

Visible-Light-Driven Rotation of Molecular Motors in a Dual-Function Metal-Organic Framework Enabled by Energy Transfer.

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The visible-light driven rotation of an overcrowded-alkene based molecular motor strut in a dual-function metal-organic framework (MOF) is reported. Two types of functional linkers, a palladium-porphyrin photosensitizer and a bispyridine derived molecular motor were used to construct the framework capable of harvesting low-energy green light to power the rotary motion. The molecular motor was introduced in the framework using the post synthetic solvent assisted linker exchange (SALE) method and the structure of the material was confirmed by powder (PXRD) and single crystal X-ray (SC-XRD) diffraction. The large decrease in the phosphorescence lifetime and intensity of the porphyrin in the MOFs upon introduction of the molecular motor pillars confirms efficient triplet-to-triplet energy transfer between the porphyrin linkers and molecular motor. Near infrared Raman spectroscopy revealed that the visible light driven rotation of the molecular motor proceeds in the solid state at rates similar to those observed in solution.

Introduction

The development of artificial molecular machines and motors allows for the design and construction of tailor-made molecular architectures capable of executing precisely controlled nanoscale structural motion.^{1–8} Among these artificial systems, overcrowded-alkene based molecular motors attract considerable attention due to their chirality controlled photochemically-driven repetitive unidirectional rotary motion.^{9–11} Although it has been demonstrated that these molecules can perform various tasks in solution, such as control over the stereochemical outcome of catalytic reactions,¹² Brownian motion precludes the cooperative action required to achieve functions beyond molecular dimensions.^{5,8,13,14} Achieving ensemble action with artificial molecular machines therefore requires that the randomizing effects of the thermal motion are eliminated by assembly on surfaces^{24–26} or integration in the larger systems.¹⁴ Incorporation and immobilization of these molecules in various supramolecular architectures, including organo¹⁵- and hydrogels,^{16,17}

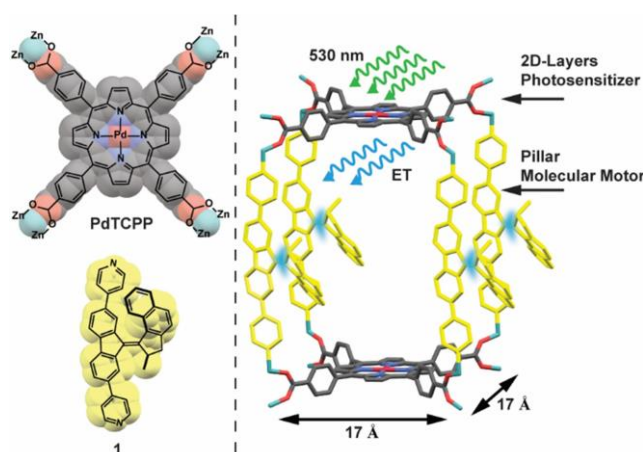


Figure 1 Structures of PdTCPP (left, top) and bispyridyl molecular motor **1** (left, bottom) used as linkers for construction of the MOF framework and the schematic representation of the rotation of molecular motor **1** incorporated as struts in the motorized pillared-paddlewheel PdTCPP MOF driven by energy transfer from a PdTCPP sensitizer (right). Relevant approximate dimensions of the unit cell are given.

polymers,^{18,19} liquid crystals^{20–23} or self-assembled monolayers^{24–26} provided a way to amplify and harness their light-induced rotational motion to form responsive materials with tunable properties, including adaptive polymers,^{18,19,27,28} artificial muscles,^{16,17} and responsive surfaces.²⁹ For overcrowded alkene-based materials the use of UV light to drive the molecular motion limits such efforts, due to limited penetration depth (due to the scattering), and potential damage by destructive photochemical processes.^{11,30,31} Therefore, development of reliable and practical visible-light excitation strategies that are compatible with a chosen material, represents a major challenge crucial for further advancement of these dynamic systems.

The most common approaches to red-shifting of the excitation wavelength of the overcrowded alkene-based molecular motors are based on HOMO-LUMO gap engineering featuring extension of the aromatic system,³² functionalization with donor-acceptor substituents^{33,34} or formation of metal complexes.³⁵ Although successful, these approaches may reduce the quantum yield of photoisomerization,³² and are so far limited in the absorption shift (only to the blue part of the visible spectrum; maximum of absorption ca. 450 nm).³⁴ Furthermore the resulting molecular architectures are synthetically more challenging to incorporate in a given material scaffold.^{32,35,36} An alternative approach, to achieve visible-light driven rotation of these molecules, is to take advantage of intra- or intermolecular sensitization through triplet energy transfer from a second chromophore.³⁷ This strategy not only reduces the synthetic efforts but also allows to tune the excitation wavelength over a broad spectral range limited only by the choice of a photosensitizer and triplet-triplet energy transfer requirements.³⁸ Furthermore, it has been successfully applied to operate several types photoswitches by visible light including, azobenzenes,^{39,40} stilbenes,^{41,42} dithienylethenes.^{43,44}

Metal-organic frameworks (MOFs) constitute a class of hybrid materials composed of inorganic nodes and organic linkers connected in a three-dimensional crystalline, highly porous network.^{45–47} Due to the high inherent porosity in these structures, sufficient internal free volume is present to allow for stimulus-responsive structural transformations,^{48–57} or rotational^{58–64} and translational⁶⁵ motion of parts of the organic linkers organized in the crystalline solid. In addition, the structural diversity and chemical tunability of these materials makes them ideal platforms to achieve spatial co-organization of functional molecules^{66,67} and chromophores.⁶⁸ Recent studies on light-harvesting multicomponent MOFs revealed that facile and long-distance energy migration can be

achieved between light-absorbing nodes and/or linkers in MOFs of various architectures.^{69–72} Furthermore, the incorporation of photochromic dithienylethenes struts in a layered porphyrin MOFs, provided a method for photocontrol over energy transfer between adjacent chromophores and efficiency of singlet oxygen generation.^{73,74}

Recently we have demonstrated that a molecular motor incorporated as a strut in a pillared-paddlewheel MOF is capable of performing unhindered, large amplitude unidirectional rotary motion fueled by UV light and heat.⁷⁵ In the present study we show that such rotary motion can be driven by visible light through linker-to-linker energy transfer. The framework was constructed from two functional linkers: a porphyrin used as both linker dictating the connectivity of the framework and light-harvesting unit, and a bispyridyl derived molecular motor serving as a pillar and able to undergo rotary motion (Figure 1). In the resulting supramolecular architecture the backbone of the framework is not only a passive ‘scaffolding’ but plays an active role by absorbing visible light and transferring the collected energy to the molecular motor struts thus driving its rotary motion. This dual-function MOF was obtained using a post-synthetic functionalization method from a parent Zn pillared-paddlewheel MOF bearing palladium porphyrin tetracarboxylic acid linker (**PdTCPP**) (Figure 1, top left panel) and bispyridyl pillars (Figure 1, bottom left panel). The chosen MOF scaffold provides proximity of both linkers allowing for efficient energy transfer between the chromophores and the large free volume that is essential for unhindered rotation of the light driven molecular motor in the solid state (Figure 1). A key challenge, presented by this approach, is in demonstrating the functioning of the material by spectroscopic methods due to the overwhelming spectroscopic properties of the porphyrin chromophore. This unit, which is central to the visible-light driven functionality, also precludes standard spectroscopic analysis of the motor function, however, near infrared Raman spectroscopy (1064 nm) enables full characterization of the motor function.

Results and discussion.

Design, Synthesis and Characterization of a Motorized Metal-Organic Framework. For the desired MOF a zinc pillared-paddlewheel scaffold was used, related to the framework we reported recently.⁷⁵ In the chosen structure, the nodes of the framework, that is the zinc paddlewheel clusters, are connected by porphyrin tetracarboxylic acid linkers (**PdTCPP**) forming two-dimensional layers, which are pillared by the bispyridine derived linker **1** (Figure 1). We designed the

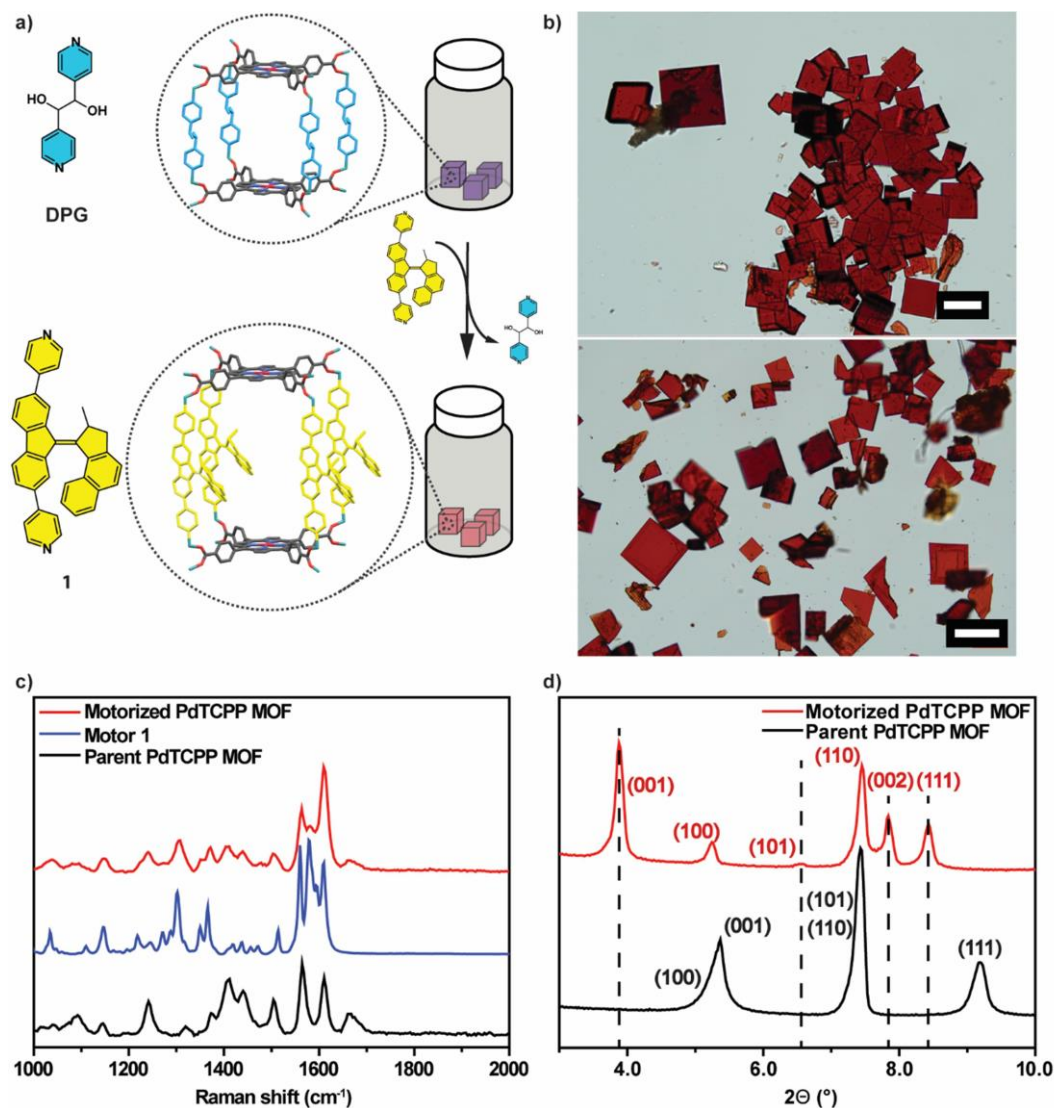


Figure 2 (a) Synthesis of the motorized pillared-paddlewheel MOF via SALE from parent MOF bearing **DPG** pillars by exchange with molecular motor **1**. (b) Optical micrograph of the parent **PdTCPP DPG**-based MOF (top panel) and motorized **PdTCPP 1**-based MOF (bottom panel) crystals obtained via linker exchange (SALE) (scale bar 100 μm). (c) Raman spectra of the parent pillared-paddlewheel MOF (black spectrum, 1064 nm, 250 mW), bispyridyl molecular motor (blue spectrum, 750 nm, 50 mW) and motorized pillared-paddlewheel MOF (red spectrum, 1064 nm, 250 mW). (d) Comparison of the experimental PXRD patterns of parent MOF (black, bottom pattern) and motorized MOF (red, top pattern). The Miller indices of planes corresponding to the peaks are given in brackets. The vertical dashed lines indicate peaks in PXRD pattern of motorized MOF, corresponding to (hkl) (where $l \neq 0$) planes.

system in such a way, that the size of **PdTCPP** linker will ensure sufficient lateral separation of the pillars bearing a molecular motor function, generating free volume critical for uncompromised rotation of the molecular motor (in the designed structure, the distance between the nodes in [100] and [010] planes is approximately 17 \AA , Figure 1). Furthermore, the length of bispyridyl derived molecular motor pillar **1** (N-N distance 15.6 \AA ⁷⁵) should separate the porphyrin layers sufficiently to prevent competing interlayer

porphyrin-porphyrin exciton transport. Finally, the nodes of the framework were based on closed-shell d^{10} configuration Zn^{2+} cations in order to exclude any undesired energy transfer between **PdTCPP** and nodes. Since, MOFs of this topology are typically synthesized under relatively harsh conditions with the presence of strong mineral acids⁷⁶, it was decided to prepare the final material using a post-synthetic method i.e. solvent assisted linker exchange (SALE) developed by Farha and Hupp.⁷⁷⁻⁸¹ In this process,

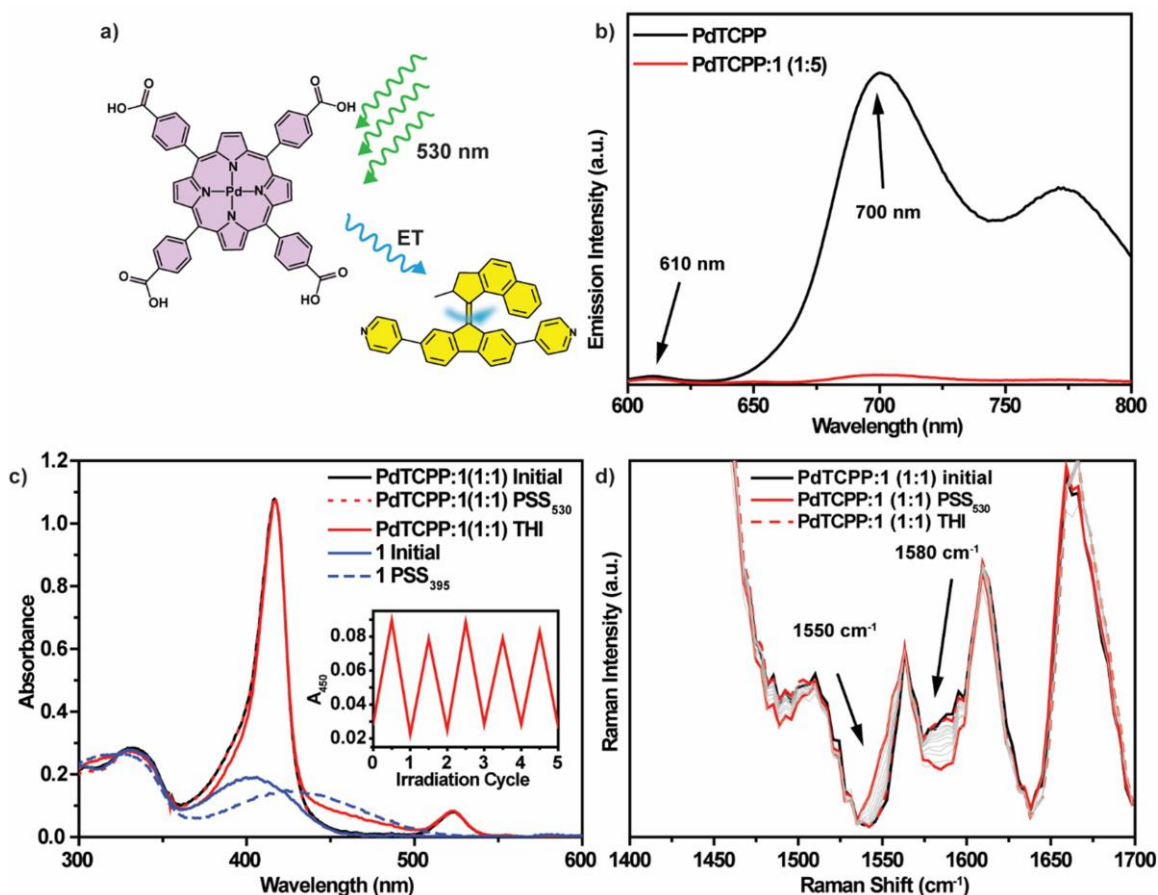


Figure 3 (a) Triplet-triplet sensitization of the light driven rotary motion of molecular motor **1** by intermolecular energy transfer from PdTCPP. (b) Emission spectra ($\lambda_{\text{exc}} = 530 \text{ nm}$) of PdTCPP (black spectrum, $44.6 \mu\text{M}$, DMF) and a mixture of PdTCPP and molecular motor **1** (red spectrum, 1:5 molar ratio of PdTCPP:**1**). The emission maxima of fluorescence (610 nm) and phosphorescence (700 nm) are indicated with arrows. (c) UV/Vis absorption spectra ($-20 \text{ }^\circ\text{C}$, $6.1 \mu\text{M}$, DMF) of **1** (blue solid line) irradiated at 395 nm to photostationary state (blue dashed line), a mixture of PdTCPP and **1** (1:1 molar ratio, black solid line), a mixture of PdTCPP and **1** irradiated at 530 nm to the photostationary state (red solid line) and photostationary state mixture after thermal helix inversion (red dashed line). Inset shows changes in absorbance followed at 450 nm upon multiple irradiations and heating cycles. (d) Changes in the Raman spectrum (1064 nm, 250 mW) of a mixture of PdTCPP and **1** in DMF (black solid line), after irradiation at 530 at $-20 \text{ }^\circ\text{C}$ to a photostationary state (red solid line) and after thermal helix inversion (red dashed line). Arrows indicate bands characteristic of the metastable isomer.

bispyridine derived pillars of the pillared MOFs can be exchanged for different bispyridyl linkers of similar length under neutral conditions, which prevents side reactions and decomposition of the acid-sensitive linkers.⁷⁷ Furthermore, it was demonstrated that with this method shorter pillars can also be exchanged for longer pillars thereby making this approach suitable for fabrication of MOFs with larger unit cell parameters.⁷⁹ Facing the problem of the absence of literature precedents for suitable MOF scaffolds that could serve as a parent MOF for the SALE process in the present design, first a novel MOF bearing *meso*- α,β -di(4-pyridyl) glycol (DPG, see Figure 2a for structure) pillar was prepared. The desired pillared-paddlewheel framework was synthesized in a solvothermal reaction between PdTCPP, DPG, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and tetrafluoroboric acid in a binary

solvent mixture (DMF/EtOH) and providing square-shaped crystals (Figure 2b, top panel). It is of note that when the reaction was carried out under less acidic conditions predominantly needle-like crystals (Figure S7a) of a three-fold interpenetrated framework with zig-zag structure were obtained (Figure S7b). Characterisation by ^1H NMR (d_6 -DMSO) spectroscopy of the digested (using D_2SO_4) square-shaped crystals of the pillared-paddlewheel MOF showed the expected 1:1 ratio of DPG and PdTCPP linkers (Figure S1, S2). The initial refinement of the single crystal (SC) X-ray diffraction data collected from the target MOF revealed the expected layered structure composed of PdTCPP and Zn cations, while the DPG pillars could not be resolved, presumably due to rotational disorder (Figure S5). Nevertheless, the interlayer distance of 9.2 \AA (N-N distance between pyridyl

nitrogens coordinated to paddle-wheel clusters) determined from the structure, corresponded well with the N-N distance (9.4 Å, see SI section 12) in the **DPG** linker, indicating that **DPG** pillars are intercalating the layers of the framework (Figure S5). The powder X-Ray diffraction data (PXRD), acquired under solvent saturated conditions, corroborated bulk crystallinity and phase purity of the sample (Figure 2d, S8). Furthermore, Pawley refinement showed negligible differences between the experimental and simulated diffraction patterns, further indicating the formation of the target pillared structure (Figure S5, S9, Table S2). Elemental analysis corroborated the anticipated elemental composition of the parent MOF (see SI, section 2). Subsequently, the parent **DPG** pillars were exchanged for bispyridyl molecular motor **1**, by means of SALE (Figure 2a), which was carried out by soaking the crystals of parent MOF in a DMF solution of bispyridyl molecular motor **1** at 80 °C for 48 h (the solution of **1** was replaced with a fresh solution after 24 h) to achieve full exchange as indicated by ¹H NMR spectroscopy of digested crystals (Figure 2b bottom panel, S1, S3). Comparison of the Raman spectra of parent and motorized **PdTCPP** MOFs revealed the presence of additional bands characteristic of molecular motor **1** in the spectrum of motorized MOF further supporting the successful exchange of the pillars (Figure 2c). As with the parent MOF, the SC X-ray structure of motorized MOF could only be partially resolved. From the refinement of the data the **PdTCPP** units and Zn paddle-wheel clusters forming a layered structure could be confirmed, while the disorder between the layers precluded the interpretation of electron density of the intercalating units (Figure S6). Nevertheless, the clear increase in the interlayer distance to 15.7 Å (N-N distance between pyridyl nitrogens coordinated to paddle-wheel clusters), corroborated the incorporation of longer pillars, consistent with length of the molecular motor **1** (N-N distance in DFT optimized structure B3LYP/6-31G(d,p) 15.4 Å).⁷⁵ In addition, the expansion of the elementary unit cell in the [001] direction was confirmed by the changes observed in positions of the peaks in the PXRD diffractograms. In comparison to the PXRD of the parent MOF, significant shifts to a smaller diffraction angle were observed for the peaks ascribed to reflections from planes perpendicular and oblique to the [001] direction, while peaks corresponding to reflections from planes parallel to the [001] direction remained unchanged (Figure 2d, S8). Furthermore, Pawley refinement showed good agreement between the dimensions of the targeted motorized **PdTCPP** MOF unit cell and the experimental PXRD pattern (Figure S8, S9, Table S2). Finally, elemental analysis was consistent with the an-

anticipated elemental composition of the parent MOF (see SI, section 2).

Energy transfer, photochemical and thermal isomerization in solution. Intermolecular energy transfer between the porphyrin (**PdTCPP**) and molecular motor **1** in solution was characterized by emission spectroscopy (Figure 3b). Deoxygenated solutions of **PdTCPP** excited at 530 nm show weak fluorescence at 610 nm and a strong emission band characteristic of phosphorescence at 700 nm (Figure 3b, black line) with a lifetime of ca. 221 μs (Figures S14-16, Table S3).⁸² For mixtures of **PdTCPP** and molecular motor **1** (1:5 ratio of **PdTCPP**:**1**) the intensity of the phosphorescence was substantially reduced with a decrease in phosphorescence lifetime to ca. 5 μs (Figure S14-16, Table S3), in line with energy transfer between triplet states of the porphyrin and motor **1** (Figure 3b, red line). Stern-Volmer plots (emission intensity and lifetime, Figures S14 and S16, respectively) with concentrations of **1** between 0.0 and 223.0 μM were linear confirming dynamic quenching of the phosphorescence of **PdTCPP** thus excluding formation of aggregates in the concentration range studied. Linear fitting of the data gave an intermolecular quenching rate constant $k_q = 0.9 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ closely matching the diffusion-limited rate constant in DMF ($7.6 \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ at 20 °C),⁸³ suggesting that the energy transfer between **PdTCPP** and **1** is under diffusion control (Figure S14, S16).

Intermolecular sensitization of the rotary motion of motor **1** in solution was studied with UV/Vis absorption, ¹H NMR and Raman spectroscopies (Figure 3c,d Figure S4). In the UV/Vis absorption spectra the region characteristic of the main absorption band of the molecular motor **1** (maximum ~ 400 nm, Figure 3c, blue solid line) is dominated by the strong Soret band of **PdTCPP** (Figure 3c, black solid line). Nevertheless, irradiation of the argon purged solution of **1** and **PdTCPP** (1:1 ratio of **1**:**PdTCPP**) at 530 nm (Q band of the porphyrin) led to a bathochromic shift of the absorption in the region of the Soret band (Figure 3c, red solid line), consistent with the formation of the metastable isomer of molecular motor (Figure 3c, blue dashed lines). Subsequent warming of the sample led to the recovery of the original spectrum, consistent with the recovery of the stable isomer by thermal helix inversion (Figure 3b, red dashed line). An isosbestic point was maintained at 323 nm throughout both photochemical and thermal processes, as expected for unimolecular reactions (Figure S12). Furthermore, the irradiation/thermal isomerization cycles could be performed for at least five consecutive cycles without noticeable fatigue or degradation (Figure 3c, inset). The rate of the thermal helix inversion of

bispyridyl motor **1** in the presence of **PdTCPP** in DMF was determined following the exponential decrease of the absorbance at 440 nm over a range of temperatures (6-14 °C, Figure S13). Eyring plot analysis showed that the Gibbs free energy of activation of the thermal helix inversion of the metastable isomer of **1** in this mixture ($\Delta^\ddagger G(20\text{ °C}) = 88.0 \pm 0.4\text{ kJ mol}^{-1}$, $t_{1/2} = 9.1\text{ min}$, Figure S13) is essentially the same as the previously determined value in DMF⁷⁵ ($\Delta^\ddagger G(20\text{ °C}) = 87.7 \pm 0.6\text{ kJ mol}^{-1}$, $t_{1/2} = 8.0$

min), thereby demonstrating that bispyridyl motor **1** can operate similarly via direct excitation and triplet sensitization. In the Raman spectra of the equimolar mixture of **PdTCPP** and **1** in DMF, bands characteristic of **PdTCPP** partially overlap and obscure bands characteristic of **1** (Figure 3d, black spectrum). Nonetheless, the features consistent with sequential photochemical and thermal isomerization of **1** could be readily observed with Raman spectroscopy. Irradiation of this mixture at 530 nm at low temperature (-20 °C, sufficient to prevent thermal helix inversion over the time scale of the experiment) led to a decrease in the Raman scattering at 1580 cm⁻¹ with concomitant increase at 1550 cm⁻¹. Warming to room temperature led to gradual recovery of the initial spectrum (Figure 3d). The intermolecular energy transfer induced photoisomerization of motor **1** was monitored with low temperature ¹H NMR spectroscopy (Figure S4). After irradiation of an equimolar mixture of **1** and **PdTCPP** at 530 nm at -30 °C, a new set of up-field shifted ¹H NMR resonances was observed in the aliphatic part of the spectrum, characteristic of the metastable isomer. Warming the sample resulted in full recovery of the original spectrum and hence of the stable isomer. The photostationary state ratio of metastable and stable isomers of **1**, established upon irradiation at 530 nm, was approximately 1:1 (Figure S4), consistent with changes observed by Raman spectroscopy (Figure 3d), which showed ~50% decrease in the intensity of the bands characteristic of the stable isomer (1580 cm⁻¹).

Energy transfer, photochemical and thermal isomerization in the solid state. The extent of the energy transfer between the **1** and **PdTCPP** linkers in motorized MOF was determined with steady-state and time-resolved emission spectroscopy. Upon excitation at 530 nm the parent **PdTCPP** MOF showed a similar emission spectrum to that of **PdTCPP** in DMF with a small hypsochromic shift of both fluorescence and phosphorescence (Figure 4a). Conversely, in the emission spectrum of the motorized **PdTCPP** MOF a strong decrease in the phosphorescence intensity was observed, consistent with the energy transfer between the linkers (Figure 4a). Furthermore a significant drop

in the porphyrin phosphorescence lifetime was observed from ca. 100 μs for the parent MOF to ca. 10 μs for the motorized MOF, demonstrating efficient

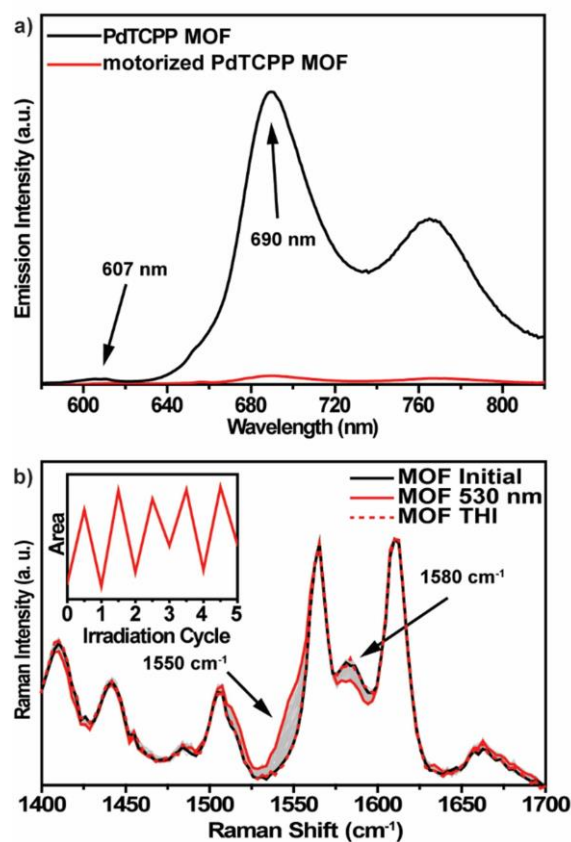


Figure 4 (a) Comparison of emission spectra ($\lambda_{exc} = 530\text{ nm}$) of DMF suspensions of parent **PdTCPP** MOF (black line) and motorized **PdTCPP** MOF (red line). (b) Changes in the Raman spectrum (1064 nm, 250 mW, 40 s integration time) of the motorized **PdTCPP** MOF sample (black solid line) upon irradiation at 530 nm (red solid line) and subsequent thermal isomerization (red dashed line). Inset shows changes in the area around 1550 cm⁻¹ followed upon multiple photochemical/thermal isomerization cycles.

energy transfer between the **1** and **PdTCPP** linkers in MOF (Figure S17, S18). The rotary motion of motor **1** inserted in the MOF scaffold was followed with NIR-Raman spectroscopy (see SI section 12 for other spectra). Previously, we demonstrated that this technique is particularly convenient to study the photochemical and thermal isomerization of rotary molecular motors in condensed phase as it allows for unambiguous correlation of spectral data with the structural changes that these molecules exhibit in response to light and heat stimuli.⁷⁵ Upon exposure of the polycrystalline motorized **PdTCPP** MOF sample to green light (530 nm) a gradual decrease in the Raman intensity at 1580 cm⁻¹ with concomitant increase in scattering intensity at 1550 cm⁻¹ was observed (Figure 4b). Similar spectral features were detected upon photo-

chemical isomerization of molecular motor **1** in solution and therefore could be ascribed to the same photochemical process. Furthermore, Raman spectroscopy showed that, for thin samples (much less than 100 μm), the photostationary state of **1** reached via triplet sensitization in motorized **PdTCPP** MOF was similar to that in solution (Figure S22). When the irradiation was discontinued, the initial Raman spectrum was recovered gradually indicating thermal relaxation of the metastable to stable isomer. The barrier of the thermal relaxation at room temperature was determined by monitoring the changes in the bands area characteristic of the metastable isomer (Figures S23-25 and Table S3). The Gibbs free energy of activation for this process ($\Delta^\ddagger G(20^\circ\text{C})$) was $88.7 \pm 0.8 \text{ kJ mol}^{-1}$, $t_{1/2} \sim 13 \text{ min}$) and corresponded well to the barrier determined in DMF solution ($88.0 \pm 0.4 \text{ kJ mol}^{-1}$, $t_{1/2} \sim 9 \text{ min}$). The good agreement between the barriers in the solution and the solid material shows that molecular motor **1** can perform its large amplitude rotary motion uncompromised while incorporated in **PdTCPP** MOF. Furthermore, irradiation/thermal relaxation steps could be repeated over five cycles (Figure 4b, inset) without any noticeable sign of fatigue or photo-degradation indicating high stability of the framework.

Conclusions

In conclusion we have established that the photoisomerization of the molecular motor pillars in a porphyrin Zn-paddlewheel MOF can be driven with visible light by triplet sensitization. The desired motorized MOF was constructed by post synthetic linker exchange (SALE) from the newly developed parent **PdTCPP** MOF bearing **DPG** pillars. Exchange of these pillars with the longer bispyridyl motor **1** resulted in the expected expansion of the elementary cell in the c direction as shown by the SC X-ray and PXRD data. Due to the spatial co-arrangement of the chromophores in the motorized MOF, the energy transfer between photosensitizer (2D layers) and molecular motor (pillars) was found to be efficient, and the photochemical isomerization of the molecular motor could be achieved with green 530 nm light. Additionally, it was shown that the rate of the thermal helix inversion step of the molecular motors incorporated in the material scaffold is essentially the same as that observed in solution, owing to the large free volume present in the framework. The demonstration of visible light driven rotary motion of a molecular motor in a metal-organic framework, opens many perspectives for future applications such as membranes and pumps able to accelerate flow of gases or in combination with catalytic function, miniaturized chemical reac-

tors able to accelerate inflow of reactants and outflow of products, powered by non-invasive visible light.⁸⁴ Furthermore, we envision that this strategy may be used to expand the scope of photosensitizers and molecular motors to achieve even further shift of the excitation wavelength towards red light.

ASSOCIATED CONTENT

Synthetic procedures and characterization, additional UV/vis and Raman spectra, Eyring plot, details on quantum yield and life time determination

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Author Contributions

W.D., F.C. synthesized MOFs; W.D. performed PXRD; W.D. analyzed rotary motion of motor in solution; W.D., A.S.S. performed emission studies in solution and solid state; S.K. performed Pawley refinement; L.P. performed SC X-Ray studies; W.D., W.R.B. studied the rotary motion in solid. W.D., W.R.B., B.L.F. conceived the project; W.R.B., B.L.F., A. C., guided the project; W.D., W.R.B., B.L.F. wrote the manuscript; all authors discussed the results and commented on the manuscript.

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Notes

The authors declare no competing financial interest.

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