This article can be cited before page numbers have been issued, to do this please use: S. Klokic, B. Marmioli, D. Naumenko, G. Birarda, S. Dal Zilio, M. D. J. Velasquez-Hernandez, P. Falcaro, L. Vaccari and H. Amenitsch, CrystEngComm, 2024, DOI: 10.1039/D4CE00221K.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Orthogonal stimulation of structural transformations in photo-responsive MOF films by linker functionalization

Sumea Klokic, a,b Benedetta Marmiroli, b Denys Naumenko, b Giovanni Birarda, b Simone Dal Zilio, b Miriam de J. Velásquez-Hernández, a Paolo Falcaro, a Lisa Vaccari a and Heinz Amenitsch b

Controlling the magnitude of structural dynamics in flexible MOF films by an applied stimulus is largely desired for specific applications such as energy storage. Herein, by introducing chlorine substituents in the azobenzene infiltrated CI-DMOF-1 film structure, a significantly slowed structural response is obtained upon photo-switching of the system.

To date, the fabrication of structurally responsive MOF films 1-2 is motivated for the development of MOF-based devices including sensors, 3,4 cargo delivery 5-7 or mechanical storage systems. 8-10 Implementing a moiety within the film assembly that is responsive to an external stimulus, allows to control the MOF film properties from remote. 11 Here, light is a particularly attractive stimulus, as it is readily available and renewable in the case of sunlight. 12 So far, a large number of structurally flexible photo-active MOFs has been reported, such as DMOF-1 ([Zn4(bdc)2(dabco)]; bdc = 1,4-benzenedicarboxylate; dabco = 1,4-diazabicyclo[2.2.2]octan), 13 or [Zn(AzDC)(4,4’-BPE)0.5] (AzDC = azobenzene-4,4’-dicarboxylic acid, 4,4’-BPE = trans-1,2-bis(4-pyridylethylene). 14 Most of such flexible structures are based on reticular design strategies, where molecular building blocks are replaced within the MOF system. 15,16 These structures exhibit a tunable flexibility that provides an extra degree of freedom which offers additional means to exploit dynamics in responsive MOF film systems alongside primary photon stimulation. This concept is introduced as orthogonal stimulation by Peh et al. 15 and holds promise for tailoring responsiveness in flexible MOF systems. Following this approach, in this work we demonstrate a chemical pathway to tune photo-induced structural transformations. 15 Replacing terephthalic acid linkers with chloro-functionalized derivatives allows the fabrication of CI-DMOF-1 films being isostructural to the DMOF-1 system (Fig. 1a, right), 13,17 while exhibiting varied flexibility with changes in growth time (Fig. 1b). Although linker functionalization has been successfully shown for bulk DMOF-1 systems, 18-21 the structural photo-response and its duration for such modified structures has not been examined so far. We tackled this by incorporating azobenzene within the CI-DMOF-1 pores to obtain a photo-responsive film system as confirmed by infrared spectroscopic measurements. Time-resolved grazing incidence wide angle X-ray scattering measurements (GIWAXS) showed a significantly slowed structural photo-response compared to the DMOF-1 structure (Fig. 1c). 22

To ensure sufficient light penetration accompanied by a controlled propagation of the structural photo-response, the CI-DMOF-1 films were fabricated as heteroepitaxial film structures following the substrate-seeded approach. 23,24 For this, in a first step, Cu(OH)2 nanobelts were deposited on glass substrates which were then converted to Cu2bdc2 (see Scheme S1). 23

Fig. 1 Schematics on the orthogonal stimulation strategy in MOF films. (a) Structure of the flexible CI-DMOF-1 framework viewed along the zinc paddlewheel units linked by functionalized C12-bdc and pillared by dobco. (b) Varying the growth time of the CI-DMOF-1 films lead to rigid or flexible structures. (c) CI-DMOF-1 films were infiltrated by azobenzene, which upon irradiation with UV light (343 nm) isomerizes from trans-to-cis, and vice versa upon the irradiation with blue light (450 nm).
Subsequently, the Cu₂bdc₂-on-Cu(OH)₂ films were treated in zinc acetate and subsequently placed at 60°C in the methanolic linker solution containing dabco and the Cl₂-bdc linker (Fig. 1a, see ESI for experimental details). However, linker functionalization in MOFs can potentially vary the thermo-dynamic stability and thus the readiness of the structure to grow.²⁵ To address this issue, in a first step, we altered the growth time of the Cl-DMOF-1 films between 10 – 270 min and studied the alignment of the structure along the Cu₂bdc₂-on-Cu(OH)₂ film surface in a combinatorial study employing SEM (Fig. 2 and Fig. S2) and GIWAXS measurements (Fig. S3 and S4), which will be discussed in the following.

In Fig. 2, the top-view SEM micrographs depict the time-dependent growth of the Cl-DMOF-1-on-Cu₂bdc₂-on-Cu(OH)₂ film structures. Initially, at a growth time of 10 min, small crystallites appear (Fig. 2a), which were determined by GIWAXS measurements to correspond to a weak growth of the Cl-DMOF-1₁₀min structure (Fig. S3, a). According to the GIWAXS pattern in Fig. S3 b, sharp reflections appear for a growth of 30 min, which are attributed to the formation of the P4/mnm phase for the Cl-DMOF-1₁₅₀min (α₀ = 10.93 Å, β₀ = 10.93 Å, c₀ = 9.61 Å).²⁷ Interestingly, the (100) reflection shows a shift of Δq₀ = 0.04 nm⁻¹ between the out-of-plane (q₀p) = 5.82 nm⁻¹ and the in-plane direction (q₀l = 5.78 nm⁻¹). On the contrary, the (001)Cl-DMOF-1 and (101)Cl-DMOF-1 reflections remain unaltered indicating that the (100) plane is distorted. This property we attribute to internal strain²² within the Cl-DMOF-1 structures which becomes more evident at a growth time of 90 min causing even a splitting of the (001)Cl₂bdc₂ reflection for the Cu₂bdc₂-on-Cu(OH)₂ substructure (Fig. S4, a, out-of-plane pattern). Kitagawa and co-workers recently delineated that with a decreasing MOF film thickness, surface effects become more pronounced,²⁸ that for heteroepitaxial structures can be a display of strain induced by the lattice mismatch.²⁴ Hence, to understand the impact of internal strain we performed GIWAXS measurements while rotating the Cl-DMOF-1₀₅₀min film sample along the azimuthal angle ϕ (rotation around the surface normal, see Fig. S5, a-b). The behaviour of the (100)Cl-DMOF-1 reflection with respect to ϕ in the out-of-plane direction indicates the presence of two crystalline phases. At ϕ = 0°, the Cl-DMOF-1₀₅₀min structure was determined to grow as the P4/mnm phase (Fig. S5, c-d), as already encountered for structures grown at short times. By rotating the sample to larger ϕ-angles, a second phase appears that is shifted towards higher ϕ, thus resembling the I4/mcm structure (Fig. S5, c). As a result of this, the characteristic (001)Cl₂bdc₂ reflection of the epitaxial substructure shifts by Δq = 0.03 nm⁻¹ towards smaller q in the out-of-plane direction (Fig. S5, d). It must be noted, that the Cu₂bdc₂ substructure of the Cl-DMOF-1₀₅₀min film was confirmed to comprise a strong azimuthal angle dependence in the in-plane direction (Fig. S5, e-g), as it was reported for the non-functionalized DMOF-1 film structure.²²,²³ The (001)Cl-DMOF-1 reflection located at q₀θ = 6.45 nm⁻¹ shows no azimuthal angle dependence in the in-plane direction (Fig. S5, b and d). Based on these findings, we consider the growth of this second I4/mcm-like phase a result of relieving the internal strain within the Cl-DMOF-1 structures that arises mainly from the urge to match the Cl-DMOF-1 lattice with the lower Cu₂bdc₂-on-Cu(OH)₂ structure. Thusly, at growth times ≤90 min, strained but heteroepitaxially grown Cl-DMOF-1-on-Cu₂bdc₂-on-Cu(OH)₂ film systems are obtained. Yet, a propagation of the growth time leads to non-epitaxially grown Cl-DMOF-1₀₅₀min (Fig. S4, b) and Cl-DMOF-1₂₇₀min structures (Fig. S4, c). Moreover, the absence of preferred alignment in both in-plane and out-of-plane directions is characteristic for non-epitaxial and bulk structures.²⁴ From SEM micrographs the evolution of the Cl-DMOF-1 crystallite growth as a function of time demonstrates the formation of very thin crystallites after 30 min with a size of 1.4 μm both in length and height (Fig. 2b). The Cl-DMOF-1₀₅₀min Crystallites continue to grow in their width (~0.1 μm; Fig. 2c), which further increases for the Cl-DMOF-1₀₅₀min system (~0.3 μm; Fig. 2d). However, prolonged growth of the Cl-DMOF-1₁₈₀min System yields crystallites of significantly different shape, where some crystallite surfaces are strongly bent inward (see red arrow in Fig. 2e). After 270 min, the crystallite size resembles those of reported bulk crystallites with the difference that most of the larger crystallites comprise cracks (see Fig. 2f), which are referred to be the result of a long-range strain within the structure.²⁹ Some of the Cl-DMOF-1₂₇₀min crystallites display a hollow core resembling a shell-like structure, which we attribute to be the ultimate product of internal stress release (Fig. 2g, see SEM image). The evolution of the Cl-DMOF-1 crystallite growth is schematically depicted in Fig. 2g, where we classify structures grown shorter than 90 min as heteroepitaxial, whilst subsequent growth yields bulk-like structures. Based on GIWAXS data, we propose for heteroepitaxial structures (growth time <90 min) that the (h00)Cl-DMOF-1 plane grows epitaxially onto the (001)Cl₂bdc₂ plane with the a-axis of the Cl-DMOF-1 system aligning perpendicular to the substrate. For these structures, the (001)Cl-DMOF-1 plane orients mainly in the out-of-plane direction, which results in the c-axis aligned parallel to the substrate (see Fig. S3, a-c). This alignment was already reported in our earlier
study of the oriented DMOF-1 film structure,22 which confirms the isoreticular growth approach for the presented functionalized heteroepitaxial film system. However, this is not the case for bulk-like Cl-DMOF-1 film structures (180 – 270 min), which show a sudden change in the alignment of their structure. This property is evidenced by the appearance of the (001)Cl-DMOF-1 plane in the in-plane direction (≥90 min, Fig. S4 a). We presume that this inversion in alignment mainly arises from the strained ≥180 min results resulting in a complete loss of heteroepitaxy accompanied by the sudden change in shape of the Cl-DMOF-1 crystallites yielding bulk-like structures (see SEM images in Fig. 2). The growth behaviour of the Cl-DMOF-1 films was additionally confirmed by infrared spectroscopic measurements. All pristine structures show strong vibrational bands located around 1388 cm<sup>-1</sup> and 1587 cm<sup>-1</sup> (Fig. 3 and S6-8), corresponding to the symmetric (υ<sub>s</sub>) and asymmetric stretching (υ<sub>as</sub>) of the carboxylic group bonded to the metal nodes, respectively.

We further investigated the structural flexibility of the Cl-DMOF-1 films. For this, the photo-active guest molecule azobenzene was incorporated within the Cl-DMOF-1 pores following the vapour-assisted approach (<0.5 molecules per pore, Table S1).22 The success of the infiltration process was confirmed by Fourier transform infrared (FT-IR) attenuated total reflectance (ATR) measurements of the respective Cl-DMOF-1 films. Results show the appearance of the characteristic trans-azo-benzene vibrational band located around 691 cm<sup>-1</sup> (see Fig. S6-8), which experiences a red-shift for structures after prolonged growth (30 – 180 min, Table S2). Similarly, a red-shift of the υ<sub>s</sub> vibrational band was determined that is attributed to the carboxylate vibrations arising from the Cl-DMOF-1 structure (Table S2). This behaviour indicates that the internal strain caused by the heteroepitaxial growth of the Cl-DMOF-1/AB structures is directly translated to the infiltrated azobenzene molecule within the pores. In the case of the weakly grown Cl-DMOF-1/AB<sub>90min</sub> structure (Fig. S6, a), where the main vibrational bands are attributed to the non-coordinated terephthalic acid linkers (see Fig. S6, b), azobenzene is expected to accumulate on the surface rather than being incorporated within the pores. Hence, this system can serve as a reference since the vibrational band of azobenzene corresponds to its non-strained, pristine trans-conformer located at υ<sub>s</sub><sub>Cl-AB</sub> = 690 cm<sup>-1</sup> (Fig. S6, c). In comparison, the Cl-DMOF-1/AB<sub>90min</sub> system contains azobenzene molecules in a relaxed state (υ<sub>s</sub><sub>AB</sub> = 691 cm<sup>-1</sup>), which is attributed to the loss of epitaxy. Hence, these findings corroborate SEM and GIWAXS measurements and show that at growth times exceeding 180 min, the internal stress is overcome which leads to bulk-like, non-epitaxially grown structures.

In the next step, to test the photo-activity of the incorporated azobenzene molecules with respect to the duration of the structural transformation of the Cl-DMOF-1/AB systems, we performed ATR measurements combined with two light-sources (343 nm, 450 nm; Scheme S2). Results show that short growth times yield rigid Cl-DMOF-1/AB structures where no azobenzene isomerization was possible (Fig. 59, a), whilst the structures obtained after longer growth times exhibit sufficient flexibility to respond to the azobenzene isomerization process (≥60 min, Fig. 59, b). For the latter films, irradiation by 343 nm prompted the azobenzene within the Cl-DMOF-1/AB<sub>90min</sub> pores to enter its cis-state (υ<sub>s</sub><sub>Cl-AB</sub> = 698 cm<sup>-1</sup>), which after exposure to 450 nm relaxed fully to its trans-conformer (υ<sub>s</sub><sub>trans-AB</sub> = 693 cm<sup>-1</sup>; OFF-state; Fig. 3b). Results for the DMOF-1/AB<sub>90min</sub> show, that in the ON state about 70% of the infiltrated azobenzene molecules convert to the cis-conformer, whilst 30% of the trans-conformer still remain (Fig. 3c). This significantly higher abundance of trans-azobenzene molecules within the Cl-DMOF-1/AB<sub>90min</sub> pores is attributed to a strong stabilization of this conformer owed to the chloro-functionalized MOF environment. The relaxed Cl-DMOF-1/AB<sub>90min</sub> structure was found to repeatedly allow the azobenzene to enter its trans-isomer, yet comprising a shift of Δυ<sub>Cl-AB</sub> = 1.05 cm<sup>-1</sup> between the ON and the OFF state (Fig. 3b).

We further performed time-resolved GIWAXS measurements to investigate the structural transformations induced within the Cl-DMOF-1/AB<sub>90min</sub> structure upon photo-excitation. Here, only the Cl-DMOF-1/AB<sub>90min</sub> structure was tested to confirm the success of the isomerization process of azobenzene upon photo-stimulation (Fig. 4). This is because azobenzene remains non-responsive at shorter growth times (Cl-DMOF-1/AB<sub>30min</sub>; Fig. S9, a), and the bulk-like growth of Cl-DMOF-1/AB structures after 180 and 270 minutes produces inhomogeneous films that hinder light penetration thus impeding their photo-physical characterization. Detailed analysis of the GIWAXS data for the Cl-DMOF-1/AB<sub>90min</sub> structure showed that 32% of the crystallites orient preferentially towards the out-of-plane direction (Fig. S10). This result is comparable to the non-functionalized DMOF-1 film structure, which confirms that an oriented and heteroepitaxial Cl-DMOF-1 structure is grown, thus allowing the characterization of its photo-switch.22 Time-resolved GIWAXS measurements revealed that upon the excitation with light of 343 nm, the (001) reflection commences a shift by Δq = 0.013 nm<sup>-1</sup>, as determined from fitting results in the in-plane direction (Fig. 4a). This value is in good agreement with findings reported for the non-functionalized DMOF-1 film system.22 Hence, the Cl-DMOF-1/AB<sub>90min</sub> structure shrinks when azobenzene enters its cis-conformer, which is reversed by light of 450 nm wavelength upon the relaxation to its trans-conformer (Fig. 4, b-c). This finding strongly supports the successful isoreticular design strategy as the structural response for the Cl-DMOF-1/AB<sub>90min</sub> system.

![Fig. 3](image-url)
Fig. 4 GIWAXS data for the Cl-DMOF-1/AB$_{0.08}$s structure. (a) Azimuthal integration of the GIWAXS pattern for the switched (ON, purple pattern) and the relaxed Cl-DMOF-1/AB$_{0.08}$ film structure (OFF, blue pattern). The change of the intensity for the (001) reflection was used to evaluate the switching times (see inset). (b) Considering the change in the normalized integrated (001) intensity, the forward switch (ON, 343 nm) occurred within $t_{\text{ON}} = 41.7 \pm 3$ s, (c) whilst the back switch (OFF, 450 nm) required $t_{\text{OFF}} = 18.4 \pm 3$ s. Switching constants represent the mean value with corresponding error derived from experiments conducted by repeating the ON/OFF switch thrice.

DMOF-1 is channelled similar as for the DMOF-1 structure.\(^{22}\) From the temporal evolution of the intensity for the (001) reflection under continuous illumination with the respective light sources, the switching constants were deduced for the ON state (343 nm, Fig. 4b) and the OFF state (450 nm, Fig. 4c). GIWAXS measurements showed, that the structural response for the ON state is reached after $t_{\text{ON}} = 41.7 \pm 3$ s (343 nm@130 mW cm$^{-2}$), which is reversed within $t_{\text{OFF}} = 18.4 \pm 3$ s (Fig. 4, b-c; 450 nm@17.2 mW cm$^{-2}$). In comparison, we reported for the non-functionalized DMOF-1 film structure that the entire switch requires 15 sec (343 nm@95 mW cm$^{-2}$, 450 nm@17.2 mW cm$^{-2}$),\(^{22}\) which therefore renders the Cl-DMOF-1/AB$_{0.08}$s film system to respond significantly slower at similar irradiances (see Table S3 for comparison of the two film systems). This finding is reasonable as chloro-functionalized switchable bulk structures are known to experience a certain loss in flexibility,\(^{36}\) as indicated by the lack of gate-opening behaviour in bulk Cl-DMOF-1 during N$_2$ sorption experiments, whilst the DMOF-1 showed a subtle step in the adsorption branch $P/P_0 = 0.003$ (Fig. S13).

In conclusion, we herein prepared Zn-based MOF films using chlorinated terephthalic acid and dabc with ligands, yielding 3D-oriented MOF crystals which were infiltrated with photo-responsive azobenzene. Upon UV irradiation, we measured the orthogonal stimulation. The chloro-functionality imparts rigidity to the oriented MOF film, leading to a strongly decelerated structural photo-response. Depending on the synthesis conditions, different photo-responsive behaviours were observed: films prepared with short reaction time (10 – 60 min) show entirely rigid frameworks, while prolonged growth of the MOF crystals (90 – 270 min) yielded more flexible structures. Moreover, the azobenzene molecules in the MOF pores can be repeatedly isomerized when triggered by light opening possibilities for their application as mechanical storage systems.\(^{10,12,15,17}\)

**Conflicts of interest**

There are no conflicts to declare.

**Notes and references**

11. Q. Huang and C. Wu, Mater. Today Sustain., 2022, 18, 100149.