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Unidirectional rotary motion in a metal–organic framework

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Overcrowded alkene-based light-driven molecular motors are able to perform large-amplitude repetitive unidirectional rotations. Their behaviour is well understood in solution. However, Brownian motion precludes the precise positioning at the nanoscale needed to harness cooperative action. Here, we demonstrate molecular motors organized in crystalline metal–organic frameworks (MOFs). The motor unit becomes a part of the organic linker (or strut), and its spatial arrangement is elucidated through powder and single-crystal X-ray analyses and polarized optical and Raman microscopies. We confirm that the light-driven unidirectional rotation of the motor units is retained in the MOF framework and that the motors can operate in the solid state with similar rotary speed (rate of thermal helix inversion) to that in solution. These ‘moto-MOFs’ could in the future be used to control dynamic function in crystalline materials.

Drawing inspiration from nature, the field of synthetic molecular machines has matured to the point that control of molecular motion can be successfully achieved in different molecular systems using external stimuli^{1–5}. However, virtually all biological counterparts exhibit collective and cooperative behaviour that requires well-defined organization along multiple length scales^{6–8}. To fully exploit the potential of artificial molecular machines and to harness their collective motion it is crucial to incorporate them into nanostructured macroscopic materials allowing for precise spatial arrangement^{9–12}.

The chiral overcrowded alkene-based rotary molecular motors are unique in the sense that these molecules use light, heat and stereochemical control to achieve unidirectional rotation^{13,14}. The full 360° rotary cycle comprises two reversible photochemical *E/Z* isomerization steps, each followed by an irreversible thermally driven helix inversion in which the photogenerated metastable isomer converts to the stable isomer (Fig. 1b), releasing steric strain. The overall unidirectionality of the rotary cycle is governed by the higher energy of the metastable isomer compared to the stable isomer, which renders the thermal helix inversion step energetically downhill. Previously, incorporation of these molecular motors into liquid crystals^{15–19}, polymer gels^{20,21} and muscle-like fibres²², as well as attachment to surfaces^{23,24} and two-dimensional (2D) organization in the pores of tris(*o*-phenylene)cyclotriphosphazene (TPP)²⁵ has enabled, to some extent, cooperative action and macroscopic function. Nevertheless, to attain a perfect ordering in 3D in a solid-state material without impeding the motor function remains a fundamental challenge^{9,26}.

Metal–organic frameworks (MOFs) are ideal platforms for spatially organizing molecular motors in a precise and predictable manner^{9,10,26–28}. They are porous 3D materials consisting of inorganic nodes (metal ions or clusters) bridged by organic linkers. Due to their inherent porosity, MOFs typically possess a large free volume, which is essential for their dynamic behaviour in solid material^{29,30}. Recent studies have shown that linker rotors can undergo small-amplitude non-directional rotations when

embedded in a MOF framework^{31–35}, while [2]rotaxane struts were shown to exhibit a large-amplitude pirouetting and shuttling motion when embedded in a MOF^{36–39}. Furthermore, electrochemical switching and large-amplitude rotational motion of a redox-active bistable catenane, introduced into the MOF framework by solvent-assisted linker incorporation (SALI), was retained⁴⁰. Nevertheless, in efforts to achieve efficient collective and cooperative behaviour and create machine-like function in the nanostructured condensed phase, it remains challenging to avoid a decrease in the rate of molecular motion and to achieve motion with directional bias.

Here we report the 3D organization of light-driven rotary molecular motors in the solid state using a MOF as a platform for achieving well-defined spatial organization. The desired motorized MOF (here denoted ‘moto-MOFs’—containing motor 1 or 2-*E/Z* as pillars, Fig. 1b) materials were prepared using a post-synthetic method, and possess sufficient free volume (larger than the volume that the molecular motor occupies) to ensure uncompromised large-amplitude unidirectional rotary motion of the linker-based motor in the solid state.

MOFs synthesis and characterization

Taking into consideration the free volume required for proper motor function in the crystalline MOF, the material of choice was a zinc pillared-paddlewheel BrYO-MOF⁴¹. This type of MOF consists of layers formed by zinc paddlewheel nodes, which are bridged by tetracarboxylic acid linkers. The layers are connected in the third dimension by 4,4′-bipyridine-derived pillars, and the distance between the nodes is approximately 10 Å (in the [100] direction) and 16 Å (in the [010] direction). It was envisioned that incorporation of the dipyriddy-functionalized motor 1 (the rotor moiety is 8 Å in length; Fig. 1a) within this framework should provide enough free space for unhindered rotation of the motor unit (for free volume analysis see Supplementary Section 4). Because the overcrowded olefinic bond of 1 might react under the relatively harsh conditions required for MOF synthesis⁴², we opted for a post-synthetic fabrication method, that is, a solvent-assisted linker exchange (SALE)⁴³. In

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Fig. 1 | Design of the moto-MOF. **a**, Schematic representation of the 3D organization of molecular motor **1** in the moto-MOF, showing packing in the crystal, the elementary cell and the structure of the linkers, tetracarboxylic acid (TCPB) and molecular motor (**1**), used to construct the framework. In the designed framework, the stator of the motor (that is, the fluorene unit) is used to bridge the 2D layers constructed from Zn paddlewheel clusters and TCPB, while the rotor moiety (the naphthyl unit) can rotate freely with respect to the other half. **b**, Structures of motors **1** and **2**, and light-powered 360° unidirectional rotary cycle of the bipyridine motor.

this process, dipyrindyl-naphthalenediimide (DPNI) pillars can be readily replaced with a broad range of bipyridines, allowing the fabrication of new MOF materials under much milder conditions than used in de novo synthesis (Fig. 2)^{43–45}.

A parent MOF constructed from 1,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene (TCPB) and DPNI was thus employed⁴¹. The dipyrindyl molecular motor strut **1** was synthesized from the appropriate thioketone and 2,7-dibromo-9-diazafluorene using a Barton–Kellogg reaction, followed by introduction of the pyridyl functionalities via a Suzuki cross-coupling step (see Methods for synthetic details). Subsequently, SALE was carried out by immersing the colourless crystals of this parent MOF (Fig. 3a) in a *N,N*-dimethylformamide (DMF) solution containing **1** at 60°C for 24 h, which afforded yellow crystals of moto-MOF1 (Fig. 3b). Moto-MOF2-*E* and moto-MOF2-*Z* were synthesized in a similar way, but the exchange was carried out over four days and the solution was replaced with a fresh batch every 24 h to achieve full exchange (see Methods for details and Supplementary Fig. 8). Characterization by ¹H NMR spectroscopy of digested (using D₂SO₄) crystals of moto-MOFs in *d*₆-dimethylsulfoxide (DMSO) showed the expected 1:1 ratio of TCPB and respective motor, supporting a successful exchange (Supplementary Figs. 82–85). In the Raman spectra of moto-MOFs, bands typical of both overcrowded olefins and TCPB are observed while bands characteristic of DPNI were not observed (Fig. 3c and Supplementary Figs. 10 and 12). The anticipated composition of moto-MOF1 was further confirmed by elemental analysis and inductively coupled plasma atomic-emission spectroscopy (ICP-AES), with the analysis results corresponding well to the anticipated 1:1:2 ratio of **1**:TCPB:Zn (see Methods for details). Powder X-ray diffraction (PXRD) data, acquired under solvent-saturated conditions, showed that the crystallinity of the material was preserved in all cases throughout the SALE process (Fig. 3d and Supplementary Figs. 1 and 3). The PXRD pattern of the

Fig. 2 | Schematic representation of the synthesis of the moto-MOFs.

Crystals of the parent framework were immersed in a solution of **1** for 24 h during which bipyridine motor **1**, **2-E** or **2-Z** (yellow) replaced the parent DPNI (green) pillars in the structure.

Fig. 3 | Structure of moto-MOF1 material. **a,b**, Optical micrographs of crystals of a parent MOF (**a**) (scale bar, $300\text{ }\mu\text{m}$) and a moto-MOF1 (**b**) (scale bar, $300\text{ }\mu\text{m}$). **c**, The Raman spectrum (785 nm , 50 mW) of a parent MOF (**c**) (black line) shows bands characteristic of both DPNI and TCPB (DPNI $1,726\text{ cm}^{-1}$ $\nu_{\text{C}=\text{O}}$ and TCPB $1,610\text{ cm}^{-1}$ $\nu_{\text{C}=\text{C}}$ of aromatic rings). In the spectrum of moto-MOF1 (red line), bands characteristic of DPNI are absent and bands consistent with **1** (blue line) are present ($\nu_{\text{C}=\text{C}}$ of the central double bond $1,562\text{ cm}^{-1}$). **d**, PXRD pattern of the parent MOF (black line) and moto-MOF1 (red line). Inset, Position of the first peak corresponding to reflection from the (001) plane.

moto-MOFs is similar to the pattern observed for the parent material in terms of peak positions, but with slight differences in terms of the relative peak intensities, assigned to the differences in electron density in the crystal structure originating from the substitution of the DPNI pillar in the framework. Nevertheless, the position of the first peak at $2\theta = 4.00^\circ$, which corresponds to the reflection from the (001) plane, remains unchanged (Fig. 3d, inset). This observation is consistent with the fact that the DPNI linker and bipyridyl-functionalized molecular motor **1** have similar N–N distances (see Supplementary Fig. 2 for a comparison of N–N distances in the DFT-optimized structures of DPNI and **1**). The single-crystal XRD data of moto-MOF1 could only be partially resolved. From the solution of the diffraction data and initial refinement, the position of the Zn cations and the TCPB fragment were located, but for the molecular motor moieties (apart from the pyridyl nitrogen atoms) this was not possible due to a degree of disorder (Supplementary Figs. 3–6). It can be calculated on the basis of the elementary cell dimensions (a , $16.202\text{ }\text{\AA}$; b , $10.742\text{ }\text{\AA}$; c , $22.258\text{ }\text{\AA}$) that one cubic centimetre of moto-MOF1 contains approximately 3×10^{20} motor units, illustrating that densely functionalized responsive materials can be created in this way. Furthermore, polarized optical microscopy showed that moto-MOF1 crystals are birefringent, indicating that the motor units are predominantly orientated in the same direction in the crystal (Supplementary Fig. 9). In addition, the polarized Raman spectra of the moto-MOF1 crystals showed significant variation of the polarizability of the bands characteristic of

the C=C stretching with respect to the polarization axis of the laser on rotation of the crystal over 180° (in 15° steps). It was found that the band ascribed to the stretching of the overcrowded double bond of **1** exhibits one maximum. A similar trend was observed in the band due to the stretching of the double bonds in the aromatic rings of both TCPB and **1** (Supplementary Fig. 11). Accordingly, the disorder in the crystal most probably arises from the different orientations of the rotor units in **1** along the [001] direction.

Photochemical and thermal isomerization in solution

The rotary behaviour of the molecular motor **1** was characterized in solution by UV–vis absorption and NMR spectroscopies. On irradiation of **1** at 395 nm at -30°C in CDCl_3 , a new set of ^1H NMR resonances appeared that are indicative of the formation of the metastable isomer, and a photostationary state ratio of 83:17 (metastable:stable) was established (Fig. 4a). Warming the sample to room temperature resulted in full conversion of the metastable isomer to the stable one (Supplementary Figs. 20 and 21). In the UV–vis absorption spectrum, a gradual bathochromic shift of the main absorption band occurred with an isosbestic point maintained at 420 nm on irradiation at 395 nm , consistent with the formation of the metastable isomer (Fig. 4b). The rate of the thermal helix inversion was determined by following the exponential decrease of the main absorption band of the metastable isomer in the temperature range 7 – 16°C in CHCl_3 , in DMF and in heptane. Eyring analysis showed that the Gibbs energy of the activation for the

Fig. 4 | Photochemical and thermal isomerization of 1 in solution. **a**, Selected region of the ^1H NMR spectra (400 MHz, -30°C , CDCl_3) of stable **1** (black line) and metastable **1** (red line), with a photostationary state ratio of 83:17 metastable:stable. **b**, UV-vis absorption spectrum of **1** before (black solid line) and after irradiation to the photostationary state (red solid line, **1-PSS**) at 395 nm (7°C , CHCl_3) and after subsequent thermal helix inversion (red dashed line, **1-THI**). An isosbestic point is maintained at 420 nm. **c**, Selected region of the Raman spectrum (785 nm, 50 mW, 3×10^{-3} M in CHCl_3) of stable **1** (black solid line). After irradiation at 395 nm at -30°C a new broad band centred at $1,550\text{ cm}^{-1}$ is present corresponding to the metastable isomer (red solid line, **1-PSS**), and after thermal helix inversion the initial spectrum was recovered (red dashed line, **1-THI**).

Table 1 | Characteristics of rotary motor 1 in solution, in moto-MOF1, in moto-MOF2-Z and calculated values

	$\Delta^\ddagger G(20^\circ\text{C})$ (kJ mol^{-1})	$t_{1/2}$ (min)
Heptane	89.5 ± 0.2^a	17
Chloroform	89.1 ± 0.7^a , (88.9 ± 0.3^c)	15
DMF	87.7 ± 0.6^a	8.0
DMF 1H $_2^{2+}$	87.7 ± 0.1^a	8.0
Calculated	90.3^b	23
Moto-MOF1	88.6 ± 0.7^c	12
Moto-MOF2-Z	88.9 ± 1.3	13

^aDetermined by UV-vis spectroscopy based on Eyring analysis. ^bDFT B3LYP/6-31G(d,p). ^cDerived from the rate constant determined by Raman spectroscopy at room temperature.

thermal helix inversion was similar in all examined solvents (Table 1, Supplementary Table 2 and Supplementary Figs. 15–17). The experimental values matched closely to the barrier for thermal helix inversion calculated by DFT methods at the B3LYP/6-31G(d,p) level of theory, confirming the unidirectional rotation of molecular motor **1** ($\Delta^\ddagger G_{\text{calc}}(20^\circ\text{C}) = 90.3\text{ kJ mol}^{-1}$, Table 1; see Supplementary Section 13 for computational details).

Additional studies were performed on bis-protonated **1**. UV-vis absorption and ^1H NMR spectroscopies confirmed that protonation of **1** did not significantly affect the photochemical isomerization behaviour or the barrier for thermal helix inversion (photostationary state ratio 68:32 metastable:stable, $\Delta^\ddagger G_{\text{DMF}}(20^\circ\text{C}) = 87.7\text{ kJ mol}^{-1}$) (Supplementary Figs. 13, 14 and 18). Hence, binding of **1** to Zn(II) in moto-MOF is unlikely to have a significant effect on the rotary behaviour of the motor. Similarly, the spectroscopic properties of desymmetrized model compound **2** (Fig. 1b; see Supplementary Section 2 for the detailed synthesis and Supplementary Figs. 24–28), for which all stereoisomers were identified with ^1H NMR, exclude possible thermal *E/Z* isomerization pathways and confirm that these pyridyl-functionalized compounds behave as unidirectional rotary molecular motors.

The Raman spectrum of stable **1** in CHCl_3 showed a sharp band centred at $1,562\text{ cm}^{-1}$, which is characteristic⁴⁶ of stretching of the overcrowded olefinic bond. On irradiation at 395 nm, an additional band appeared at $1,550\text{ cm}^{-1}$ that is characteristic⁴⁶ of the stretching of the central double bond of the metastable isomer (Fig. 4c). The gradual decrease of this band corresponds to the thermal helix inversion and was followed over time. The rate constant ($k = 8.8 \times 10^{-4}\text{ s}^{-1}$) at room temperature was used to calculate the activation barrier $\Delta^\ddagger G(20^\circ\text{C}) = 88.9\text{ kJ mol}^{-1}$ (Table 1 and Supplementary Fig. 19). The value obtained by Raman spectroscopic analysis is in good agreement with the barrier determined by UV-vis absorption spectroscopy ($\Delta^\ddagger G_{\text{CHCl}_3}(20^\circ\text{C}) = 89.1\text{ kJ mol}^{-1}$). Additionally, the unidirectional rotary motion of the desymmetrized analogue **2** was followed by Raman spectroscopy in CHCl_3 . The respective *2-E/Z* isomers were identified quantitatively from the intensity of bands in the $1,290\text{ cm}^{-1}$ region (Supplementary Figs. 29–36).

Photochemical and thermal isomerization in the solid state

The rotary behaviour of molecular motor **1** in the confined environment of the moto-MOF (Fig. 5a) was studied with Raman spectroscopy. This technique is particularly convenient, as it allows for the in situ monitoring of structural changes in the individual molecular components in the framework (that is, the molecular motor, TCPB). It is known for this particular family of MOFs that solvent removal leads to collapse of the porous structure^{41,47}, so experiments were performed on moto-MOF crystals immersed in DMF. Photoswitchable MOFs, for example bearing azobenzene^{48,49} or diarylethylene^{50,51} struts, have recently been studied and proven to be stable following exposure to

Fig. 5 | Photochemical and thermal isomerization studies of 1 in moto-MOF1. a, Schematic representation of structural changes during the photochemical and subsequent thermal isomerization (half of the rotary cycle) of 1 incorporated in moto-MOF1. **b**, Changes in the Raman spectrum of moto-MOF1 (black solid line, initial) following irradiation at 395 nm (red solid line) and upon subsequent thermal isomerization (red dashed line) at 20 °C. Inset, Multiple irradiation/thermal helix inversion cycles (all Raman spectra were recorded at 785 nm with power density sufficient to avoid sample heating; Supplementary Figs. 37–43).

UV light⁵². Nevertheless, the stability of the framework following irradiation at 395 nm was verified with PXRD, which showed no changes even over 5 h (Supplementary Fig. 1). Also, no leakage of the linkers to the solution took place, as Raman spectra for the solvent only showed bands corresponding to DMF, while the spectra of the single-crystal moto-MOF1 showed bands corresponding to the components of the framework. During irradiation of a crystal at 395 nm at room temperature, a gradual decrease in the area of the band at 1,562 cm⁻¹ was observed, accompanied by a gradual increase in the broad band centred at 1,550 cm⁻¹ (Fig. 5b). These spectral changes correspond well to those observed in solution and can therefore be ascribed to the same isomerization process. Furthermore, irradiation of moto-MOF1 crystals at low temperature (−5 °C) showed that, depending on the crystal thickness, the metastable to stable isomers ratio in moto-MOF1 can be as high as in solution (Supplementary Figs. 44–48). Hence, the molecular motors can still undergo their usual photoisomerization when embedded in the MOF.

When irradiation was discontinued and the sample was kept in the dark, the band characteristic of the metastable isomer disappeared and the original spectrum was recovered, indicating that thermal relaxation to the stable isomer had taken place (Fig. 5b). These irradiation and thermal relaxation steps could be repeated multiple times without any noticeable signs of fatigue (Fig. 5b, inset). Additionally, for moto-MOF2-E/Z the changes in intensity around 1,290 cm⁻¹ upon prolonged irradiation were followed by Raman microscopy. The spectral features in this area are characteristic of the 2-E and 2-Z isomers. The same Raman spectrum was obtained following prolonged irradiation at 395 nm (1 h) of either moto-MOF2-E or moto-MOF2-Z corresponding to a 1:1 ratio of 2-E/Z pillars, thereby indicating the unidirectional motion of the molecular motor (Supplementary Fig. 49). Furthermore ¹H NMR spectroscopy of digested crystals of both moto-MOF2-Z and moto-MOF2-E revealed that the irradiation and subsequent heating to induce thermal helix inversion results in conversion of the respective pillars into the opposite geometrical isomer (2-E and 2-Z, respectively), further corroborating unidirectional rotation of the molecular motor (Supplementary Figs. 50 and 51). As in solution, the thermal isomerization of the metastable isomer in both moto-MOF1 and moto-MOF2-Z was followed in time by monitoring the

decrease of the band area at 1,550 cm⁻¹ (Supplementary Sections 10 and 11). The barrier ($\Delta^{\ddagger}G$) of thermal helix inversion at room temperature in the moto-MOFs was 88.6 ± 0.7 kJ mol⁻¹ for moto-MOF1 and 88.9 ± 1.3 kJ mol⁻¹ for moto-MOF2-Z (Supplementary Figs. 42, 43, 47 and 48 and Supplementary Tables 3 and 4; for discussion about the possible effects of the MOF confined solvents see Supplementary Information page 39)⁵³. These values are in excellent agreement with the barrier determined in solution (Table 1), and the good agreement between the barriers for thermal helix inversion of 1 and 2-E in moto-MOF excludes a thermal E/Z isomerization pathway, confirming that the unidirectional rotation of the molecular motor is not compromised by confinement in moto-MOF.

Conclusions

In summary, we have devised a simple strategy, using SALE, to achieve spatial 3D organization of light-driven molecular motors using a MOF platform. By using Raman spectroscopy, the photochemically and thermally driven rotary motion in solution could be compared to that in the crystalline solid. It is shown that the motor units in the struts are able to perform unhindered 360° unidirectional rotations owing to a design that allows for sufficient free volume, provided by the chosen framework. These findings are remarkable, as it was shown previously that the incorporation of rotaxanes in MOFs influences their dynamics^{39,42}. The successful preparation of a fully operational motorized MOF will allow, in the future, exploration of the collective behaviour of 3D-organized rotary molecular motors and tailoring of crystalline materials for a specific light-responsive function, for example, control of the diffusion of gases, directional light-powered mass transport or miniature light-powered pumps in microfluidic devices.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, statements of data availability and associated accession codes are available at <https://doi.org/10.1038/s41565-019-0401-6>.

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Author contributions

W.D., S.J.W. and B.L.F. conceived the project. W.D. and D.R. synthesized compounds and W.D. carried out studies in solution. W.D., S.A. and W.R.B. performed Raman micro-spectroscopy studies of the solid material. W.D. and T.v.L. performed DFT studies. S.J.W., W.R.B. and B.L.F. guided the project. W.D., T.v.L., S.J.W. and B.L.F. wrote the manuscript. All authors discussed the results and commented on the manuscript.

Competing interests

The authors declare no competing interests.

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Methods

Synthesis of 2,7-dibromo-9-(2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene (5). A two-neck flask was charged with 2,7-dibromo-9-diazo-9H-fluorene (**3**) (690 mg, 1.97 mmol) and a solution of thioketone **4** (1.3 equiv., 550 mg, 2.59 mmol) in dry THF (20 ml) was added. The reaction mixture was stirred at room temperature for 16 h. Subsequently, tris(dimethylamino)phosphine (1.29 g, 7.90 mmol, 1.4 ml) was added and the resulting mixture was stirred at room temperature for 16 h and purified by column chromatography (SiO₂, pentane/CH₂Cl₂) to afford **5** as a yellow solid (720 mg, 1.43 mmol, 73%). ¹H NMR (CDCl₃, 400 MHz): δ 8.08 (d, *J* = 1.6 Hz, 1H), 7.98 (dd, *J* = 8.3 Hz, 2.0 Hz, 2H), 7.70–7.45 (m, 6H), 7.47–7.34 (m, 1H), 7.33 (dd, *J* = 8.1 Hz, 1.8 Hz, 1H), 6.75 (d, *J* = 1.7 Hz, 1H), 4.30 (p, *J* = 6.6 Hz, 1H), 3.59 (dd, *J* = 15.2 Hz, 5.6 Hz, 1H), 2.82 (d, *J* = 15.2 Hz, 1H), 1.41 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 154.2, 148.1, 141.1, 138.3, 137.6, 137.0, 135.2, 132.5, 131.8, 129.5, 129.4, 129.3, 128.9, 128.8, 127.8, 127.0, 126.9, 126.8, 125.5, 123.8, 120.9, 120.7, 119.9, 119.9, 45.1, 41.8, 19.2; HRMS (ESI) calcd C₂₇H₁₉Br₂ [M+H]⁺ 502.9827, found 502.9830.

Synthesis of 4,4'-(9-(2-methyl-2,3-dihydro-1H-cyclopenta[a]naphthalen-1-ylidene)-9H-fluorene-2,7-diyl)dipyridine (1). A two-neck round-bottomed flask equipped with a reflux condenser was charged with **5** (400 mg 0.80 mmol), 4-pyridinylboronic acid (2.2 equiv., 216 mg, 1.76 mmol) and Pd(PPh₃)₄ (0.05 equiv., 46 mg, 0.04 mmol). A degassed aqueous solution of K₂CO₃ (1 M, 7.9 ml) and THF (15 ml) were added and the resulting mixture was heated at reflux and stirred at this temperature for 16 h. Subsequently, the reaction mixture was cooled to room temperature, after which EtOAc (30 ml) was added and the aqueous phase extracted with EtOAc (2 × 10 ml). The combined organic layers were washed with brine (20 ml), dried over MgSO₄ and concentrated in vacuo, and the crude product was purified by column chromatography (SiO₂, pentane/EtOAc) to afford **1** as a yellow solid (0.60 mmol, 299 mg, 75%). ¹H NMR (CDCl₃, 400 MHz): δ 8.78–8.70 (m, 2H), 8.38–8.27 (m, 3H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.99 (t, *J* = 7.8 Hz, 2H), 7.87 (dd, *J* = 13.2 Hz, 8.2 Hz, 2H), 7.71 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.67–7.50 (m, 5H), 7.41 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.05 (d, *J* = 1.5 Hz, 1H), 6.66–6.60 (m, 2H), 4.45 (p, *J* = 6.6 Hz, 1H), 3.62 (dd, *J* = 15.3 Hz, 5.7 Hz, 1H), 2.86 (d, *J* = 15.3 Hz, 1H), 1.52 (d, *J* = 6.7 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 152.8, 150.2, 149.7, 148.8, 147.9, 147.9, 140.8, 139.9, 139.2, 137.9, 137.1, 135.6, 135.6, 132.6, 131.6, 129.7, 129.3, 129.0, 127.2, 127.0, 125.8, 125.4, 125.2, 124.4, 124.1, 122.6, 121.4, 120.8,

120.5, 119.7, 45.1, 41.8, 19.2. HRMS (ESI) calcd C₃₇H₂₇N₂ [M+H]⁺ 499.2169, found 499.2167.

Synthesis of moto-MOF via SALE. Crystals of parent BrYO-MOF⁴¹ (30 mg) were placed in a 2 ml screw-cap vial and a 1 ml solution of motor **1** (30 mg, 0.06 mmol) in DMF was added. Next, the vial was capped and placed in an oven at 60 °C for 24 h. For moto-MOF2-**Z** and moto-MOF2-**E** a similar procedure was used but the exchange was performed on 15 mg of parent BrYO-MOF with a solution of either **2-E** or **2-Z** (1 ml, 30 mg) for 96 h; the exchange solution was replaced with a fresh batch every 24 h. For moto-MOF2-**E** the exchange was carried out in a 1:1 (vol:vol) mixture of NMP/DMF due to the low solubility of **2-E** in pure DMF. Subsequently, the vial was removed from the oven and the supernatant solution was immediately replaced with 1 ml of fresh DMF. To remove the excess of **1**, the supernatant solution was replaced with fresh portions of DMF after 0.5, 1, 2, 6, 24 and 48 h. For elemental analysis, the MOF crystals were extensively washed with DCM and dried in vacuo. For NMR studies, the MOF crystals were extensively washed with DCM, dried in vacuo, and 0.5 ml of *d*₆-DMSO and two drops of D₂SO₄ were added. The sample was sonicated until complete dissolution of the MOF crystals was achieved (Supplementary Figs. 82–84). Elemental analysis moto-MOF1 calcd [C₇₁H₄₂O₈N₂Zn₃Br₃·3H₂O] %C 61.10; %H 3.47; %N 2.01; %Zn 9.37; found %C 60.87, %H 3.45, %N 2.06, %Zn 9.00.

Irradiation experiments. For solid-state Raman spectroscopy, samples of moto-MOF crystals were kept at room temperature, in a 1 mm capped quartz cuvette filled with DMF or between two quartz slides sealed with polytetrafluoroethylene paste to avoid drying. Raman spectra were acquired using a RamanStation400F (PerkinElmer) employing multimode fibres for both excitation and collection. The sample was placed on the Olympus BX51 microscope stage and a chosen single crystal of moto-MOF was aligned with the laser beam (785 nm, 50 mW) at ×50 lens magnification. Irradiations were carried with a 395 nm light-emitting diode (Thorlab M395F1) connected to a 0.6 mm optical fibre, which guided the light to the position of the laser beam.

Data availability

The data associated with the reported findings are available in the manuscript or the Supplementary Information. Other related data are available from the corresponding author upon request.