU-8 prepared under these conditions were persistent without the precipitation of any solid particle for periods of time longer than those required for the laser flash photolysis experiments, about 3 h, allowing the use of transmission techniques for the detection of transient spectra.[29,37] The third harmonic of a Nd:YAG nanosecond laser apparatus operating at 355 nm was used as an excitation light.

Upon excitation of the acetonitrile suspensions of CAU-8, the generation of a transient signal decaying in the microsecond scale time was observed (Fig. 2). The transient spectra consist of an intense sharp peak at 350 nm accompanied by a less-intense absorption with relative maxima at 390 nm, 580 nm and in the region 620 to 780 nm. In comparison, irradiation of BPDC in the same solvent gives a transient signal that is shorter lived than that recorded for CAU-8. Thus, for BPDC, the best fit to first-order decay gives lifetimes of 4.0 and 3.6 μs for the signals at 350 and 580 nm, while for CAU-8 the corresponding lifetimes are 8.1 and 6.6 μs, respectively. This is somewhat unexpected since benzophenone is known to undergo triplet–triplet annihilation that leads to shorter lifetimes as the concentration increases.[31–35] We propose that the strict spatial arrangement and immobilization provided by the framework disfavors the operation of triplet–triplet self quenching.

Fig. 2 shows the transient spectra recorded at 0.1, 1 and 10 μs after the laser flash in an Ar-purged acetonitrile suspension of CAU-8. There are precedents in the literature showing that transient spectra recorded in transmission mode can be conveniently obtained for MOF suspensions in various solvents.[29,38] Apparently, due to the small particle size and the composition, sonication of the MOF in an appropriate solvent results in colloidal dispersions that are persistent enough to allow monitoring of the transient absorption spectra. This experimental procedure has proved to be advantageous with respect to recording diffuse reflectance transient spectra of opaque powders, since very frequently no signals are observed for powdered samples. In the present case, sonication of CAU-8 in acetonitrile results in the generation of a dispersion that contains particles with an average size of about 500 nm, as determined by dynamic laser scattering measurements. Furthermore, after subjecting the dispersion to extended laser flash exposure, chemical analysis of the acetonitrile solution after removal of the suspended particles showed that the aluminum content in the solution was lower than 1 ppb, corresponding to $<0.01\%$ of the total Al^{3+} suspended. Also, PXRD analysis of the recovered solid material suspended in acetonitrile after the laser measurements still exhibited the same diffraction pattern, although with broader peaks and lower crystallinity. This lower crystallinity following the photochemical study could be attributed to the smaller particle size of the sample present in the acetonitrile dispersion after laser flash exposure, compared to the fresh CAU-8 solids before sonication. It has been frequently observed that exposure of dispersed submicrometric particles to laser pulses leads to a decrease in the average particle size, likely due to the deaggregation caused by the impact of the laser energy.[37,39]

As can be seen in Fig. 2, the transient spectra of the acetonitrile dispersion CAU-8 have two relative maxima peaking at 350 and 580 nm, accompanied by the transient signals decaying faster from 620 to 780 nm. For the signal monitored at 390 nm, a fast component in the first μs was observed. This fast component of the 390 nm signal, that lived about 1 μs and overlapped with the tail of the 350 nm band, could correspond to the expected triplet excited state of the benzophenone moiety, considering the same λ_{max} for this transient signal and its short life time have been reported previously.[40] Fig. 2 also presents the temporal profile of the signals monitored at three other wavelengths that correspond with the relative intensity maxima in the transient spectra.

The transient signal did not decay completely after tens of μs, for both the BPDC linker and CAU-8. At delay times longer than 30 μs, the transient absorption spectra of BPDC linker and CAU-8 were observed to be remarkably different. While for BPDC, the 350 and 580 nm bands were still present at 30 μs, in the case of CAU-8 the transient spectrum was continuous, spanning from 300 to 800 nm. This could reflect the relaxation of the initial exciton localized on the BPDC linker through the MOF network over this time scale. Fig. 3 shows the transient absorption spectra for Ar-purged BPDC and CAU-8 suspended in acetonitrile recorded 30 μs after the laser pulse.

Regarding the assignment of the bands at 350 and 580 nm, the coincidence of their decay after 1 μs suggests that they may correspond to the same species. Based on their relative long life times and the position of the peaks, we assigned this long-lived transient species to ketyl radicals that would be generated from the triplet excited state by abstraction of one hydrogen atom from the medium.[40–43] The most likely origin of the hydrogen donor would be DMF solvent molecules trapped in CAU-8 during its synthesis in this solvent. Although less likely, acetonitrile could also play the role of hydrogen donor.

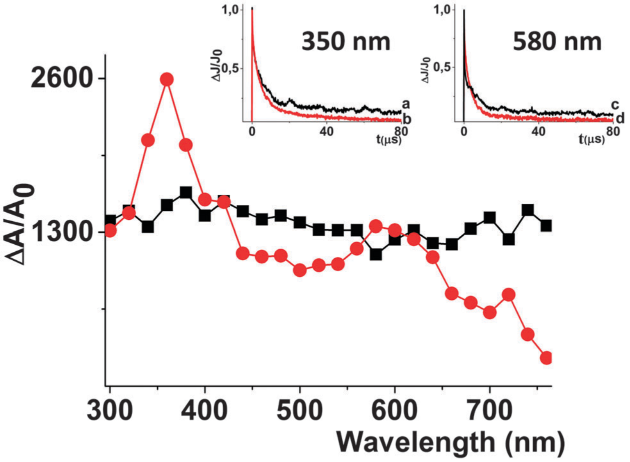


Fig. 3 Transient spectra recorded at 30 μs after laser excitation (355 nm, 7 ns fwhp, 30 mJ per pulse) for an Ar-purged solution of BPDC and CAU-8 suspensions in acetonitrile. The signal from CAU-8 was about twice more intense than that recorded for BPDC and has been normalized at 300 nm for clarity. The insets shows the comparison of the signals for CAU-8 (a, c) and BPDC (b, d) monitored at 350 and 580 nm.

Evidence in support of this rationalization was obtained by quenching experiments. The presence of molecular oxygen results in the complete disappearance of the transient signal. This observation is in agreement with the fact that all photogenerated transient species derive from the triplet state of the excited linker. Triplet excited states of benzophenone are efficiently quenched by oxygen.[40] In addition, the presence of electron donors such as $N(C_2H_5)_3$ (Fig. 4) or hydrogen donor quenchers such as ethanol or isopropanol (Fig. 5) leads to very similar transient spectra with the notable difference that the absorption bands are much narrower and better defined and also that the lifetime of the transient signal increases significantly, indicating that they correspond to longer lived species.

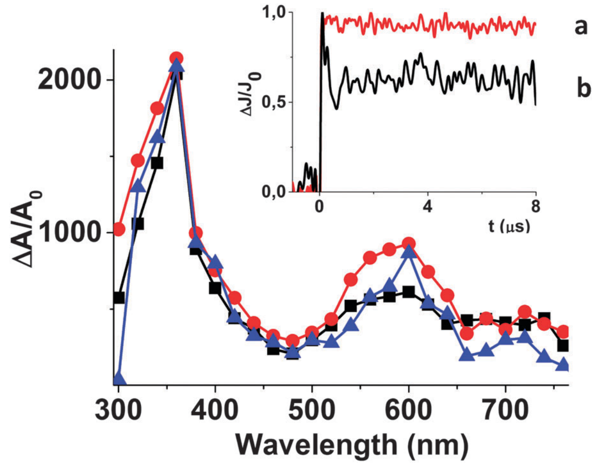


Fig. 4 Transient absorption spectra recorded 0.1 (red), 1 (blue) and 10 (black) μs after 355 nm laser excitation (7 ns fwhp, 225 J per pulse) for an acetonitrile suspension of CAU-8 (O.D. at 355 nm is 0.3) in the presence of 10^{-5} M aqueous solution of $N(C_2H_5)_3$. The inset shows the transient signal monitored at 340 (a) and 600 (b) nm.

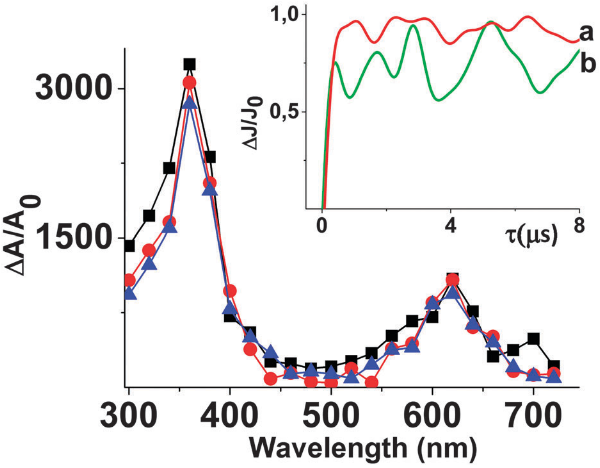
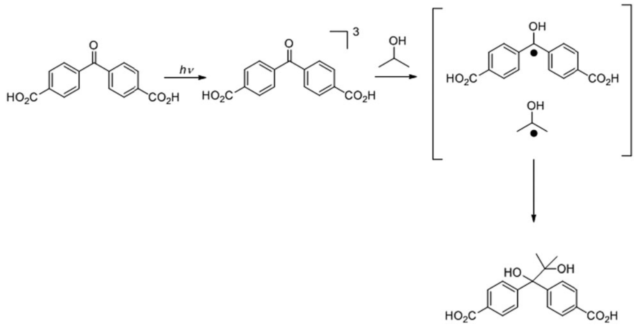


Fig. 5 Transient absorption spectra recorded 0.1 (black), 1 (red) and 10 (blue) μs after 355 nm excitation (7 ns fwhp, 25 mJ per pulse) for an acetonitrile dispersion of CAU-8 containing isopropanol as a hydrogen donor. The inset shows the temporal profile of the transient signal monitored at 350 (a) and 580 (b) nm.

Fig. 4 shows the transient spectra of CAU-8 dispersions in acetonitrile in the presence of $N(C_2H_5)_3$ at three different delay times after the laser pulse. A comparison of the spectra at delays of 0.1 and 10 μs shows that the residual absorbance from 400 to 520 nm and the broad envelope from 480 to 650 nm present in the spectrum recorded at 0.1 μs have disappeared in the spectrum at 5 μs, due to the faster triplet state decay leaving the spectrum of the pure benzophenone radical anion. Fig. 4 also shows the temporal profile of the signal at 340 and 600 nm, showing that in the presence of $N(C_2H_5)_3$the transient is very long-lived. It is well known that $N(C_2H_5)_3$ reacts with benzophenone by electron transfer giving the corresponding ketyl radical anion.[42,44] This ketyl radical is formed concomitantly with $N(C_2H_5)_3^{+\bullet}$, but the diffusion and decomposition of $N(C_2H_5)_3^{+*}$ radical cation determines that, in excess of amine, the ketyl radical anion of benzophenone lives hundreds of microseconds. This lifetime of the benzophenone ketyl radical anion is much longer than that of the triplet excited state that only lives a few microseconds. Accordingly, the transient spectra obtained for the acetonitrile dispersion of CAU-8 in the presence of $N(C_2H_5)_3$ recorded 10 μs after the laser pulse should be safely attributed to the ketyl radical anion of the benzophenone linker without contamination of signals due to the triplet state that should have completely decayed at this time. Comparison of the transient spectra under these conditions immediately after laser pulse and 10 μs after reveals many similarities, but they do not exactly coincide as the initial transient spectrum is broader, particularly between 380 and 420 nm and from 480 to 620 nm. The broadness of some of the bands in Fig. 4 for the transient spectrum recorded for CAU-8 in the presence of $N(C_2H_5)_3$ immediately after the laser pulse can be attributed to the residual triplet states of the linker. In other words, even though the transient spectra of the benzophenone triplet and ketyl radical anion are similar, they can be resolved in time due to their different lifetimes.



Scheme 2 Generation of a ketyl radical from the BPDC triplet excited state and the final radical coupling leading to a *vic*-diol.

Another well documented behavior of benzophenone triplet reactivity, due to the n–π* character of this excited state, is its ability to abstract hydrogen atoms from hydrogen donor molecules (Scheme 1).[1,3,45] Isopropanol is one of the favorite quenchers for this process. Therefore, we also performed laser flash measurements of dispersions of CAU-8 in acetonitrile in the presence of isopropanol as a hydrogen donor. The transient spectra recorded at 0.1, 1 and 10 μs after the laser pulse are presented in Fig. 5.

In the transient spectra of Fig. 5 we observed a sharp peak at 360 nm accompanied by a broader, but less intense, absorption band from 530 to 650 nm. In addition, the transient signals of the bands monitored at 350 and 580 nm exhibited identical temporal profiles that were remarkably long-lived, indicating that they correspond to the ketyl radical formed from the benzophenone triplet excited state by hydrogen abstraction from isopropanol, as indicated in Scheme 2. It is worth commenting that essentially the same transient signal and spectra were recorded for measurements performed in ethanol as a quencher.

To summarize the results, the transient signal of CAU-8 is longer lived than that of BPDC and at long delay times the initially similar transient spectra of CAU-8 and BPDC become remarkably different due to delocalization of the exciton in CAU-8. At short delay times, the UV-Vis absorption transient spectra of CAU-8 are attributable to the absorption a triplet excited state (Fig. 2), radical anion (Fig. 4) and ketyl radical (Fig. 5) localised on the benzophenone linker. The transient spectra of these species are very similar, the main difference being in the life times and the conditions in which they are generated.

The previous transient absorption study has revealed that the BPDC linker in CAU-8 has a photochemical behavior typical of benzophenone with a triplet excited state decaying in a few μs and being able to accept electrons or hydrogen atoms from appropriate quenchers. Therefore, we investigated the photochemical reactivity of CAU-8 when acting as a photosensitizer for the chemical transformation of guest molecules included in the pores.

To study the activity of CAU-8, we performed two types of photochemical reaction using CAU-8. In the first one, CAU-8 was dispersed in styrene, or a styrene–divinylbenzene mixture, a small amount of ethanol was added and the system was irradiated with a medium pressure mercury lamp. As expected, the dispersion gradually increased in viscosity until all styrene

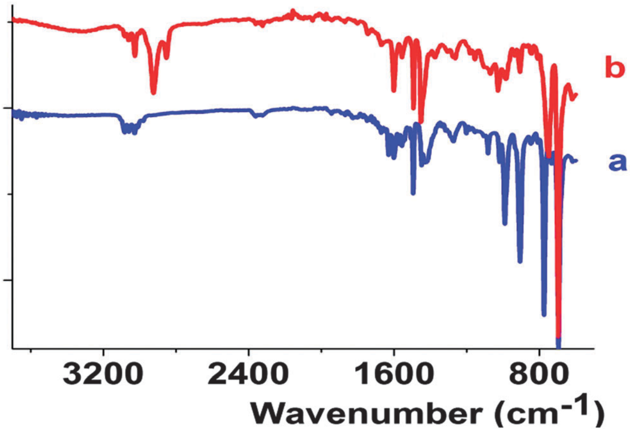


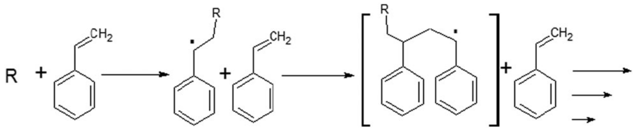
Fig. 6 FT-IR spectra of a mixture of styrene/*p*-divinylbenzene 84/16 (6 mL) with 50 mg CAU-8 and 150 μL of EtOH before (a) and after (b) 30 min irradiation with a 400 W medium pressure Hg lamp.

molecules were finally polymerized. The success of the styrene polymerization was assessed by comparison of the IR spectra before and after irradiation (Fig. 6). Of particular note was the appearance of the vibrations at 2950 and 2890 cm^{-1}, characteristic of aliphatic C–H bonds, and the disappearance of the C=C stretching band of medium intensity that is present in styrene before polymerization.

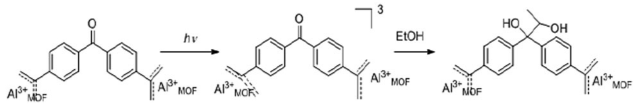
We propose that the styrene polymerization is promoted by CAU-8 and takes place according to Scheme 3. Blank controls showed that styrene polymerization does not take place under the same conditions in the absence of CAU-8 acting as photosensitizer. In addition, CAU-8 behaves differently to BPDC under the same conditions, since BPDC was unable to promote styrene polymerization. The reason for the failure of BPDC to act as a photosensitizer is probably its high insolubility in the styrene liquid phase. The porosity of CAU-8 and its high adsorption capacity is apparently advantageous to promote polymerization.

The second type of photochemical reaction that was performed involves the reaction of the BPDC linkers in CAU-8 with alcohols. It is well known that benzophenone can react with alcohols giving rise to the corresponding *vic*-diol coupling products as indicated in Scheme 4.[1]

We were unsuccessful in the photochemical transformation of CAU-8 to another MOF in which the linker should correspond to the product generated photochemically as indicated in Scheme 4. For this purpose, CAU-8 solid was dispersed in ethanol and submitted to lamp irradiation. As expected, the spectroscopic properties of the CAU-8 sample changed after irradiation in accordance with the reactivity of benzophenone.



Scheme 3 Radical chain styrene polymerization initiated by the irradiation of a suspension of CAU-8 in styrene or a styrene–divinylbenzene mixture.



Scheme 4 Photochemical reaction of BPDC linker by irradiation of CAU-8 in ethanol.

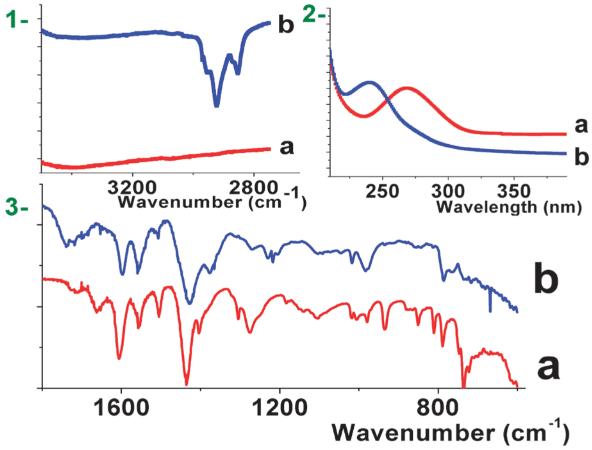


Fig. 7 Comparison of FT-IR and UV-Vis spectra of CAU-8 fresh and after irradiation in ethanol for 30 min with a 400 W medium-pressure Hg lamp: (1) part of the FT-IR spectra before (a) and after (b) irradiation; (2) UV-Vis spectra of CAU-8 resuspended in acetonitrile before (a) and after (b) irradiation in ethanol, and (3) part of the FI-IR spectra before (a) and after (b) irradiation.

Fig. 7 shows a comparison of the UV-Vis spectra of pristine CAU-8 and the resulting material after irradiation (CAU-8/I). As can be seen, CAU-8 exhibits a band at λ_{max} 265 nm which, after irradiation, is converted into a new band at λ_{max} 238 nm for CAU-8/I, indicating the disappearance of the benzophenone chromophore.

The IR spectrum of CAU-8/I, after evacuation under a reduced pressure to remove unreacted ethanol, also reveals the disappearance of the benzophenone carbonyl band at 1640 cm^{-1}, which is compatible with the transformation of the carbonyl group in the photochemical reaction with ethanol. In addition, a very broad OH vibration at 3450 cm^{-1}, together with sharp peaks at 2980 and 2890 cm^{-1} attributable to the asymmetric and symmetric stretching of C–H bonds appear in the FT-IR spectrum (see Fig. 7). The aromatic region of the irradiated CAU-8/I sample was also different from that of the initial CAU-8. All of these spectroscopic changes indicate the disappearance of carbonyl groups and the incorporation of a hydroxyethyl moiety in the resulting product (Scheme 4).

PXRD patterns of the samples before and after irradiation in ethanol demonstrate that CAU-8 becomes increasingly amorphous upon irradiation, without the appearance of a new crystalline phase (Fig. 8). The structural stress is responsible for the lack of crystallinity of the framework and is a consequence of the changes in the geometry of the benzophenone linker where the planar trigonal C=O is converted into a tetrahedral C atom in the *vic*-diol. Optical microscopy showed that the crystallite size of the fresh material is maintained upon irradiation in ethanol.

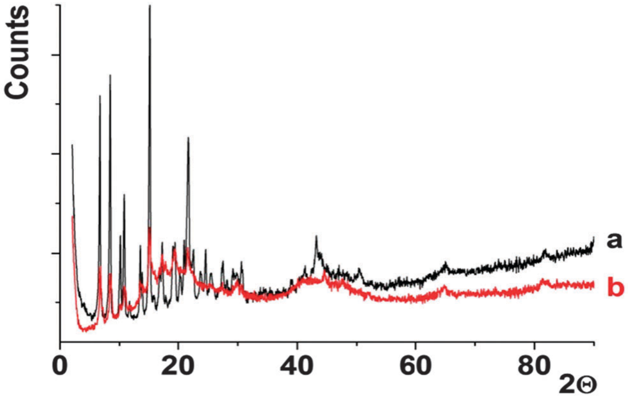


Fig. 8 Powder XRD pattern of CAU-8 before (a) and after (b) 30 min irradiation in ethanol with a 400 W medium-pressure Hg lamp.

Conclusions

The present study has shown that CAU-8, having a benzophenone subunit, exhibits the characteristic photochemical behavior expected for this chromophore. Irradiation of CAU-8 allows the detection of the triplet excited state of BPDC that lives a few μs. This BPDC triplet excited state is able to react with electron and hydrogen donors forming the corresponding radical anion or ketyl radical, detectable by transient spectroscopy as long-lived transients. This photochemical behavior can be used to perform the photosensitized polymerization of styrene and also to convert the BPDC ligand from benzophenone to a *vic*-diol derivative. In this way, irradiation in the presence of ethanol results in the transformation of the BPDC ligand, causing a change of the solid framework as a consequence of the change in the geometry of the BPDC linker.

Experimental section

Characterisation techniques

UV/Vis absorption spectra were recorded in transmission mode with a Jasco V-650 spectrophotometer by dispersing CAU-8 in acetonitrile by sonication. X-ray powder diffraction data was measured on a PANalytical Empyrean diffractometer (CuKα radiation) in transmission mode. FT-IR spectra of self-supported compressed wafers (10 mg) were recorded in a Bruker FT-IR spectrophotometer.

Synthesis of CAU-8

Phase-pure CAU-8 was obtained as a sub-microcrystalline powder following a previously reported procedure.[36] In brief, 2 g of H_2BPDC (7.4 mmol), 14.8 mL of a 0.5 M solution of $Al_2(SO_4)\cdot18H_2O$ (7.4 mmol), 0.6 mL of milliQ water and 12 mL of DMF (resulting volume ratio water : DMF 2 : 3) were heated up to 140 °C over 1 h. The reactor was kept at this temperature for 12 h. After this time, the autoclave was cooled down to room temperature over 1 h. The resulting solid was treated with 20 mL of DMF and heated to 85 °C overnight, thoroughly washed with water and dried under room conditions.

Transient absorption spectroscopy studies

Laser Flash Photolysis (LFP) measurements were performed using a Q-switched Nd:YAG laser (Quantel Brilliant, 355 nm, 20 mJ per pulse, 5 ns fwhm) coupled to a mLFP-111 Luzchem miniaturized equipment. This transient absorption spectrometer includes a ceramic xenon light source, a 125 mm monochromator, a Tektronix 9-bit digitizer TDS-3000 series with 300 MHz bandwidth, a compact photomultiplier and a power supply, a cell holder and fiber optic connectors, a fiber optic sensor for laser-sensing pretrigger signal, computer interfaces, and a software package developed in the LabVIEW environment from National Instruments. The LFP equipment supplies 5 V trigger pulses with a programmable frequency and delay. All transient spectra were recorded using 10 mm × 10 mm quartz cells with a capacity of 4 mL and were bubbled for 30 min with Ar or the appropriate quencher before signal acquisition. The absorbance of the samples was O.D. 0.3 at the laser excitation wavelength (355 nm).

Photochemical polymerisation of styrene

Two different polymerization reactions were performed by irradiating CAU-8 (50 mg) in freshly distilled styrene (5 mL) with or without distilled 1,4-divinylbenzene (1 mL). The suspension was stirred magnetically in a Pyrex glass vial of 20 mL capacity. After 5 min, 150 μL of ethanol were added using a syringe and the suspension was irradiated at room temperature in a water bath using the output of a 400 W high-pressure Hg lamp for 30 min. During this time the liquid phase become very viscous, particularly when 1,4-divinylbenzene was present. The course of the polymerization was followed by monitoring the disappearance of the styrene vibration band at 1630 cm^{-1} in the IR spectra of the mixture.

CAU-8 irradiation in ethanol

100 mg of CAU-8 were suspended in 20 mL of ethanol and the suspension was stirred magnetically in a Pyrex round bottom flask of a 50 mL capacity that was capped with a rubber septum. The suspension was purged with argon 30 min before irradiation with a 400 W Hg lamp. Initially the temperature was 22 °C but the system underwent some heating during irradiation, although the temperature was never above 60 °C. The photochemical reaction was carried out for 10 h. At the end of the reaction the solid was recovered and dried in an oven at 90 °C overnight. The crystallinity of the material was surveyed by XRD. UV-Vis spectra were recorded in transmission mode suspending a small amount of the sample in acetonitrile. FT-IR spectra of the irradiated powders were recorded by attenuated total reflectance (ATR) spectroscopy. These ATR IR spectra were recorded with a Bruker ATR spectrophotometer.

Acknowledgements

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References

1 A. Gilbert and J. E. Baggot, *Essentials of Molecular Photochemistry*, CRC, Boca Raton, 1991.
2 N. J. Turro, V. Ramamrthy and J. C. Scaiano, *Principles of Organic Photochemistry*, University Science Books, New York, 2009.
3 N. J. Turro, J. C. Scaiano and V. Ramamurthy, *Principles of Organic Photochemistry. An Introduction*, 2008.
4 V. Ramamurthy, *Photochemistry in Organized and Confined Media*, Wiley, New York, 1995.
5 D. Avnir, L. J. Johnston, P. Demayo and S. K. Wong, *J. Chem. Soc., Chem. Commun.*, 1981, 958.
6 R. K. Bauer, R. Borenstein, P. Demayo, K. Okada, M. Rafalska, W. R. Ware and K. C. Wu, *J. Am. Chem. Soc.*, 1982, **104**, 4635.
7 P. Demayo, A. Nakamura, P. W. K. Tsang and S. K. Wong, *J. Am. Chem. Soc.*, 1982, **104**, 6824.
8 P. Demayo, K. Okada, M. Rafalska, A. C. Weedon and G. S. K. Wong, *J. Chem. Soc., Chem. Commun.*, 1981, 820.
9 L. J. Johnston, P. Demayo and S. K. Wong, *J. Chem. Soc., Chem. Commun.*, 1982, 1106.
10 M. Alvaro, V. Fornes, S. Garcia, H. Garcia and J. C. Scaiano, *J. Phys. Chem. B*, 1998, **102**, 8744.
11 M. Alvaro, H. Garcia, S. Garcia, F. Marquez and J. C. Scaiano, *J. Phys. Chem. B*, 1997, **101**, 3043.
12 J. C. Scaiano and H. Garcia, *Acc. Chem. Res.*, 1999, **32**, 783.
13 S. Hashimoto, *J. Phys. Chem. Lett.*, 2011, **2**, 509.
14 S. Hashimoto, H. R. Moon and K. B. Yoon, *Microporous Mesoporous Mater.*, 2007, **101**, 10.
15 S. Hashimoto, K. Uehara, K. Sogawa, M. Takada and H. Fukumura, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1451.
16 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Science*, 2002, **295**, 469.
17 M. Eddaoudi, D. B. Moler, H. L. Li, B. L. Chen, T. M. Reineke, M. O'Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
18 G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191.
19 C. Janiak, *Dalton Trans.*, 2003, 2781.
20 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.
21 O. M. Yaghi, M. O'Keeffe, N. W. Ockwig, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.
22 M. D. Allendorf, C. A. Bauer, R. K. Bhakta and R. J. T. Houk, *Chem. Soc. Rev.*, 2009, **38**, 1330.
23 Y. Cui, Y. Yue, G. Qian and B. Chen, *Chem. Rev.*, 2012, **112**, 1126.
24 C. Gomes Silva, A. Corma and H. Garcia, *J. Mater. Chem.*, 2010, **20**, 3141.
25 C. A. Kent, B. P. Mehl, L. Ma, J. M. Papanikolas, T. J. Meyer and W. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 12767.
26 P. Mahata, G. Madras and S. Natarajan, *J. Phys. Chem. B*, 2006, **110**, 13759.
27 M. Alvaro, E. Carbonell, B. Ferrer, F. X. Llabres i Xamena and H. Garcia, *Chem. – Eur. J.*, 2007, **13**, 5106.
28 M. de Miguel, F. Ragon, T. Devic, C. Serre, P. Horcajada and H. Garcia, *ChemPhysChem*, 2012, **13**, 3651.
29 H. A. Lopez, A. Dhakshinamoorthy, B. Ferrer, P. Atienzar, M. Alvaro and H. Garcia, *J. Phys. Chem. C*, 2011, **115**, 22200.
30 T. Tachikawa, J. R. Choi, M. Fujitsuka and T. Majima, *J. Phys. Chem. C*, 2008, **112**, 14090.
31 A. Beckett and G. Porter, *Trans. Faraday Soc.*, 1963, **59**, 2038.
32 F. Bosca, M. A. Miranda, G. Carganico and D. Mauleon, *Photochem. Photobiol.*, 1994, **60**, 96.
33 S. Kazanis, A. Azarani and L. J. Johnston, *J. Phys. Chem.*, 1991, **95**, 4430.
34 M. Sakamoto, M. Fujistuka and T. Majima, *J. Photochem. Photobiol., C*, 2009, **10**, 33.
35 J. C. Scaiano, E. B. Abuin and L. C. Stewart, *J. Am. Chem. Soc.*, 1982, **104**, 5673.
36 H. Reinsch, M. Krueger, J. Marrot and N. Stock, *Inorg. Chem.*, 2013, **52**, 1854.
37 H. G. Baldovi, B. Ferrer, M. Alvaro and H. Garcia, *J. Phys. Chem. C*, 2013, **118**, 9275.
38 K. G. M. Laurier, E. Fron, P. Atienzar, K. Kennes, H. Garcia, M. Van der Auweraer, D. E. De Vos, J. Hofkens and M. B. J. Roeffaers, *Phys. Chem. Chem. Phys.*, 2014, **16**, 5044.
39 M. Alvaro, C. Aprile, B. Ferrer and H. Garcia, *J. Am. Chem. Soc.*, 2007, **129**, 5647.
40 L. J. Martinez and J. C. Scaiano, *J. Am. Chem. Soc.*, 1997, **119**, 11066.
41 L. F. V. Ferreira, M. R. V. Ferreira, A. S. Oliveira, T. J. F. Branco, J. V. Prata and J. C. Moreira, *Phys. Chem. Chem. Phys.*, 2002, **4**, 204.
42 M. Sakamoto, X. C. Cai, M. Hara, S. Tojo, M. Fujitsuka and T. Majima, *J. Phys. Chem. A*, 2004, **108**, 8147.
43 H. Tsubomura, N. Yamamoto and S. Tanaka, *Chem. Phys. Lett.*, 1967, **1**, 309.
44 C. Devadoss and R. W. Fessenden, *J. Phys. Chem.*, 1991, **95**, 7253.
45 C. V. Costa, M. A. Grela and M. S. Churio, *J. Photochem. Photobiol., A*, 1996, **99**, 51.