

# Visible Light [2+2] Photocycloaddition Mediated by Flavin Derivative Immobilized on Mesoporous Silica

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**Abstract:** 7,8-Dimethoxy-3-methylalloxazine was immobilized on mesoporous silica (MCM-41) to provide a heterogenized flavin photocatalyst. Thus, the prepared heterogeneous catalyst **2** was found to sensitize the visible light [2+2] cycloaddition of various types of dienes to produce corresponding cyclobutanes in high yields and diastereoselectivities. Use of **2** allows procedure which is advantageous by its simple operation and workup, no additives requirement and minimum waste generation.

The rapid development of visible-light photocatalysis has produced many procedures that are useful in organic synthesis; most of them are based on transition metal chromophores.<sup>[1]</sup> Nowadays, metal-free alternatives are of a growing interest thanks to the lower price of organic dyes, which may even allow other chemistry to occur.<sup>[2]</sup> Regardless of their nature, dyes have mostly been used as homogeneous catalysts. The number of "heterogenized" photocatalysts has still been limited despite their advantages such as the ease of separation from the reaction mixtures.<sup>[3]</sup>

Mesoporous silica nanoparticles<sup>[4]</sup> seem to be suitable solid supports for photocatalysts because of their thermal stability, versatile surface functionalisation, large surface area and, importantly, good transparency over a broad range of wavelengths.<sup>[5]</sup> Yet their use in the immobilization of molecular photocatalysts is still uncommon. He<sup>[6]</sup> used Ru(bpy)<sub>3</sub><sup>2+</sup> anchored on mesoporous silica for the photooxidation of thioanisole. Mori attached [Ir(Mebib)(ppy)CI]<sup>[7]</sup> and [Pt(tpy)CI]Cl<sup>[8]</sup> with several types of mesoporous silica, including MCM-41, MCM-48 and SBA-15 with differing in pore dimensions and structures, and used them for the photooxidation of *trans*-stilbene, styrene and 1-naphtol. Regarding organic photocatalysts, iodo-Bodipy on the siliceous mesoporous molecular sieve, KIT-1, was used for an aerobic oxidation – [3+2] cycloaddition cascade and is a rare example.<sup>[9]</sup> Rose-bengal immobilized on Wang resin used for

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aerial photosulfoxidation can be given<sup>[10]</sup> as one of the few examples of an heterogeneous photoorganocatalyst utilizing another material.

The UV light promoted [2+2] cycloaddition of alkenes providing cyclobutane derivatives is a textbook example of the usefulness of light in organic synthesis because this process is thermally disfavoured.<sup>[11,12]</sup> Recently, [2+2] photocycloadditions have been described to also occur under visible light, which is allowed when using a suitable photocatalyst/sensitiser<sup>[2,11d,13]</sup> that absorbs in the appropriate region. Initially, Yoon<sup>[14]</sup> reported visible-light procedures utilising the transition metal complexes, Ru(bpy)<sub>3</sub><sup>2+</sup> and Ir[(<sup>F</sup>bpy)<sub>2</sub>(<sup>tBu</sup>bpy)]<sup>+</sup>, which mediated the [2+2] photocycloaddition via electron and energy transfer, respectively Later attempts to replace these metal ion chromophores with an organic photocatalyst resulted in a few metal-free procedures.<sup>[15,16]</sup> We described one using the flavin derivative, 1butyl-7,8-dimethoxy-3-methylalloxazine (1), selected as suitable alloxazine as it has absorption maximum in visible region (400 nm) while keeping its triplet energy high enough to excite activated double bonds by energy transfer. System with 1 excelled with its versatility since upon irradiation with visible light it promoted the [2+2] photocycloaddition of both styrene dienes, which are considered as electron-rich substrates, and electronpoor bis(arylenones).<sup>[16]</sup> Very recently, we showed catalyst 1 can be applied even for nitrogen, sulfur and anhydride function containing dienes.<sup>[17]</sup> Despite the effectiveness of this photoorganocatalytic method, it suffers from some drawbacks: i) the homogeneous flavin catalyst 1 must be removed by chromatography, which is, moreover, not fully tolerated by some cyclobutane products and ii) less reactive substrates did not achieve full conversion under the homogeneous conditions.

Herein, we report anchoring flavin **1** (Figure 1) on mesoporous silica nanoparticles, which we envisage will solve the aforementioned specific problems with homogeneous photoorganocatalytic [2+2] photocycloaddition. From a more general point of view, we expect it could be a proof of concept for the immobilization of flavin photocatalysts. To the best of our knowledge, the use of a flavin-thiourea derivative anchored on silica gel for benzyl alcohol oxidation<sup>[18]</sup> has still been the only application of an immobilized flavin photocatalyst. Notably, dark oxidations with flavin immobilized in an ionic liquid<sup>[19]</sup> or gold nanoparticles<sup>[20]</sup> have been described.





MeO

MeC

MeC

MeC

2 HCL 80 °C

3. SOCI2

3

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Mesoporous silica MCM-41 was selected as a readily available siliceous matrix to support flavin; it was prepared in two steps via the graft method.<sup>[21]</sup> Initially, a silica polymer was formed after adding tetraethoxysilane (TEOS) to a waterammonia solution of hexadecyltrimethylammonium bromide (CTABr). Then, the surfactant was removed using ethanolic hydrogen chloride. Next, the surface of the nanoparticles was modified<sup>[6,22]</sup> with an aminopropyl group using aminopropyltriethoxysilane (APTES), followed by flavin unit attachment using acyl chloride 3 to form an amide bond (Scheme 1; for details, see Supporting Information). The catalyst (Figure 2a) was analyzed by SEM showing spherical shaped particles with diameter in the range approximately 450-650 nm (Figure 2b). A hexagonal pore structure was confirmed by powder X-ray diffraction (XRD). Using this method, each step was monitored to prove a degree of structural ordering and invariability of the (100) interplanar spacing correlating with mesopore diameter (Figure 2d).<sup>[4d]</sup> Absorption and emission maxima of alloxazine dve were found not to be affected by its anchoring on solid phase (see Figure 2c).

With the prepared heterogeneous catalyst 2, we optimized conditions for the visible light [2+2] the reaction photocycloadditions using the same apparatus (including light source) and model substrate (styryl ether 5) as in our previous study with homogeneous catalyst 1.<sup>[16]</sup> As previously described, the initial experiments were performed in a Schlenk tube in 1 mL of deuterated solvent under an argon atmosphere (Table 1). The solvents were selected to be easily removable by evaporation since this single operation was thought to be needed for the product isolation when using heterogeneous catalyst. The amount of catalyst 2 (2 mg) was chosen as it contains approximately the same amount of anchored alloxazine as that used in the homogeneous catalysis with 1 (2.5-2.7 mol% relative to the substrate).[23]

Table 1. [2+2] Photocycloaddition of diene 5 mediated by heterogeneous catalyst 2 and visible light (400 nm) on an analytical scale.<sup>[a]</sup> A result<sup>[16]</sup> for homogeneous conditions with 1 is given for comparison.

MeO

2

400 nm



MeC



Figure 2. Photograph (a) and SEM image (b) of the catalyst 2. Comparison of UV-VIS absorption and emission spectra of 1 and 2 (solid state) (c). CuK $\alpha$  Xray diffraction patterns of the catalyst 2 and intermediates MCM-41 and 4 (d).

Entry	Solvent	Time [min]	Conversion <sup>[b]</sup> [%]	Impurities <sup>[c]</sup>
1	CD <sub>3</sub> CN	60	quant.	no
2	Toluene-D <sub>8</sub>	60	quant.	no
3	CDCI <sub>3</sub>	60	55	yes
4	CDCI <sub>3</sub>	120	70	yes
5	CD <sub>3</sub> OD	60	55	no
6	CD <sub>3</sub> OD	120	60	no
<b>7</b> <sup>[d]</sup>	CD <sub>3</sub> OD	60	quant.	yes
8 <sup>[e]</sup>	CD <sub>3</sub> CN	120	0	-
9 <sup>[f]</sup>	CD <sub>3</sub> CN	120	0	-
10 <sup>[g]</sup>	CD <sub>3</sub> CN	60	quant.	no
11 <sup>[h]</sup>	CD <sub>3</sub> CN	10	87	no
12h <sup>[i]</sup>	CD <sub>3</sub> CN	10	55	no

<sup>[a]</sup> Reaction was performed in a Schlenk tube in 1 mL of deuterated solvent under an argon atmosphere; m(2) = 2 mg, i.e.  $n(2) = 5.4 \times 10^{-4} \text{ mmol}$ , c(5)= 2 x 10<sup>-2</sup> mol.L<sup>-1</sup>. <sup>[b]</sup> Conversion determined by <sup>1</sup>H NMR. <sup>[c]</sup> GC-HRMS. <sup>[d]</sup> m(2) = 10 mg, i.e.  $n(2) = 2.7 \times 10^{-3}$  mmol. <sup>[e]</sup> In the presence of mesoporous silica MCM-41 instead of catalyst. [f] In the presence of 4 instead of catalyst 2. <sup>[g]</sup> Reaction performed under air. <sup>[h]</sup> In the presence of catalyst 1 from ref.

Analogously to homogeneous conditions, the best results were achieved in acetonitrile and also in toluene where the pure cycloaddition product 6 was quantitatively formed within 60 min of irradiation (Entries 1 and 2); quantitative conversion in acetonitrile was observed even under aerial conditions (entry 10).



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On the other hand, in chloroform and methanol (Entries 3 and 5), the reaction proceeded more slowly and did not give complete conversion even after a prolonged reaction time (Entries 4 and 6). In methanol, attempts to improve the conversion by using a higher amount of catalyst resulted in the disappearance of all the starting diene but at the expense of purity (Entry 7). Importantly, the blank experiments showed the reaction does not occur either with mesoporous silica MCM-41 or with its APTES-modified version 4 used instead of 2 (Entries 8 and 9). Short experiments (10 min) demonstrated that the efficiency 2 is somewhat lower when compared to 1 under homogeneous conditions (cf. Entries 11 and 12) nevertheless one should take in mind that the result with the heterogeneous catalyst can be underestimated since some alloxazine units may not participate in the catalysis.

In acetonitrile, we investigated the substrate scope of our method with heterogeneous catalyst 2 both on an analytical and semipreparative scale using substrates studied previously<sup>[16,17]</sup> under homogeneous conditions with 1 (Table 2): electron-rich non-symmetrical and symmetrical styrenes 5 and 7. electronpoor bis(arylenone) 8, sulfur (9) and nitrogen (10, 11) containing dienes and anhydrides 12 and 13. Using immobilized catalyst 2, quantitative conversions were achieved in semipreparative (0.2 mmol) experiments within 120 min of irradiation with the exception of bis(arylenone) 8, sulfone 9 and amide 11 (Entries 3, 4 and 6) which required longer reaction times or a higher catalyst loading (in the case of 8). On the other hand, due to its high reactivity, methoxyphenyl derivative 13 cyclised almost quantitatively after 30 min of irradiation (Entry 8). We found this time as optimal for 13 to avoid decomposition of the product 20 observable after longer irradiation.

Compared to reactions under homogeneous conditions with 1 (see Table 2, last two columns) cycloaddition with 2 required longer reaction times with some exceptions: (i) cyclization of anhydrides 12 and 13 which was faster with heterogenized catalyst 2, (ii) cyclization of 9 which did not reach quantitative conversion under homogeneous conditions even after longer reaction time while complete formation of 16 was observed with solid-supported catalyst 2.

Importantly, contrary to the crude product obtained from the homogeneous photocycloaddition using 1 which required the chromatographic purification to remove catalyst. cyclobutanes with acceptable purity were obtained by simply filtering off the catalyst 2 followed by solvent evaporation after the cycloaddition under heterogeneous conditions (for a comparison of <sup>13</sup>C NMR data; see the Supporting Information). Neither alloxazine dye nor possible products of its decomposition were observed as impurities in the product. This is advantageous mainly from the point of view of preparative yields of cyclobutanes which were always higher using new procedure with heterogenized catalyst 2 compared to method with 1 (cf. data in Table 2). The differences in the yields are significant mainly when less stable cyclobutanes 16, 18 and 20 were prepared (Entries 4, 6 and 8).

Notably, the stereoselectivity of the cycloadditions using **2** was the same as that found under homogeneous conditions using **1** affording the exclusive formation of *exo*-cyclobutanes with a relative *cis*-configuration of the aryl groups (if appropriate) with diastereoselectivity d.r. >10:1 (Table 2). The ratio of the

*cis:trans*-benzoylcyclobutanes **15** was 4:1 (Entry 3), which was similar to that obtained using 1 (5:1).<sup>[16]</sup>

**Table 2.** Substrate scope investigation for [2+2] photocycloadditions mediated by **2** and visible light (400 nm) on an analytical<sup>[a]</sup> and semipreparative scale<sup>[b]</sup>. Data for homogeneous reactions with **1** (ref.<sup>16,17</sup>) are given for comparison.

			Heterogeneous reaction with <b>2</b> (2.7 %)			Homogeneous reaction with 1 <sup>[f]</sup> (2.5 %)	
Entry	Substrate (	Cyclobutane	Conv. 60min [%] <sup>[a,c]</sup>	Yield [%] <sup>[b,d]</sup> (time [min])	d.r. <sup>[e]</sup>	Yield [%] (time [min])	d.r. <sup>[e]</sup>
1	OMe Control	Meo H 6 H	quant.	96 (60)	>10:1	82 <sup>[m]</sup> (10)	>10:1
2			quant. <sup>[g]</sup>	98 (120)	-	80 <sup>[m]</sup> (25)	-
3			quant. <sup>[g]</sup>	93 <sup>[h]</sup> (120)	4:1	70 <sup>[m]</sup> (45)	5:1
4			quant. <sup>[g]</sup>	91 (300)	>10:1	51 <sup>[I,n]</sup> (40)	>10:1
5	V 10 O Me		quant.	96 (120)	10:1	70 <sup>[m]</sup> (40)	10:1
6			70 <sup>[9]</sup>	96 (300)	-	53 <sup>[m]</sup> (40)	-
7			quant.	93 (90)	>10:1	96 <sup>[k,l,m]</sup> (180)	>10:1
8	OMe OMe		<sup>vie</sup> 85	80 (30)	>10:1	46 <sup>[l,n]</sup> (120)	>10:1

<sup>[a]</sup> For conditions, see Table 1. <sup>[b]</sup> Reaction was performed in a Schlenk tube i 10 mL of anhydrous acetonitrile under an argon atmosphere; m(2) = 20 mg, i.e  $n(2) = 5.4 \times 10^{-3}$  mmol, n(substrate) = 0.2 mmol. <sup>[c]</sup> Relative conversio determined using <sup>1</sup>H NMR. <sup>[d]</sup> Preparative yield after filtration of catalyst. <sup>[L]</sup>, Diastereoisomeric ratio determined from <sup>1</sup>H NMR spectra of the reaction mixtures. <sup>[II]</sup> Yields (after column chromatography) and selectivities of cycloadditions with 1 under homogeneous conditions<sup>[16,17]</sup> obtained on the same apparatus. <sup>[G]</sup> m(2) = 5 mg, i.e.  $n(2) = 1.4 \times 10^{-3}$  mmol. <sup>[h]</sup> m(2) = 40 mg and new portion (m(2) = 20 mg) of 2 after 1 hour. <sup>[II]</sup> 10 % of 1. <sup>[K]</sup> Without column chromatography which causes decomposition of the product. <sup>[II]</sup> 5 % of 1. <sup>[m]</sup> Quantitative conversion. <sup>[n]</sup> Conversion 90%.

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We also attempted to reuse catalyst 2 in subsequent experiments but we observed significant drop of its activity becoming less active (12%) and inactive for the second and third round. respectively. Deactivation is caused by photodecomposition of flavin dye as evident from UV-VIS and fluorescence spectra (see Supporting Information) which also show that any aromatic, probably flavin decomposition product, remains anchored on MCM-41 after photocycloaddition. Thus the stability remains an issue to be solved in photocatalysis with flavins regardless they are used as homogeneous<sup>[16,17]</sup> or heterogenized catalysts.

In conclusion, we have found a simple way of heterogenisation of the flavin photocatalyst **1** by its covalent bonding on mesoporous silica MCM-41, which is still rarely used to anchor molecular organocatalysts. We demonstrated the usefulness of the prepared heterogeneous alloxazine catalyst **2** in the visible light [2+2] photocycloaddition of various dienes with a special focus on the transformations characterized by lower conversion and/or problematic product isolation under homogeneous conditions. We believe this approach to prepare the solid supported catalyst may be useful for other flavin derivatives whose photocatalytic properties have been of high research interest.<sup>[17a,24]</sup> It should bring new environmentaly benign photoorganocatalytic procedures.

#### **Experimental Section**

#### [2+2] Photocycloadditions on preparative scale

In a representative experiment, the reactions were performed in a Schlenk tube. Solid phase catalyst **2** (20 mg, containing  $5.4 \times 10^{-3}$  mmol of active units) and a substrate (0.2 mmol) were suspended/dissolved in acetonitrile (10 mL), tube was closed and air was removed by three freeze-pump-thaw cycles using argon as an inert gas. Schlenk tube was irradiated for an appropriate time (usually 30 - 300 minutes) on apparatus with six high power LED emitors (LED Engin LZ4-00UA00) directly shining on the tube from three directions at distance of 5 mm from the tube wall (see Supporting Information). The cycloaduct was obtained by removing the catalyst by filtration and by evaporation of solvent.

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### Entry for the Table of Contents (Please choose one layout)

Layout 1:

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We proved immobilization of flavin on mesoporous silica MCM-41 as effective way to prepare a heterogeneous flavin photocatalyst. Its possible application was demonstrated in visible light [2+2] photocycloaddition which is advantageous compared to analogous homogeneous procedure.



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