

Document downloaded from:

<http://hdl.handle.net/10251/148856>

This paper must be cited as:

Wang, D.; Albero-Sancho, J.; García Gómez, H.; Li, Z. (2017). 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. *Journal of Catalysis*. 349:156-162. <https://doi.org/10.1016/j.jcat.2017.01.014>



The final publication is available at

<https://doi.org/10.1016/j.jcat.2017.01.014>

Copyright Elsevier

Additional Information

## **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**

### **Abstract**

MIL-100(Fe) and MIL-68(Fe), two Fe-based MOFs, were found to be active for the oxidative condensation between alcohols and *o*-aminothiophenols to form 2-substituted benzothiazoles under visible light irradiations using oxygen (O<sub>2</sub>) as an 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<sub>2</sub><sup>•-</sup>) mediated pathway, which is derived from the reduction of O<sub>2</sub> by photo-generated Fe<sup>2+</sup> on Fe-O clusters. The whole multi-step reaction is limited by the step of the photo-oxidation of alcohols to aldehydes. MIL-100(Fe) showed superior catalytic performance as compared with MIL-68(Fe), due to higher concentration of long lived transient species with positive charge can be photo-generated over MIL-100(Fe) than over 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 TAS as an important tool to understand the photophysics of MOFs, which are believed to show great potential as multifunctional catalysts for light-induced organic transformations.

**Keywords:** oxidative condensation, 2-substituted benzothiazole, Fe-based MOFs, transient absorption spectroscopy, light-induced organic transformations

## Introduction

As an important class of heterocycles, 2-substituted benzothiazoles are important building blocks for the generation of many biologically active products, pharmaceuticals compounds and functional materials. The traditional transition metal-catalyzed intramolecular cyclization of *o*-halothiobenzanilides or the condensation between carbonyl-containing compounds and *o*-aminothiophenol to produce 2-substituted benzothiazoles involve either the costly dehydrating reagents or toxic oxidant like benzoquinone. A direct oxidative condensation of alcohols with *o*-aminothiophenols using environmentally friendly oxidant like molecular oxygen (O<sub>2</sub>) to produce 2-substituted benzothiazoles is attractive since alcohols are readily available chemical feedstock and such a process is high atom efficiency and clean, producing water as the only byproduct. 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 alcohols. Unfortunately, the performance of these catalytic systems for the direct oxidative condensation is still unsatisfactory. In addition to their difficulty in recycling, the homogeneous systems also require more than stoichiometric amount of basic additives or excess amount of alcohols, which results in low atom-efficiency. High catalyst usage and prolonged reaction time are necessary for most of the heterogeneous systems. Moreover, elevated temperature is required for almost all these systems, in which by-products due to the over-alkylation of 2-substituted benzothiazole are produced.

With an aim to development of renewable energy based processes, the utilization of light to trigger the chemical reactions has attracted extensive recent research interest. Light induced chemical reaction can usually be carried out in mild conditions, which make them to be more selective than those carried out with the traditional thermal activated processes since some thermally induced undesirable side reactions can be inhibited. Light induced formations of 2-substituted benzothiazoles from reactions between *o*-aminothiophenols and aldehydes have already been realized over several photocatalytic systems like CdS, boron-dipyrromethene and tetrazine-based catalytic systems. Considering alcohols are readily available, it is therefore attractive to direct use of alcohols as starting material to react with *o*-aminothiophenols to produce 2-substituted benzothiazoles. Since the oxidative condensation between

alcohols and *o*-aminothiophenols to produce 2-substituted benzothiazoles 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, a multifunctional catalyst is therefore required for such a one-pot multi-step reaction.

Metal-organic frameworks (MOFs), a class of 3D crystalline micro-mesoporous hybrid material constructed from metal or metal clusters nodes interconnected with multi-dentated organic linkers, have already shown a variety of applications. 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 as antenna to activate these semiconductor quantum dots via the linker-to-metal cluster charge-transfer (LCCT) upon light excitation, the use of MOFs for photocatalysis have attracted extensive research interest. Actually MOFs are emerging as a new type of promising photocatalysts and have already been applied for photocatalytic CO<sub>2</sub> reduction, organic transformations, hydrogen evolutions as well as pollutant degradations. The use of MOFs for light-induced organic transformations is in particular appealing due to the existence of the order but tunable cavity in the MOFs, which can ensure a fast mass transportation, as well as the presence of different catalytic sites which enables them to behave as multifunctional catalysts. 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 intensive absorption in the visible light region because of the existence of iron-oxo (Fe-O) clusters.

In this manuscript, we reported the direct oxidative condensation between *o*-aminothiophenols and alcohols to produce 2-substituted benzothiazoles over MIL-100(Fe) and MIL-68(Fe), two Fe-based MOFs, under visible light irradiations using O<sub>2</sub> as an oxidant. It was found that the structure of MOFs influences their catalytic performance, which was explained well by 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 between structure of MOF-based catalysts and their catalytic activity.

## **Experimental Sections**

**Synthesis.** MIL-100(Fe) was prepared following previously reported procedures. Fe(NO<sub>3</sub>)·9H<sub>2</sub>O (484 mg, 1.2 mmol) and 1,3,5-benzenetricarboxylic 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 12h. The resultant product was recovered by filtration, washed with water and methanol. The synthesized MIL-100(Fe) was dried overnight at 60 °C in oven.

MIL-68(Fe) was synthesized according to the literature. A mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (324 mg, 1.2 mmol), 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 oven.

**Characterizations.** X-ray diffraction (XRD) patterns were collected on a D8 Advance X-ray diffractometer (Bruker, Germany) with Cu K<sub>α</sub> radiation. The accelerating voltage and the applied current were 40 kV and 40 mA, respectively. Data were recorded at a scanning rate of 0.02° 2θ s<sup>-1</sup> in the 2θ range of 5° to 30°. UV-visible diffuse reflectance spectra (UV-vis DRS) of the powders were obtained with BaSO<sub>4</sub> used as a reflectance standard. BET surface area was 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 performed on a Bruker A300 ESR spectrometer. Fe content in filtrate was determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin-Elmer, OPTIMA 8000). Before ICP-OES experiment, the solid was digested in a mixture of HNO<sub>3</sub> and milli-Q water. The reactions were performed with a 300 W Xe arc lamp (Beijing Perfectlight, PLS-SXE300c).

**Light-induced reactions.** The synthesis of 2-substituted benzothiazoles from *o*-aminothiophenols and alcohols were performed in a sealed Schlenk tube under visible light irradiations. Typically, a mixture of *o*-aminothiophenol (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 it 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 UV-cut filter to remove all irradiations with wavelengths less than 420 nm and an IR-cut filter to remove all irradiations with wavelengths larger than 800 nm. After the reaction, the suspension

was filtered through a porous membrane (20  $\mu\text{m}$  in diameter) and the products were analyzed by GC-MS and GC-FID (Shimadzu GC-2014) equipped with a HP-5 capillary column. The reaction scaled up by 10 times was conducted under similar conditions in a home-made reactor. A mixture of *o*-aminothiophenol (1 mmol) and benzyl alcohol (3 mmol) in  $\text{CH}_3\text{CN}$  (20 ml) saturated with  $\text{O}_2$  was transferred to the home-made 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.

**Transient absorption spectroscopy studies.** MIL-100(Fe) and MIL-68(Fe) were dispersed in  $\text{CH}_3\text{CN}$  with concentration approximate 0.1 mg/ml by sonication for 30 minutes, respectively. Subsequently, the resultant dispersions were purged with Ar for 10 minutes. Transient signals of MIL-100(Fe) and MIL-68(Fe) dispersions were acquired at 3  $\mu\text{s}$  upon 532 nm excitation using same laser power (25 mJ, 1 Hz). The transient kinetic of MIL-100(Fe) and MIL-68(Fe) dispersions were acquired at 560 nm upon 532 nm laser excitation. Quenching experiments were carried out by monitoring the transient signals of the MOFs dispersions at 560 nm upon addition of small amounts of Methanol (MeOH), ethanol (EtOH) and 2-propanol (IPA), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), cerium (IV) ammonium nitrate (Ce(IV)) and oxygen ( $\text{O}_2$ ), respectively. Quenching of the transient signals allowed us to build the Stern-Volmer plots following the equation:

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

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

## Results and discussion

MIL-100(Fe), a three-dimensional Fe-based MOF material, was first chosen for the photo-induced oxidative condensation between *o*-aminothiophenol and alcohol to produce 2-substituted benzothiazole, due to its very good resistance to water and organic solvent. MIL-100(Fe) is built up from supertetrahedra consisting of trimers of  $\text{FeO}_6$  octahedra sharing a common vertex  $\mu_3\text{-O}$ , which delimits two types of mesoporous cages. MIL-100(Fe) was prepared by a solvothermal reaction following the previously reported methods with slight modifications. The good agreement between the XRD patterns of the as-prepared product and the calculated MIL-100(Fe) indicates the formation of pure phase of MIL-100(Fe) (Figure 1). The  $\text{N}_2$

adsorption/desorption analysis on the as-obtained MIL-100(Fe) reveals a BET specific surface area to be 2021 m<sup>2</sup>/g, comparable to that reported previously (2050 m<sup>2</sup>/g) (Figure S1a). The UV-vis diffuse reflectance spectra (DRS) of the as-prepared MIL-100(Fe) shows a broad intense absorption in 200-550nm, with the absorption edge extending to around 600 nm (Figure 2).

The direct oxidative condensation between *o*-aminothiophenol and benzyl alcohol was carried out over MIL-100(Fe) in the presence of O<sub>2</sub> in CH<sub>3</sub>CN under visible light irradiation. It was found that 2-phenylbenzothiazole as the main product was obtained over irradiated MIL-100(Fe), while negligible 2-phenylbenzothiazole was obtained in either absence of MIL-100(Fe) or visible light irradiations (Table S1, entry 1-2). The reaction medium played an important role in this reaction (Table S1, entry 3-7). 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 irradiated for 6 h (Table S1, entry 3). Benzaldehyde was detected, but no other by-products like imine/benzothiazoline or other over-alkylated tertiary amine were observed. Since the oxidative condensation between benzyl alcohol and *o*-aminothiophenol 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, no observation of imine/banzothiazoline during the reaction process indicates that its transformation to 2-phenylbenzothiazole is fast. Prolonged reaction time of 10 h led to a higher conversion of *o*-aminothiophenol (91%) without sacrificing the selectivity to 2-phenylbenzothiazole (98%) (Table S1, entry 8). Filtrate reaction revealed that no further reaction occurred after MIL-100(Fe) was removed from the reaction system at 4 h (Table S1, entry 9). The ICP analysis of the filtrate showed no detectable Fe<sup>3+</sup>. All these results indicate that the formation of 2-phenylbenzothiazole from the reaction between *o*-aminothiophenol and benzyl alcohol is truly induced by heterogeneous MIL-100(Fe) under visible light irradiations. The recycling use of MIL-100(Fe) for three runs showed no obvious decrease of the catalytic activity (Figure 3). The XRD of the used MIL-100(Fe) did not change and its surface area is comparable to that of the fresh one (Figure S1b and S2), indicating that MIL-100(Fe) is stable during the catalytic reaction and is reusable.

With the optimized reaction condition, the substrate scope of this reaction was

also investigated and the results were shown in Table 1. All the aromatic alcohols with different substituted groups, aliphatic alcohols as well as heterocyclic alcohols were found to react with *o*-aminothiophenol to give 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 like -Cl and -NO<sub>2</sub> showed decreased conversion rate (46-56%, **3b-c**) in 10 h. On the contrary, aromatic alcohols bearing electron-donating groups like *p*-OCH<sub>3</sub> and *p*-CH<sub>3</sub> exhibited enhanced conversion ratio (92-96%, **3d-e**), 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-h**) as compared with bare benzyl alcohol. This suggests the existence of both an electronic and steric effect in this reaction. Aliphatic alcohols can also react with *o*-aminothiophenol over irradiated MIL-100(Fe), but with a much lower conversion of *o*-aminothiophenol (38-42%) to their corresponding 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 alcohols also occurred. 2-amino-4-chlorobenzenethiol and 2-amino-4-(tri-fluoromethyl)benzenethiol reacted with benzyl alcohol with a high conversion ratio (87-90%) and a high selectivity (≥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 generally applicable to a wide scope of substrates.

Previous study revealed that the visible light induced synthesis of 2-substituted benzothiazoles over a homogeneous Ru-containing catalytic system involves O<sub>2</sub><sup>•-</sup> as an active species. 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 and thus confirms the formation of O<sub>2</sub><sup>•-</sup> radicals during the catalytic reaction (Figure 4). Moreover, the addition of benzoquinone, an O<sub>2</sub><sup>•-</sup> radical scavenger, into the catalytic system completely quench the reaction, another confirmation that the synthesis of 2-phenylbenzothiazole over MIL-100(Fe) truly follows an O<sub>2</sub><sup>•-</sup> radical mediated oxygenation pathway. It was



proposed that the  $O_2^{\cdot-}$  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  $O_2^{\cdot-}$  radical was previously observed over  $NH_2$ -MIL-101(Fe), which was found to be responsible for the oxidation of benzyl alcohol to realize the one pot tandem photo-oxidation/Knoevenagel condensation between aromatic alcohols and active methylene compounds. 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  $CO_2$  reduction.

Based on the ESR result, the mechanism for the visible light induced synthesis of 2-phenylbenzothiazole from *o*-aminothiophenols and alcohols over MIL-100(Fe) was proposed in Scheme 1. First, an excited charge separation state occurs in MIL-100(Fe) upon irradiation, with the electron transferred from  $O^{2-}$  to  $Fe^{3+}$  in the Fe-O clusters to form  $Fe^{2+}$  (step i). The as-formed  $Fe^{2+}$  can reduce  $O_2$  to form  $O_2^{\cdot-}$  radicals, while  $Fe^{2+}$  itself was oxidized back to  $Fe^{3+}$  (step ii). In the meantime, by donating an electron to MIL-100(Fe), alcohol is transformed to alkoxide intermediate (step iii), which can further react with  $O_2^{\cdot-}$  radical to form the aldehyde via an oxidative dehydrogenation process (step iv). Such an  $O_2^{\cdot-}$  radical mediated oxidative dehydrogenation process have been previously reported over a series of MOFs as well as some semiconductor photocatalysts in oxygenation reactions. The condensation between the in-situ generated aldehyde and *o*-aminothiophenol can be promoted by Lewis acidic  $Fe^{3+}$  sites in MIL-100(Fe) to produce 2-substituted benzothiazoline, which can be further oxidized by the active  $O_2^{\cdot-}$  radicals to form 2-substituted benzothiazole (step v and vi).

Based on the above proposed mechanism, it is believed that other Fe-containing MOFs may also be active for the light induced formation of 2-substituted benzothiazole. To explore how the structure of the MOFs can influence the reaction, MIL-68(Fe), another Fe-containing MOF, was also applied in the 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 corner-sharing  $FeO_4(OH)_2$  octahedra connected through a terephthalate linker, defining two types of one-dimensional channels. MIL-68(Fe) with high quality as evidenced from XRD pattern and  $N_2$  adsorption/desorption was also obtained following the previous reported method (Figure S3). Although the reaction also

occurred over MIL-68(Fe), as compared to that over MIL-100(Fe) (conversion, 91%; selectivity, 98%) (Table S1, entry 8), MIL-68(Fe) showed a lower *o*-aminothiophenol conversion of 66% and a selectivity of 97% to 2-phenzylbenzothiazole (Table S1, entry 10).

To explain why MIL-100(Fe) shows superior performance to MIL-68(Fe), transient absorption spectroscopy studies were carried out over MIL-100(Fe) and MIL-68(Fe) dispersions in CH<sub>3</sub>CN under inert atmosphere. To exclude the influence of their different light absorption, the transient spectra of MIL-100(Fe) and MIL-68(Fe) were acquired using same laser power (25 mJ, 1 Hz) on both MOFs dispersions with similar absorption at 532 nm. As shown in Figure 5a, although both the transient spectra of MIL-100(Fe) and MIL-68(Fe) show negative signal 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 over MIL-68(Fe). These signals are related to the bleaching of the steady states, in good agreement with their UV-vis spectra (Figure 2). Since the laser power over the dispersions of both MOFs and their light absorption is similar, the higher intensity of the transient signal observed over the dispersion of MIL-100(Fe) indicates a higher concentration of excited species formed 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 (Figure 5b). The lifetime ( $\tau$ ) of the excited state generated over MIL-100(Fe) was estimated to be 1.48  $\mu$ s, while that for MIL-68(Fe) is only 0.63  $\mu$ s. These results indicate that higher concentration of transient species 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 origin of the transient signals, quenching experiments were also carried out by monitoring the transient signals of these two MOF dispersions at 560 nm by adding small amounts of either electro-withdrawing or electro-donating chemicals (Figure S4). The Stern-Volmer plots built from the quenching results revealed that for both MOFs, electron donors are better quenchers than electron acceptors. This suggests that the negative signal ranging from 450 to 700 nm observed on both MIL-100(Fe) and MIL-68(Fe) correspond to trapped positive charges.

The photophysical results help us to explain why MIL-100(Fe) is more active than

MIL-68(Fe) in the light induced formation of 2-substituted benzothiazoles. Scheme 1 show that alcohols act as electron donors and by donating electrons to MIL-100(Fe), alcohols are transformed to alkoxide intermediates, which is an important step in the whole catalytic cycle. The observations that higher concentration of long lived transient species with positive charge are generated over MIL-100(Fe) as compared with those over MIL-68(Fe) upon laser excitation at 532 nm indicate that MIL-100(Fe) should be more active in this photo-oxidation reaction. Actually, our previous experimental result indicated that MIL-100(Fe) is more active than MIL-68(Fe) in the photocatalytic oxidation of benzyl alcohol to form benzaldehyde. The photophysical results also imply that the whole formation of 2-substituted benzothiazoles from the reaction between *o*-aminothiophenols and alcohols is limited by the step of the oxidation of the alcohols. This is consistent with our experimental results that show the existence of aldehyde as the by-product and the almost complete transformation of *o*-aminothiophenol with aldehyde to 2-substituted benzothiazole.

## Conclusions

In summary, MIL-100(Fe) and MIL-68(Fe), two Fe-based MOFs, were found to be active for direct oxidative condensation between *o*-aminothiophenols and alcohols to produce 2-substituted benzothiazoles under visible light irradiations using O<sub>2</sub> as an oxidant. Due to the photo-generation of higher concentration of long lived transient species with positive charge over MIL-100(Fe) than over MIL-68(Fe), MIL-100(Fe) showed superior catalytic performance. 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 TAS as an important tool to understand the photophysics of MOFs, which are believed to show great potential as multifunctional catalysts for light-induced organic transformations.

## Acknowledgements

This work was supported by 973 Program (2014CB239303), NSFC (21273035), Specialized Research Fund for the Doctoral Program of Higher Education (20123514110002) and Independent Research Project of State Key Laboratory of Photocatalysis on Energy and Environment (2014A03). Z. Li also thanks the Award Program for Minjiang Scholar Professorship for financial support.

### Captions for Figures

**Figure 1** The XRD patterns of as-synthesized MIL-100(Fe) and calculated MIL-100(Fe).

**Figure 2** The UV-vis DRS spectra of MIL-100(Fe) and MIL-68(Fe).

**Figure 3** The cycling use of MIL-100(Fe) for the oxidative condensation of *o*-aminothiophenol with benzyl alcohol to produce 2- phenylbenzothiazole.

**Figure 4** The DMPO spin-trapping ESR spectra for  $O_2^{\cdot-}$  radical in the presence of MIL-100(Fe), benzyl alcohol and *o*-aminothiophenol in dark and upon irradiations ( $\lambda \geq 420\text{nm}$ ).

**Figure 5** (a) Transient spectra of MIL-100(Fe) and MIL-68(Fe) dispersions were acquired at 3  $\mu\text{s}$  upon 532 nm excitation using same laser power (25 mJ, 1 Hz); (b) Transient kinetics of MIL-100(Fe) (black dots) and MIL-68(Fe) (red dots) acquired at 560 nm upon 532 nm excitation at 25 mJ and 1 Hz. The green and blue lines corresponds to raw data fitting to a single exponential function of MIL-100(Fe) and MIL-68(Fe), respectively.

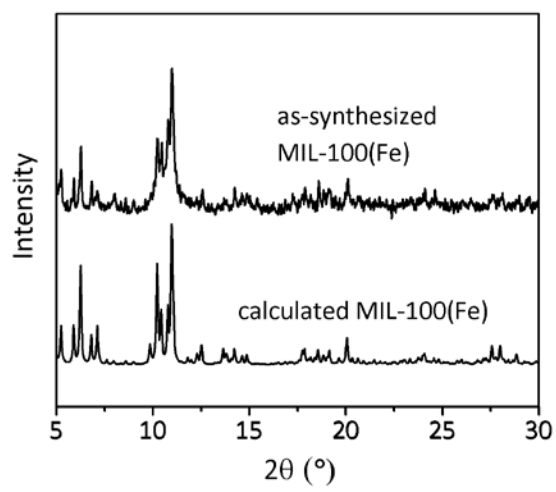
### Caption for Table

**Table 1** Synthesis of 2-substituted benzothiazoles from different *o*-aminothiophenols and alcohols over MIL-100(Fe).

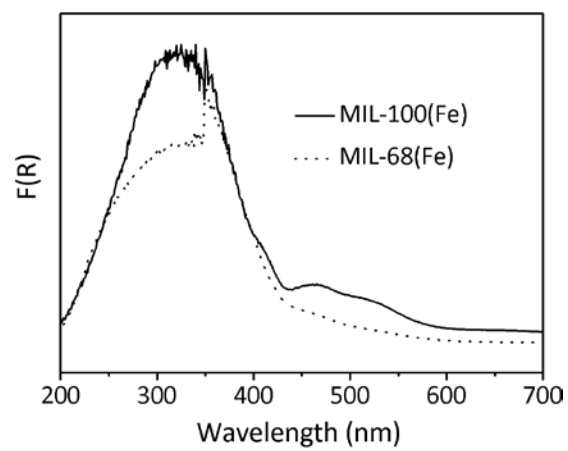
### Caption for Scheme

**Scheme 1** Proposed mechanism for the visible-light-induced synthesis of 2-substituted benzothiazole from *o*-aminothiophenols and alcohols over MIL-100(Fe).

**Figure 1**



**Figure 2**



**Figure 3**

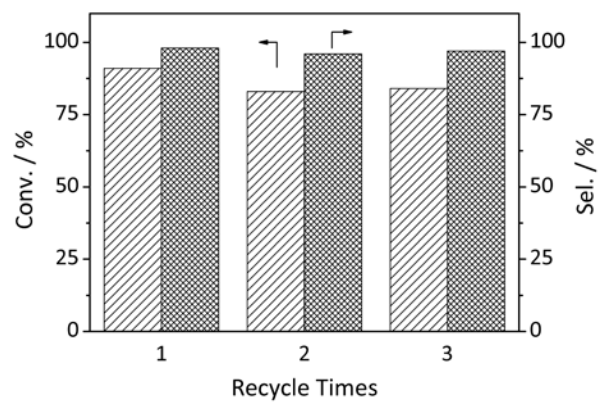


Figure 4

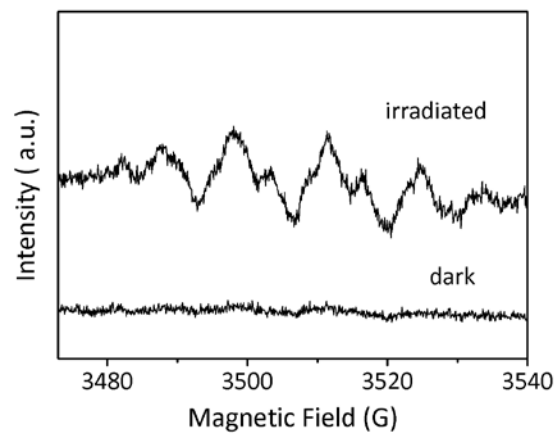
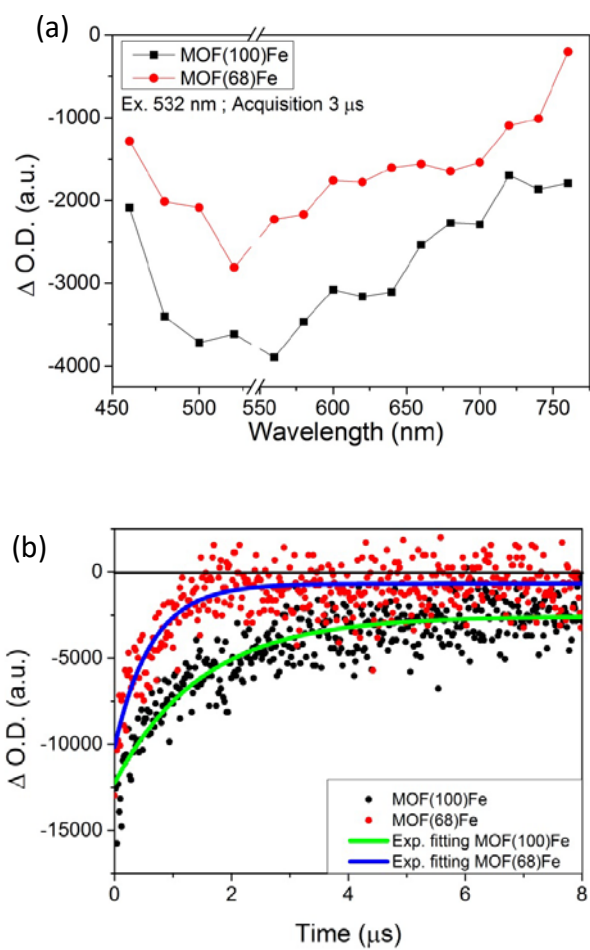
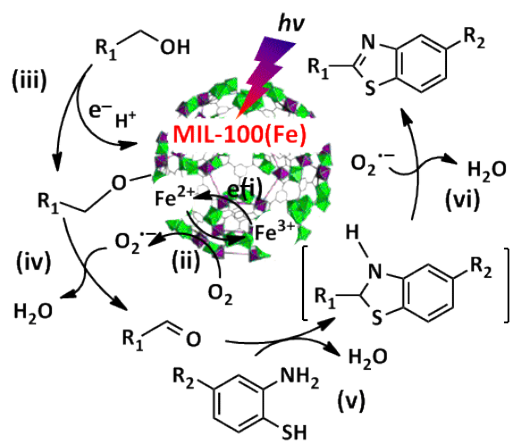




Figure 5



Scheme 1

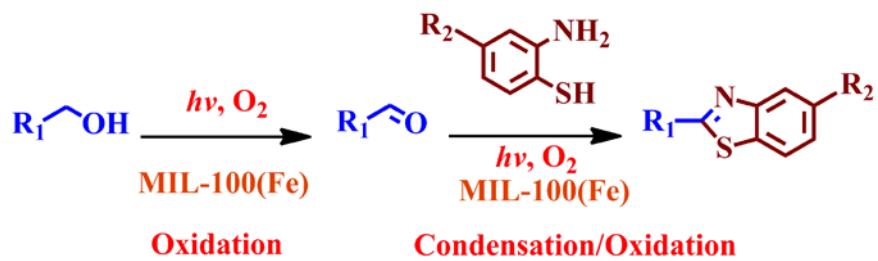


**Table 1**

<b>1</b>	<b>2</b>	<b>3</b>
<b>3a</b> 91% (98%) <sup>a</sup>	<b>3b</b> 56% (97%)	<b>3c</b> 46% (>99%)
<b>3d</b> 96% (97%)	<b>3e</b> 92% (99%)	<b>3f</b> 78% (97%)
<b>3g</b> 80% (98%)	<b>3h</b> 85% (98%)	<b>3i</b> 42% (98%)
<b>3j</b> 38% (97%)	<b>3k</b> 90% (99%)	<b>3l</b> 84% (97%)
<b>3m</b> 86% (96%)	<b>3n</b> 90% (99%)	<b>3o</b> 87% (>99%)

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), 10h. <sup>a</sup> The conversion of **2** and the selectivity of **3** in bracket.

## Table of Content Graphic



$R_1$  = aryl, alkyl, heterocycle ...

$R_2$  = -H, -Cl, -CF<sub>3</sub> ...