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Tracking the Light-Induced Isomerization Processes and the Photostability of Spiroyrans embedded in the Pores of Crystalline Nanoporous MOFs via IR Spectroscopy

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Abstract

The embedment of photochromic dyes into porous host matrices has attracted increasing interest in recent years. Especially the class of spiroyrans has been considered because of its outstanding photochromic and solvatochromic response. We herein present a comprehensive infrared spectroscopic characterization of the photoresponse and photostability of a nitro-substituted spiroyan “SP-Nitro” (namely 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran) non-covalently attached to different crystalline nanoporous MOF (metal-organic framework) host lattices. The TTC mesomeric form of SP-Nitro has been found to be preferably generated upon UV light exposure inside the different MOF hosts. Additionally, the excited isomer was found to be stable for prolonged irradiation times of 1-1.5 h.

Introduction

Photoswitchable molecules undergo the phenomenon called photochromism, which has firstly been described by *Hirshberg* as the reversible transformation of a chemical species upon exposure to electromagnetic radiation of a specific wavelength.^[1] The light induced transformation can cause *E*-to-*Z* isomerizations (e.g. for azobenzenes) or ring-opening/-closing reactions, which are known for e.g. spiroyrans or diarylethenes.^[2] With respect to spiroyrans, most of the investigations have focused on the switching processes in solution^[3-6], as the light induced SP-to-MC conversion (SP denotes the closed spiroyan form and MC the open

merocyanine form) is sterically hindered in the pure solid. The light induced SP-to-MC isomerization is depicted in Figure 1. The closed SP form converts to the open MC form by irradiation with UV light. Re-conversion to the ground state is either achieved by visible light exposure or by heat treatment, which makes spiropyrans T-type chromophores.^[2]

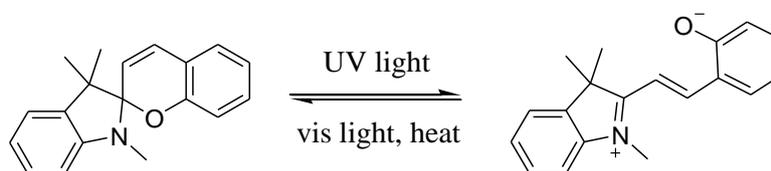


Figure 1. Photoisomerization of a spiropyran between its closed spiropyran form (SP form, left) and its open merocyanine form (MC form, right).

To enable photoswitching in the solid state, metal-organic frameworks (MOFs)^[7] have recently been applied as porous host materials not only for spiropyrans^[8–11] but for various photochromic molecules.^[12–18] MOFs are composed of inorganic nodes and organic linker molecules that form 3 D frameworks with potential voids.^[7] These voids have been intensively exploited regarding various applicabilities. For detailed information on the different applications of MOFs, we refer to more in-depth literature on this topic.^[19–40] With respect to the embedment of photochromic molecules as non-covalently attached guest molecules, many functional materials with promising properties were obtained. Here, stilbenes^[41], 2-(phenylazo)pyridine^[42,43], azobenzenes and (fluorinated) derivatives^[44–49], diarylethenes^[50], spiropyrans^[8–11] and spirooxazines^[51] were applied and extrinsically introduced into different MOF host scaffolds. For azobenzene@MOF^[44,49] and spirooxazine@MOF^[51] composites, it was possible to obtain IR spectroscopic data of both the ground and excited species in solid state for the first time. Focusing on spirooxazines embedded inside different MOF matrices, the merocyanine form in its TTC^[52] form was generated upon UV light irradiation^[51]. Additionally, high fatigue resistance upon prolonged and repetitive UV light exposure was found, which was tracked via IR and UV/vis spectroscopic measurements.^[51] Following the results of the IR spectroscopic investigations on azobenzenes and spirooxazines inside different MOF hosts, we present the first detailed IR-spectroscopic data of the nitro-substituted spiropyran, denoted as SP-Nitro in the following, non-covalently attached to MOF-5^[53], MIL-68(In)^[54] and MIL-68(Ga)^[54] in this work. The vibrational changes of these SP-Nitro@MOF composite materials^[8] were studied before and after irradiation with UV light (short and prolonged irradiation times) in order

- a) to give a complete assignment of all IR bands of the closed SP-form and the open MC form in the solid state
and
- b) to probe the photostability of these hybrid systems.

Furthermore, the reversibility of switching after prolonged irradiation was studied by photochemical and thermal means. That way, possible re-conversion to the closed SP-form was followed.

Results

For SP-Nitro@MOF composite materials, successful isomerization of the closed SP form to the open MC form was found to occur upon irradiation with UV light, which was published in a previous study.^[8] Here, we found that the optical properties of the excited isomer strongly depend on the surrounding host matrix, which resulted in solid-state solvatochromism of these switch@MOF systems. Therefore, we denoted MOFs as “solid solvents” since the embedded and irradiated nitro-substituted spiropyran showed absorption properties ranging from its optical behavior in toluene to methanol: when embedded inside MOF-5, the absorption maximum was found to be similar as when the dye was dissolved in methanol, whereas inside MIL-68(In) and MIL-68(Ga) an optical behavior like in acetone/acetonitrile was observed.^[8] Further, the light induced changes were followed by IR spectroscopic measurements focusing on the characteristic C_{Spiro-O} band at approx. 950 cm⁻¹, of which the amplitude decreased as a result of the C_{Spiro-O} bond cleavage and the associated formation of the merocyanine species. Thus, this bond cleavage is a good indicator for the successful SP-to-MC conversion. Nevertheless, upon irradiation with UV light simple photodegradation of SP-Nitro might occur resulting also in a decrease of the amplitude of this characteristic vibrational band. To study the light induced changes and the formation of the merocyanine species, a clear assignment of all increasing and decreasing vibrational bands is obligatory, which is the focus of this work. All decreasing IR bands must, in case of the successful SP-to-MC conversion, belong to the closed SP isomer, whereas all increasing IR bands correspond to the open MC isomer. In order to understand the resulting IR spectra, the merocyanine moiety must be examined more precisely. In the following, the occurring isomers are discussed in detail.

MC-Nitro is known to occur in four different isomers, which are shown in figure 2. Here, T denotes “*trans*” and C denotes “*cis*”. The four isomers are the TTC, TTT, CTT and CTC form.

The first letter refers to the first double bond connected to the indoline part, the second one to the second double bond and the third to the position of the O_{Spiro}-atom. According to quantum chemical calculations, the TTC form has the lowest energy (23.8 kJ mol⁻¹, whereas the calculated relative energies for TTT, CTC, and CTT are 30.6, 32.9 and 35.9 kJ mol⁻¹, respectively) and is thus most preferably produced upon photoirradiation followed by TTT, CTC and CTT.^[52]

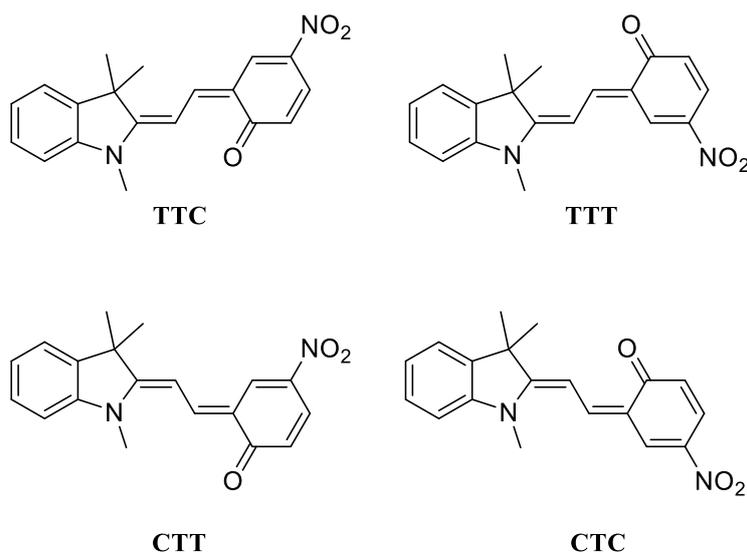


Figure 2. Different isomers of the open merocyanine form of MC-Nitro.

In an experimental and associated theoretical work, *Nakata* and co-workers determined and calculated the vibrational frequencies of the closed SP form and the corresponding merocyanine moiety of SP-Nitro.^[52] Here, the authors found the TTC form to be generated upon UV light irradiation inside an argon matrix at 8 K. From both the experimental and calculated data, the authors found IR bands with the highest intensities relative to the strongest IR band (> 30%) of SP-Nitro and MC-Nitro for the following wavenumbers (tables 1 and 2):

Table 1 Observed and calculated vibrational bands $\tilde{\nu}$ (in cm⁻¹) and relative intensities (in %) for SP-Nitro.^[52]

obs.	rel. intensity / %	calc.	rel. intensity / %
1487	36		
1482	36		
1472	30		

1348	100	1334	100
1275	57	1264	54
		1072	33
959	40		
		934	47

Table 2 Observed and calculated vibrational bands $\tilde{\nu}$ (in cm^{-1}) and relative intensities (in %) for the TTC isomer of the merocyanine moiety.^[52]

obs.	rel. intensity / %	calc.	rel. intensity / %
1628	33	1627	33
		1551	88
		1490	68
1469	75		
1324	100	1316	100
1252	44	1247	42
1229	48		
1209	46	1210	31
1086	38		

The authors experimentally determined the most intensive bands for each isomer at 1348 cm^{-1} for the closed SP form and at 1324 cm^{-1} for the open MC form (highlighted in both tables), which is also in agreement with their theoretical calculations. Upon irradiation with UV light, these authors found the most intensive band for the SP form to lose intensity and the most intensive IR band for the MC form to increase. Using the experimental and calculated data of *Nakata* and co-workers on SP-Nitro^[52] inside an argon matrix at 8 K as a reference, we analyzed and assigned decreasing and increasing IR bands of both the closed and the open isomer of SP-Nitro we studied inside different MOF host matrices at ambient conditions (room temperature). For this purpose, the spectra of the non-irradiated species were subtracted from the irradiated ones to obtain $\text{ext}_{\text{irrad}} - \text{ext}_{\text{ground state}}$ difference spectra, which has successfully been applied for spirooxazine@MOF composite materials in a study prior to this work^[51]. These

difference spectra were then used to study IR band alterations upon UV light irradiation. The assignment was exclusively done by analyzing these difference spectra, which only show IR bands of the SP and MC form of SP-Nitro, since the MOF host frameworks remain unaffected. In prior experiments, the ideal irradiation times for the formation of maximal MC-Nitro bands with maximal intensity were determined, which were then applied for the following analysis.

The method of using difference spectra is an elegant way to analyze photodynamic processes. In case of spiropyrans, the open merocyanine form is formed by exposure to UV light. Consequently, merocyanine bands are formed, while the vibrational bands belonging to the SP form lose intensity. This means that positive values in the difference spectra are associated with the excited species, and negative values are associated with the closed spiropyran form.

The resulting difference spectra after different irradiation times of SP-Nitro inside MOF-5 are depicted in figure 3. Difference spectra of SP-Nitro inside MIL-68(In) and MIL-68(Ga) can be found in the Supporting Information (figures S1 and S2). The discussion of these spectra will be exemplarily conducted for the SP-Nitro@MOF-5 system.

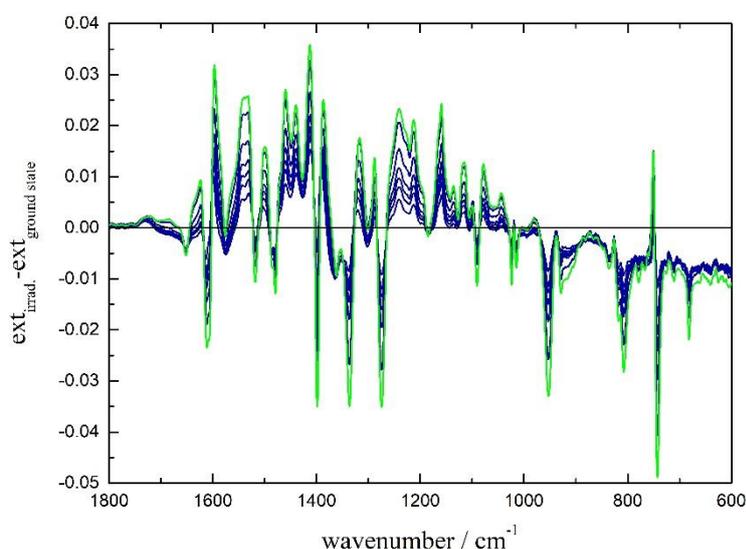


Figure 3. Difference IR spectra of SP-Nitro@MOF-5 under irradiation with UV light ($\lambda = 365$ nm). The green line shows the spectrum, for which the maximum intensity of MC bands was observed (60 min irradiation time).

In figure 3, the difference spectra of SP-Nitro@MOF-5 after irradiation at different times are depicted. Here, the green spectrum corresponds to an irradiation of 60 min, where MC IR bands with maximal intensity are observed. This spectrum is relevant for the assignment of increasing

and decreasing IR bands. The blue colored difference spectra display the proceeding formation of the open merocyanine species at irradiation times of 1, 2, 3, 5, 10 and 30 min. Upon irradiation with UV light, several IR bands gain and lose intensity, which corresponds to the formation of the MC form and the decreasing fraction of the SP form. In order to adequately assign the occurring IR bands, the TTC mesomeric form of the merocyanine moiety must be examined more precisely regarding changing bonds in comparison to the closed SP-Nitro form. The structure of the TTC form is depicted in figure 4 and compared to the closed SP form. The rings I and II remain unaffected by the light induced cleavage of the C_{Spiro}-O bond, whereas ring I' is opened and II' changes structurally. Consequently, we expect only small changes for all vibrational modes related to rings I and II, while vibrations related to rings I' and II' as well as the spiro C-O group will exhibit more pronounced changes upon photoisomerisation.

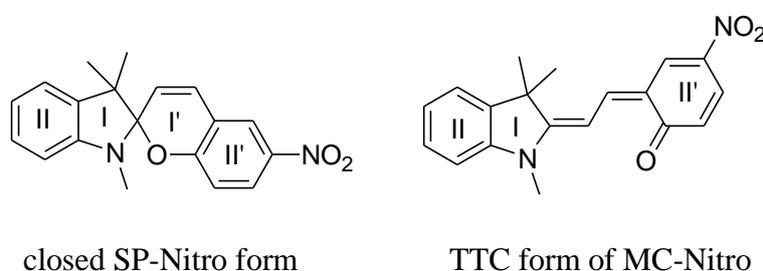


Figure 4. Comparison of SP-Nitro in its closed form and the TTC form of the respective merocyanine.

In tables 3 and 4, the changes upon UV light irradiation of the vibrational bands of SP-Nitro@MOF-5 are listed (for SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga) see tables S1 to S4, Supporting Information). We performed a comprehensive assignment of all bands making use of the available literature. Values marked with an “*” were taken from the theoretical and without an “*” from the experimental data of *Nakata* and co-workers.^[55] Highlighted data represent the strongest bands with regard to intensity (bold: relative intensity > 30%; bold and underlined: intensity = 100%). Modes of vibrations were assigned according to *Lyubimov* and co-workers^[55], *Paal* and *Arnold*^[56] and *Hesse, Meyer & Zeeh*^[57].

Table 3. Observed decreasing IR bands of SP-Nitro@MOF-5. The given assignment is based on the experimental and calculated (“*”) data of *Nakata* and co-workers^[52]. Modes of vibration were attributed according to *Lyubimov* and co-workers^[55], *Paal* and *Arnold*^[56] and *Hesse, Meyer & Zeeh*^[57].

decreasing bands / cm ⁻¹	assignment / cm ⁻¹	vibration mode
1652	SP(1654)	$\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N})$ ^[56]
1610	SP(1615)	$\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N})$ ^[56]
1589/1578	SP(1583)	ring-valence vibration $\nu(\text{C}=\text{C})$ ^[56]
1517	SP(1508)	ring-valence vibration $\nu(\text{C}=\text{C})$ ^[56]
1479	SP(1482/1472)	ring-valence vibration $\nu(\text{C}=\text{C})$ ^[56]
1398	SP(1388) SP(1398)	<u>theoretical</u> ^[55] : $\nu(\text{C}-\text{C})$ (ring II) $\nu(\text{C}-\text{C})$ (ring II’) $\nu(\text{C}-\text{N})$ (ring I) $\nu(\text{H}-\text{C}_{\text{Methyl}}-\text{H})$ bound to N atom
1361	SP(1363)	$\nu(\text{C}-\text{N})$ ^[56]
<u>1334</u>	<u>SP(1334)*</u>	<u>theoretical</u> ^[55] : $\nu(\text{C}-\text{C})$ (ring I’-II’) $\nu(\text{C}-\text{C}-\text{H})$ (ring I)
1299	SP(1300)	<u>theoretical</u> ^[55] : $\nu(\text{C}-\text{N})$ (ring I) $\nu(\text{N}-\text{C}_{\text{Methyl}})$ (ring I) $\nu(\text{C}-\text{C}-\text{H})$ (ring II) $\nu(\text{C}-\text{N}-\text{C})$ (ring I)

1275	SP(1275)	<u>theoretical</u> ^[55] : $\nu(\text{C-O})$ $\nu(\text{C-C-H})$ (ring II) $\nu(\text{N-C}_{\text{Methyl}})$ (ring I) $\nu(\text{C-C-N})$ (ring I)
1220	SP(1221)	<u>theoretical</u> ^[55] : $\nu(\text{C-C})$ (ring II')
1184	SP(1187)	<u>theoretical</u> ^[55] : $\nu(\text{C}_{\text{Spiro-O}})$ $\nu(\text{C-C}_{\text{Methyl}})$ (ring I) $\nu(\text{C-C})$ (ring I) $\nu(\text{C-C}_{\text{Methyl-H}})$ (ring I) $\nu(\text{C}_{\text{Spiro-N}})$ $\nu(\text{C-N})$ (ring I) $\nu(\text{C-C})$ (ring I) $\nu(\text{N-C}_{\text{Methyl}})$ (ring I) $\nu(\text{H-C}_{\text{Methyl-H}})$
1126	SP(1125)	<u>theoretical</u> ^[55] : $\nu(\text{N-C}_{\text{Methyl}})$ $\nu(\text{C-C})$ (ring I)
1089	SP(1101)	$\delta(\text{C-H})_{\text{arom.}}$ ^[56]
1023	SP(1025)	<u>theoretical</u> ^[55] : $\nu(\text{O-C}_{\text{Spiro-C}})$ (ring I') $\nu(\text{C}_{\text{Spiro-O}})$ $\nu(\text{N-C-C})$ (ring I')
1013	SP(1013)	<u>theoretical</u> ^[55] : $\nu(\text{C-C})$ (ring II) $\nu(\text{C-N})$ (ring I)

951	SP(959)	$\nu(\text{O}-\text{C}_{\text{Spiro}}-\text{N})^{[56]}$
927	SP(929)	<u>theoretical</u> ^[55] : $\nu(\text{C}-\text{C}_{\text{Methyl}}-\text{H})$
835	SP(838)	<u>theoretical</u> ^[55] : deviation of H atoms from the plane (ring I') out-of-plane vibrations (ring I' - II') $\nu(\text{C}_{\text{Spiro}}-\text{O})$
806	SP(810)	<u>theoretical</u> ^[55] : deviation of H atoms from the plane (ring II) out-of-plane vibrations (ring II)
777	SP(777)	<u>theoretical</u> ^[55] : deviation of H atoms from the plane (ring II) out-of-plane vibrations (ring II) $\nu(\text{C}-\text{C})$ (ring I) δ (ring II)
743	SP(743)	$\gamma(\text{C}-\text{H})$ benzene ring ^[56]
681	SP(685)	<u>theoretical</u> ^[55] : out-of-plane vibrations (rings I', II')
628	SP(635)	<u>theoretical</u> ^[55] : in-plane-ring bending vibrations/bond bending vibrations of (rings I', II') and (ring II)

Table 4. Observed increasing IR bands of SP-Nitro@MOF-5. The indicated assignment is based on the experimental and calculated (“**”) data of *Nakata* and co-workers^[52]. Modes of vibration were attributed according to *Lyubimov* and co-workers^[55], *Paal* and *Arnold*^[56] and *Hesse, Meyer & Zeeh*^[57].

increasing bands / cm ⁻¹	assignment / cm ⁻¹	vibration mode
1686	MC (1642)	$\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N})$ ^[56]
1633	MC(1628)	$\nu(\text{C}=\text{C}), \nu(\text{C}=\text{N})$ ^[56]
1617	MC(1617)	ring-valence vibration $\nu(\text{C}=\text{C})$ ^[56]
1596	MC(1595)*	<u>theoretical</u> ^[55] $\nu(\text{C}-\text{C})$ (ring II) $\nu(\text{C}-\text{C})$ (ring II)
1561	MC(1560)*	<u>theoretical</u> ^[55] $\nu(\text{C}-\text{C})$ (ring II')
1536	MC(1600-1500)	ring-valence vibration $\nu(\text{C}=\text{C})$ ^[56,57]
1500	MC(1490)*	ring-valence vibration $\nu(\text{C}=\text{C})$ ^[56,57]
1459	MC(1459)	<u>theoretical</u> ^[55] $\nu(\text{C}-\text{C})$ (ring II) $\nu(\text{C}-\text{N})$ (ring I) $\nu(\text{C}-\text{C}-\text{H})$ (ring II)
1436	MC(1430)*	<u>theoretical</u> ^[55] $\nu(\text{H}-\text{C}_{\text{Methyl}}-\text{H})$ on N atom $\nu(\text{H}-\text{C}_{\text{Methyl}}-\text{H})$ on C atom
1410	MC(1407)*	$\delta(\text{C}-\text{H})$ neighboring $\text{C}=\text{O}$ ^[57]
1385	MC(1388)	$\delta(\text{C}-\text{H})$ methyl-group of I ^[57]
1317	MC(1316)*	$\delta(\text{C}-\text{H})$ methyl-group of I ^[57]
1288	MC(1281)	<u>theoretical</u> ^[55] $\nu(\text{C}-\text{O})$

		v(N-C _{Methyl}) (ring I) v(C-C-N) (ring I) v(C-C-H) (ring II)
1241	MC(1247)*	<u>theoretical</u> ^[55] v(C-C-O)
1210	MC(1210)*	<u>theoretical</u> ^[55] v(C-C) (ring II')
1159	MC(1159)*	<u>theoretical</u> ^[55] v(C-C) (ring I) v(C-C _{Methyl} -H) (ring I) v(C-C -C _{Methyl}) (ring I)
1117	MC(1118)*	δ (C-H) _{arom.} ^[56]
1097	MC(1090)	δ (C-H) _{arom.} ^[56]
1078	MC(1073)*	<u>theoretical</u> ^[55] v(C-O)
1052	MC(1048)	<u>theoretical</u> ^[55] δ (ring II) v(N-C _{Methyl})
750	MC(745)	γ (C-H) (II) ^[57]

For all SP-Nitro@MOF compounds, the IR bands of decreasing and increasing intensities were completely attributed to the SP or the MC form of the embedded guest molecule. The light induced changes are followed by the formation of the merocyanine moiety, that is, increasing IR bands point to the formation of the MC form, whereas decreasing bands to the SP form. The assigned MC-Nitro IR bands all belong to the TTC isomer of the merocyanine form, which is the isomer to be preferably formed according to quantum chemical calculations.^[52] Accordingly, this classification leads to the conclusion that exposure to UV light causes the formation of the merocyanine in its TTC form, and indicate, thus, a successful light induced SP-to-MC conversion.

After this comprehensive characterization of the infrared spectra of the two isomers, we applied prolonged irradiation times to probe the photostability of the embedded MC-Nitro guest. If MC-Nitro is photostable inside the different host matrices, prolonged UV light irradiation should not affect the IR spectra, which has recently been observed for spirooxazine@MOF composite materials [51]. However, for photodegradation of MC-Nitro, decrease of both the spiropyran and the merocyanine IR bands and the occurrence of new IR bands (of photodegradation products) is expected. In figure 5, the difference spectra of SP-O@MOF-5 after 60 min (green line) and 720 min (orange line) UV light exposure is shown. For clarity, we marked decreasing MC bands with an arrow, whereas new increasing IR bands are labeled with an asterisk. The corresponding spectra for SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga) can be found in figure S3 and S4, Supporting Information.

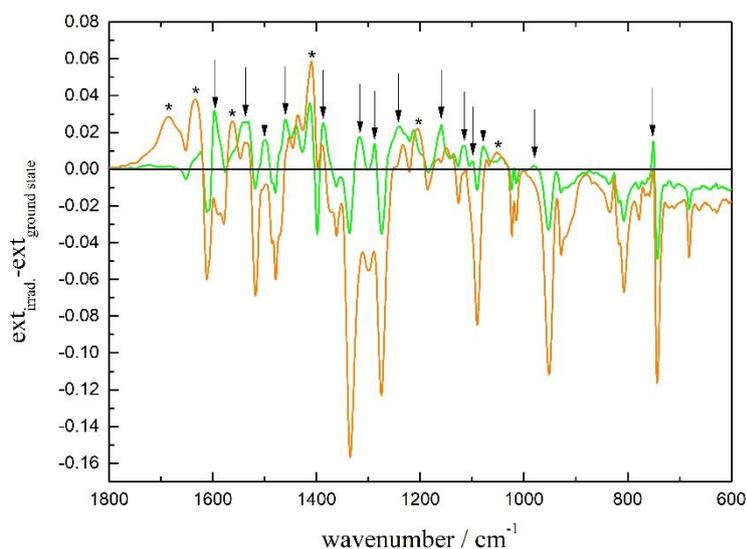


Figure 5. Difference IR spectra of SP-Nitro@MOF-5 under irradiation with UV light ($\lambda = 365$ nm) for 60 min to 720 min. The green line shows the spectrum, for which the maximum intensity of MC bands was observed (60 min irradiation time), the orange line corresponds to an irradiation time of 720 min. Decreasing MC bands are marked with an arrow, whereas new increasing IR bands are labeled with an asterisk.

By exceeding the UV light exposure time to $t \gg 60$ min, a significant decrease of several IR bands is observed. The decreasing IR bands for the MC form are marked with an arrow. Furthermore, a proceeding decrease in the SP form IR bands is also present. Both the decrease of the MC and SP IR bands point to photodegradation processes upon prolonged irradiation. In addition to the decreasing bands of the studied MC and SP species, new IR bands occur. For

irradiated SP-Nitro inside MIL-68(In) and MIL-68(Ga), these findings are similar. In a comparable manner to the UV light response of SP-Nitro@MOF-5, the intensity of typical merocyanine bands diminishes with extended irradiation times for SP-Nitro@MIL-68(In) (>> 60 min) and SP-Nitro@MIL-68(Ga) (>> 90 min). These decreasing bands are listed in Table 5.

Table 5. List of decreasing IR bands (in cm^{-1}) for MC-Nitro embedded in MIL-68(In) (left) and MIL-68(Ga) (right) upon prolonged UV irradiation. Bold values refer to the characteristic MC vibrational mode.

decreasing IR bands in cm^{-1}	
MC-Nitro@MIL-68(In) after 1000 min UV light exposure	MC-Nitro@MIL-68(Ga) after 210 min UV light exposure
1603	1603
1532	1531
1498	1504
1458	1459
1438	1438
1412	1415
1309	1309
1286	1287
1255	1256
1212	1213
1157	1158
1134	1133
1115	1116
1080	1082
1043	1042
938	940

Interestingly, decreasing bands are the same for both compounds, pointing to an analogous behavior of the embedded MC-Nitro guest inside these MIL-68 matrices. Since MIL-68(In) and MIL-68(Ga) show the same topology, but different metal nodes, this result is not surprising. The most intensive band at $\tilde{\nu} = 1309 \text{ cm}^{-1}$ for the open merocyanine form according to *Nakata* and co-workers^[52] significantly loses intensity for both compounds, which is in accordance to the results of MC-Nitro inside MOF-5.

In order to spot the alterations in intensity easier, we subtracted the IR spectrum after 60 min of irradiation from the IR spectrum after 720 min UV light exposure to obtain $\text{ext}_{\text{irrad. long}} - \text{ext}_{\text{irrad. max.}}$. In figure 6, these intensity alterations are shown for SP-Nitro@MOF-5. For SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga), these difference spectra are depicted in figure S5 and S6, Supporting Information.

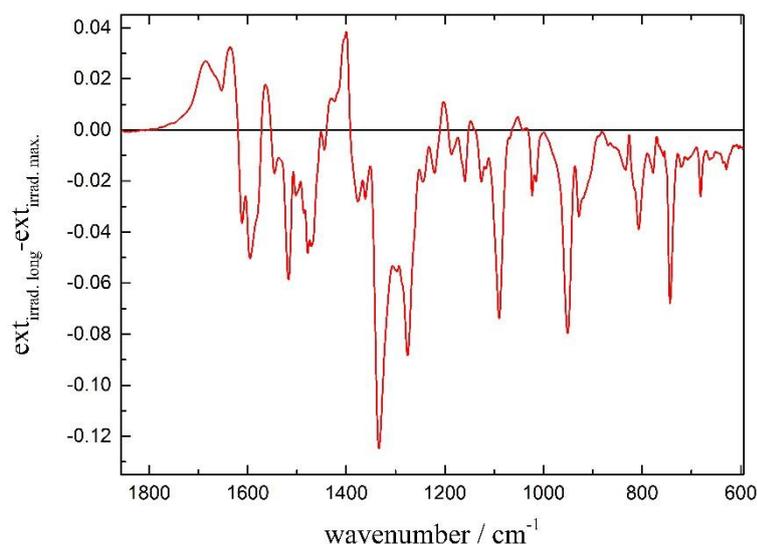


Figure 6. Difference IR spectrum of SP-Nitro@MOF-5 after irradiation with UV light (365 nm, 720 min) after subtracting the difference spectrum obtained after 60 min UV light exposure.

In addition to the already discussed decrease of the IR bands of the merocyanine and spiropyran form, increasing IR bands at wavenumbers of 1050, 1147, 1204, 1400, 1431, 1563, 1634 and 1684 cm^{-1} become visible. Interestingly, for SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga) similar and even additional increasing IR bands are observed upon prolonged UV light irradiation, which must be the result of photodegradation product formation. The values of the increasing IR bands of all studied compounds are compared in the

following table 6. Notably, small changes in the range of 700-600 cm^{-1} were not listed. Increasing IR bands, which are present in all three compounds, are highlighted.

Table 6. List of increasing IR bands (in cm^{-1}) for MC-Nitro embedded in MOF-5, MIL-68(In) (left) and MIL-68(Ga) (right) upon prolonged UV irradiation. In bold, increasing IR bands, which are present in all three compounds, are highlighted.

Increasing IR bands in cm^{-1}		
MC-Nitro@MOF-5 after 720 min UV light exposure	MC-Nitro@MIL-68(In) after 1000 min UV light exposure	MC-Nitro@MIL-68(Ga) after 210 min UV light exposure
1684	1674	1674
1634	1641	1641
1563	1563	1573
1431	1428	1427
1398	1397	1404
	1370	1349
1202	1198	
1147	1148	
	1138	
1053	1053	1056
1035	1033	1030
	993	982
	880	883
	826	824
		789
		770
		748

As the given values in table 6 indicate, the investigated systems show the same increasing IR bands, except for a few differences. Consequently, we suggest the local environment having an impact on the kind of photodegradation product formation. To understand the presence of new IR bands, the photodegradation products of SP-Nitro must be known. Already in the 1970s, *Gautron* reported on decomposition of SP-Nitro and other spiroopyran derivatives.^[58] In the solid state, the author mainly found three compounds to be generated upon prolonged UV light excitation: 3,3-dimethyloxindole, 1,3,3-trimethyloxindole and 5-nitrosalicylaldehyde. The structures of these compounds are found in figure 7.

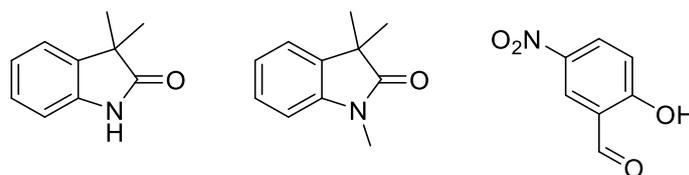


Figure 7. Structures of the products mainly formed upon prolonged UV light irradiation: 3,3-dimethyloxindole (left); 1,3,3-trimethyloxindole (middle) and 5-nitrosalicylaldehyde (right).

By comparing the IR data of these three compounds to our obtained values, we propose the formation of 1,3,3-trimethyloxindole and 5-nitrosalicylaldehyde: For 3,3-dimethyloxindole, the known IR bands do not fit to the observed ones,^[59] whereas for the combination of 1,3,3-trimethyloxindole^[60] and 5-nitrosalicylaldehyde^[61] published IR data are almost consistent with our data. We attribute the differences of the occurring IR bands between the studied hybrid systems to the different local environments within the MOF host scaffolds, which are also reflected in the stability of the MC form at UV light exposure.

Although these results clearly show the occurring photodegradation of SP-Nitro, we conducted both photochemical and thermal treatment of the long-irradiated samples to induce possible re-conversion of still intact MC-Nitro. Therefore, we exposed the samples to light of different wavelengths ($\lambda = 450, 530, 590$ and 660 nm). Additionally, all compounds were thermally treated at 50 °C in a laboratory oven. Since spiroopyrans belong to the T-type chromophores, both ways (thermal and photochemical) were applied to achieve re-conversion to the ground state. In the following, the results of these experiments are exemplarily discussed for SP-Nitro@MOF. The resulting spectra for SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga) can be found in figure S7 to S10, Supporting Information. In figure 8, the C_{Spiro-O} bond region of SP-Nitro inside MOF-5 is depicted. The C_{Spiro-O} bond features an IR band at approx. 950 cm⁻¹. As shown in figure 1, UV light exposure causes decreasing of this band as a result of bond

cleavage. We already reported this in a previous study on this systems.^[8] By excitation with electromagnetic radiation of the wavelength with $\lambda = 450, 530, 590$ and 660 nm (colored broken lines), no increase in intensity for the characteristic spiropyran band is found (see figure 8). Upon light exposure, the IR band of the excited species (orange solid line, 720 min of irradiation) remains unaffected for three possible reasons: SP-Nitro becomes a pure T-type chromophore inside MOF-5 or the MOF host matrix might fully stabilize the dipolar merocyanine as either isolated molecules or associated in aggregates. Further, photodegradation takes place, which has already been discussed previously.

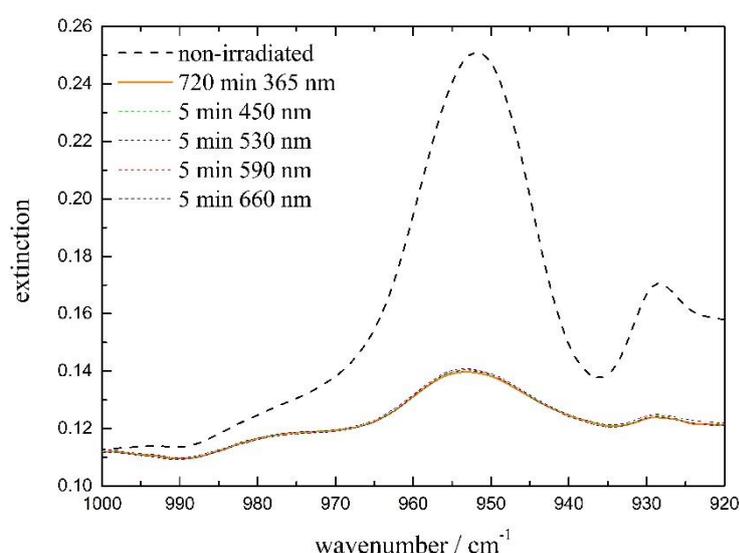


Figure 8. Light excitation of SP-Nitro@MOF-5 with different wavelengths to induce re-conversion to the ground state.

If being a pure T-type chromophore, heat treatment would cause intensity increase of the $C_{\text{Spiro-O}}$ band. The resulting spectra after different heat treatment times are depicted in figure 9. Here, heat supply causes the formation of a small band (cyan and dark cyan broken lines), but with lower intensity than the irradiated species (orange solid line). Consequently, small amounts of MC-Nitro still seem to be intact and able to re-convert to the closed SP-form, but only by thermal treatment. However, the initial state is not recovered again, which, again, confirms the low photostability at prolonged irradiation.

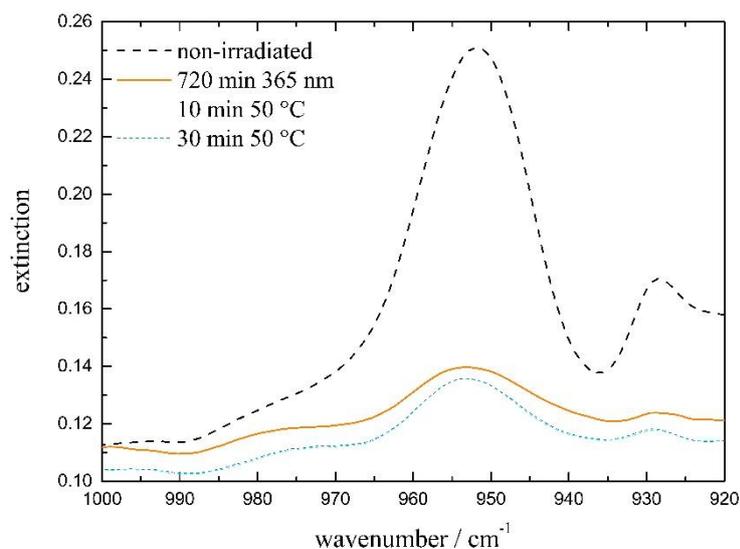


Figure 9. Heat treatment of SP-Nitro@MOF-5 at 50 °C for different times to induce the re-conversion to the initial state thermally.

For compounds SP-Nitro@MIL-68(In) and SP-Nitro@MIL-68(Ga), an almost identical behavior to SP-Nitro@MOF-5 is observed for illumination with electromagnetic radiation of different wavelengths: Upon irradiation of the excited species (orange solid line, figure S7 and figure S9, Supporting Information) the intensity value of the $C_{\text{Spiro-O}}$ band remains unaffected (colored broken lines, respectively). However, heat treatment causes a slight increase in comparison to the excited state in both cases (figure S8 and figure S10, Supporting Information).

Conclusion

In this study, we present a comprehensive infrared spectroscopic characterization including assignment of all relevant vibrational bands of SP-Nitro (namely 1,3,3-trimethylindolino-6'-nitrobenzopyrlospiran) inside different porous host materials, namely MOF-5, MIL-68(In) and MIL-68(Ga) at ambient conditions. These spiropyran@MOF hybrid materials^[8] are known to allow photoswitching in the solid state. Upon irradiation with UV light ($\lambda = 365$ nm), the open MC form is generated. This formation can be tracked by IR spectroscopy, particularly by using difference IR spectra. These difference spectra were employed to identify the SP and MC bands. Here, bands with increasing intensity were assigned to the excited state (TTC isomer of the MC

form), whereas decreasing bands to the ground state (SP form). That way, a complete IR signature for both the closed and open form of SP-Nitro was obtained.

Based on these results, the photostability of the three spiropyran@MOF systems was studied. IR bands of both the SP and the MC forms continuously decreased upon irradiation times exceeding 60 min and 90 min, respectively. The decrease of these IR bands clearly showed the photodegradation of the studied systems for long UV irradiation times. Additionally, the presence of new IR bands after prolonged irradiation was attributed to photodegradation products. Here, we found a different behavior for the three host materials, which suggests not only an influence of the host matrix on the optical properties^[8] of the embedded SP-Nitro, but also on the photostability of the excited species and the type of degradation products. To understand these findings in more detail, further investigations on the formation of degradation products during UV light exposure as a function of local environment is in the focus of our current research.

In a last step, we conducted irradiation and heat treatment experiments to induce the photochemical and/or thermal re-conversion, respectively. Here, neither exposure to light of different wavelengths nor heating the sample caused the re-isomerization. These experiments further validate the obtained results of the prolonged UV light exposure, which showed the photodegradation of the embedded SP-Nitro.

Conclusively, in this study, we confirmed that like for azobenzenes^[44,49] and spirooxazines^[51], the IR signature of spiropyrans can be obtained at room temperature by embedding them in the pores of MOFs. These results indicate that MOFs as hosts have a high potential for IR spectroscopic investigations of photoswitchable molecules. Future work will focus on photoswitches, whose excited species have short lifetimes, but which might be stabilized by embedding them in a MOF, which would allow for their IR spectroscopic characterization.

Experimental

The synthesis and characterization of all investigated compounds have already been described and can be found in the respective literature^[8].

IR spectroscopic measurements. Measurements were carried out on a *Nicolet7500* FT-IR-Spectrometer under reduced pressure to avoid any contact with humidity. Samples were prepared as follows: half a spatula of substance was thoroughly ground with six spatulas of KBr. Afterwards the mixture was pressed for 30 min at a pressure of ~530 bar yielding a thin and transparent slightly colored pellet. The pellet was placed into the sample holder. The sample

chamber was evacuated to 10^{-5} mbar in order to improve the quality of the resulting spectra and for keeping the quality of the pellet high. Scans were recorded in the range 360 cm^{-1} to 4000 cm^{-1} with a resolution of 2 cm^{-1} and 90 scans per sample. Backgrounds were measured after every sample replacement to ensure the results being as exact as possible. The samples underwent different irradiation programs, which are given with the respective spectra. Processing of the resulting spectra was carried out using the program package *OriginPro 8.50G*^[62]. Irradiation experiments were conducted with *ThorLabs* LEDs. Details of the illumination times and applied wavelengths can be found in the respective spectra.

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