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Stereoselective Solid-State Synthesis of Substituted Cyclobutanes Assisted by Pseudorotaxane-like MOFs

Fei-Long Hu,^[a,b] Yan Mi,^[b] Chen Zhu,^[a] Brendan F. Abrahams,^[c] Pierre Bruanstein,^[d] and Jian-Ping Lang^{*[a]}

Abstract: Regioselective photodimerization of *trans*-4-styrylpyridine (4-spy) derivatives is performed using pseudorotaxane-like Zn-based metal organic frameworks MOFs as templates. The formation of *rcct*-HT (head-to-tail) dimers is achieved by confining pairs of coordinated 4-spy derivative ligands within hexagonal windows and then irradiating them with UV light. It is also possible to achieve a photodimerization reaction where two different substituted 4-spy ligands are included in such a MOF material. The ether bond formation is employed to protect the sensitive -OH group of HO-spy and the methyl group of CH₃O-spy is subsequently removed after the formation of cyclobutane derivative in the CH₃O-Spy-based MOF. Introducing substituents at the 2- or 3-position of the phenyl group of 4-spy does not significantly affect the rate of the dimerization process except in the case of the strongly electron-withdrawing nitro group where the rate is significantly decreased. These results are in striking contrast to the mixtures of photoproducts and low yields obtained by untemplated photodimerization in organic solvents.

Stereoselective photodimerization reactions of alkenes remain elusive because of unfavorable interference of non-selective background reactions.^[1] The physical state of the precursor alkene is one factor that can impact the reaction outcome.^[2] For example, photoirradiation of a dilute solution of *trans*-4-styrylpyridine (4-spy) affords only the *cis*-isomer because of an accompanying *trans*-to-*cis* photoisomerization reaction.^[3] In contrast, photodimerization of an asymmetrical, substituted 4-spy in a concentrated solution generally produces a mixture of stereo- and regio-isomeric cyclobutanes, the formation of which is governed by Woodward-Hoffman rules, electronic and steric effects, and the thermodynamic stability of the diradical intermediates.^[4] Inspired by nature, which exploits tailored microenvironments within enzymes to promote a variety of biological reactions with high regio- and stereo-selectivity, it should be possible to obtain unique stereoselectivity and quantitative yields by preorganizing the reactants within an appropriately structured environment.^[5]

The generation of an environment that not only brings

alkene groups in close proximity and alignment for reaction but also imposes physical constraints that prevent conformational change during the lifetime of the excited states, offers the enticing prospect of stereoselectivity.^[6] Although establishing such molecular environments is challenging, the development of host structures which can be used as well-ordered templates or vessels to efficiently control the selectivity is clearly desirable.^[1b] Discrete supramolecular species, including cyclodextrins and calixarenes, etc, have served as hosts that offer the appropriate confinement of olefin pairs necessary for the photodimerization process.^[8]

The regulation of chemical reactions in the solid state by supramolecular confinement has attracted considerable interest^[1b, 7a, 7b, 9] because the rigid molecular environment of the reacting molecules in the solid state limits the opportunity for conformational change, thus promoting regio- and stereoselective processes.^[10] For example, the photodimerization of olefins can proceed stereoselectively in the solid state. According to Schmidt's criteria, solid state [2+2] photodimerization of olefins can occur when C=C bonds are parallel and the separation between the alkene groups is < 4.2 Å.^[11] A solid state approach of increasing importance involves the use of metal-organic frameworks (MOFs) in which the reacting molecules are confined within the framework voids.^[8b, 12] The design and synthesis of a MOF that holds voids capable of not only accommodating but also aligning an isolated pair of olefins represents a significant challenge.^[12a, 13] One way of exerting some control over the organization of pairs of reacting molecules within the voids, involves tethering the olefins to the framework via coordinate bonds. Herein, we report a pseudorotaxane-like MOF-based approach for the generation of a wide range of substituted cyclobutanes through stereoselective photodimerization reactions.

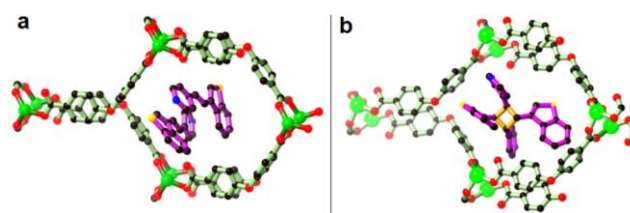


Figure 1. (a) A depiction of part of the Zn(obn) network (green bonds) showing btpy ligands (pink bonds) penetrating the hexagonal window. (b) The photoproduct 4,4'-(2,4-bis(benzo[b]thiophen-3-yl)cyclobutane-1,3-diyl)dipyridine (btcb) enclosed in a hexagonal window.

The combination of Zn(II) centers with the V-shaped dianionic ligand 4,4'-oxybis(benzoate) (oba²⁻), in the presence of 4-spy (**1**) and its derivatives S-spy (**1a-1v**) (Scheme S1), leads to the formation of neutral 2D networks [Zn(oba)(S-spy)]₂(S-spy)_x (**C1-C22**, Supporting Information). As depicted in Figure 1 and Figure S1, pairs of Zn(II) centers are linked by the bridging oba²⁻ ligands to other pairs of Zn(II) centers. Although

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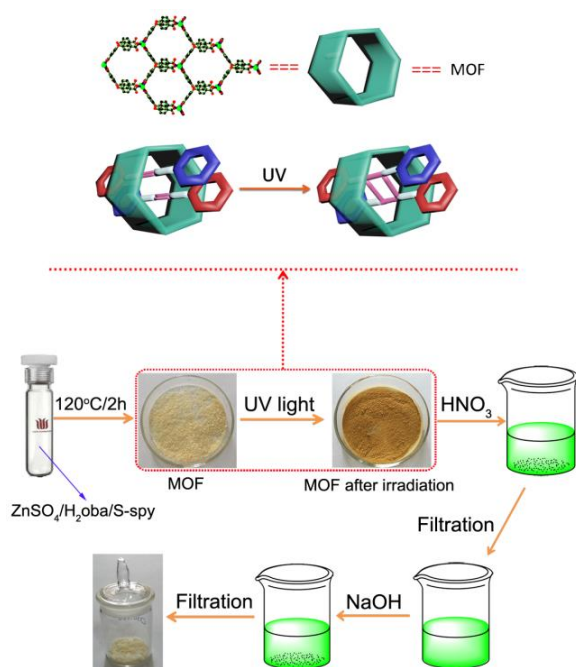
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each pair is linked to four other pairs, generating a network with the (4,4) topology, the use of a V-shaped oba²⁻ ligand results in the formation of a network that contains hexagonal windows. The S-spy ligands, binding through pyridyl groups to Zn(II) centers, are directed above and below the mean plane of the Zn(oba) network and extend through hexagonal windows of adjacent 2D networks, giving rise to a pseudorotaxane arrangement. The two molecules indicated in Figure 1a with pink bonds represent (E)-4-(2-(benzo[b]thiophen-3-yl)vinyl)pyridine (btpy, **1p**) ligands that are bound to Zn centers (Figure S2) of the Zn(oba)(S-spy) networks (S-spy<MOF) situated above and below the green network shown. The hexagonal cavities, in which the S-spy ligands are located, have approximate dimensions of 8 x 14 Å and possess a size and shape comparable to those found in cyclodextrin and cucurbit[8]ril.^[7d, 14] As can be appreciated from inspection of Figure 1a, the two btpy ligands are arranged in a head-to-tail manner and appear to be suitably positioned for a solid state photodimerization reaction.

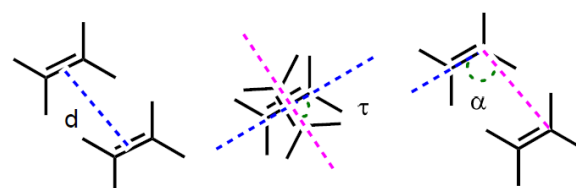


Scheme 1. (top) Preorganization of spy derivatives face-to-face using the coordination template and the [2+2] photodimerization reaction. (below) The procedure of the synthesis of the cyclobutane derivatives.

Previously it has been reported that both **1** and (E)-4-(2-(naphthalen-1-yl)vinyl)pyridine (4-npy, **1a**) are able to undergo [2+2] photodimerization when each is appended to Zn centers of the Zn(oba) network.^[15] This leads to the formation of *rctt*-1,3-bis(4-pyridyl)-2,4-bis(phenyl)cyclobutane (HT-ppcb) from 4-spy and *rctt*-1,3-bis(4-pyridyl)-2,4-bis(1-naphthyl)cyclobutane from 4-npy (*rctt* refers to the stereochemistry of the cyclobutane ring, *cis*, *trans*, *trans*). We have now developed a protocol for the generation of a wide range of head-to-tail *rctt*-cyclobutane molecules. The synthetic approach is summarized in Scheme 1 and involves, firstly, the solvothermal synthesis of S-spy<MOF. Upon UV irradiation, the photodimerization occurs, leading to the

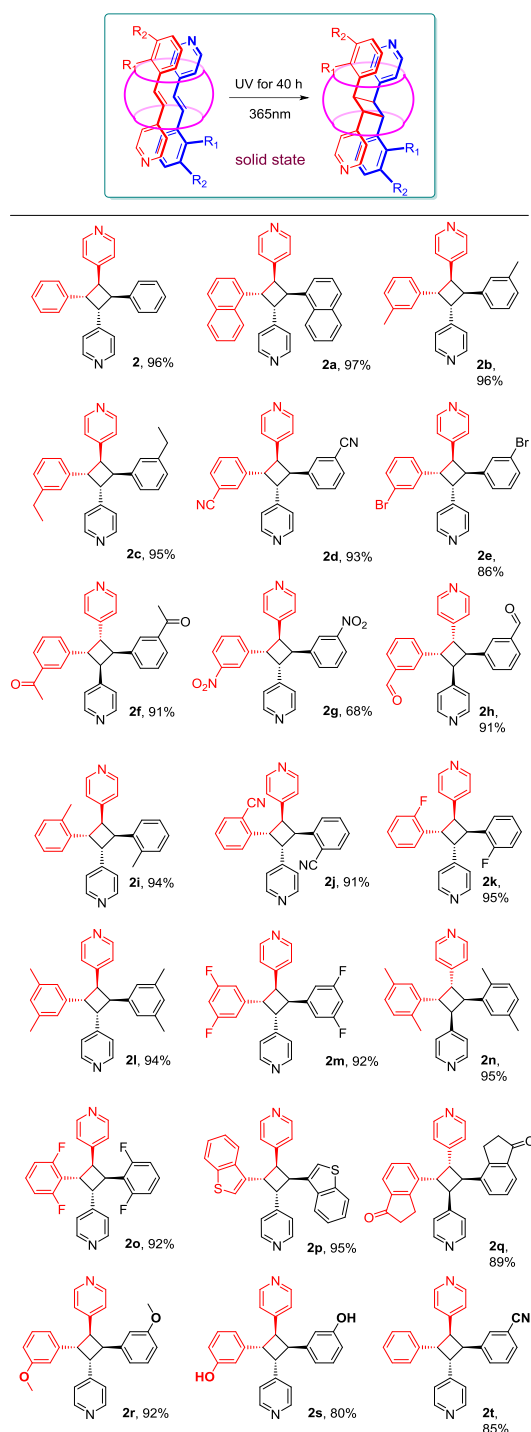
generation of the substituted *rctt*-cyclobutane in the solid product. The network material is then placed in nitric acid, resulting in the destruction of the network and the precipitation of H₂oba which may then be filtered and recycled (Figure S3). Upon addition of base to the acidic solution, the substituted cyclobutane precipitates and is isolated by filtration. The intermolecular photodimerization of the pre-organized olefins generates head-to-tail *rctt*-cyclobutanes in almost quantitative yields and with unique stereo- and regio-selectivities.

Crystal structure analysis of the parent S-spy<MOF crystals (Table S1) allows an accurate determination of the separation and relative orientation of the olefinic groups before photo-irradiation. Of particular importance are three parameters d , τ and α indicated in Scheme 2 and Table S2. The d parameter represents the separation of the mid-points of the double bonds, the τ parameter provides an angular indication of how close the double bonds are to being parallel and the α parameter is referred to the slip angle. For an ideal alignment, d should be as small as possible and certainly less than 4.2 Å, τ and α can be 0° and 90°, respectively. In the case of the btpy ligands depicted in Figure 1a, $d = 3.844$ Å, $\tau = 4.78^\circ$ and $\alpha = 75.99^\circ$. The photodimerization occurs with retention of single crystal character and the substituted *rctt*-cyclobutane, 4,4'-(2,4-bis(benzo[b]thiophen-3-yl)cyclobutane-1,3-diyl)dipyridine (btcb), is apparent from a single crystal structure determination, where it is still coordinated to the Zn centers (Figure 1b). The crystal structure of the pure substituted cyclobutane (Figure S4) confirms the successful generation and isolation of the intended product.



Scheme 2. Geometrical parameters used to evaluate the potential for photoreactivity.

The substituted cyclobutane products (**2**, **2a-2t**) (Scheme 3) were obtained upon UV irradiation over S-spy<MOF crystals at a wavelength of 365 nm for a period of 40 h. The ¹H NMR spectrum of each of the compounds represented in Scheme 3 showed the appearance of signals at 4-6 ppm which can be attributed to the cyclobutane rings (Figure S5). Signals associated with the olefinic protons were absent from the spectra. The pyridyl proton signals were shifted from 8.6 to 8.3 ppm, which is consistent with the formation of the substituted cyclobutane.^[10b, 16] Following the recovery of the dicarboxylate ligand, the ¹H NMR spectrum showed no changes for the proton signals of oba (7.0 and 8.0 ppm), indicating that the oba²⁻ ligands which form the frames of the hexagonal windows are unaffected by the photo-irradiation process (Figure S3). The thermal gravimetric analysis showed that the as-prepared compounds display two weight loss stages, while the photo-irradiated samples exhibit only one weight loss stage (Figure S6). The different weight loss stages of the compounds before and after photo-irradiation can be attributed to the new cyclobutane derivatives formed from the cycloaddition reaction.



Scheme 3. Synthesis of cyclobutane derivatives **2-2t**.

As indicated in Scheme 3, all substrates gave high yields of photodimerization products (**2-2q**), even those bearing bulky substituents, such as 3,5-dimethylphenyl (**2i**), benzothiophene (**2p**) and indanone (**2q**). Interestingly, the formation of **2i** did not occur in solution (Figure S7) and its formation in the network is presumably facilitated by the entropically favorable containment in the hexagonal windows. In the case of even larger

substituents, such as anthacyl in (*E*)-4-(2-(anthracen-9-yl)vinyl)pyridine (**4-atpy**, **1r**), the formation of $[\text{Zn}(\text{oba})(4\text{-atpy})]_2$ was inaccessible. Presumably the hexagonal window is not large enough to host this large substrate. It remains to be seen whether a different choice of metal and/or auxiliary ligands could afford a larger pore size to accommodate such a bulky ligand.

Attempts to synthesize the expected cognate product from HO-spy ligand failed due to the fact that the -OH group usually forms multiple hydrogen bonds in the assembly process. A protecting-group strategy was employed to avoid the formation of such hydrogen bonds. Thus, the methoxy derivative, (*E*)-4-(3-methoxyphenyl)pyridine (**3-OCH₃-spy**, **1t**) was easily obtained by treating (*E*)-4-(3-hydroxyphenyl)vinylpyridine (**3-HO-spy**, **1s**) with CH_3I under mild conditions.^[17] Formation of $[\text{Zn}(\text{oba})(3\text{-OCH}_3\text{-spy})]_2$ (**C19**) followed by the above method gave 4,4'-(2,4-bis(3-methoxyphenyl) cyclobutane-1,3-diyl)dipyridine (pocb, **2r**). The demethylation of **2r** worked efficiently using HBr or BCl_3 ,^[18] generating the final product 3,3'-(2,4-di(pyridin-4-yl)cyclobutane-1,3-diyl)diphenol (pdcb, **2s**) in 80% yield (Figure S8).

In all cases except for **2a**, **2c**, **2i**, **2m** and **2n**, structural analyses revealed *d*, *r* and *α* values which indicate a favorable arrangement with respect to the formation of the intended *rc**tt*-cyclobutane upon photo-irradiation. In the case of **2c**, **2i**, **2m** and **2n**, it was not possible to solve the crystal structures of the parent network compounds and thus it is not certain that an appropriate alignment and separation of the double bonds are present. In the known **2a**,^[15] the double bonds of the 4-npy ligands are in a criss-cross arrangement ($\tau = 93.16^\circ$). Given that such an arrangement would be incompatible with the formation of the intended substituted cyclobutane, it is proposed that the photodimerization to produce **2a** is preceded by a pedal motion rearrangement, resulting in a 180° rotation of the naphthyl group as shown in Scheme S2.

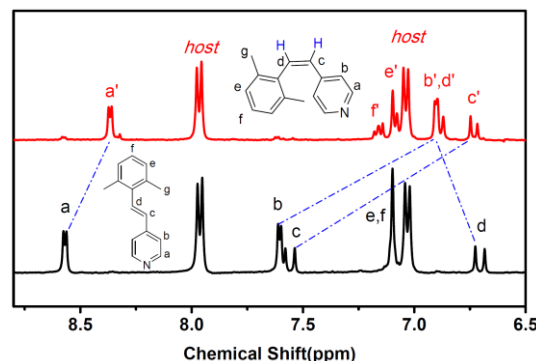


Figure 2. The ^1H NMR spectra of $[\text{Zn}(\text{oba})(2,6\text{-Me-spy})]_2$ before and after UV light irradiation.

The crystal structure of $[\text{Zn}(\text{oba})(2,6\text{-Me-spy})]_2$ (**C21**, 2,6-Me-spy = (*E*)-4-(2,6-dimethylphenylvinyl)pyridine, **1u**) also showed a criss-cross arrangement of the double bonds with an angle of 95.04° . On the basis of the successful formation of **2a**, it was anticipated that the conformational change involving a pedal motion process would bring the pair of substituted olefins into an arrangement suitable for photodimerization. However, the ^1H NMR spectrum of the irradiated **C21** showed the absence of signals in the 4-6 ppm range, thus indicating that the photodimerization reaction had failed to occur. Close inspection

of the ^1H NMR spectrum revealed that it was different to that of the parent ligand **1u**. In particular, the signals associated with the olefin protons of **1u** shifted from 7.53 and 6.68 ppm to 6.74 and 6.87 ppm, respectively. Such a change suggests conversion of a *trans* to a *cis* isomer upon irradiation (Figure 2). Corresponding shifts of the signals of protons bound to the pyridyl and methyl groups were also observed, from 8.57 to 8.37 ppm, 7.61 to 6.87 ppm and 2.33 to 2.08 ppm. The isomerization process was clearly confirmed by the ^1H - ^1H COSY spectrum of the *cis* product (Figure S9).

The unexpected *trans*-*cis* isomerization of **1u** rather than photodimerization, prompted closer examination of the parent coordination network and a comparison with the initial arrangement of criss-cross olefins, depicted in Figure 3, from which **2a** was isolated. Clearly, the presence of two methyl groups bound to the phenyl ring increases the bulkiness of the ligand and this may prevent the necessary rotation within the hexagonal window that is required before photodimerization can occur. However, the successful formation of **2l** and **2n** from (E)-4-(3,5-dimethylstyryl)pyridine (3,5-Me-spy, **1l**) and (E)-4-(2,5-dimethylstyryl)pyridine (2,5-Me-spy, **1n**), respectively, suggests that the position of the methyl groups on the ring is critical to the outcome of the irradiation process. It is proposed that the arrangement for **1u** (Figure 3), in which the methyl groups flank the link to the double bond, impedes the required pedal motion rearrangement which is necessary for the alignment of the double bonds. In order to further examine the steric effect of the methyl groups, a ligand resembling 4-npy but with an additional methyl group, (E)-4-(2-(2-methylnaphthalen-1-yl)vinyl)pyridine (3-Me-4-npy, **1v**) (Figure 3), and its corresponding complex $[\text{Zn}(\text{oba})(3\text{-Me-4-npy})]_2$ were prepared. No photodimerization occurred for **1v** (Figure S10), probably because the additional methyl group hindered the necessary pedal motion process required for the alignment of the double bonds.

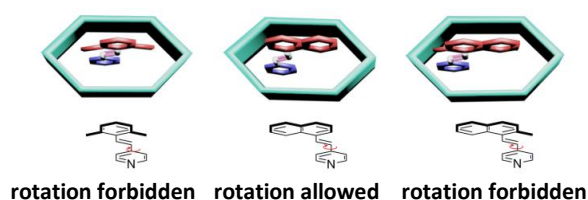
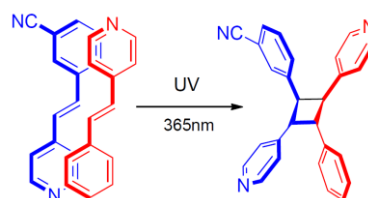


Figure 3. Representation of the possible rotation of **1u** (left), **1a** (middle) or **1v** (right) in the limited space of a pseudorotaxane window of each MOF.

Cross-dimerization reactions in which mixtures of S-spy ligands were used, were also studied. In particular, pairs of different ligands were combined in order to determine whether a heterodimer could be generated by using the synthetic approach successfully employed to produce the homodimers. The combination of **1** and (E)-3-(2-(pyridin-4-yl)vinyl)benzonitrile (3-CN-spy, **1d**) as indicated in Scheme 4 led to the formation of the heterodimer as only one single cross photodimerization product **2t** (Scheme 3) was detected by LC-MS (Figures S11-S12). Moreover, the ^1H NMR and ^1H - ^1H COSY spectra clearly showed that nearly equivalent **1** and **1d** crystallized in the same MOF **C20** (Figures S13-S14). In contrast, mixtures of **1/1a**, **1/(E)-4-(3-**

bromostyryl)pyridine (3-Br-spy, **1e**), and **1a/1e** using the Zn(oba) synthetic approach all gave mixtures of two homo- and one hetero-dimers in the ratio of 1:1:1 (Figure S15).

Whilst the regioselectivity of S-spy photodimerization reactions can be reliably controlled by templation, finding an appropriate template for a specific reaction type is challenging. In nature, enzymes provide highly tailored microenvironments that can promote reactions with high regio- and stereo-selectivity.^[19] With respect to the reaction of olefins, the pre-organization prior to UV irradiation provided by small molecule H-bonding templates such as resorcinol (and various substituted resorcinols) allows asymmetrical olefins to be arranged in a head-to-head^[1b, 20] or head-to-tail^[21] orientation. Other templates such as cucurbit[8]rill^[3, 22] can also facilitate the regiospecific formation of cyclobutanes. This effect is enhanced by adding hydrochloric acid. We have found that no photodimeric products were observed upon UV irradiation over crystalline samples of uncoordinated (E)-2-(2-(pyridin-4-yl)vinyl)benzonitrile (2-CN-spy, **1j**) or (E)-4-(2-(pyridin-4-yl)vinyl)-2,3-dihydro-1H-inden-1-one (idpy, **1q**). The failure to achieve dimerization is attributed to poor alignment and separation of the C=C bonds of neighboring molecules (Figures S16-S17). When a template is employed, a parallel alignment yields head-to-head dimers while the antiparallel orientation produces the head-to-tail cyclobutane products. When framework voids are exploited for templating purposes, antiparallel orientation is commonly observed because of steric repulsion between bulky groups in the parallel orientation.^[23] The regiospecificity of the photodimerization of S-spy ligands is governed by the balance of different types of interactions in the solid state. The successful cross photodimerization of **1** and **1d** in the hexagonal window of **1/1d**-MOF (**C20**) leads to the formation of a single heterodimer product **2t**. This result demonstrates the power of the MOF-templation method given that in theory six possible products may be formed in the solution reaction of **1** and **1d** (Figure S18). However, in the absence of the coordination network, no photodimer was formed from the batch of **1/1a**, **1/1b** or **1/(E)-4-(2-fluorostyryl)pyridine** (2-F-spy, **1k**) even at very high concentration (Figures S19-S21). These results demonstrate that for **1/1d** the exclusive formation of the hetero-photodimer was clearly controlled by steric factors associated with the hexagonal window of the appropriate MOF.



Scheme 4. Cross photodimerization between **1** and **1d**.

The time-dependent ^1H NMR spectra were recorded to examine the kinetics of the photodimerization reaction (Figure 4).^[24] The significant difference among the reaction rates of S-spy-MOF (S = H, -Me, -Et, -CN, -Br, -F, -CHO, -OCH₃, -aceto, -NO₂) was attributed to the very strong electron withdrawing 3-nitro group of (E)-4-(3-nitrostyryl)pyridine (3-NO₂-spy, **1g**) in **C8**.

Another reason for this was probably due to the relatively strong intermolecular H-bonding interactions between the HC=CH group of 3-NO₂-spy and O atom of the NO₂ group of one nearby 3-NO₂-spy (C20-H20...O2 ($x, 0.5-y, -0.5+z$), 2.48 Å) or O atom of oba²⁻ (C19-H19...O10 ($x, 0.5-y, 0.5+z$), 2.48 Å) in **C8** (Figure S24). Interestingly, the presence of weakly donating alkyl, weakly withdrawing halo or strongly withdrawing cyano substituents at the 2- or 3-position had virtually no influence on the reaction rate. The influence of substituents on the rate of solid state photodimerization reaction has rarely been reported.^[25]

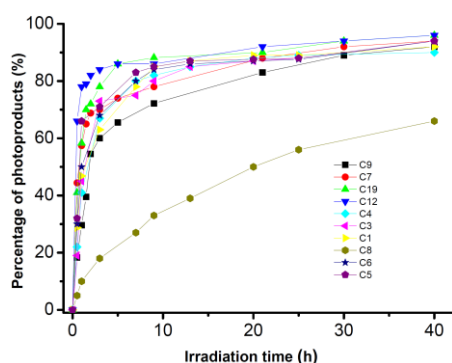


Figure 4. The percentage of S-spy ligand in **C1**, **C3**, **C4**, **C5**, **C6**, **C7**, **C8**, **C9**, **C12** and **C19** converted to *rctt*-ppcb derivatives under UV irradiation at different time intervals.

In summary, a series of *rctt*-HT substituted cyclobutanes have been synthesized in a stereoselective, photodimerization process within a crystalline pseudorotaxane-like Zn(II)-based MOF material. The results indicate that in cases where steric effects greatly impact the ability of the olefin to undergo pedal motion, *trans*-to-*cis* isomerization can occur instead of dimerization upon UV irradiation. The electronic nature of the substituents at the 2- or 3-position of the phenyl group is shown to have little impact on the reaction results except for the strongly electron-withdrawing nitro group. Cross-dimerization involving some of the smaller substrates is shown to be possible by including two different S-spy ligands in the S-spyc-MOF crystals. In cases where C=C bonds are arranged in a criss-cross style, the ability of the molecule to undergo the necessary pedal motion to achieve the C=C alignment, is found to depend on the extent of steric crowding near the double bond. This work offers a promising protocol for the quantitative solid-state synthesis of cyclobutane derivatives with excellent selectivity, which cannot be replicated in solution phase reactions.

Acknowledgements

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Conflict of interest

The authors declare no conflict of interest.

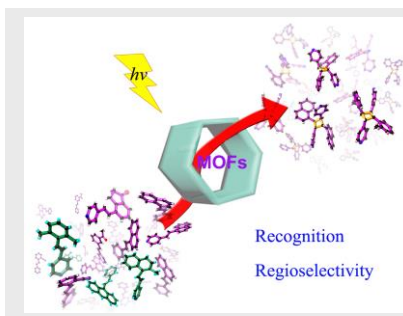
Keywords: MOFs • regioselectivity • photodimerization • solid-state organic synthesis • preorganization

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COMMUNICATION

Pairs of *trans*-4-styrylpyridine or its derivatives are oriented in a parallel and head-to-tail manner for the solid-state photodimerization within a pseudorotaxane-like MOF. The high selectivity for the *rctt*-HT (head-to-tail) dimers provides a controlled photodimerization within a confined environment. These results are in striking contrast to the mixtures of products and low yields obtained by untemplated photodimerization in organic solvents.



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Brendan F. Abrahams, Pierre Braunstein
and Jian-Ping Lang*

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**Stereoselective Solid-State Synthesis
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by Pseudorotaxane-like MOFs**