Supplementary Information

Reversible structural switching of a metal-organic framework by photoirradiation

Varvara I. Nikolayenko, Simon A. Herbert and Leonard J. Barbour*

Department of Chemistry and Polymer Science, University of Stellenbosch, Stellenbosch 7600, South Africa. ljb@sun.ac.za

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1.1 General information

Apart from the synthesised ligands L1 and L2, all reagents were used as purchased from commercial sources with no further purification.

1.2 Ligand synthesis

Both the 1,2 bis[2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene (L1) and 1,2 bis[2-ethyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene (L2) ligands were synthesized according to a previously reported synthetic procedure and were isolated as the ring-open conformers.^{1,2,3}

1.3 Physical measurements

X-ray intensity data were recorded on either a Bruker SMART APEX II or a Bruker APEX II DUO X-ray diffractometer.⁴ The former is equipped with a Mo sealed tube source and the latter with an Incoatec IµS Mo source. Each diffractometer employs an Oxford Cryosystems 700+ Plus cryostat to control the temperature of the sample. Data reduction was carried out by means of standard procedures using the Bruker software package SAINT.⁵ Absorption corrections and correction of other systematic errors were carried out using SADABS.⁶ All structures were solved by direct methods using SHELXS-2016 and refined using SHELXL-2016.⁷ X-Seed⁸ was used as the graphical interface for the SHELX program suite. Hydrogen atoms were placed in calculated positions using riding models.

Thermogravimetric analyses were carried out using a TA Instruments Q500 thermogravimetric analyser to record the weight loss of the metal-organic frameworks as a function of temperature. The balance and sample were purged with dry N_2 gas flowing at rates of 50 and 70 cm³ min⁻¹, respectively. Samples masses typically ranged from 2-7 mg and samples were heated at a constant rate of 10 °C min⁻¹ from 25 °C to 600 °C. Thermograms were analyzed using the TA Instruments Universal Analysis program.

X-ray powder diffractograms were recorded with a Bruker D2 PHASER equipped with a Lynxeye 1D detector and Ni-filtered Cu K α radiation (30 kV, 10 mA generator parameters; restricted by a 1.0 mm divergence slit and a 2.5° Soller collimator) with a 0.02° step width. All samples were first ground into a powder (using a mortar and pestle) and loaded onto zero-background sample holders.

Gravimetric sorption isotherms were recorded using an Intelligent Gravimetric Analyser (IGA-002) supplied by Hiden Analytical (Ltd), Warrington, UK.⁹ The instrument records the change in mass of a sample under controlled pressure and temperature conditions. It is equipped with an advanced pressure rating that allows measurements up to 20 bar. The pressure is monitored using a pressure transducer with a range of 0-20 bar and buoyancy effects are corrected for automatically by the control software. An accurate estimate of the sample density is required for the buoyancy correction. Densities are generally estimated from the singlecrystal structure or, in the absence of a structure, by means of a buoyancy scan under helium pressure. Ultra-high purity CO₂ gas was used for the measurements. Temperature control was maintained to an accuracy of ± 0.05 °C using a Grant refrigerated recirculation bath. Sorption data were monitored by real-time software that analyses the pressure and weight equilibrium using least-squares regression to extrapolate a value for the asymptote.^{10,11,12,13,14} A Linear Driving Force (LDF) relaxation model was used and each point was recorded once a 99% fit to the model was achieved, or a pre-set time-out was reached (set at 120 minutes). Although there are various options for reporting data, the data were exported as the number of guest CO₂ molecules per formula unit of host.

Solid-state UV-visible spectra were recorded on an Analytik Jena SPECORD 210 PLUS spectrophotometer equipped with an integrating sphere. Photoirradiation was carried out using either a hand held UV-Groebel UV-LED SOLO photodiode emitting UV light of wavelength 365 nm at 4,200 mW cm⁻², or a high intensity laser emitting green light with a wavelength of 532 nm at ca 800 mW.

1.4 Activation methods

For each sample the optimum activation temperature was determined from thermogravimetric analyses which were carried out for all solvates except **DMOF3** (crystals of **DMOF3** are very difficult to grow and there was not enough material for TGA). Once the guest-loss onset temperature had been established for a particular solvate, several crystals were then heated at that temperature under dynamic vacuum in a Büchi glass oven for 24 hours. In the case of DMOF2 and DMOF3, this conventional activation method proved too extreme, resulting in loss of crystal singularity. Therefore, a milder activation method involving exposure of the material to super critical CO₂ (scCO₂) was employed instead. ScCO₂, possesses properties of both a liquid and a gas it thus exerts little to no surface tension on the walls of the channels in the crystal. Depending on the solvent present in the channels, and the exact conditions of temperature and pressure, scCO₂ is often able to dissolve the solvent molecules and leave behind the activated phase. **DMOF2** and **DMOF3** were activated with scCO₂ in a Tousimis[™] Samdri® PVT-30 critical point dryer. Each sample was placed in the steel pressure chamber of the dryer, which was then sealed, filled with liquid CO₂, and warmed to 40 °C. This brought the chamber pressure to approximately 100 bar. The contents of the chamber were kept above the critical point for 24 hours, after which the chamber was slowly vented over the course of 1 hour.

1.5 Void volume calculations

Accessible and *contact* surfaces can be calculated and visualised using a number of different software packages. We have used the programs Mercury,^{15,16} MS-Roll ^{17,18} or a combination thereof. These surfaces are mapped by tracing the passage of a spherical probe (of a specified radius) through the structure. Lee and Richards¹⁹ defined the *accessible surface* as the surface enclosing the space that can be accessed by the centre of the probe. The *contact surface* encloses the space that can be accessed by the exterior of the probe. These concepts were originally developed to describe the topologies of protein cavities but they are now also applied to mapping the open spaces of porous crystals. In the latter context (and in hindsight), the term *accessible space* is a poor linguistic choice. For example, use surfaces for the purpose of illustrating void volumes, but we prefer to refer to the volume rather than the surface when discussing the space available to a guest. It is therefore linguistically comfortable to discuss an *accessible volume* but it is awkward to refer to a *contact volume*.

Besides, there is no clear reason to use the term *accessible* to describe the trajectory of the probe's centre rather than its surface. Therefore, the term *accessible volume* is often used to describe the space enclosed by either the *accessible* surface <u>or</u> the *contact* surface. Until these terminological difficulties are addressed by authorities in the field, this will continue to happen – in the interim, confusion can be avoided if the authors clearly state which term they are using in which context. We prefer to use the terms *solvent-accessible volume* or *guest-accessible volume* to refer to the space enclosed by the *contact surface*. With regard to maps of guest-accessible space in crystal structures we should be aware of a number of considerations that are generally not discussed. Some of these are:

- The selection of probe radius affects the map of the accessible volume there are no guidelines for the selection but it seems sensible to choose a radius that represents the atoms at the extremities of possible guest volumes. Of course, when comparing accessible volumes, the radius of the probe should be standardised.
- Static atomic coordinates of the host framework are used when computing accessible volumes. Computer programs do not accommodate possible movement of the host atoms due to thermal vibration or structural flexibility. Therefore, in many structures the true accessible volume is a dynamic entity.
- 3. Calculations are susceptible to the atomic radii assigned to the host atoms, and all host atoms of the same element are assumed to be spheres with a consistent radius regardless of their chemical environment.
- 4. Calculations generally do not consider kinetic radii of potential guests.
- Different programs use different algorithms for the calculations for example, the results from Mercury depend on the grid spacing chosen while MSRoll does not use a grid approach.
- 6. When structures are disordered it becomes necessary to delete one or more of the disordered components. This complicates volume calculations because volumes may be different depending on which component is deleted. Moreover, in such cases it is often impossible to know whether there is a cooperative effect that synchronises the disorder of neighbouring molecules.

Until these issues are addressed properly, we need to consider that maps of accessible volumes are only useful in a qualitative sense.

Our typical mapping procedure involves deletion of the guest molecules from the atom list and specification of an 'appropriate' probe radius. The MSRoll output file *name*.cav is imported into X-Seed and the mapped surface can be incorporated into the final structure visualisation using POV-Ray.²⁰ Although our graphics were generated using MSRoll, both MSRoll and Mercury were used for the volume calculations, as appropriate (each has its advantages and disadvantages). Unless otherwise stated, Mercury values were calculated using a probe radius of 1.5 Å and a grid spacing of 0.1 Å (since these numbers are adjustable, void volume calculations without specification of these parameters are meaningless). Although Mercury provides a percentage of the unit cell volume that is occupied by voids and a void volume, it does not provide any details regarding the number of voids or their individual volumes. In contrast, MS-Roll maps a more accurate surface (no grid spacing) and provides individual void volumes but no percentage of the unit cell volume. It should be noted that, in cases where structures contained host disorder, the minor fragment was removed when modelling solvent accessible surfaces and pockets of 18 Å or less were ignored.

1.6 Disorder and modelling of solvent molecules

For the structure of **DMOF** it was not possible to model all of the solvent crystallographically. However, it was possible to model one DMF molecule disordered over two positions with site occupancies of 63% and 37%. The remaining electron density within the channel was removed using the SQUEEZE²¹ routine of PLATON.²² However, TGA is consistent with the presence of two DMF molecules per formula unit.

For **DMOF1**, the entire ligand L2 was modelled as disordered over two very similar positions with site occupancies that refined to 51 and 49%. L2 was therefore refined isotropically. It was possible to model one DMF molecule with 50% site occupancy. TGA and SQUEEZE are consistent with the presence of a second DMF molecule, which could not be modelled.

In **DMOF1'** and **iDMOF1'** one of the alkyl chains was modelled as disordered over two positions with site occupancies of 53% and 47% (for **DMOF1'**) and 58% and 42% (for **DMOF1'**).

In DMOF2 three DMF molecules were modelled with site occupancies of 93%, 90% and 57%.

In **DMOF3** three DMF molecules were modelled, of which two are disordered over two positions. The ordered DMF molecule was modelled with a site occupancy of 54%.

The two disordered molecules were modelled with site occupancies of 59%/41% and 54%/46%. TGA and SQUEEZE are consistent with the presence of a fourth molecule, which could not be modelled.

In **DMOF3'** one alkyl chain was modelled as disordered over two potions with site occupancies of 53% and 47%.

1.7 Irradiation procedures

Photochromic samples were interconverted between the open and closed forms using either an 800 W green laser ($\lambda = 532$ nm) or a high-intensity UV photodiode ($\lambda = 365$ nm). In order to carry out continuous irradiation experiments while recording diffraction data, it was necessary to construct a suitable device to hold the photodiode in place while ensuring sufficient incident intensity at the crystal without impeding the motion of the X-Ray detector. Space considerations dictated that the only location for the source was directly beneath the crystal (which is also directly in the flow of the nitrogen crystostream). This configuration prevents simultaneous irradiation and cooling owing to the risk of cracking the glass lens of the photodiode. As a result, continuous (*in situ*) UV irradiation experiments during intensity data collection were carried at room temperature (Fig. S1).



Figure S1. Photographs showing **a**) *in situ* and **b**) *ex situ* UV irradiation experimental configurations.

In the case of **iDMOF'** and **iDMOF1'** multiple SCD experiments were carried out with sequentially prolonged *in situ* exposure to UV-Irradiation.

1.8 BPTC chirality

BPTC molecules exhibit atropisomerism and are usually synthesised under non-stereospecific conditions. The final product is therefore isolated as a racemic mixture of P and M isomers that are helical conformers of one another (Fig. S2).²³ A racemic compound could crystallise either as a collection of centrosymmetric crystals that contain an equal number of both enantiomers, or as a conglomerate (i.e. a mechanical mixture of enantiomerically pure crystals of isomers).



Figure S2. *P* and *M* helical conformers found in BTCP ligands.

1.9 MOF synthesis and discussion

1.9.1 Comparison of the published structure of DMOF and that determined in the present study

The structure of **DMOF** was first reported in 2014 by Luo *et al.* We were independently studying the same material at approximately the same time. Some of our experiments were carried out in the same manner as those of Luo *et al.*, with similar outcomes. However, it is important to note that there are several difference between our results and theirs, and these will be discussed below. Although L1 is prepared as a racemic mixture of P and M enantiomers, **DMOF** crystallises as a conglomerate of chiral crystals. Luo *et al.* prepared **DMOF** from a DMF-H₂O solution, and then selected and analysed a crystal containing L1 as the M enantiomer. We crystallised **DMOF** from DMF and selected a crystal containing the P

enantiomer of L1. Luo *et al.* did not model any solvent molecules and the identity of the guest was established using elemental analysis and TGA. Our model of **DMOF** includes a model for one of the two unique guest molecules.

Luo *et al.* did not report SCD analysis for the activated or irradiated forms of **DMOF** (**DMOF**' or **iDMOF**'). Further differences include the type and wavelength of the UV source used to irradiate the crystals.

Luo et al. used an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp instrument, all emitting 300 nm radiation. We used a hand held UV-Groebel UV-LED SOLO lamp emitting a 365 nm UV light at 4,200 mW cm⁻². Luo et al. apparently recorded CO₂ gas sorption in the range 0-1 bar (erroneously reported as $P/P_0 = 0-1$) at 298 K using "an ASAP 2020 from Quantachrome" (we note that the ASAP 2020 is an instrument supplied by Micromeritics). Assuming that they used a Micromeritics ASAP 2020 instrument, we are aware that the system uses glass sample tubes. In their experiment the material was irradiated *in-situ* during the gas sorption experiments. In an attempt to further understand the results reported by Luo et al., we extended our sorption study by measuring CO₂ uptake in the range 1-20 bar at 298 K. This was carried out using an Intelligent Gravimetric Analyser (IGA-002) supplied by Hiden Analytical (Ltd). The stainless steel sample compartment of the IGA-002 precludes in situ irradiation of the sample during sorption analysis. After the original **DMOF'** sample had undergone one CO₂ sorption/desorption cycle, the material was removed from the instrument and irradiated ex situ using our UV source for 3 hours. The sample was then reloaded into the IGA-002 sample pan in the dark and the CO₂ sorption cycle repeated. The powdered sample was stirred periodically during irradiation in order to expose as many of the particles as possible to the light.

1.9.2 DMOF

L1, Zn(NO₃)₂·6H₂O and 4-4'-biphenyl carboxylic acid (bpdc) were dissolved in a 1:1:1 ratio in 2 mL DMF, sealed in a Teflon-lined steel autoclave and heated at 100 °C for 24 hours (Fig. S3). Upon cooling to room temperature, colourless rectangular crystals were obtained in 85% yield.



Figure S3. Synthesis of **DMOF** from the solvothermal reaction of L1, bpdc and zinc nitrate.

DMOF crystallises in the orthorhombic space group $P2_12_12_1$. The asymmetric unit (ASU) consists of one zinc cation, one ligand L1, one bpdc ligand and one DMF molecule disordered over two positions (the second DMF molecule was too diffuse to model but its presence was suggested by TGA and SQUEEZE). Each metal centre possesses tetrahedral coordination geometry (Fig. S4a) comprised of two L1 ligands and two bpdc ligands.

The L1 ligands are present in the ring-open form (Fig. S4a) with the distance between carbon atoms associated with ring closure measuring 3.652(7) Å. Although the 3D network is fivefold interpenetrated, there are large corrugated channels running along [100]. Fig. S4b shows DMF molecules (i.e. those that could be modelled) occupying these channels.



Figure S4. a) Tetrahedral geometry around Zn in **DMOF**. b) View along [100] showing fivefold interpenetration (yellow, orange, pink, green, blue) and solvent-filled channels.

The modelled DMF molecule is disordered over two positions with site occupancies of 63% and 37%. TGA (**Fig. S5**) shows some initial mass loss attributed to surface solvent, with an additional 20% mass loss occurring in the temperature range of 50-150 °C. This corresponds to two DMF molecules per formula unit. Decomposition of the framework begins at approximately 325 °C.



Figure S5. TGA of the as-synthesised (green) as well as the evacuated (blue) phases of **DMOF**.

While activating bulk material by heating above 150 °C the crystals of **DMOF** did not appear to deteriorate. An SCD experiment was therefore undertaken to obtain the structure of the activated form **DMOF'** (Table S1). **DMOF'** shows no significant change *viz*. cell parameters and an examination of the ASU shows that the host coordination mode is unaltered. Large 1D channels are apparent when viewing **DMOF'** along [100] (Fig. S6).

	DMOF	DMOF'	iDMOF′
Formula	$C_{42}H_{31}F_6N_3O_5S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$	$C_{39}H_{24}F_6N_2O_4S_2Zn$
Formula weight	901.21 g mol ⁻¹	828.11 g mol ⁻¹	828.11 g mol ⁻¹
Temperature* / K	100(2)	100(2)	297(2)
Wavelength/ Å	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁
<i>a</i> / Å	7.217(6)	7.106(2)	7.166(9)
b / Å	24.471(3)	24.681(7)	24.540(3)
<i>c</i> / Å	28.683(3)	29.181(9)	29.480(3)
$\mathbf{V}/\mathrm{\AA}^3$	5066(1)	5118(3)	5184(1)
Z	4	4	4
CC / Å	3.652(7)	3.675(7)	3.668(9)

Table S1.Crystallographic data for **DMOF**.

* Where possible, intensity data were recorded at 100 K in order to obtain the best possible crystallographic model. Owing to space limitations, the UV source was mounted directly beneath the crystal. It was not possible to irradiate the crystal at cryogenic temperatures because of the possibility of cracking the lens of the UV source.



Figure S6. DMOF' viewed along [100], showing solvent-accessible voids.

A UV-visible spectrum of the apohost of **DMOF'** was recorded. The same sample was then irradiated (365 nm) for one minute and the spectrum rerecorded. Fig. S7 shows that the original form contains two bands, one at 353 nm and one at 425 nm. These bands are attributed to π - π * transitions in the ligand, and metal-to-ligand charge transfer of the divalent zinc to the π * orbital of the bridging ligand. The spectrum of the irradiated material shows a broad peak with a maximum at 614 nm.



Figure S7. Solid-state UV-visible spectra of **DMOF1'** recorded after exposure to visible (green) and ultraviolet (blue) light, with associated sample photomicrographs.

Fig. S8 shows that irradiation does not discernibly diminish the quality of the crystals and single-crystal to single-crystal (SC-SC) transformation experiments were thus undertaken in an attempt to verify the hypothesis proposed by Luo *et al.* Despite the vivid colour change and numerous data collections with varying degrees of exposure to UV irradiation, **iDMOF'** did not exhibit any significant change in its unit cell parameters. Neither could we establish a structural change, nor the presence of residual electron density peaks in the region associated with ring closure. Furthermore, the distance between the two carbon atoms involved in ring closure is measured at 3.668(9) Å, regardless of the colour change.



Figure S8. Photomicrographs showing a crystal of **DMOF'** undergoing a reversible colour change when exposed to ultraviolet and green light.

Several **DMOF'** crystals were irradiated overnight using a high intensity 365 nm photodiode. The crystals were then broken into fragments and Fig. S9 shows that the blue colour only penetrates a short distance beyond the original crystal surface, with the bulk of the crystal remaining colourless. We believe that this is why we were unable to detect any crystallographic evidence for bulk photocyclisation.



Figure S9. Photomicrographs showing fragments of **iDMOF'** crystals with the blue colour only penetrating a short distance beyond the original surface.

Since we were unable to obtain SCD evidence of ring-closure, we postulate that particle size distribution is critical, and that the crystals studied where simply too large for conversion to occur in significant yield. Thus powder diffraction experiments were carried out; the overlaid PXRD patterns in Fig S10 show little difference between **DMOF'** and **iDMOF'**. Owing to the limited space within the sample compartment of the XRD instrument (Bruker D2 Phaser), it was not possible to irradiate samples *in situ* during PXRD analysis. Samples were therefore irradiated before they were transferred to the instrument under low light conditions.



Figure S10. Overlaid experimenatal PXRD patterns of **DMOF'** and **iDMOF'** exposed to UV irradiation *ex situ*.

Since UV-visible spectroscopy was the principle technique used by Luo *et al.* to infer ring closure, we recorded multiple sequential scans for a non-irradiated sample of **DMOF'** in an attempt to determine what effect extended exposure to the full spectral window of the UV-visible spectrophotometer would have on the material. Fig. S11 shows that **DMOF'** undergoes a consistent increase in absorbance intensity in both the π - π * region and in the blue region associated with ring closure.

An examination of the sample also showed a change in colour of the previously colourless sample to blue. Since the sample undergoes a colour change (which is generally associated with ring closure) under these conditions, the use of solid-state UV-visible spectroscopy seems ill-advised as a monitoring technique.



Figure S11. Sequential solid-state UV-visible spectra of DMOF'.

The UV-visible spectra recorded after various durations of *ex situ* UV irradiation (Fig. S12) revealed that the band associated with combined π - π * and MLCT interactions at 375 nm increase, while the band attributed to ring closure at 625 nm decreases with extended exposure. Thus, **DMOF'** appears to undergo some conversion to the ring-closed form upon initial exposure, but that no more material is converted to the closed form upon continued exposure. Indeed, it is even possible that prolonged irradiation generates sufficient heat to cause cycloreversion such that an equilibrium is reached between the photoinduced ring-closed and heat-induced ring-open forms.



Figure S12. Sequential solid-state UV-visible spectra of **DMOF'** after varying durations of *ex situ* UV irradiation.

Having failed to obtain solid-state (single-crystal or PXRD) evidence that **DMOF**' is indeed undergoing complete ring closure, we carried out an extended version of the sorption experiment reported by Luo *et al.* with a view to gaining further insight. **DMOF**' shows conventional Type I sorption behaviour with no hysteresis, absorbing approximately one and a half molecules of CO₂ (7.9 wt %) per formula unit (Fig. S13) at 20 bar and 298 K. Even at 20 bar the shape of the sorption isotherm implies that full occupancy is not reached (i.e. the isotherm does not plateau at the pressure limit of the instrument). Thus it appears that **DMOF**' could potentially accommodate even more guest molecules at pressures exceeding 20 bar. Our isotherm correlates well with that reported by Luo *et al.* for **DMOF**'. However, it is important to note that at 1 bar, the reported CO₂ occupancy of 5.0 cm³g⁻¹ is equivalent to 0.15 molecules per formula unit. The isotherm recorded for the UV irradiated (*ex situ*) form showed a negligible increase in uptake and release of the CO₂ guest by the **iDMOF**' host.



Figure S13. CO₂ sorption (solid lines) and desorption (dashed lines) isotherms at 298 K for the **DMOF'** (green) and **iDMOF'** (blue). Solid lines represent sorption while dashed lines represent desorption.

1.9.3 DMOF1

DMOF1 was crystallised using a solvothermal process similar to that described for **DMOF**; L2 was used instead of L1. Colourless rectangular crystals where obtained in a 75% yield. **DMOF1** also crystallises in the orthorhombic space group $P2_12_12_1$ (Table S2) and may be considered homeotypic to **DMOF1**; the ASU consists of one zinc cation, one L2 ligand (disordered over two positions), (Fig. S14) one bpdc ligand and one DMF molecule.



Figure S14. The ASU of **DMOF1** showing disordered L2 ligand molecules in green and orange. Hydrogen atoms and solvent molecule are omitted for clarity.

TGA (Fig. S15) shows a 20% mass loss in the temperature range 30-150 °C. This corresponds to two DMF molecules per formula unit. Due to diffuse electron density the second DMF molecule could not be modelled. Decomposition of the framework begins at 335 °C. During bulk material activation it was observed that the crystals did not deteriorate visibly and SCD analysis was undertaken to determine the activated structure **DMOF1'** (Table S2). **DMOF1'** shows no significant change in unit cell parameters and an examination of the ASU shows that the coordination mode of the host remains unaltered. A UV-visible spectrum of the apohost of **DMOF1'** was recorded. The same sample was then irradiated (365 nm) for one minute and the spectrum rerecorded. Fig. S16 shows that the original form gives rise to two bands, one at 473 nm and one at 640 nm. These bands are once again attributed to π - π * transitions in the ligand, and metal-to-ligand charge transfer of the divalent zinc to the π * orbital of the bridging ligand. The spectrum of the irradiated form shows a broad peak maximizing at 660 nm. Fig. S17 shows that irradiation does not discernibly diminish the quality of the crystals. SCD experiments were carried out but, similar to **iDMOF1'** idoes not show any evidence of bulk ring-closure (Table S2).



Figure S15. TGA of the as-synthesised (green) and the evacuated (blue) phases of DMOF1.



Figure S16. Solid-state UV-visible spectra of the original and *ex situ* UV-irradiated forms of **DMOF1'**, hinting at ring closure upon irradiation with UV light.



Figure S17. Photomicrographs showing a crystal of **DMOF1'** undergoing a reversible colour change when exposed to ultraviolet and green light.

	DMOF1	DMOF1'	iDMOF1'	
Formula	$C_{43}H_{32}N_3O_5F_6S_2Zn$	$C_{41}H_{28}N_2O_4F_6S_2Zn$	$C_{41}H_{28}N_2O_4F_6S_2Zn$	
Formula weight	895.56 gmol ⁻¹	856.16 gmol ⁻¹	856.18 gmol ⁻¹	
Temperature* / K	100(2)	100(2)	296(2)	
Wavelength/ Å	0.71073	0.71073	0.71073	
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	
Space group	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	P2 ₁ 2 ₁ 2 ₁	
<i>a</i> / Å	7.519(7)	7.592(9)	7.635(8)	
b / Å	23.292(9)	23.821(3)	23.650(2)	
<i>c</i> / Å	29.563(2)	28.799(4)	29.184(8)	
$\mathbf{V}/\mathrm{\AA}^3$	5178(2)	5209(1)	5270(4)	
Z / Å	4	4	4	
CC / Å	3.850(2) and 3.480(2)	3.725(1)	3.762(8)	

Table S2.Crystallographic data for **DMOF1**.

* Where possible, intensity data were recorded at 100 K in order to obtain the best possible crystallographic model. Owing to space limitations, the UV source was mounted directly beneath the crystal. It was not possible to irradiate the crystal at cryogenic temperatures because of the possibility of cracking the lens of the UV source.

1.9.4 DMOF2

L1, $Zn(NO_3)_2 \cdot 6H_2O$ and 4,4'-oxybisbenzoic acid (oba) were dissolved in a 1:2:2 ratio in 2 mL DMF, sealed in a Teflon-lined steel autoclave and heated at 100 °C for 48 hours. Upon cooling to room temperature, yellow block-shaped crystals were obtained in 70% yield, based on Zn. **DMOF2** crystallises in the triclinic space group *P*-1 (Table S3). The ASU consists of two zinc cations, two oba ligands, one L1 ligand in the ring-open conformation and three DMF molecules.



Figure S18. Synthesis of **DMOF2** from the solvothermal reaction of L1, oba and zinc nitrate hexahydrate.

Each Zn center has a highly distorted square pyramidal geometry with four oxygen atoms from three oba ligands in the square plane and one nitrogen atom from the L1 ligand in the axial position. One bidentate carboxylate group is asymmetrically bound to the Zn center, while the other two are symmetrically bridging carboxylate groups in the $\mu_{1,2}$ mode between the two metal centers. The crystallographic inversion symmetry produces [Zn₂(L1)₂(oba)₄] (Fig. S19a). This highly unusual "half paddle-wheel"²⁴ secondary building unit (SBU) is the building block for the pillared MOF and generates a 3D two-fold interpenetrated framework structure (Fig. S19b). The reactive carbon…carbon distance is 3.883(8) Å.



Figure S19. a) Half paddlewheel moiety in DMOF2. b) Solvent filled channels viewed along [010].

TGA (Fig. S20) shows a 16% mass loss in the temperature range 0-125 °C, which corresponds to three DMF molecules per formula unit. Decomposition of the framework commences at 375 °C. Although TGA showed complete solvent removal at a relatively low temperature, neither solvent exchange (with a series of organic solvents, including acetonitrile, acetone, chloroform and dioxane) nor the use of scCO₂ activation resulted in retention of crystal singularity.

A UV-visible spectrum of the original solvate **DMOF2** was recorded. The same sample was then irradiated (365 nm) for one minute and the spectrum rerecorded. Fig. S21 shows two bands for the original, one at 350 nm and one at 465 nm. These bands are also attributed to π - π * transitions in the ligand and metal-to-ligand charge transfer of the divalent zinc to the π * orbital of the bridging ligand, respectively. The spectrum of the *ex situ* UV-irradiated sample shows a very broad peak above 550 nm.

Figure S20. TGA of the as-synthesised (green) and the evacuated (blue) phases of DMOF2.

Figure S21. Solid-state UV-visible spectra of as synthesised **DMOF2** before (green) and after (blue) *ex situ* exposure to UV light, with associated sample photomicrographs.

Figure S22. Photomicrographs showing a crystal of **DMOF2** undergoing a reversible colour change when exposed to UV and green light.

Table S3.Crystallographic data for **DMOF2**.

	DMOF2
Formula	$C_{60}H_{53}F_6N_4O_{12}S_2Zn_2$
Formula weight	1345.45gmol ⁻¹
Temperature / K	100(2)
Wavelength/ Å	0.71073
Crystal system	Triclinic
Space group	<i>P</i> -1
<i>a</i> / Å	11.169(3)
b / Å	14.536(4)
<i>c</i> / Å	21.343(6)
α / °	71.760(4)
β/°	76.741(4)
γ / °	68.321(5)
$\mathbf{V}/\ \mathrm{\AA}^3$	3033(1)
CC / Å	3.883(8)

1.9.5 DMOF3

DMOF3 was crystallised using a solvothermal process similar to that described for **DMOF2**; L2 was used instead of L1. Orange block-shaped crystals where obtained in a 30% yield, based on Zn. **DMOF3** crystallises in the triclinic space group *P*-1 (Table S4) with the ASU consisting of two zinc cations, two oba ligands, one L2 ligand in the ring-open conformation and three DMF molecules (a fourth DMF molecule could not be modelled). The structure of **DMOF3** is very similar to that of **DMOF2**, also containing a distorted version of the half-paddlewheel SBU (Fig. S23a). A notable difference between the two structures is the distance seperating the two oxygen atoms of adjacent oba ligands (4.37 Å in **DMOF3** and 4.53 Å in **DMOF2**). A single net of **DMOF3** shows the linear almost parallel alignent of oba ligands (Fig. S23b). The reactive carbon…carbon distance is 3.735(7) Å. The structure is twofold interpenetrated and contains channels along [011], which are occupied by DMF molecules (Fig. S23c).

Figure S23. a) Simplified rendition of the half-paddlewheel moiety in **DMOF3**. b) A single net of **DMOF3** showing arrangement of the oba ligands. c) Solvent-filled channels viewed along [010].

	DMOF3	DMOF3'	iDMOF3'
Formula	$C_{63}H_{54}F_6N_5O_{13}S_2Zn_2$	$C_{55}H_{36}F_6N_2O_{10}S_2Zn_2$	$C_{55}H_{36}F_6N_2O_{10}S_2Zn_2$
Formula weight	1378.18 g mol ⁻¹	1193.76g mol ⁻¹	1193.76g mol ⁻¹
Temperature* / K	100(2)	100(2)	298(2)
Wavelength / Å	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> / Å	13.355(9)	13.426(3)	12.260(1)
b / Å	14.136(9)	13.645(3)	13.257(2)
<i>c</i> / Å	19.632(7)	17.046(4)	17.620(2)
α / °	84.267(2)	90.202(3)	78.598(1)
β / °	77.664(2)	91.831(3)	89.230(1)
γ/°	66.013(2)	114.465(3)	67.499(1)
\mathbf{V} / Å ³	3307(9)	2841(1)	2587(5)
Z	2	2	2
C····C / Å	3.735(7)	3.513(1)	1.486(2)

Table S4.Crystallographic data for **DMOF3**.

* Where possible, intensity data were recorded at 100 K in order to obtain the best possible crystallographic model. Owing to space limitations, the UV source was mounted directly beneath the crystal. It was not possible to irradiate the crystal at cryogenic temperatures because of the possibility of cracking the lens of the UV source.

Unfortunately, no TGA could be carried out for **DMOF3** owing to an insufficient amount of sample (crystals are very difficult to grow). The apohost form (**DMOF3'**) was generated by immersion of the solvate in a solution of scCO₂ for 12 h. Although the crystals exhibited some visible deterioration and striation as a result of scCO₂ activation, the framework is sufficiently robust for activation to proceed as a SC-SC transformation. The activated structure **DMOF3'** exhibits a dramatic change in unit cell parameters (Table S4), the reason for which becomes apparent upon examination of the half-paddlewheel SBU. Fig.S24a shows a dramatic change in the orientation of the oba and pyridyl ligands of **DMOF3'** as compared to **DMOF3**. The distance seperating the central oxygen atoms of adjacent oba ligands increases to 6.00 Å upon activation. Extension of the aperture of each net of **DMOF3'** (cf Fig. S23b).

SQUEEZE analysis of **DMOF3'** indicates that only 46 residual electrons are present in the formula unit. We attribute this to the presence of one diffuse CO_2 molecule per ASU. Interestingly the carbon…carbon distance associated with ring closure contracts to 3.513(1) Å.

Figure S24. a) Half paddlewheel moiety of **DMOF3'**. b) A single net showing extended framework structure.

A UV-visible spectrum was recorded for the apohost **DMOF3'**. The same sample was then irradiated (365 nm) *ex situ* for one minute and the UV-visible spectrum rerecorded. Fig. S25 shows that the original form contains two bands, one at 360 and one at 465 nm. The UV-irradiated sample shows a broad band, which is attributed to the blue colour observed. Similar to the previous examples, exposure of **DMOF3'** crystals to UV light induced a colour change (Fig. S26) from bright orange to blue. This process is reversible – however, the change from blue back to the original colour appears to be slower than it is for **DMOF1**. It is important to note that activation causes deterioration crystal.

Figure S25. Solid-state UV-visible spectra of **DMOF3'** before (green) and after (blue) *ex situ* exposure to UV light.

Figure S26. Photomicrographs showing a crystal of **DMOF3'** undergoing a reversible colour change when exposed to UV and then green light.

In order to determine the extent of photoconversion in the solid state, a SC-SC transformation experiment was carried out. A crystal of **DMOF3'** was glued to the tip of a glass fibre and irradiated for one hour using 365 nm ultraviolet light. Diffraction data were then recorded for this crystal under *in situ* UV irradiation at room temperature.

iDMOF3' (Fig. S27a) has the same space group as **DMOF3'** but exhibits a further reduction in cell parameters and, most importantly, ring-closure. Fig. S27b shows the change in the orientation of the half-paddlewheel, with the distance separating the oxygen atoms of adjacent oba ligands increasing to 6.42 Å.

Not surprisingly, a reduction in unit cell parameters leads to a further reduction in solvent accessible space. The distance between the two carbon atoms involved in ring closure becomes 1.486(2), a typical value for a C–C single bond.

Figure S27. a) A simplified rendition of the SBU of **iDMOF3'** showing relative positions of the shifted ligands. **b)** A single net of **iDMOF3'** showing the extended structure with further slanted and decreased pore size relative to of **DMOF3'**.

It is interesting to map the progression of guest-accessible space as **DMOF3** is activated to give **DMOF3'**, which is in turn irradiated to give **iDMOF3'** (see Table S5). The program Mercury was used to determine the 'virtual' guest-accessible volume for each structure (guest atomic coordinates were deleted for **DMOF3**). Calculations were carried out using a grid spacing of 0.2 Å and probe radii ranging from 1.2 to 1.6 Å. We have already discussed some of the issues that should be considered when determining void volumes (section 1.5 above). We are aware that the volume reported by Mercury for an idealised spherical void would be insensitive to the probe radius (assuming a probe that is smaller than the void).

However, the calculation of void volume becomes more susceptible to the probe radius as the shape of the void becomes more irregular and the numbers that we generate therefore need to be taken at face-value. Table S5 shows that, for the commonly used probe radii the general trend is that **DMOF3** undergoes a substantial decrease in guest-accessible volume upon activation, followed by another substantial decrease after ring-closure of L2. It is also interesting that slight positional disorder of one ethyl moiety has a marked effect on the calculated values of the guest-accessible volumes of **DMOF3**'.

Structure	Probe radius (Å)	Guest-accessible volume	Percentage free volume
		per unit cell (ų)	
	1.2	1066	32.2
	1.3	1020	30.8
DMOF3	1.4	977	29.5
	1.5	880	26.6
	1.6	843	25.5
	1.2	631	22.2
	1.3	573	20.2
DMOF3'a	1.4	509	17.9
	1.5	423	14.9
	1.6	352	12.4
	1.2	490	17.3
	1.3	414	14.6
DMOF3'b	1.4	346	12.2
	1.5	262	9.2
	1.6	179	6.3
	1.2	142	5.5
	1.3	87	3.3
iDMOF3'	1.4	45	1.7
	1.5	40	1.6
	1.6	35	1.4
1	1	1	

Table S5. Guest-accessible volumes for the three forms of DMOF3, calculated using Mercury.

^a minor component of ethyl disorder removed

^b major component of ethyl disorder removed

To understand the effect that photocyclisation has on the overall structure we need carefully compare the crystal structures of **DMOF3'** (pre-irradiation) and **iDMOF3'** (post-irradiation). We begin by creating a "dummy atom" at the centroid of the two metal ions in the ASU to represent a metal cluster node (each node is 6-connected in the framework structure).

These nodes are then connected to one another by linkages that represent two L2 ligands and 4 oba ligands. These interconnections form a conceptually infinite arrangement of corner-, edge- and face-sharing parallelepipeds reminiscent of the propagation of triclinic unit cells. We can therefore describe and compare the interconnection geometries of **DMOF3'** and **iDMOF3'** using the six parameters (a', b', c', a', β' and γ') that define the parallelepiped in each case (Fig S28 and Table S6). For each structure, note that the framework parallelepiped (framework cell) and crystallographic unit cell are not superimposable – however, they are related by a matrix transformation and have the same volumes. Fig. 28 shows an overlay of the framework cells of **DMOF3'** and **iDMOF3'** with a common origin and oriented such that the coordinating nitrogen atoms of L2 are located as close to one another as possible. We note that the node-node link across L1 remains almost the same length (c' changes from 21.35 to 21.33 Å upon UV irradiation). The corresponding oba node-node linkages change from 13.64 to 14.20 and 14.65 to 13.25 Å. The volume of the framework cell reduces from 2840 to 2587 Å³ upon UV irradiation.

Figure S28. Overlay of the asymmetric units and framework cells of **DMOF3'** (orange) and **iDMOF3'** (blue). The newly formed C-C bond of **iDMOF3'** is shown as a green cylinder.

	DMOF3'	iDMOF3′
<i>a'</i> / Å	13.64(5)	14.20(1)
<i>b' /</i> Å	14.65(3)	13.25(8)
<i>c'</i> / Å	21.35(9)	21.33(0)
α'/°	107.9	93.3
β'/°	105.3	115.7
γ′/°	123.5	127.1

Table S6.Comparison of the framework cells of **DMOF3'** and **iDMOF3'**.

1.9.6 X-ray powder diffraction analysis of DMOF3

The structural changes experienced by **DMOF3**, first upon activation and then upon irradiation, impart a considerable amount of strain on the crystals. Therefore, it was not possible to record single-crystal diffraction data for **iDMOF3'** during green light irradiation. We instead present experimental and simulated PXRD diffractograms (Fig. S29) for all three forms of **DMOF3**. We also include an experimental powder pattern for **iDMOF3'** after three days of exposure to green light. It appears that **iDMOF3'** undergoes ring opening and begins to revert to the apohost form **DMOF3'**. The cycloreversion process appears to be slow and the diffractogram is consistent with a mixture of predominately ring-open material with a small amount of ring-closed material present. Pawley refinement (see below) was attempted with a view to determining the relative amount of each form but this was unsuccessful due to poor resolution. Ten consecutive diffractograms were recorded for each of **DMOF3'** and **iDMOF3'** (Figs S30 and 31), thereby establishing that these materials do not appear to be susceptible to prolonged exposure to X-rays.

Figure S29. Simulated and experimental PXRD diffractograms of the various forms of DMOF3.

Figure S30. Ten consecutive PXRD patterns of the apohost **DMOF3'** with no visible effect as a result of diffraction X-rays.

Figure S31. Ten consecutive PXRD patterns of the ring-closed **iDMOF3'** with no visible effect as a result of diffraction X-rays.

1.9.7 Pawley refinements for DMOF3' and iDMOF3'

The PXRD pattern of **iDMOF3'** exposed to green laser light for three days indicated that the sample had not converted completely to the activated form **DMOF3'**. In an attempt to establish the extent to which cycloreversion had occurred, and how much **iDMOF3'** relative to **DMOF3'** was present, a Pawley refinement was carried out. The experimental X-ray powder patterns were refined using the Pawley method in the program TOPAS²⁵. Since the quality of the experimental XRPD patterns was poor, we could only obtain the lattice parameters in each case. These are similar to those obtained from SCD analysis (*min* and *max* constraints were used in TOPAS, Tables S7 and S8) and the resulting difference plots are given in Figs S32 and S33.

Parameters from SCXRD	Parameters from Pawley
Space group= <i>P</i> -1	Space group = $P-1$
Temperature = 298K	Temperature = 298K
<i>a</i> = 12.259(8) Å	<i>a</i> = 13.35 Å
<i>b</i> = 13.257(5) Å	<i>b</i> = 13.68 Å
<i>c</i> = 17.619(9) Å	<i>c</i> = 16.36 Å
$\alpha = 78.59(8)^{\circ}$	$\alpha = 76.77^{\circ}$
$\beta = 89.23(3)^{\circ}$	$\beta = 88.53^{\circ}$
$\gamma = 67.49(9)^{\circ}$	$\gamma = 68.99^{\circ}$
$V = 2587.48 \text{ Å}^3$	$V = 2712.55 \text{ Å}^3$
D_{1} , 2.77 D_{2} , 4.57 D_{2} , 2.52 COE, 1.21	

Table S7.Comparison of the SCD and PXRD data of iDMOF3'

 $R_{exp}: 3.77, Rwp: 4.57, Rp: 3.52, GOF: 1.21$

Parameters from SCXRD	Parameters from Pawley
Space group= <i>P</i> -1	Space group = $P-1$
Temperature = 100K	Temperature = 298K
<i>a</i> = 13.426(2) Å	<i>a</i> = 14.08 Å
<i>b</i> = 13.644(6) Å	<i>b</i> = 14.32 Å
<i>c</i> = 17.045(8)	<i>c</i> = 16.26 Å
$\alpha = 90.20(2)^{\circ}$	$\alpha = 90.72^{\circ}$
$\beta = 91.83(1)^{\circ}$	$\beta = 91.48^{\circ}$
$\gamma = 114.46(5)^{\circ}$	$\gamma = 114.55^{\circ}$
$V = 2840.40 \text{ Å}^3$	$V = 2977.82 \text{ Å}^3$

 $R_{exp}: 4.82, Rwp: 6.87, Rp: 5.42, GOF: 1.43$

Figure S32. Experimental (blue) and Pawley refined (red) powder diffractograms for iDMOF3'.

Figure S33. Experimental (blue) and Pawley refined (red) powder diffractograms for **iDMOF3'** after exposure to green laser light for three days.

1.9.8 Sorption data for DMOF3' and iDMOF3'

As with **DMOF'**, we carried out sorption experiments on both **DMOF3'** and **iDMOF3'** in order to determine whether the light induced changes observed crystallographically could in fact affect the sorption capabilities of the material thus confirming this a molecular switch. **DMOF3'** shows conventional Type I sorption behaviour with no hysteresis, absorbing approximately four molecules of CO_2 (15 wt %) per formula unit (Fig. S34) at 20 bar and 298 K. Once again the shape of the sorption isotherm implies that full occupancy is not reached and that **DMOF3'** could potentially accommodate even more guest molecules at pressures exceeding 20 bar. The isotherm recorded for the UV irradiated (*ex situ*) form **iDMOF3'** also shows the uptake reduced by half (approximately two molecules of CO_2 (7.4 wt %) are absorbed per formula unit at 20 bar). Since the structure of **iDMOF3'** shows negligible solvent accessible space it is postulated that the material has not undergone complete ring-closure due to the need for *ex situ* irradiation.

Figure S34. CO₂ sorption (solid lines) and desorption (dashed lines) isotherms at 298 K for the **DMOF3'** (green) and **iDMOF3'** (blue). Solid lines represent sorption while dashed lines represent desorption.

1.9.9 Summary of results

Table S9	Summary	of	photoactivity	of DN	AOF-I	OMOF3
	,					

Sample	Photoactivity	Structural change
DMOF	Not in bulk	No
DMOF1	Not in bulk	No
DMOF2	Inconclusive	Inconclusive
DMOF3	Yes	Yes

1.9.10 Description of Supplementary Videos

Supplementary Video 1: An orange crystal of **DMOF3'** is exposed to 365 nm UV irradiation. The crystal changes colour to blue and appears to contract. The crystal is then irradiated with 532 nm green light and reverts to its original orange colour. The irradiation sequence is then repeated.

Supplementary Video 2: Animation showing an overlay of ligand L2 from the crystal structures of **DMOF3'** (orange) and **iDMOF3'** (blue). Note that there is little difference in the cross-ligand N····N distances. Both ligands occupy a similar amount of space – note that, UV irradiation causes the central part of the ligand to flatten due to ring closure. However, in terms of the overall bulk of the ligand, the ethyl groups of **iDMOF3'** twist outwards such that they occupy approximately the same relative space as in **DMOF3'**.

Supplementary Video 3: Animation showing ligand L2 from the crystal structures of **DMOF3'** (top) and **iDMOF3'** (bottom). The yellow vectors extend along coordinating axes of the pyridyl groups. Note that these vectors are offset relative to one another (by approximately 3 Å) in **DMOF3'** while they almost cross one another in **iDMOF3'**. This conformational change in L2 has the effect of requiring the framework structure to distort its framework cell – this transformation is most likely facilitated by the relatively flexible oba co-ligands.

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