

Solution-Like Behavior of Photoswitchable Spiropyrans Embedded in Metal-Organic Frameworks

Heidi A. Schwartz,[†] Selina Olthof,[‡] Dominik Schaniel,[§] Klaus Meerholz,[‡] and Uwe Ruschewitz^{*,†}

[†]University of Cologne, Institute of Inorganic Chemistry, Greinstraße 6, D-50939 Cologne, Germany

[‡]University of Cologne, Institute of Physical Chemistry, Luxemburger Straße 116, D-50939 Cologne, Germany

[§]Université de Lorraine, CNRS, CRM², F-54506 Nancy, France

Supporting Information

ABSTRACT: 1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran (SP-1) as an example of a photoswitchable spiropyran was loaded into the pores of different prototypical metal-organic frameworks, namely MOF-5, MIL-68(In), and MIL-68(Ga), by a vapor-phase process. The successful incorporation in the pores of the MOF was proven by X-ray powder diffraction, and the amount of the embedded photoswitchable guest was determined by X-ray photoelectron spectroscopy and elemental analysis. In contrast to the sterically hindered crystalline state, SP-1 embedded in solid MOF hosts shows photoswitching under irradiation with UV light from the spiropyran to its merocyanine form with a nearly complete photoisomerization. Switching can be reversed by heat treatment. These switching properties were confirmed by means of UV/vis and IR spectroscopy. Remarkably, the embedded guest molecules show photoswitching and absorption properties similar to those in the dissolved state,



so that MOFs might be considered as "solid solvents" for photoswitchable spiropyrans. In contrast to that, embedment of SP-1 in the smaller pores of MIL-53(Al) was not successful. SP-1 is mainly adsorbed on the surfaces of the MIL-53(Al) particles, which also leads to photoswitching properties.

INTRODUCTION

Photochromism is defined as the reversible transformation of a molecule between two configurations induced by irradiation with light, which results in changes in its absorption spectra.¹ Depending on the nature of the molecule, light-triggered structural changes may cause E/Z isomerizations (e.g., azobenzenes) or ring-opening/-closing reactions (e.g., diarylethenes/spiropyrans); retransformation can be induced by either light (P-type chromophores) and/or heat treatment (Ttype chromophores).²

Among the different types of photoresponsive molecules, spiropyrans have been intensely studied since their discovery by Hirshberg and Fischer in 1952³ and independently by Chaudé and Rumpf in 1953.⁴ These molecules consist of two π systems linked by a tetrahedral spiro carbon. They are known to be in equilibrium with their two metastable merocyanine forms. Upon irradiation with UV light the stable, closed, and rather nonpolar spiropyran form (SP) transforms to an open, highly polar merocyanine form (MC), which may exist in chargeseparated zwitterionic and quinoidal forms.^{3,4} UV light irradiation causes cleavage of the C_{Spiro} -O bond and formation of a larger π -conjugated system, whereas ring reclosure is achieved by visible light or heat, which makes spiropyrans Ttype chromophores.^{3,4} In Figure 1 the ring-opening/-closing reaction is shown for 1,3,3-trimethylindolino-6'-nitrobenzopyr-



Figure 1. Photoinduced isomerization of the spiropyran SP-1 to its zwitterionic merocyanine form via cleavage of the C_{Spiro}-O bond.

ylospiran (SP-1), which was used as an example of a photoswitchable spiropyran in this work.

Due to the substantial structural reorganization, the switching of spiropyrans is hindered by spatial confinement in pure solids, such as crystals or crystalline powders. Therefore, photochromic behavior of spiropyrans has mainly been studied in solution.⁵⁻⁸ It is noteworthy that the polarity of the solvent influences the absorption properties of the resulting merocyanine dye by changing the energy gap between the ground state and excited state.² This solvatochromism results in red-shifted absorption bands (bathochromic shift) in nonpolar solvents, leading to a bluish appearance (cf. Figure $6\overline{)}$. Blue-shifted absorption bands (hypsochromic shifts) appear in polar solvents, leading to reddish colors. Furthermore, the highly

Received: July 27, 2017

polar merocyanine molecules have a strong tendency to aggregate.9 Arrangement of the dipoles occurs in either an antiparallel (side by side, H-aggregates) or parallel fashion (head to tail, J-aggregates), leading to additional blue- or redshifted absorption peaks, respectively, in comparison to the isolated merocyanine molecule. These two aspects, solvatochromism and aggregation of the merocyanine dyes, have to be considered when the switching behavior of spiropyrans in solution is investigated. Similar effects are expected in the solid state for spiropyrans either incorporated in porous matrices and polymers or deposited as thin films.¹⁰⁻²¹ Here, the necessary steric degree of freedom is realized by separating the single molecules from each other. Surprisingly, only one publication up to now has dealt with the incorporation of a spiropyran into a thin film of a metal-organic framework (MOF),²² even though MOFs appear to be ideal and very versatile host matrices, which has already been shown for other photo-chromic molecules.^{23–28}

Since the first presentation of MOF-5 by Yaghi and co-workers in 1999, 29 metal–organic frameworks have become a promising field of research. MOFs are hybrid materials, consisting of an inorganic node and an organic linker molecule, forming structures with potential voids.³⁰ MOFs offer various potential applications such as gas adsorption,^{31,32} separation of gases^{33,34} and liquids,^{34–36} heterogeneous catalysis,³⁷ and drug molecule encapsulation.^{38,39} The variable design and possible functionalization of the linker molecules lead to MOFs with a wide variety of properties.⁴⁰ The specific design of MOF pores results in different chemical and physical environments; hence, various forms of host-guest interactions may be expected for photoswitches embedded in different MOF host materials. Therefore, it is the aim of this work to synthesize and characterize different SP-1@MOF systems to examine the influence of the MOF hosts on the optical and photoswitching properties of the embedded SP-1 molecules and to compare the resulting properties with those obtained in solution. It should be noted that our approach is different from the concept, where the photoactive functionality is part of the backbone^{26,41} or a substituent^{25,42,43} of the linker forming the MOF framework. This necessarily leads to a high immobilization of the photoswitchable unit, whereas in our guest@host systems a higher mobility of the embedded guest molecules is expected.

EXPERIMENTAL SECTION

1,3,3-Trimethylindolino-6'-nitrobenzopyrylospiran (SP-1, $C_{19}H_{18}N_2O_3$). SP-1 was used as purchased (TCI) without further purification. The purity of SP-1 was confirmed by ¹H and ¹³C NMR spectroscopy.

MOF Synthesis. MOF-5 $(Zn_4O(C_8H_4O_4)_3)$ was provided by BASF SE and used without further purification. The phase purity was checked by XRPD (X-ray powder diffraction).

MIL-68(*Ga*) (*GaOH*($C_8H_4O_4$)·0.9*DMF*·*zH*₂O) and *MIL-68*(*In*) (*InOH*-($C_8H_4O_4$)·1.0*DMF*·*zH*₂O). MIL-68(Ga) and MIL-68(In) were synthesized by following mainly the protocol given in the literature.⁴⁴ The corresponding metal salt and terephthalic acid were mixed with 5.0 mL of DMF in a 23 mL Teflon lined autoclave. The mixture was heated to 100 °C at 20 °C/h, kept at this temperature for 48 h, and afterward cooled to room temperature at 5 °C/h. The resulting colorless powder was washed several times with DMF and dried in air. To remove the embedded DMF molecules, the residue was heated in air at 200 °C for 12 h and then at 100 °C for 1 h under reduced pressure and was stored afterward under an argon atmosphere. In a typical synthesis 207.40 mg of Ga(NO₃)₃·*x*H₂O (0.81 mmol calculated for *x* = 0) and 100.00 mg of H₂bdc (0.60 mmol) or 408.20 mg of In(NO₃)₃·*x*H₂O (1.04 mmol calculated for *x* = 0) and 200.00 mg of H₂bdc (1.20 mmol) were used

 $(H_2bdc = C_8H_6O_4$, terephthalic acid). The phase purity of both compounds was checked by XRPD.

*MIL-53(AI) (AIOH(C*₈*H*₄*O*₄*I*). MIL-53(AI) was synthesized according to the protocol known in the literature⁴⁵ with variations in the amount of the starting materials and the applied temperature programs. A 1.95 g portion of Al(NO₃)₃·9H₂O (5.20 mmol) and 432.00 mg of terephthalic acid (2.60 mmol) were mixed with 5.0 mL of deionized water in a 23 mL Teflon lined autoclave. The mixture was heated to 180 °C at 10 °C/h, kept at this temperature for 72 h, and afterward cooled to room temperature at 5 °C/h. The resulting colorless powder was washed with deionized water several times and dried in air. To remove the embedded terephthalic acid molecules, the residue was heated in air at 350 °C for 7 days followed by 3 days of heating at 400 °C. Finally, the resulting powder was heated at 100 °C for 1 h under reduced pressure and stored under an argon atmosphere. The phase purity was confirmed by XRPD.

Commercially available N,N'-dimethylformamide (Acros Organics), Ga(NO₃)₃:xH₂O (ABCR), In(NO₃)₃:xH₂O (ABCR), Al(NO₃)₃: 9H₂O (ABCR), and terephthalic acid (Alfa Aesar) were used without further purification.

Preparation of SP-1@MOF Systems. A mixture of the respective activated MOF and SP-1 was ground under an argon atmosphere. The resulting homogeneous powder was placed into a small glass vessel inside a Schlenk tube and heated at 145-150 °C and a reduced pressure of $\sim 5 \times 10^{-2}$ mbar for several hours. The excess of SP-1 resublimated at the top of the glass tube. To prevent the absorption of water and decomposition upon contact with air and moisture, all compounds were stored in a glovebox under an argon atmosphere.

 $SP-1_x@MOF-5$ (1). The synthesis was carried out as described above with 60.00 mg (0.08 mmol) of MOF-5 and 126.00 mg (0.4 mmol) of SP-1, yielding a pink powder.

 $SP-1_x@MlL-68(ln)$ (2). The synthesis was carried out as described above with 60.00 mg (0.20 mmol) of MIL-68(ln) and 64.00 mg (0.20 mmol) of SP-1, yielding a pastel pink powder.

 $SP-1_x@MIL-68(Ga)$ (3). The synthesis was carried out as described above with 60.00 mg (0.24 mmol) of MIL-68(Ga) and 77.00 mg (0.24 mmol) of SP-1, yielding a pastel pink powder.

The purities of the resulting guest@MOF materials were checked by XRPD. The XRPD patterns of 1-3 (loaded and unloaded) are shown in Figure 2 and Figures S1 and S2 in the Supporting Information. The resulting unit cell volumes are given in Table 1. The composition, i.e. the amount of loading, of 1-3 was obtained from elemental analysis and XPS measurements, which are summarized in Table 2. Details are given in Figures S3–S5 and Tables S1–S4 in the Supporting Information.



Figure 2. XRPD patterns of SP-1@MOF-5 (1) (red) and unloaded MOF-5 (black), measured at 298 K (BM01B/ESRF: $\lambda = 0.50561$ Å (1) and $\lambda = 0.504477$ Å (unloaded MOF-5)). As both patterns were recorded with different wavelengths 1/d was chosen as the *x* axis and a small offset along *y* (+ 4%) was applied.

Table 1. Results of Le Bail Fits of High-Resolution Synchrotron Powder Diffraction Data of Compounds 1-3 in Comparison with the Unit Cell Volumes of the Respective Unloaded MOF

	1	2	3
T/K	298	298	298
GOF	0.80	0.97	0.91
R _p	0.186	0.167	0.205
R _{wp}	0.291	0.248	0.325
$V/Å^3$	17111.8(3)	5911.5(2)	5217(1)
$V/Å^3$ (unloaded MOF)	17156.0(4)	5901.1(2)	5197.0(7)

 $SP-1_x@MIL-53(AI)$ (4). The synthesis was carried out as described above with 60 mg (0.28 mmol) of MIL-53(AI) and 92 mg (0.28 mmol) of SP-1, yielding a pastel pink powder. The purity of the resulting guest@MOF material was checked by XRPD. No obvious changes in intensities in comparison to pristine MIL-53(AI) were found (Figure S6 in the Supporting Information); therefore, it was concluded that obviously only a very small amount of SP-1 was embedded in the pores of the MOF. As no additional peaks for SP-1 were found, we concluded that SP-1 was adsorbed as an amorphous thin film on the surfaces of MIL-53(AI) particles. Nonetheless, the composition of this SP-1@MIL-53(AI) system was determined from elemental analysis and XPS measurements: The results are also presented in Table 2. Details of these investigations can be found in Figure S7 and Tables S1 and S5 in the Supporting Information.

Synchrotron Powder Diffraction. High-resolution synchrotron powder diffraction data of pristine and loaded MOFs were recorded at the Swiss Norwegian BeamLine (SNBL, BM01B) at the European Synchrotron (ESRF, Grenoble/France). The wavelength was calibrated with a Si standard NIST 640c to 0.50561 and 0.504477 Å, respectively. The diffractometer is equipped with five counting channels, delivering five complete patterns collected with a small 1.1° offset in 2 θ . A Si(111) analyzer crystal is mounted in front of each NaI scintillator/photomultiplier detector.

For all experiments the substances were filled in glass capillaries (1.0 mm i.d., Hilgenberg) and sealed under an argon atmosphere. The capillaries were mounted on a spinning goniometer. Data were collected at 298 K between 1.1 and 25° in 2θ with steps of 0.002° and 100 ms of integration time per data point. Typical recording times were ~20 min per scan. For each sample five such scans were added. Data from all detectors and scans were averaged and added to one pattern with local software. To determine the unit cell parameters precisely, Le Bail fits in Jana2006⁴⁶ were performed by refining the lattice parameters, zero shifts, background (manual background function with 30 points), and profile parameters (TCH profile function with GW and LY as refined parameters). In all Le Bail fits the same set of parameters was used. These Le Bail fits are given in Figures S8–S10 in the Supporting Information.

X-ray Powder Diffraction. To check the purity of the crystalline samples, laboratory measurements were carried out on a STOE Stadi P diffractometer (Ge monochromator, PSD detector) with Cu K α_1 radiation. Data were collected at 298 K between 4 and 80.70° in 2θ with steps of 0.01° and a measurement time of 5 s/step. For each sample seven such scans were added.

XPS. For XPS measurements, SP-1@MOF powders were placed on an adhesive copper foil. Measurements were performed on a

multichamber UHV system at a pressure of 5×10^{-10} mbar using a Phoibos 100 hemispherical analyzer (Specs). As the excitation source a Mg K α anode was used ($h\nu$ = 1252.6 eV, probing depth ~10 nm).

Due to charging effects during measurements caused by the low conductivity of the powder samples, the binding energy scale as measured by XPS was shifted by a few electronvolts for the different samples. To account for this, the binding energies were corrected such that adventitious carbon is positioned at 284.8 eV. Integrated peak areas of characteristic core level excitations were used to calculate the embedded amount of SP-1 inside the MOF matrices. For this, the peak areas of N, Zn, In, Ga, and Al were evaluated and corrected by their relative sensitivity factors (RSF).⁴⁷ Details are given in Figures S3–S5 and S7 and Table S1 in the Supporting Information.

Elemental Analysis. Elemental analysis of carbon, hydrogen, and nitrogen was carried out with a HEKAtech GmbH EuroEA 3000 Analyzer. Approximately 2 mg of each compound was filled into a tin cartridge under an argon atmosphere. For each sample three measurements were carried out, from which a mean value was calculated (Tables S2–S5 in the Supporting Information). To estimate the SP-1 to MOF ratio the following procedure was applied: as only the SP-1 guest contains nitrogen, *x* in SP-1_{*x*}@MOF was optimized in a way that calculated and found nitrogen contents agree as well as possible. For SP-1_{*x*}@MOF-5 this leads to very good agreements between the calculated and found carbon and hydrogen values as well. However, significant discrepancies are found for the systems based on the MIL family as hosts. This is discussed in more detail below.

Reflection Spectroscopy. Measurements were carried out with a PerkinElmer Lambda 1050 spectrometer. Samples were measured on an adhesive film in the range 250–750 nm. Data were recorded before and after irradiation with UV light ($\lambda = 365$ nm, 1 min).

UV/vis Spectroscopy. UV/vis spectra of the SP-1@MOF systems were recorded using transparent KBr pellets with a Varian CARY 4000 spectrometer.

Transparent pellets were prepared as follows: half a spatula of the substance was carefully ground with six spatulas of dried KBr. The mixture was pressed for 30 min at a pressure of ~530 bar, yielding a thin, transparent, slightly colored pellet. The KBr pellet was placed into the sample holder, and the sample chamber was evacuated to 10^{-5} mbar. Spectra were recorded before and during irradiation with UV light ($\lambda = 365$ nm). For thermal relaxation, the pellet was placed in a furnace; details of the irradiation and relaxation times as well as applied temperatures are given in Table S6 in the Supporting Information.

UV/vis spectra of SP-1 dissolved in different solvents were measured on a Varian Cary50 Scan photospectrometer (Figure S11 in the Supporting Information).

IR Spectroscopy. IR spectra of solid SP-1@MOF compounds were measured with a Nicolet7500 FT-IR spectrometer using transparent KBr pellets. Transparent pellets were prepared as described for the UV/vis experiments. The KBr pellet was placed into the sample holder, and the sample chamber was evacuated to 10^{-5} mbar. Scans were recorded in the range 360–4000 cm⁻¹ with a resolution of 2 cm⁻¹. Ninety scans for each sample were recorded and added. Irradiation times varied. They are given in the figures of the respective spectra.

IR spectra of pristine MIL-68(In) and MIL-68(Ga) were measured as pure solids with a PerkinElmer Spectrum 400 FT-IR/FT-FIR spectrometer. Scans were recorded in the range 400–4000 cm⁻¹ with a resolution of 4 cm⁻¹. One scan for each sample was recorded. Selected

Table 2. Ratio of SP-1 per Formula Unit of the Respective MOF for 1–4 Calculated from XPS Measurements and Elemental Analysis

		XPS	elemental analysis
$SP-1_x @MOF-5 (1)$	$SP-1:(Zn_4O(bdc)_3)$	2.26:1	2.4:1
SP-1 _x @MIL-68(In) (2)	SP-1:(In(OH)(bdc))	0.30:1	0.45:1
SP-1 _x @MIL-68(Ga) (3)	SP-1:(Ga(OH)(bdc))	0.24:1	0.25:1
$SP-1_x@MIL-53(Al)$ (4)	SP-1:(Al(OH)(bdc))	0.10:1	0.06:1

IR spectra are shown in Figure 8 and in Figures S12–S16 in the Supporting Information, focusing on the ν (OH) region.

RESULTS AND DISCUSSION

In this work we present our results on MOFs as suitable hosts for photoswitchable spiropyrans and, in a second step, how the MOF matrix influences the switching properties of the embedded dye. In this first systematic investigation we have concentrated on the influence of the metal node so that only MOFs with bdc^{2–} as a linker ligand (H₂bdc = C₈H₆O₄, 1,4benzenedicarboxylic acid = terephthalic acid) were selected. Furthermore, suitable MOFs for this investigation were chosen to meet the following requirements:

- (1) The guest SP-1 has to fit into the pores of the MOF, and photoswitching inside these pores has to be possible; therefore, an adequate pore size is required.
- (2) The absorption maxima of guest and host should not overlap so that the switching process can be followed by spectroscopic methods. Basically, colorless MOFs are preferable.

Therefore, we have chosen MOF-5 $(Zn_4O(bdc)_3)$,²⁹ MIL-68(In) (In(OH)(bdc)),⁴⁴ MIL-68(Ga) (Ga(OH)(bdc)),⁴⁴ and MIL-53(Al) (Al(OH)(bdc)),⁴⁵ as suitable MOFs for this study, while 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran (denoted SP-1 in the following) was selected as the photoactive guest molecule. From the crystal structure of SP-1⁴⁸ the size of one molecule including van der Waals radii was estimated (~15 Å × 8 Å × 8 Å), which should fit into the pores of the MOFs we have selected for this investigation. The crystal structure of the merocyanine form of SP-1 is not known, but from a similar merocyanine⁴⁹ its molecular size can be estimated to be ~16.5 Å × 7 Å × 9.5 Å. Thus, during and after switching it should also fit into the pores of the selected MOFs. Note: for the MOFs of the MIL series an embedment of the guest molecules along the porous channels is assumed.

The MOFs were loaded via a gas-phase reaction to exclude any influence of solvent molecules in these investigations. During the loading process, the mixture of the previously colorless MOF and yellow SP-1 forms a slightly colored powder, giving a first impression of the successful combination of MOF and guest.

Embedment. The successful embedment of SP-1 into the MOF's pores was confirmed by X-ray powder diffraction (XRPD). After the MOF's pores were loaded, the integrity of the MOF framework remained intact, as indicated by the almost unaltered reflection positions. However, significant changes in the reflection intensities were observed for SP-1(a) MOF-5 (1), SP-1(a)MIL-68(In) (2), and SP-1(a)MIL-68(Ga) (3). The changes in the reflection intensities indicate that the electron density within the MOF's pores must have changed, as expected after embedment of a guest. No additional reflections pointing to free dye molecules were observed. In Figure 2 the diffraction patterns of the unloaded MOF-5 as well as 1 are shown as examples (for diffraction patterns of unloaded/loaded MIL-68(In) and MIL-68(Ga), see Figures S1 and S2 in the Supporting Information).

It is remarkable that the Bragg peaks of 1 are shifted to higher angles in comparison to unloaded MOF-5, indicating a contraction of the MOF-5 framework upon incorporation of SP-1. Le Bail fits using the software Jana2006⁴⁶ confirm the observed decrease of the unit cell volume. In Table 1 the unit cell volumes of 1-3 are given. It is noteworthy that the unit cell

volumes of the MIL-68 family show a slightly increased unit cell volume upon loading, which might indicate repulsive interactions between guest and host, whereas the decrease of the unit cell volume of MOF-5 upon loading might point to attractive interactions between guest and host. However, as these changes are very small (approximately 0.2-0.4%), it will be essential to confirm this finding by complementary methods: e.g., quantum chemical calculations.

In contrast, for MIL-53(Al) no changes in reflection positions and intensities were observed after loading, although especially the reflection positions of such flexible ("breathing") MOFs should be very sensitive to guest incorporation. As in the diffraction pattern of loaded MIL-53(Al) (Figure S6 in the Supporting Information) no reflections in addition to the expected MOF structure were found, though a color change occurred during the loading process (see above), we concluded that only a very little amount of SP-1 was embedded in the pores of MIL-53(Al) and/or merely adsorption on the MOF's surface as an amorphous thin film took place. Nonetheless, SP-1@MIL-53(Al) (4) was further investigated by XPS, IR, and UV/vis spectroscopy in order to clarify the interaction between MIL-53(Al) and SP-1. However, these investigations cannot unambiguously prove whether SP-1 is adsorbed in the pores of MIL-53(Al) or on its surface.

The successful embedment of SP-1 into the pores of MIL-68(In) and MIL-68(Ga) can also be concluded from the shifts of the OH frequencies in the IR spectra before and after loading (Table S7 in the Supporting Information). These OH groups of the MIL-68 frameworks are a sensitive probe for guest uptake.⁵⁰ Shifts of -14 cm^{-1} (MIL-68(In)) and -6 cm^{-1} (MIL-68(Ga)) confirm the successful embedment of SP-1, whereas for MIL-53(AI) a shift of $+4 \text{ cm}^{-1}$ indicates a different behavior for this system, as already concluded from the XRPD measurements.

Composition (Degree of Loading). To understand the switching behavior of the synthesized SP-1@MOF systems and to correctly interpret possible host-guest and guest-guest interactions, it is essential to know the composition of these systems: i.e., to which fraction the MOF's pores are filled with guests. The ratio of guest molecule per formula unit of the respective MOF was determined by means of XPS and elemental analysis. In our previous work on azobenzene (AZB) embedded in different MOF hosts, we only used elemental analysis to determine the composition of the guest@ MOF systems.⁵¹ These results were in good agreement with the results of Rietveld refinements on AZB_{0.5}@MIL-53(Al) and AZB_{0.66}@MIL-68(Ga).⁵¹ However, the molecular structure of SP-1 is much more complex than that of AZB so that we have failed up to now to obtain a reliable structure model for SP-1@ MOF from powder diffraction data. Therefore, we used XPS data in this work to corroborate the results of the elemental analysis by a second method. As nitrogen is only found in the guest, not in the MOF framework, we compared the nitrogen intensities of typical XPS signals with the intensities of XPS signals of the respective metal cations of the MOF host. The results of the XPS measurements are shown in Table 2 and compared with the results of the elemental analysis. More detailed information is given in Figures S3-S5 and S7 and Tables S1–S5 in the Supporting Information. The results of the elemental analysis and the XPS measurements are in the same range. However, larger discrepancies are found for the MIL-68(In) and MIL-53(Al) samples. But, as the calculated and measured CHN values already show some significant deviations (Tables S2–S5), we conclude that XPS analysis seems to be the



Figure 3. Reflection spectra (298 K) of 1–4 (respectively (a)–(d)) before (blue) and after (red) irradiation with UV light (λ = 365 nm, 1 min) with photographs of 1–4 before and after irradiation with UV light.

much more accurate method to determine the degree of loading in such guest@MOF systems.

On comparison of the XPS peaks of nitrogen in Figures S3– S5 and S7 in the Supporting Information, the peaks in compounds 1–3 appear somewhat broader than the nitrogen peak for compound 4. As an interaction of the guest with the MOF framework might lead to such a broadening, this can be interpreted as another confirmation that SP-1 was successfully incorporated in 1–3 but not in 4.

Photoswitching. In solution, spiropyrans show transformation to their merocyanine form upon irradiation with UV light. The planar structure and extended π conjugation between the chromene and indoline parts of the merocyanine leads to a reduction of the band gap, where the absorption maximum is located between 500 and 600 nm, being strongly dependent upon the polarity of the surrounding environment.^{52,53} Recovery of the closed spiropyran form is achieved by irradiation with visible light or heat treatment. It is known that the acidity of the environment (saltlike structures are formed in the presence of acids) $^{54-59}$ and metal complexalso influence the stability and the absorption ation^{60–68} properties of the merocyanine dye. However, these two aspects do not have to be taken into consideration in our investigation, as the MOFs we have used do not contain any coordinatively unsaturated metal sites (CUM) for complexation and its ligand (bdc^{2-}) is not acidic enough to protonate the merocyanine.

To compare the results of the switching properties of SP-1 embedded in different MOF hosts, UV/vis spectra of all compounds 1-4 were recorded before and after irradiation with UV light ($\lambda = 365$ nm, 1 min). In Figure 3 the resulting reflection spectra of 1-4 are shown and compared. It should be noted that additional adsorption of SP-1 as an amorphous film on the surface of the respective metal-organic framework is expected to lead to a shoulder in the reflection spectrum, as the different host-guest interactions within a pore and on a surface will affect the optical properties. However, even for MIL-53(Al), for which such a scenario has been assumed, no shoulder is visible in the spectra shown in Figure 3. For the latter this leads to the assumption that only a very small amount of SP-1 is embedded in the pores of MIL-53(Al) and the reflection spectrum is dominated by the species adsorbed on the surfaces of the MOF's particles.

Immediately after loading, a deep pink color is observed for **1** without UV light irradiation (Figure 3a)). The local minimum in the reflection spectrum of nonirradiated **1** at ~520 nm can be assigned to the open merocyanine form of SP-1. On irradiation ($\lambda = 365$ nm, 1 min), the reflection further decreases in this range, indicating a proceeding isomerization of SP-1 to its merocyanine configuration (MC-1) inside the pores of MOF-5. This process can be reversed by heating the sample, but a complete isomerization back to the SP-1 form was not achieved. A similar finding was reported by Zhang et al., stating

Article



Figure 4. (a) Absorption spectra of **2** after irradiation with UV light ($\lambda = 365 \text{ nm}$) and heat treatment. (b) Photographs of the switching process of a pressed powder of **2** (for details see text).

that 1-(2-hydroxyethyl)-3,3-dimethylindolino-6'-nitrobenzopyrylospiran is also stabilized in its open MC form within the pores of JUC-120, an analogue of MIL-100.²² We think that these results clearly show that the pores of MOF-5 and JUC-120 establish a chemical environment, which is preferred by molecules with a high dipole moment such as spiropyrans in their open MC form.

For 2 and 3 a somewhat different behavior of the SP-1 molecule in the pores of MIL-68(In) and MIL-68(Ga) is observed. When they are embedded in the respective MOF, nonirradiated 2 and 3 show only slight coloration (Figure 3b,c). After irradiation with UV light the color changes to deep purple and the reflection spectra of 2 and 3 show minima at \sim 560 nm for 2 and at ~566 nm for 3 (Figures 3b,c), which can be assigned to the open MC-1 form. The reflection minima of 2 and 3 are shifted to slightly longer wavelengths in comparison to 1, leading to a more bluish color. Similar to the results shown above for 1, the isomerization between SP-1 and MC-1 is not sterically hindered inside the pores of MIL-68(In) and MIL-68(Ga). Switching of 2 and 3 is fully reversible by heating the sample. This is shown for 2 as an example in Figure 4. Figure 4a shows the absorption spectra of 2 irradiated with UV light (solid line) and after heating (broken line). The MC-1 band decreases significantly after heating. In Figure 4b a pressed powder of nonirradiated whitish 2 is irradiated with UV light (λ = 365 nm) using a shadow mask. After irradiation, a powder with a deep purple color is obtained. The nonirradiated sections of the pressed powder show the pastel pink color of nonirradiated 2 after removal of the shadow mask. After heating pastel pink 2 is recovered in the whole powder.

In Figure 3d the reflection spectra of 4 are shown. Even though a successful embedment of the dye molecule in the pores of MIL-53(Al) could not be confirmed, photochromic behavior of the combination of this MOF with SP-1 was observed. Comparable to the case for 2 and 3, 4 shows photochromic behavior upon irradiation with UV light (see Figure 3). Interestingly, the light-induced transformation of SP-1 to its MC-1 form causes a deep blue color with a reflection minimum at ~599 nm, which is significantly red shifted in comparison to 2 and 3.

It is obvious from Figure 3 that the colors of irradiated 1–4, i.e. MC-1 embedded in different MOFs, vary significantly: a more reddish color is found for MC-1 embedded in MOF-5, whereas a shift to bluish colors is found for MC-1 embedded in different MOFs of the MIL series. These results are summarized in Figures 5 and 6 (right), which show the reflection spectra of 1–4 after irradiation with UV light ($\lambda =$



Figure 5. Reflection spectra (298 K) of 1–4 after irradiation with UV light ($\lambda = 365$ nm, 1 min).



Figure 6. Photographs of (left) MC-1 dissolved in solvents with different polarities after irradiation with UV light ($\lambda = 365 \text{ nm}, 1 \text{ min}$) and (right) 1–4 (from left to right) after irradiation with UV light ($\lambda = 365 \text{ nm}, 1 \text{ min}$).

365 nm) and the colors of the resulting powders. As mentioned above, the energy gap between the ground and excited states of MC-1 is influenced by the polarity of the solvent in solution. Therefore, we conclude that the different colors and reflection spectra found for irradiated 1–4 can be ascribed to variations in polarity inside the different MOF pores. Thus, the pores within MOF-5 should be rather polar, leading to a blue (hypsochromic) shifted absorption band and a reddish color. For MIL-68(In) and MIL-68(Ga) the difference between the ground state and excited state of the merocyanine form in 2 and 3 is not as high as in 1, as a bathochromic shift of the absorption band is found leading to a more bluish color. Therefore, it can be concluded that the pores within MIL-68(In) and MIL-68(Ga) establish an environment which is less polar than that of MOF-5. As the same bdc^{2-} linker is used in these MOFs, this

difference must be related to their knots, which are $[{\rm Zn_4O}]^{6+}$ (MOF-5) and $[{\rm Ga(OH)}]^{2+}/[{\rm In(OH)}]^{2+}$ units (MIL-68). Just focusing on the charges of these knots, one indeed expects a higher polarity for pores in MOF-5, as has been experimentally observed. The difference between Ga(OH)^{2+} and In(OH)^{2+} due to the increasing charge/radius ratio from ${\rm In^{3+}}$ to Ga^{3+} is obviously too small to lead to a significant change in the recorded spectra.

For 4 the situation is not as clear as for 1-3. As already mentioned, apparently only a small amount of SP-1/MC-1 is embedded in the pores of MIL-53(Al), which are the smallest of all MOF pores of this investigation. Additionally, SP-1/MC-1 is assumed to be adsorbed on the surfaces of the MOF particles. For the $[Al(OH)]^{2+}$ knots in MIL-53(Al) a polarity between those of MOF-5 and MIL-68 is expected, whereas an adsorption on the surface should be less polar. From the reflection measurements we conclude that SP-1 must be mainly adsorbed on the surfaces of MIL-53(Al) particles, resulting in a red-shifted reflection minimum in comparison to 1-3 (Figure 5). This red-shifted minimum leads to a bluish color of 4 (Figure 6, right).

It is also remarkable that the colors of the nonirradiated guest@MOF systems 1–4 differ significantly, which can be directly correlated to the amount of MC-1 embedded in the pores of the respective MOF (in addition to SP-1, see absorption spectra in Figure 3). With increasing polarity of the pores the amount of the open polar MC-1 form increases. As already mentioned, a similar finding was reported for thin films of JUC-120, an analogue of MIL-100,²² where after embedment of a spiropyran larger amounts of the open merocyanine form were found, which was also attributed to the polarity of the pores in JUC-120.²²

As all these observations (switching properties, dependence of the MC-1 color on the MOF's polarity) resemble very much the behavior of spiropyrans dissolved in solvents with different polarities,² we conclude that MOFs might be considered as *"solid solvents"* for this class of photochromic molecules. In Figure 6 the correspondence between MC-1 dissolved in different MOFs and solvents is shown. From methanol to toluene the polarity of the solvent decreases (Figure 6, left) and the absorption of MC-1 is increasingly red shifted, leading to a more bluish color. This correlates nicely with the colors of MC-1 embedded in different MOFs (Figure 6, right).

To classify the polarities of the different MOFs used in this investigation, the absorption maxima of the merocyanine (MC-1) dissolved in solvents of different polarities (Figure S11 in the Supporting Information) were plotted against the elution power ε^0 of the respective solvent on alumina, which was taken from Snyder.⁶⁹ In Figure 7 the resulting values (blue dots) are shown, which give an almost linear fit (blue dotted line). Adding the reflection minima of the different SP-1@MOF systems (green diamonds), one can estimate the polarity of the respective MOF host compared to these solvents.

According to the plot in Figure 7, MOF-5 is even more polar than methanol and both MOFs of the MIL-68 series show polarities between those of acetonitrile and acetone, whereas the polarity of MIL-53(Al) (better: it's surface) almost equals that of toluene. However, note that for SP-1@MIL-53(Al) our results indicate that SP-1 is merely adsorbed on the surfaces of the MOF particles. These results nicely show the similarity between SP-1 dissolved in different solvents and embedded in different MOFs so that our conclusion to understand MOFs as "solid solvents" for such solvatochromes seems to be reasonable.



Figure 7. Plot of the absorption maxima (in nm) of MC-1 dissolved in different solvents (blue dots) against the elution power ε^0 on alumina taken from Snyder.⁶⁹ These values were linearly fitted (blue dotted line). The reflection minima of the different SP-1@MOF systems (green diamonds) were added to this curve classifying the polarity of the respective MOFs.

Of course, more examples with other solvatochromes embedded in different MOFs are needed to support this hypothesis. This is part of our current investigations in this field.

As shown above, the successful isomerization of SP-1 to its MC-1 form was confirmed by means of UV/vis spectroscopy (Figure 3). In addition, IR spectroscopy was employed as a powerful tool to gain more detailed information about the amount of switching from SP-1 to MC-1 in 1–4, as has previously been shown for some azobenzene@MOF systems.⁵¹ As the formation of the merocyanine moiety leads to a cleavage of the C_{Spiro}–O bond in SP-1 (Figure 1), the decrease of this band at ~950 cm⁻¹ can be used to follow the formation of MC-1.⁷⁰ Therefore, IR spectra on polycrystalline powders of 1–4 pressed to thin transparent KBr pellets were recorded before and during irradiation with UV light ($\lambda = 365$ nm). These spectra are shown in Figure 8.

Formation of the merocyanine moiety is proven for all compounds 1–4, as the intensity of the band at ~950 cm⁻¹ decreases upon irradiation with UV light ($\lambda = 365$ nm). Depending on the MOF host, a complete isomerization took up to ~17 h. Long irradiation times are required, as MC-1 formed at the surface of the pellets strongly absorbs the incoming UV light, such that SP-1 molecules in the bulk receive a significantly lower UV dose, which hinders their switching. This assumption is validated by a significant decrease in the C_{spiro}–O absorption band after turning the KBr pellets to their opposite sides (cf. Figure 8).

CONCLUSION

In conclusion, we synthesized four new switching systems consisting of a photoswitchable spiropyran (SP-1) embedded in four different metal—organic frameworks: namely, MOF-5, MIL-68(In), MIL-68(Ga), and MIL-53(Al). The resulting SP-1@MOF systems were thoroughly investigated by means of XRPD, XPS, and elemental analysis to confirm the successful loading and the degree of loading. It was found that the pores of MOF-5, MIL-68(In), and MIL-68(Ga) were successfully filled with SP-1, whereas the smaller pores of MIL-53(Al) were only filled with a minor amount of SP-1 and the major amount



Figure 8. IR spectra of 1–4 (respectively (a)–(d)) during irradiation with UV light (λ = 365 nm) focusing on the decrease (the direction of the decrease is marked with an arrow) of the band of the C_{spiro}–O bond at approximately 950 cm⁻¹. Measurements labeled with an asterisk mark the spectra which were recorded after turning the KBr pellets of 1–4 to their opposite sides.

was adsorbed on the surfaces of the MIL-53(Al) particles. Nonetheless, photochromic behavior was confirmed for all compounds by UV/vis and IR spectroscopy.

It is a remarkable finding that the photoswitching properties of embedded SP-1 strongly depend on the MOF host. Before irradiation with UV light already a larger amount of SP-1 switched to its merocyanine form (MC-1) after embedment in MOF-5, whereas in MIL-68(In) and MIL-68(Ga) only minor amounts of MC-1 were found before UV irradiation. After irradiation with UV light ($\lambda = 365$ nm) increasing amounts of MC-1 were found, depending on the time of the irradiation (also for SP-1@MIL-53(Al)). However, the color of the MC-1 form strongly depends on the MOF host, as a more reddish color was found in MOF-5 and more bluish colors were found in the MOFs of the MIL series. We were able to show that this is due to the larger polarity within the pores of MOF-5 in comparison to MIL-68. As this behavior resembles very much the behavior of SP-1 dissolved in solvents with different polarities, MOFs might be considered as "solid solvents" for such photoswitchable molecules. During the preparation of this paper a similar finding was reported by Shustova and coworkers, who found that after embedment of the chromophore MeO-oHBI in different MOF types the emission wavelength varies by 100 nm depending on the respective MOF.⁷¹

However, these authors did not ascribe their finding to the different polarities within the MOF pores.

As mentioned in the Introduction, merocyanines in their zwitterionic forms are known to have a strong tendency to form aggregates. However, as in the spectra shown in this contribution no additional blue (*H*-aggregates)- or red-shifted (*J*-aggregates) absorption bands were found, no such aggregation can be concluded from our spectra. However, after very long irradiation times with UV light (>12 h) we observed some hints that aggregation might take place. This is currently being investigated by our group.

Recently Gascon and co-workers⁷² gave an interesting overview on photoswitch@MOF hybrid materials. Most of the presented approaches contain the photoswitchable moiety as a part of the MOF linker, which typically requires complex syntheses. Our approach to embed readily available photoswitchable molecules in the pores of well-known MOFs seems to be an easy alternative, which is not restricted to bulk materials, but can also be extended to thin films.⁷³ In their review Gascon and co-workers state that "... SP/MC-based MOFs still remain unexplored."⁷² With this contribution we present the very first results on these SP/MC-based MOFs, which seem to offer new and remarkable photophysical properties.

Article

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01908.

Details of XPS measurements/calculations and elemental analyses, IR and UV/vis spectra, XRPD patterns of loaded and unloaded MOFs, and XRPD patterns with Le Bail fits (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail for U.R.: Uwe.Ruschewitz@uni-koeln.de.

ORCID [©]

Selina Olthof: 0000-0002-8871-1549 Uwe Ruschewitz: 0000-0002-6511-6894

Author Contributions

H.A.S. performed the syntheses and all experiments, which were coplanned by H.A.S. and U.R.. S.O., D.S., and K.M. provided the different spectroscopic instruments as well as their expertise in these methods. All authors discussed the results and the final version of the manuscript, which was written by H.A.S. and U.R.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors gratefully acknowledge H. Emerich for his technical support and expertise at the Swiss Norwegian BeamLine (SNBL BM01B) at the ESRF (Grenoble), S. Kremer for the elemental analyses, and BASF SE for providing MOF-5.

REFERENCES

(1) Hirshberg, Y. Photochromie Dans Le Série de La Bianthrone. C. R. Hebd. Séances Acad. Sci. **1950**, 116, 903–904.

(2) Bouas-Laurent, H.; Dürr, H. Organic Photochromism (IUPAC Technical Report). *Pure Appl. Chem.* 2001, 73, 639–665.

(3) Fischer, E.; Hirshberg, Y. Formation of Coloured Forms of Spirans by Low-Temperature Irradiation. *J. Chem. Soc.* **1952**, *11*, 4522–4524.

(4) Chaudé, O.; Rumpf, R. Sur la double phototropic de certains spiranes. C. R. Hebd. Séances Acad. Sci. 1953, 236, 697–699.

(5) Li, C.; Zhang, Y.; Hu, J.; Cheng, J.; Liu, S. Reversible Three-State Switching of Multicolor Fluorescence Emission by Multiple Stimuli Modulated FRET Processes within Thermoresponsive Polymeric Micelles. *Angew. Chem., Int. Ed.* **2010**, *49*, 5120–5124.

(6) Chen, J.; Zeng, F.; Wu, S.; Zhao, J.; Chen, Q.; Tong, Z. Reversible Fluorescence Modulation through Energy Transfer with ABC Triblock Copolymer Micelles as Scaffolds. *Chem. Commun.* **2008**, *13*, 5580–5582.

(7) Liao, B.; Long, P.; He, B.; Yi, S.; Ou, B.; Shen, S.; Chen, J. Reversible Fluorescence Modulation of Spiropyran-Functionalized Carbon Nanoparticles. *J. Mater. Chem. C* **2013**, *1*, 3716–3721.

(8) Zhu, L.; Zhu, M.-Q.; Hurst, J. K.; Li, A. D. Q. Light-Controlled Molecular Switches Modulate Nanocrystal Fluorescence. *J. Am. Chem. Soc.* **2005**, *127*, 8968–8970.

(9) Berkovic, G.; Krongauz, V.; Weiss, V. Spiropyrans and Spirooxazines for Memories and Switches. *Chem. Rev.* **2000**, *100*, 1741–1754.

(10) Parthenopoulos, D. A.; Rentzepis, P. M. Three-Dimensional Optical Storage Memory. *Science* **1989**, *245*, 843–845.

(11) Tomioka, H.; İtoh, T. Photochromism of Spiropyrans in Organized Molecular Assemblies. Formation of J- and H-Aggregates of Photomerocyanines in Bilayers-Clay Matrices. J. Chem. Soc., Chem. Commun. 1991, 7, 532-533.

(12) Casades, I.; Constantine, S.; Cardin, D.; García, H.; Gilbert, A.; Márquez, F. "Ship-in-a-Bottle" Synthesis and Photochromism of Spiropyrans Encapsulated within Zeolite Y Supercages. *Tetrahedron* **2000**, *56*, 6951–6956.

(13) Schomburg, C.; Wark, M.; Rohlfing, Y.; Schulz-Ekloff, G.; Wöhrle, D. Photochromism of Spiropyran in Molecular Sieve Voids: Effects of Host-guest Interaction on Isomer Status, Switching Stability and Reversibility. *J. Mater. Chem.* **2001**, *11*, 2014–2021.

(14) Casades, I.; Alvaro, M.; García, H.; Pillai, M. N. Modified Mesoporous MCM-41 as Hosts for Photochromic Spirobenzopyrans. *Photochem. Photobiol. Sci.* **2002**, *1*, 219–223.

(15) Kinashi, K.; Harada, Y.; Ueda, Y. Thermal Stability of Merocyanine Form in Spiropyran/silica Composite Film. *Thin Solid Films* **2008**, *516*, 2532–2536.

(16) Dattilo, D.; Armelao, L.; Fois, G.; Mistura, G.; Maggini, M. Wetting Properties of Flat and Porous Silicon Surfaces Coated with a Spiropyran. *Langmuir* **2007**, *23*, 12945–12950.

(17) Renkecz, T.; Mistlberger, G.; Pawlak, M.; Horváth, V.; Bakker, E. Molecularly Imprinted Polymer Microspheres Containing Photoswitchable Spiropyran-Based Binding Sites. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8537–8545.

(18) Kundu, P. K.; Olsen, G. L.; Kiss, V.; Klajn, R. Nanoporous Frameworks Exhibiting Multiple Stimuli Responsiveness. *Nat. Commun.* **2014**, *5*, 3588.

(19) Li, Z.; Wan, S.; Shi, W.; Wei, M.; Yin, M.; Yang, W.; Evans, D. G.; Duan, X. A Light-Triggered Switch Based on Spiropyran/Layered Double Hydroxide Ultrathin Films. *J. Phys. Chem. C* **2015**, *119*, 7428–7435.

(20) Lee, C.-Y.; Hu, C.-H.; Cheng, S.-L.; Chu, C.-C.; Hsiao, V. K. S. Reversible Photoluminescence in Spiropyran-Modified Porous Silicon. *J. Lumin.* **2015**, *159*, 246–250.

(21) Lukyanov, B. S.; Metelitsa, A. V.; Voloshin, N. A.; Alexeenko, Y. S.; Lukyanova, M. B.; Vasilyuk, G. T.; Maskevich, S. A.; Mukhanov, E. L. Solid State Photochromism of Spiropyrans. *Int. J. Photoenergy* **2005**, 7, 17–22.

(22) Zhang, F.; Zou, X.; Feng, W.; Zhao, X.; Jing, X.; Sun, F.; Ren, H.; Zhu, G. Microwave-Assisted Crystallization Inclusion of Spiropyran Molecules in Indium Trimesate Films with Antidromic Reversible Photochromism. *J. Mater. Chem.* **2012**, *22*, 25019–25026. (23) Ohara, K.; Inokuma, Y.; Fujita, M. The Catalytic Z to E Isomerization of Stilbenes in a Photosensitizing Porous Coordination Network. Angew. Chem., Int. Ed. **2010**, *49*, 5507–5509.

(24) Ruschewitz, U.; Hermann, D. Metal-Organic Frameworks as Host Materials for Azobenzene Molecules. *Z. Anorg. Allg. Chem.* **2012**, 638, 1574.

(25) Yu, X.; Wang, Z.; Buchholz, M.; Füllgrabe, N.; Grosjean, S.; Bebensee, F.; Bräse, S.; Wöll, C.; Heinke, L. Cis-To-Trans Isomerization of Azobenzene Investigated By Using Thin Films of Metal–Organic Frameworks. *Phys. Chem. Chem. Phys.* **2015**, *17*, 22721–22725.

(26) Walton, I. M.; Cox, J. M.; Coppin, J. A.; Linderman, C. M.; Patel, D. G. (Dan); Benedict, J. B. Photo-Responsive MOFs: Light-Induced Switching of Porous Single Crystals Containing a Photochromic Diarylethene. *Chem. Commun.* **2013**, *49*, 8012–8014.

(27) Yanai, N.; Uemura, T.; Kitagawa, S. Behavior of Binary Guests in a Porous Coordination Polymer. *Chem. Mater.* **2012**, *24*, 4744– 4749.

(28) Yanai, N.; Uemura, T.; Inoue, M.; Matsuda, R.; Fukushima, T.; Tsujimoto, M.; Isoda, S.; Kitagawa, S. Guest-to-Host Transmission of Structural Changes for Stimuli- Responsive Adsorption Property. *J. Am. Chem. Soc.* **2012**, *134*, 4501–4504.

(29) Yaghi, O. M.; Li, H.; Eddaoudi, M.; O'Keeffe, M. Design and Synthesis of an Exceptionally Stable and Highly Porous Metal-Organic Framework. *Nature* **1999**, *402*, 276–279.

(30) Batten, S. R.; Champness, N. R.; Chen, X.-M.; Garcia-Martinez, J.; Kitagawa, S.; Öhrström, L.; O 'Keeffe, M.; Suh, M. P.; Reedijk, J. Terminology of Metal–organic Frameworks and Coordination

Polymers (IUPAC Recommendations 2013). Pure Appl. Chem. 2013, 85, 1715–1724.

(31) Zlotea, C.; Campesi, R.; Cuevas, F.; Leroy, E.; Dibandjo, P.; Volkringer, C.; Loiseau, T.; Férey, G.; Latroche, M. Pd Nanoparticles Embedded into a Metal-Organic Framework: Synthesis, Structural Characteristics, and Hydrogen Sorption Properties. *J. Am. Chem. Soc.* **2010**, *132*, 2991–2997.

(32) Suh, M. P.; Park, H. J.; Prasad, T. K.; Lim, D.-W. Hydrogen Storage in Metal–Organic Frameworks. *Chem. Rev.* 2012, *112*, 782–835.

(33) Wu, H.; Reali, R. S.; Smith, D. A.; Trachtenberg, M. C.; Li, J. Highly Selective CO_2 Capture by a Flexible Microporous Metal-Organic Framework (MMOF) Material. *Chem. - Eur. J.* **2010**, *16*, 13951–13954.

(34) Li, J. R.; Sculley, J.; Zhou, H. C. Metal-Organic Frameworks for Separations. *Chem. Rev.* 2012, *112*, 869–932.

(35) Alaerts, L.; Maes, M.; Giebeler, L.; Jacobs, P. A.; Martens, J. A.; Denayer, J. F. M.; Kirschhock, C. E. A.; De Vos, D. E. Selective Adsorption and Separation of ortho-Substituted Alkylaromatics with the Microporous Aluminum Terephthalate MIL-53. *J. Am. Chem. Soc.* **2008**, *130*, 14170–14178.

(36) Maes, M.; Vermoortele, F.; Alaerts, L.; Couck, S.; Kirschhock, C. E. a.; Denayer, J. F. M.; De Vos, D. E. Separation of Styrene and Ethylbenzene on Metal-Organic Frameworks: Analogous Structures with Different Adsorption Mechanisms. *J. Am. Chem. Soc.* **2010**, *132*, 15277–15285.

(37) Lee, J.; Farha, O. K.; Roberts, J.; Scheidt, K. A.; Nguyen, S. T.; Hupp, J. T. Metal-Organic Framework Materials as Catalysts. *Chem. Soc. Rev.* **2009**, *38*, 1450–1459.

(38) Horcajada, P.; Serre, C.; Vallet-Regí, M.; Sebban, M.; Taulelle, F.; Férey, G. Metal-Organic Frameworks as Efficient Materials for Drug Delivery. *Angew. Chem., Int. Ed.* **2006**, *45*, 5974–5978.

(39) Horcajada, P.; Chalati, T.; Serre, C.; Gillet, B.; Sebrie, C.; Baati, T.; Eubank, J. F.; Heurtaux, D.; Clayette, P.; Kreuz, C.; Chang, J.-S.; Hwang, Y. K.; Marsaud, V.; Bories, P.-N.; Cynober, L.; Gil, S.; Férey, G.; Couvreur, P.; Gref, R. Porous Metal–organic-Framework Nanoscale Carriers as a Potential Platform for Drug Delivery and Imaging. *Nat. Mater.* **2010**, *9*, 172–178.

(40) Yaghi, O. M.; O 'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. Reticular Synthesis and the Design of New Materials. *Nature* **2003**, *423*, 705–714.

(41) Lyndon, R.; Konstas, K.; Ladewig, B. P.; Southon, P. D.; Kepert, P. C. J.; Hill, M. R. Dynamic Photo-Switching in Metal-Organic Frameworks as a Route to Low-Energy Carbon Dioxide Capture and Release. *Angew. Chem., Int. Ed.* **2013**, *52*, 3695–3698.

(42) Park, J.; Yuan, D.; Pham, K. T.; Li, J.-R.; Yakovenko, A.; Zhou, H.-C. Reversible Alteration of CO₂ Adsorption upon Photochemical or Thermal Treatment in a Metal–Organic Framework. *J. Am. Chem. Soc.* **2012**, *134*, 99–102.

(43) Healey, K.; Liang, W.; Southon, P. D.; Church, T. L.; D'Alessandro, D. M. Photoresponsive Spiropyran-Functionalised MOF-808: Postsynthetic Incorporation and Light Dependent Gas Adsorption Properties. J. Mater. Chem. A **2016**, *4*, 10816–10819.

(44) Volkringer, C.; Meddouri, M.; Loiseau, T.; Guillou, N.; Marrot, J.; Férey, G.; Haouas, M.; Taulelle, F.; Audebrand, N.; Latroche, M. The Kagomé Topology of the Gallium and Indium Metal-Organic Framework Types with a MIL-68 Structure: Synthesis, XRD, Solid-State NMR Characterizations, and Hydrogen Adsorption. *Inorg. Chem.* **2008**, *47*, 11892–11901.

(45) Loiseau, T.; Serre, C.; Huguenard, C.; Fink, G.; Taulelle, F.; Henry, M.; Bataille, T.; Férey, G. A Rationale for the Large Breathing of the Porous Aluminum Terephthalate (MIL-53) Upon Hydration. *Chem. - Eur. J.* **2004**, *10*, 1373–1382.

(46) Petríček, V.; Dušek, M.; Palatinus, L. Jana2006: The Crystallographic Computing System; Institute of Physics, Praha, Czech Republic, 2006.

(47) Scofield, J. H. Hartree-Slater Subshell Photoionization Cross-Sections at 1254 and 1487 eV. J. Electron Spectrosc. Relat. Phenom. 1976, 8, 129–137.

(48) Clegg, W.; Norman, N. C. Structures of Three Photochromic Compounds and Three Non-Photochromic Derivatives; the Effect of Methyl Substituents. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, 47, 817–824.

(49) Hirano, M.; Osakada, K.; Nohira, H.; Miyashita, A. Crystal and Solution Structures of Photochromic Spirobenzothiopyran. First Full Characterization of the Meta-Stable Colored Species. *J. Org. Chem.* **2002**, *67*, 533–540.

(50) Hermann, D. Ph.D. Thesis, University of Cologne, 2013.

(51) Hermann, D.; Emerich, H.; Lepski, R.; Schaniel, D.; Ruschewitz, U. Metal–Organic Frameworks as Hosts for Photochromic Guest Molecules. *Inorg. Chem.* **2013**, *52*, 2744–2749.

(52) Florea, L.; McKeon, A.; Diamond, D.; Benito-Lopez, F. Spiropyran Polymeric Microcapillary Coatings for Photodetection of Solvent Polarity. *Langmuir* **2013**, *29*, 2790–2797.

(53) Florea, L.; Hennart, A.; Diamond, D.; Benito-Lopez, F. Synthesis and Characterisation of Spiropyran-Polymer Brushes in Micro-Capillaries: Towards an Integrated Optical Sensor for Continuous Flow Analysis. *Sens. Actuators, B* **2012**, *175*, 92–99.

(54) Shimizu, I.; Kokado, H.; Inoue, E. Photoreversible Photographic Systems. VI Reverse Photochromism of 1,3,3-Trimethylspiro[indoline-2,2'-benzopyran]-8'-carboxylic Acid. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1730–1734.

(55) Shimizu, I.; Kokado, H.; Inoue, E. Photoreversible Photographic Systems. V. Reverse Photochromism of (Photospiran/Acid) System in Acetone. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1726–1729.

(56) Schneider, S.; Grau, H.; Ringer, J. Surface-Enhanced Resonance Raman Studies of Spiropyrans (Bips and Derivatives). *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **1994**, *246*, 267–274.

(57) Roxburgh, C. J.; Sammes, P. G. On the acid catalysed isomerisation of some substituted spirobenzopyrans. *Dyes Pigm.* **1995**, 27, 63–69.

(58) Gaeva, E. B.; Pimienta, V.; Delbaere, S.; Metelitsa, A. V.; Voloshin, N. A.; Minkin, V. I.; Vermeersch, G.; Micheau, J. C. Spectral and kinetic properties of a red-blue pH-sensitive photochromic spirooxazine. *J. Photochem. Photobiol.*, A 2007, 191, 114–121.

(59) Sugahara, A.; Tanaka, N.; Okazawa, A.; Matsushita, N.; Kojima, N. Photochromic Property of Anionic Spiropyran with Sulfonatesubstituted Indoline Moiety. *Chem. Lett.* **2014**, *43*, 281–283.

(60) Winkler, J. D.; Deshayes, K.; Shao, B. Photodynamic transport of metal ions. J. Am. Chem. Soc. 1989, 111, 769–770.

(61) Inouye, M.; Noguchi, Y.; Isagawa, K. Sensitive and Selective Coloration of Cryptand-Type Crown Spirobenzopyrans for Alkaline-Earth Metal Cations. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 1163–1166.

(62) Winkler, J. D.; Bowen, C. M.; Michelet, V. Photodynamic Fluorescent Metal Ion Sensors with Parts per Billion Sensitivity. *J. Am. Chem. Soc.* **1998**, *120*, 3237–3242.

(63) Wojtyk, J. T. C.; Kazmaier, P. M.; Buncel, E. Modulation of the Spiropyran–Merocyanine Reversion via Metal-Ion Selective Complexation: Trapping of the "Transient" cis-Merocyanine. *Chem. Mater.* **2001**, *13*, 2547–2551.

(64) Tanaka, M.; Nakamura, M.; Salhin, M. A. A.; Ikeda, T.; Kamada, K.; Ando, H.; Shibutani, Y.; Kimura, K. Synthesis and Photochromism of Spirobenzopyran Derivatives Bearing an Oxymethylcrown Ether Moiety: Metal Ion-Induced Switching between Positive and Negative Photochromisms. *J. Org. Chem.* **2001**, *66*, 1533–1537.

(65) Tanaka, M.; Ikeda, T.; Xu, Q.; Ando, H.; Shibutani, Y.; Nakamura, M.; Sakamoto, H.; Yajima, S.; Kimura, K. Synthesis and Photochromism of Spirobenzopyrans and Spirobenzothiapyran Derivatives Bearing Monoazathiacrown Ethers and Noncyclic Analogues in the Presence of Metal Ions. J. Org. Chem. **2002**, 67, 2223–2227.

(66) Kopelman, R. A.; Snyder, S. M.; Frank, N. L. Tunable Photochromism of Spirooxazines via Metal Coordination. *J. Am. Chem. Soc.* **2003**, *125*, 13684–13685.

(67) Guo, X.; Zhang, D.; Zhang, G.; Zhu, D. Monomolecular Logic: "Half-Adder" Based on Multistate/Multifunctional Photochromic Spiropyrans. J. Phys. Chem. B **2004**, 108, 11942–11945. (68) Zhang, C.; Zhang, Z.; Fan, M.; Yan, W. Positive and negative photochromism of novel spiro[indoline-phenanthrolinoxazines]. *Dyes Pigm.* **2008**, *76*, 832–835.

(69) Snyder, L. R. In High-Performance Liquid Chromatography (Horváth, C., Ed.); Academic Press: New York, 1983; Vol. 3.

(70) Arnold, G.; Schiele, C. Notizen: IR-Untersuchungen an 6-, 7und 8-Substituierten Spiro[2H-1-Benzopyran-2.2'-1'.3'.3'-Trimethylindolinen]. Z. Naturforsch., B: J. Chem. Sci. **1967**, 22, 1228–1230.

(71) Dolgopolova, E. A.; Moore, T. M.; Ejegbavwo, O. A.; Pellechia, P. J.; Smith, M. D.; Shustova, N. B. A metal–organic framework as a flask: photophysics of confined chromophores with a benzylidene imidazolinone core. *Chem. Commun.* **2017**, *53*, 7361–7364.

(72) Castellanos, S.; Kapteijn, F.; Gascon, J. Photoswitchable Metal Organic Frameworks: Turn on the Lights and Close the Windows. *CrystEngComm* **2016**, *18*, 4006–4012.

(73) Müller, K.; Wadhwa, J.; Malhi, J. S.; Schöttner, L.; Welle, A.; Schwartz, H.; Hermann, D.; Ruschewitz, U.; Heinke, L. Photoswitchable nanoporous films by loading azobenzene in metal–organic frameworks of type HKUST-1. *Chem. Commun.* **2017**, *53*, 8070–8073.