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# Visible-light-induced tandem reaction of *o*-aminothiophenols and alcohols to benzothiazoles over Fe-based MOFs: Influence of the structure elucidated by transient absorption spectroscopy



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# ABSTRACT

MIL-100(Fe) and MIL-68(Fe), two Fe-based MOFs, were found to be active for oxidative condensation between alcohols and o-aminothiophenols to form 2-substituted benzothiazoles under visible light irradiation using oxygen ( $O_2$ ) as oxidant. This reaction can be applied to a wide range of substrates with medium to high yield. Controlled experiments and ESR results revealed a superoxide radical ( $O_2^-$ )-mediated pathway, which is derived from the reduction of  $O_2$  by photogenerated Fe<sup>2+</sup> on Fe–O clusters. The whole multistep reaction is limited by the step of the photo-oxidation of alcohols to aldehydes. MIL-100(Fe) showed catalytic performance superior to that of MIL-68(Fe) because its higher concentration of longlived ( $\mu$ s time scale) positive holes can be photogenerated over MIL-100(Fe), in contrast to MIL-68(Fe). This study not only provides an economical, sustainable, and thus green process for the production of 2-substituted benzothiazoles, but also illustrates the potential of using transient absorption spectroscopy as an important tool for understanding the photophysics of MOFs, which are believed to show great potential as multifunctional catalysts for light-induced organic transformations.

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# 1. Introduction

As an important class of heterocycles, 2-substituted benzothiazoles are building blocks for the generation of many biologically active products, pharmaceutical compounds, and functional materials [1–3]. The traditional transition metal-catalyzed intramolecular cyclization of o-halothiobenzanilides and the condensation between carbonyl-containing compounds and o-aminothiophenol to produce 2-substituted benzothiazoles involve either costly dehydrating reagents or toxic oxidants such as benzoquinones [4-8]. Direct oxidative condensation of alcohols with oaminothiophenols using an environmentally friendly oxidant such as molecular oxygen  $(O_2)$  to produce 2-substituted benzothiazoles is an attractive alternative, since alcohols are readily available substrates, and this process has high atom efficiency and is clean, producing water as the only byproduct [9–11]. Both Ru- and Ir-based homogeneous and noble metal-doped heterogeneous systems have already been explored for the direct formation of 2-substituted

benzothiazole from oxidative condensation between *o*aminothiophenol and alcohol [12,13]. Unfortunately, the performance of these catalytic systems for direct oxidative condensation is still unsatisfactory. In addition to the difficulty of recycling them, the homogeneous systems also require more than stoichiometric amounts of basic additives or excess amounts of alcohols, which results in low atom efficiency. Large catalyst amounts and long reaction times are necessary for most of the heterogeneous systems. Moreover, elevated temperatures are required for almost all these systems, in which by-products due to the overalkylation of 2-substituted benzothiazoles are produced.

With the aim of developing renewable-energy-based processes, the utilization of natural light to trigger chemical reactions is attracting increasing research interest [14-18]. Light-induced chemical reactions can usually be carried out under mild conditions, which frequently makes them more selective than those carried out following the traditional thermally activated processes, since some thermally induced undesirable side reactions can be inhibited. Light-induced formation of 2-substituted benzothiazoles by reaction of *o*-aminothiophenols and aldehydes has already been realized over several photocatalytic systems, such as CdS [19,20], boron dipyrromethene [21], and tetrazine-based catalytic systems



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[22]. Considering that alcohols are readily available, the direct use of alcohols as starting material to react with *o*-aminothiophenols to produce 2-substituted benzothiazoles is therefore attractive. Since this reaction involves the oxidation of alcohols to aldehydes, condensation of aldehydes with *o*-aminothiophenols to imine/benzothiazolines, and oxidation of imine/benzothiazolines to 2-substituted benzothiazoles in consecutive steps (as shown in Scheme 1), a multifunctional catalyst is required for such a one-pot multistep reaction [9–11,23–27].

Metal-organic frameworks (MOFs), a class of 3D crystalline micro-mesoporous hybrid materials constructed from metal or metal cluster nodes interconnected with multidentate organic linkers, have already shown a variety of photocatalytic applications [28-36]. Ever since previous studies on MOF-5 revealed that metal clusters in MOFs can be regarded as inorganic semiconductor quantum entities, while the organic linkers act as antennae to activate these semiconductor quantum dots via linker-to-metal cluster charge transfer (LCCT) upon light excitation, the use of MOFs for photocatalysis has attracted extensive research interest [37,38]. Actually, MOFs are emerging as a new type of promising photocatalysts and have already been applied for photocatalytic CO<sub>2</sub> reduction [39-45], organic transformations [46-52], and hydrogen evolution [53–59], as well as pollutant degradation [60,61]. The use of MOFs for light-induced organic transformations where photocatalytic and catalytic steps are consecutively taking place is particularly appealing [62–72]. The high porosity of MOFs can ensure fast mass transport, while the presence of different catalytic sites in different places in the MOF structure enables them to behave as multifunctional catalysts [52,69–72]. Actually, the use of MOFs, especially the Matériaux de l'Institut Lavoisier (MILs) for other types of catalysis, such as Brønsted and Lewis acid catalysis, as well as tandem reactions, has already been reported previously [73–76]. Among all the reported MOF-based photocatalysts, Fe-containing MOFs are extremely attractive because Fe is an earth-abundant element and Fe-based MOFs show relatively intense absorption in the visible light region localized at the iron-oxo (Fe-O) clusters [45.51.52.60.77-80].

In this article, we report direct oxidative condensation between o-aminothiophenols and alcohols to produce 2-substituted benzothiazoles under visible light irradiations using  $O_2$  as an oxidant over MIL-100(Fe) and MIL-68(Fe), two Fe-based MOFs. It was found that the structure of MOF influences its catalytic performance, which was explained well using transient absorption spectroscopy (TAS). This study not only provides an economical, sustainable, and thus green process for the production of 2-substituted benzothiazoles, but also gives us a better understanding of the relationship



**Scheme 1.** Oxidative condensation of alcohols and *o*-aminothiophenols to produce 2-substituted benzothiazoles.

between the structure of MOF-based catalysts and their catalytic activity.

# 2. Experimental

## 2.1. Synthesis

MIL-100(Fe) was prepared following previously reported procedures [81,82]. Fe(NO<sub>3</sub>)·9H<sub>2</sub>O (484 mg, 1.2 mmol) and 1,3,5benzenetricarboxylic acid (H<sub>3</sub>BTC, 210 mg, 1.0 mmol) were dissolved in deionized water (5 mL) and were treated thermally in a stainless steel autoclave at 180 °C for 12 h. The resultant product was recovered by filtration and washed with water and methanol. The synthesized MIL-100(Fe) was dried overnight at 60 °C in an oven.

MIL-68(Fe) was synthesized according to the literature [83,84]. A mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (324 mg, 1.2 mmol), 1,4benzenedicarboxylic acid (H<sub>2</sub>BDC, 798 mg, 4.8 mmol), hydrofluoric acid (5 mol/L, 0.12 mL), and hydrous hydrochloride (1 mol/L, 0.12 mL) was dissolved in N,N-dimethylformamide (18 mL) in a Teflon-lined autoclave. The resultant mixture was heated at 100 °C for 120 h. The obtained solid product was recovered by filtration, washed with water and methanol, and then dried overnight at 60 °C in an oven.

### 2.2. Characterization techniques

X-ray diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu Ka radiation. XRD patterns were scanned over the angular range of  $5^{\circ}$ - $30^{\circ}$  $(2\theta)$  with a step size of 0.02°. The UV-vis diffuse reflectance spectra (UV-vis DRS) were obtained with a UV-vis spectrophotometer (Varian Cary 500). Barium sulfate (BaSO<sub>4</sub>) was used as a reference. BET surface area measurements were carried out on an ASAP 2020M apparatus (Micromeritics Instrument Corp., USA). The samples were degassed in vacuum at 150 °C for 10 h and then measured at -196 °C. The ESR spectra were determined on a Bruker A300 ESR spectrometer. Fe content in the filtrate was determined using inductively coupled plasma optical emission spectroscopy (ICP-OES, Perkin-Elmer, OPTIMA 8000). Before ICP-OES analyses, the solid was digested in a mixture of HNO<sub>3</sub> and milli-Q water. The reactions were carried out with a 300 W Xe arc lamp (Beijing Perfectlight, PLS-SXE300c).

#### 2.3. Light-induced reactions

The synthesis of 2-substituted benzothiazoles from oaminothiophenols and alcohols was performed in a sealed Schlenk tube under visible light irradiation. Typically, a mixture of oaminothiophenol (0.1 mmol) and alcohol (0.3 mmol) in acetonitrile (CH<sub>3</sub>CN, 2 mL) was saturated with O<sub>2</sub> before the mixture was transferred into a 10 mL tube containing 10 mg of MOFs. The suspension was irradiated with a 300 W Xe lamp equipped with a UVcut filter to remove all irradiations with wavelengths less than 420 nm and an IR-cut filter to remove all irradiations with wavelengths greater than 800 nm. After the reaction, the suspension was filtered through a porous membrane (diameter 20 µm) and the products were analyzed by GC-MS and GC-FID (Shimadzu GC-2014) with an HP-5 capillary column. The reaction, scaled up by 10 times, was conducted under similar conditions in a homemade reactor. A mixture of o-aminothiophenol (1 mmol) and benzyl alcohol (3 mmol) in CH<sub>3</sub>CN (20 ml) saturated with O<sub>2</sub> was transferred to the homemade reactor containing 100 mg of MIL-100(Fe). The reactor was irradiated with a 300 W Xe lamp equipped with both a UV-cut filter and an IR-cut filter.

## 2.4. TAS studies

MIL-100(Fe) and MIL-68(Fe) were dispersed in CH<sub>3</sub>CN with an approximate concentration of 0.1 mg/ml by sonication for 30 min. Subsequently, the resultant dispersions were purged with Ar for 10 min. Transient signals of MIL-100(Fe) and MIL-68(Fe) dispersions were acquired at 3  $\mu$ s upon 532 nm excitation using the same laser power (25 mJ, 7 ns pulse). Quenching experiments were carried out by monitoring the transient signals of the MOF dispersions at 560 nm upon addition of quenchers, including methanol (MeOH), ethanol (EtOH), 2-propanol (IPA), dichloromethane (CH<sub>2</sub>-Cl<sub>2</sub>), cerium (IV) ammonium nitrate (Ce(IV)), and oxygen (O<sub>2</sub>). Quenching of the transient signals allowed us to build Stern–Volmer plots following the equation

$$\frac{I_0}{I} - 1 = K_{SV} \cdot [Q]$$

where  $I_0$  is the initial and I the after-quencher addition transient signal intensity,  $K_{SV}$  is the Stern–Volmer constant, and [Q] is the quencher concentration.

# 3. Results and discussion

MIL-100(Fe), a three-dimensional Fe-based MOF material, was initially chosen to promote photoinduced oxidative condensation between o-aminothiophenol and alcohol to produce 2substituted benzothiazole, due to its very good resistance to water and organic solvents. MIL-100(Fe) is built up from supertetrahedra consisting of trimers of FeO<sub>6</sub> octahedra sharing a common vertex  $\mu_3$ -O, which delimits two types of mesoporous cages (Fig. S1a) [81,82]. MIL-100(Fe) was prepared by a solvothermal reaction following a previously reported method [81,82]. Formation of the pure phase of MIL-100(Fe) was confirmed by the good agreement between the XRD patterns of the as-prepared MIL-100(Fe) and those calculated for it (Fig. 1a). The N<sub>2</sub> adsorption/desorption measurements on the as-obtained MIL-100(Fe) reveal a specific BET surface area of 2021 m<sup>2</sup>/g, comparable to that reported previously  $(2050 \text{ m}^2/\text{g})$  (Fig. S2a) [82]. The UV-vis diffuse reflectance spectra (DRS) of the as-prepared MIL-100(Fe) show a broad intense absorption at 200-550 nm, with the absorption edge extending to around 600 nm (Fig. 2).

The direct oxidative condensation between *o*-aminothiophenol and benzyl alcohol was carried out over MIL-100(Fe) in the presence of  $O_2$  in CH<sub>3</sub>CN under visible light irradiation. It was found that 2-phenylbenzothiazole was obtained as the main product over irradiated MIL-100(Fe), while negligible 2-phenylbenzothiazole was obtained either in the absence of MIL-100(Fe) or in its presence but in the dark (Table 1, entries 1, 2). The reaction medium played an important role in this reaction (Table 1, entries 3–7).



Fig. 2. The DR UV-vis spectra of MIL-100(Fe) and MIL-68(Fe).

Among all the solvents investigated, CH<sub>3</sub>CN showed the best performance by giving the highest o-aminothiophenol conversion of 78% and a selectivity of 99% to 2-phenylbenzothiazole after 6 h irradiation (Table 1, entry 3). Benzaldehyde was detected, but no other reaction intermediates or by-products such as imine/benzothiazoline or other overalkylated tertiary amine were observed. Since the oxidative condensation between benzyl alcohol and oaminothiophenol to produce 2-phenylbenzothiazole involves the oxidation of alcohol to aldehyde, condensation of aldehyde with o-aminothiophenol to imine/benzothiazoline, and its transformation to 2-substituted benzothiazole in consecutive steps (Scheme 1) [9–13,19–22], the nonobservation of imine/benzothiazoline during the reaction process indicates that its transformation to 2phenylbenzothiazole is fast and that the rate-controlling step in the overall process is benzyl alcohol photo-oxidation. A prolonged reaction time of 10 h led to a greater conversion of oaminothiophenol (91%) without sacrificing the selectivity to 2phenylbenzothiazole (98%) (Table 1, entry 8). A filtration test revealed that no further reaction occurred after MIL-100(Fe) was removed from the reaction system at 4 h (Table 1, entry 9). The ICP analysis of the filtrate showed that the amount of Fe<sup>3+</sup> was below the detection limit ( $\sim$ 1 ppm). All the available data indicate that the formation of 2-phenylbenzothiazole from the reaction between o-aminothiophenol and benzyl alcohol is a truly heterogeneous process induced by the presence of MIL-100(Fe) and requiring visible light irradiation. Recyclability tests for three runs showed no obvious decrease in the catalytic activity of MIL-100(Fe) (Fig. 3). The XRD of MIL-100(Fe) after three runs did not change and its surface area is comparable to that of the fresh sample (Figs. 1a and S2b), indicating that MIL-100(Fe) is stable during the catalytic reaction and is reusable. Furthermore, it was found that the experiment can be scaled up without obvious decrease



Fig. 1. XRD patterns of (a) as-synthesized MIL-100(Fe), used MIL-100(Fe), and calculated MIL-100(Fe); (b) as-synthesized MIL-68(Fe) and calculated MIL-68(Fe).



*Notes:* Reaction conditions: *o*-aminothiophenol (0.1 mmol), benzyl alcohol (0.3 mmol), solvent (2 mL), MIL-100(Fe) (10 mg),  $O_2$  (1 atm), light irradiation (800 nm  $\geq \lambda \geq 420$  nm).

<sup>a</sup> Without visible light irradiation.

<sup>b</sup> No products or negligible products were detected.

<sup>c</sup> No catalyst.

Table 1

<sup>d</sup> The catalyst was filtrated after being irradiated for 4 h.

<sup>e</sup> The reaction was scaled up by 10 times.

<sup>f</sup> The reaction was quenched by benzoquinone.

<sup>g</sup> MIL-68(Fe) was used as catalyst.



**Fig. 3.** Recycling of MIL-100(Fe) as catalyst for the oxidative condensation of *o*-aminothiophenol with benzyl alcohol to produce 2-phenylbenzothiazole.

in performance. Comparable *o*-aminothiophenol conversion (90%) was still observed with high selectivity of 97% to 2-phenylbenzothiazole when the reaction was scaled up by a factor of 10 (Table 1, entry 10).

Under the optimized reaction condition, the substrate scope of this reaction was also investigated and the results are shown in Table 2. All the aromatic alcohols with different substituents, aliphatic alcohols as well as heterocyclic alcohols, were found to react with o-aminothiophenol to give the corresponding 2-substituted benzothiazoles (3a-3m) over irradiated MIL-100(Fe), although with different activity. As compared with bare benzyl alcohol, aromatic alcohols with electron-withdrawing groups such as -Cl and -NO<sub>2</sub> showed lower conversions (46-56%, 3b-3c) in 10 h. In contrast, aromatic alcohols bearing electron-donating groups such as p-OCH<sub>3</sub> and p-CH<sub>3</sub> exhibited enhanced conversion values (92-96%, 3d-3e), with the exception observed over benzyl alcohol with o-OCH<sub>3</sub>, o-CH<sub>3</sub>, and p-CH(CH<sub>3</sub>)<sub>2</sub> groups, which exhibited a slightly lower conversion ratio (78–85%, 3f–3 h) than bare benzyl alcohol. This suggests the existence of both electronic and steric effects in this reaction. Aliphatic alcohols can also react with oaminothiophenol over irradiated MIL-100(Fe), but with a much lower conversion of o-aminothiophenol (38-42%) to their corre-

#### Table 2

Conversion and selectivity data for the formation of 2-substituted benzohiazoles from different *o*-aminothiophenols and alcohols over MIL-100(Fe).



Notes: Reaction conditions: substituted o-aminothiophenol (0.1 mmol), alcohol (0.3 mmol), CH<sub>3</sub>CN (2 mL), MIL-100(Fe) (10 mg), O<sub>2</sub> (1 atm), light irradiation (800 nm  $\geq \lambda \geq 420$  nm), 10 h.

<sup>a</sup> The conversion of **2** and the selectivity of **3** in parentheses.

sponding 2-substituted benzothiazoles (3i-3j). The reaction between heterocyclic alcohols and *o*-aminothiophenol also afforded a high conversion rate (84-90%) to 2-substituted benzothiazoles (3k-3m) over MIL-100(Fe). On the other hand, the reactions between substituted *o*-aminothiophenols and benzyl alcohol also occurred. 2-Amino-4-chlorobenzenethiol and 2-amino-4-(trifluoro methyl)benzenethiol reacted with benzyl alcohol with high conversion values (87-90%) and a high selectivity ( $\geq 99\%$ ) to substituted benzothiazoles (3n-3o). These results indicate that the light-induced reaction between *o*-aminothiophenols and alcohols to synthesize 2-substituted benzothiazoles over MIL-100(Fe) is a general process applicable to a wide scope of substrates.

Previous studies revealed that the visible-light-induced synthesis of 2-substituted benzothiazoles over a homogeneous Rucontaining catalytic system involves  $O_2^-$  as an active species [85]. The ESR spectrum of our reaction system, which contained MIL-100(Fe), benzyl alcohol, and o-aminothiophenol in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a trapping agent also shows typical signals for the DMPO-O<sub>2</sub><sup>-</sup> adduct when irradiated, thus, confirming the formation of O<sub>2</sub><sup>-</sup> radicals during the catalytic reaction (Fig. 4) [86]. Previous studies revealed that the oxidative coupling of amines may also go through the singlet oxygen  $({}^{1}O_{2})$ -mediated pathway [87]. To investigated whether  ${}^{1}O_{2}$ was involved in the reaction, an ESR study using 2,2,6,6-tetrame thylpiperidinyloxyl (TEMPO) as a <sup>1</sup>O<sub>2</sub>-trapping agent was carried out. No typical signals for the TEMPO-<sup>1</sup>O<sub>2</sub> adduct were observed in the ESR spectrum under visible light irradiation (Fig. S3). This suggested that no  ${}^{1}O_{2}$  was involved during the tandem reaction. Moreover, addition of benzoquinone, an 0<sup>5–</sup> radical scavenger, into the catalytic system completely quenched the reaction, further evidence that the synthesis of 2-phenzylbenzothiazole over MIL-100 (Fe) can follow an  $O_2^{-}$  radical mediated oxygenation pathway (Table 1, entry 11). It was proposed that the  $O_2^-$  radical in this system can be generated via the reduction of  $O_2$  by  $Fe^{2+}$  formed over the irradiated MIL-100(Fe). A similar formation of O<sub>2</sub><sup>-</sup> radicals was previously observed over NH<sub>2</sub>-MIL-101(Fe), which was found to be responsible for the oxidation of benzyl alcohol to realize one-pot tandem photo-oxidation/Knoevenagel condensation between aromatic alcohols and active methylene compounds [77]. In addition, the reduction of  $Fe^{3+}$  to form  $Fe^{2+}$  upon light irradiation in Fe-based MOFs has also been reported over MIL-100(Fe) for benzene hydroxylation as well as MIL-101(Fe) for photocatalytic CO<sub>2</sub> reduction [45,51].

Based on the ESR results, a reasonable mechanism for the visible-light-induced synthesis of 2-phenylbenzothiazole from oaminothiophenols and alcohols over MIL-100(Fe) can be proposed in Scheme 2. First, an excited charge separation state occurs in MIL-100(Fe) upon irradiation, with the electron transferred from  $O^{2-}$  to Fe<sup>3+</sup> in the Fe<sub>3</sub>O clusters to form Fe<sup>2+</sup> (step i). The asformed  $Fe^{2+}$  can reduce  $O_2$  to form  $O_2^-$  radicals, while  $Fe^{2+}$  itself is oxidized back to Fe<sup>3+</sup> (step ii). In the meantime, by the quenching of the hole in MIL-100(Fe), alcohol becomes oxidized through the benzylic intermediate (step iii), which can further react with the O<sub>2</sub><sup>-</sup> radical to form the aldehyde via an oxidative dehydrogenation process (step iv). Such an O<sub>2</sub><sup>-</sup> radical-mediated oxidative dehydrogenation process of alcohols has been previously reported over a series of MOFs as well as some semiconductor photocatalysts in oxygenation reactions [14,47,88,89]. The condensation between the in situ generated aldehyde and o-aminothiophenol can be promoted by Lewis acidic Fe<sup>3+</sup> sites in MIL-100(Fe) to produce



**Fig. 4.** ESR spectra for DMPO- $O_2^-$  adduct in the presence of MIL-100(Fe), benzyl alcohol, and o-aminothiophenol in the dark and upon irradiation ( $\lambda \ge 420$  nm).



**Scheme 2.** Proposed mechanism for the visible-light-induced synthesis of 2-substituted benzothiazoles from *o*-aminothiophenols and alcohols over MIL-100 (Fe).

2-substituted benzothiazoline, which can be further oxidized by the active  $O_2^-$  radicals to form 2-substituted benzothiazole (step v and vi). According to this mechanistic proposal, MIL-100(Fe) has to act as a photocatalyst and as a solid Lewis acid to successfully promote the tandem reaction.

Based on the above proposed mechanism, it is believed that other Fe-containing MOFs may also be active in the light-induced formation of 2-substituted benzothiazole. To explore how the structure of the MOF can influence the reaction, MIL-68(Fe), another Fe-containing MOF, was also applied as a catalyst in the light-assisted reaction between *o*-aminothiophenol and benzyl alcohol under otherwise similar conditions. Unlike MIL-100(Fe), MIL-68(Fe) is assembled from an infinite straight chain of cornersharing FeO<sub>4</sub>(OH)<sub>2</sub> octahedra connected through terephthalate linkers, defining two types of one-dimensional channels (Fig. S1b) [83,84]. MIL-68(Fe) with high quality, as evidenced from the XRD pattern and N<sub>2</sub> adsorption/desorption, was also obtained following the previous reported method (Figs. 1b and S4). Although, as anticipated, the reaction also occurred over MIL-68 (Fe), compared with MIL-100(Fe) (conversion, 91%; selectivity, 98%) (Table 1, entry 8), MIL-68(Fe) showed a lower oaminothiophenol conversion of 66% and a selectivity of 97% to 2phenzylbenzothiazole (Table 1, entry 12). Similarly to MIL-100 (Fe), MIL-68(Fe) also showed high stability, as evidenced from the unchanged XRD patterns of the used MIL-68(Fe) (Fig. S5).

To provide some evidence supporting the photocatalytic activity of Fe-based MOFs and explain why MIL-100(Fe) shows superior performance to MIL-68(Fe), TAS studies were carried out over MIL-100(Fe) and MIL-68(Fe) dispersions in CH<sub>3</sub>CN under an inert atmosphere. To exclude the influence of their different light absorption coefficients, the transient spectra of MIL-100(Fe) and MIL-68(Fe) were acquired using the same laser power (25 mJ, 1 Hz) on both MOFs dispersions with optically matched dispersions at 532 nm, the wavelength of the laser excitation. As shown in Fig. 5a, although both the transient spectra of MIL-100(Fe) and MIL-68 (Fe) show negative signals ranging from 450 to 700 nm centered at approximately 550 nm, the intensity of the transient signal observed over the dispersion of MIL-100(Fe) is higher than that observed over MIL-68(Fe). These signals are related to the bleaching of the ground state absorption and they are in good agreement with their UV-vis spectra (Fig. 2). Since the laser power over the dispersions of both MOFs and their light absorption is the same within experimental error, the higher intensity of the transient signal observed over the dispersion of MIL-100(Fe) indicates a higher concentration of excited species reaching the microsecond time



**Fig. 5.** (a) Transient spectra of optically matched MIL-100(Fe) (black squares) and MIL-68(Fe) (red dots) dispersions acquired 3 μs upon 532 nm excitation using same laser power (25 mJ, 7 ns fwhp); (b) Transient kinetics of MIL-100(Fe) (black triangles) and MIL-68(Fe) (red dots) at 560 nm upon 532 nm excitation at 25 mJ. The green and blue lines correspond to raw data fitting to a single exponential function of MIL-100(Fe) and MIL-68(Fe), respectively.

scale in MIL-100(Fe) than in MIL-68(Fe) upon 532 nm laser excitation. The transient kinetics of MIL-100(Fe) and MIL-68(Fe) dispersions acquired at 560 nm upon 532 nm laser excitation can be fit to a single exponential function (Fig. 5b):

$$y = y_o + C \exp(t/\tau), \tag{1}$$

where *y* and *y*<sub>o</sub> are the transient signals at time *t* and 0, respectively, *C* is a constant, and  $\tau$  is the half-life constant. The lifetime ( $\tau$ ) of the excited state generated over MIL-100(Fe) was estimated to be 1.48 µs, while that for MIL-68(Fe) was only 0.63 µs. These results indicate that a higher concentration of transient species reaching microseconds with a longer lifetime is generated over MIL-100(Fe) as compared with MIL-68(Fe) upon laser excitation at 532 nm.

To elucidate the nature of the photogenerated transient signals, quenching experiments were carried out by monitoring the recovery of the ground state for these two MOF dispersions at 560 nm by adding either electron or hole quenchers (Fig. S6). The Stern–Volmer plots obtained from the quenching results revealed that for both MOFs, electron donors are better quenchers than electron acceptors. This suggests that the recovery of the ground state corresponding to the negative signal from 450 to 700 nm observed for both MIL-100(Fe) and MIL-68(Fe) is controlled mainly by the kinetics of the holes. The decay of the holes is believed to be the rate-determining step in the recovery of the ground state.

The photophysical data provide some rationalization for why MIL-100(Fe) is more active than MIL-68(Fe) in the light-induced formation of 2-substituted benzothiazoles. Scheme 2 shows that alcohols act as electron donors, and by donating electrons to MIL-100(Fe), alcohols become oxidized through the corresponding benzylic intermediates, which is an important step in the whole catalytic cycle. TAS data show that higher concentrations of transient species with positive charge reaching the relevant microsecond are generated over MIL-100(Fe) than over MIL-68(Fe) upon laser excitation at 532 nm, indicating that MIL-100(Fe) should be more active in this photo-oxidation reaction. Actually, our previous experimental results indicated that MIL-100(Fe) is more active than MIL-68(Fe) in the photocatalytic oxidation of benzyl alcohol to form benzaldehyde [46–50]. The photophysical data also imply that the overall formation of 2-substituted benzothiazoles by the reaction of o-aminothiophenols and alcohols should be limited by the ability of alcohols to act as electron donors to quench the positive holes. This is consistent with our experimental results, which show the existence of aldehyde as the by-product and the almost complete transformation of o-aminothiophenol with aldehyde to 2-substituted benzothiazole.

# 4. Conclusions

MIL-100(Fe) and MIL-68(Fe), two Fe-based MOFs, have been found to be active for tandem oxidative coupling of *o*aminothiophenols and alcohols to produce 2-substituted benzothiazoles under visible light irradiation using  $O_2$  as an oxidant. Due to the photogeneration of higher concentrations of long-lived transient species with positive charges over MIL-100(Fe) than over MIL-68(Fe), MIL-100(Fe) showed superior catalytic performance. The process has been scaled up to gram amounts. This study not only provides an economical, sustainable, and thus green process for the production of 2-substituted benzothiazoles, but also illustrates the potential for using TAS to explain the activity data and understand the photophysics of MOFs, which are believed to show great potential as multifunctional catalysts for light-induced organic transformations.

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## Appendix A. Supplementary material

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