# Green Chemistry

# Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: Y. Li, J. Cai, M. Hao and Z. Li, *Green Chem.*, 2019, DOI: 10.1039/C9GC00328B.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/green-chem

# Visible Light Initiated Hydrothiolation of Alkenes and Alkynes/C9GC00328B over ZnIn<sub>2</sub>S<sub>4</sub>

Yuanyuan Li, Jingyu Cai, Mingming Hao, Zhaohui Li\*

Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350116, P. R. China

#### Abstract

Published on 21 March 2019. Downloaded by University of Western Ontario on 3/21/2019 1:33:28 AM.

View Article Online DOI: 10.1039/C9GC00328B

The construction of C-S bonds is very important. The hydrothiolation of alkenes or alkynes with thiols, represents an attractive and atom economic approach for the formation of C-S bonds. In this manuscript, flowerlike microspheres of ZnIn<sub>2</sub>S<sub>4</sub> consisting of interweaving nanoflakes were prepared by a solvothermal method and for the first time applied in visible light initiated hydrothiolation of alkenes and alkynes. The reactions between a broad range of thiols and alkynes or alkenes over irradiated ZnIn<sub>2</sub>S<sub>4</sub> afford corresponding hydrothiolated products in moderate to excellent yields. The mechanism proposed based on the ESR results suggests that the holes generated over irradiated ZnIn<sub>2</sub>S<sub>4</sub> are reductively quenched by the thiols to generate the third radicals, which are added to the alkynes/alkenes to generate the alkene/alkyl radicals for propagation of the thiol-ene/thiol-yne coupling reactions. The use of solar light and a semiconductor-based photocatalyst to realize the thiol-ene and thiol-yne coupling reactions in a green solvent (methanol), with only stoichiometric thiols required and applicable to a broad substrate scope, makes this reaction protocol to be a green, sustainable and cost-effectively strategy for the synthesis of thiolated products. This study also highlights the great potential of semiconductor-based photocatalysis for advanced organic syntheses.

**Keywords:** hydrothiolation reaction; visible light; ZnIn<sub>2</sub>S<sub>4</sub>; alkenes; alkynes.

#### Introduction

The construction of C-S bonds is synthetically important because of the large numbers of sulfur-containing natural products and pharmaceuticals as well as the increasing importance of the sulfur-containing products in polymer and material chemistry.<sup>1</sup> The most classical and important method for the construction of C-S bonds is the substitution reaction of alkyl halides and mercaptans under strong alkaline conditions.<sup>2</sup> These reactions have several drawbacks such as low efficiency, limited substrate scopes and harsh reaction conditions. Although an efficient method to construct C-S bond has been realized through the transition-metal-catalyzed cross-coupling reactions between activated Csp<sup>2</sup>-X (aryl halides/aryl boronic acids) and thiols,<sup>3-6</sup> most of the involved catalysts are based on noble metals like Pd, Rh, Au, Ag etc.<sup>7-8</sup> In particular, this protocol is applied only to prefunctionalized arenes and harsh reaction conditions are usually required.

The thiol-ene and thiol-yne reactions, the hydrothiolation reaction of alkenes or alkynes with thiols, represent an attractive and atom economic approach for the formation of C-S bond.<sup>9-10</sup> Initially, the addition of thiols to alkenes or alkynes is achieved via a radical pathway initiated by thermal or UV activation of a radical initiator or by direct irradiation with UV light.<sup>11-12</sup> However, this kind of free-radical addition suffers from harsh reaction conditions and low selectivity with the possible formation of by-products, which makes its application to only simple systems.<sup>13</sup> The development of hydrothiolations of alkynes/alkenes with thiols based on metal catalysts represents an important progress in this field since it offers great potential for hydrothiolation with high degree of region- and stereoselectivity.<sup>14-16</sup> Recently, with the aim of developing green and sustainable process for organic syntheses, the use of light to drive chemical transformations has attracted extensive current research interest.<sup>17-21</sup> The development of the photoredox catalysis has provided an attractive alternative to traditional methods to generate synthetically useful radical intermediates in complex systems.<sup>22-24</sup> Up to date, the hydrothiolation of alkenes and alkynes have been realized over homogeneous photocatalysts like Ru(II) complexes<sup>25-26</sup>, dyes (Eosin Y)<sup>27</sup> as well as heterogeneous semiconducting TiO<sub>2</sub>.<sup>28</sup> Using the photocatalyst to mediate the electron transfer not only enables these hydrothiolation reactions to be more selective with expanded substrate scopes, but also can be realized under mild conditions without the requirement of special UV equipments.

The first demonstration of the photoredox hydrothiolation reaction was reported

3

by Yoon and co-workers, in which the reactions between alkenes and thiply werse/CogCoo328B realized under visible light over  $[Ru(bpz)_3](PF_6)_2$  (bpz = 2,2'-bipyrazine).<sup>25</sup> It was proposed that when irradiated,  $[Ru(bpz)_3](PF_6)_2$  is excited to its excited state, which via a reductive quenching by a thiol generates [Ru(bpz)<sub>3</sub>]<sup>+</sup> accompanied with a thivl radical cation. Deprotonation of the thiyl radical cation generates a thiyl radical, which abstracts hydrogen from an un-reacted thiol to produce the hydrothiolated product and another equivalent of thivl radical to propagate the radical reaction, while the as-formed  $[Ru(bpz)_3]^+$  can be regenerated by reacting with oxygen. To realize such a hydrothiolation system, a photoredox cycle for initiation of the thiyl radical and the radical propagation cycle for the generation of the thiolated products are both required and operate synergistically. However, due to the consumption of the protons by oxygen in the system, excess thiols (4 equivalents) are required to achieve a high yield to the thiolation products, which not only is not economic, but also produces unnecessary by-products. Later, Ru(bpy)<sub>3</sub>Cl<sub>2</sub>-based photocatalytic radical initiation system for thiol-ene reactions was also developed.<sup>26</sup> Unlike that in  $[Ru(bpz)_3](PF_6)_2$ system, via a single electron oxidation of the sacrificial electron donor in the system, the photoexcited [Ru(bpy)<sub>3</sub>Cl<sub>2</sub>]\* is transform to a [Ru] species capable of reduction of bromotrichloromethane to form trichloromethyl radicals. The further reaction between the thiols and the trichloromethyl radicals yield the active thiyl radicals for the radical thiol-ene coupling. Similar hydrothiolation reactions between thiols and alkynes were also realized over Eosin Y,<sup>27</sup> a metal-free dye photocatalyst, via a similar strategy as that over  $[Ru(bpz)_3](PF_6)_2$ . The use of a cheap dye to replace expensive Ru complexes as photocatalyst in light initiated hydrothiolation reactions represents a significant advance in the synthetic methodology since it can significantly reduce the cost for the reaction. However, the organic dyes usually lack a long-term stability due to their degradations upon irradiations.

Recently, semiconducting  $TiO_2$  was also reported for the hydrothiolation reactions between alkenes and thiols.<sup>28</sup> The light initiated thiol-ene reactions over  $TiO_2$  also involves the thiyl radicals, which are generated by the deprotonation of the thiyl radical cations via the reaction between the thiol and the photogenerated holes. To complete a photocatalytic cycle over  $TiO_2$ , oxygen as a sacrificial electron acceptor should also be used in the reaction system. As compared with homogeneous Ru complexes and the dyes, the use of  $TiO_2$  as photocatalyst for hydrothiolation reactions obviously has advantages since  $TiO_2$  is cheap, nontoxic and readily

#### Green Chemistry

**Experimental** 

#### Preparations

All the reagents were commercial available and used without further purifications. ZnIn<sub>2</sub>S<sub>4</sub> was synthesized according to our previously reported method.<sup>40</sup> Characterizations

Powder XRD data were collected by using a Bruker D8 Advance X-ray diffractometer (CuKa irradiations). The morphology of the samples was characterized by field-emission SEM (JSM-6700F). UV-visible diffuse reflectance spectra (UV-DRS) of the powders were obtained for the dry-pressed disk samples using a Cary 500 Scan Spectrophotometer (Varian, USA), with BaSO<sub>4</sub> used as a reflectance standard. The ESR spectra were recorded on a Bruker A300 ESR spectrometer.

accessible. In addition, as a heterogeneous semiconductor photocatalyst, TiQ<sub>20</sub> can by View Article Online easily removed from the reaction system by filtering for recycling, which not only can avoid the possible contamination of the products by the catalyst, but also reduce the cost of the reaction. However, bare TiO<sub>2</sub> only absorb weakly in the visible light due to its relatively large band gap. The visible light initiated hydrothiolation reactions over TiO<sub>2</sub> are only applicable to those substrates that adsorbed and bound to its surface since the formation of the surface complexes between the substrates and the surface of TiO<sub>2</sub> is responsible for the absorption of TiO<sub>2</sub> in visible light region.<sup>29-30</sup> In addition, like that in  $[Ru(bpz)_3](PF_6)_2$  system, oxygen introduce into the reaction system consume the protons and therefore an excess of the thiol are required.

Hexagonal ZnIn<sub>2</sub>S<sub>4</sub>, a ternary chalcogenide semiconductor with a band gap well responsive in visible light region, has been extensively studied as a photocatalyst for hydrogen evolution and advanced organics synthesis.<sup>31-38</sup> In particular, our recent studies revealed that PtS/ZnIn<sub>2</sub>S<sub>4</sub> nanocomposites can split thiols to produce disulfides under visible light, via thiyl radicals (RS·) generated between the reaction of thiols and the photogenerated holes over ZnIn<sub>2</sub>S<sub>4</sub>.<sup>39</sup> Stimulated by this previous observation, in this manuscript, we investigated the visible light initiated hydrothiolation reactions over ZnIn<sub>2</sub>S<sub>4</sub>. Both aromatic and aliphatic thiols as well as thiophenols were found to react with a variety of alkynes and styrene to afford the corresponding thiolated products in moderate to excellent yields. This study provides a green, sustainable and cost-effective strategy for realization of hydrothiolation reactions and highlights the great potential of semiconductor-based photocatalysis in light initiated organics synthesis.

Catalytic reactions

View Article Online DOI: 10.1039/C9GC00328B

The visible light initiated hydrothiolation reactions were carried out in a sealed reaction tube with a LED lamp (Beijing Perfect Light, PCX50B). The catalyst (10 mg), thiols (0.1 mmol) and alkynes/styrene (0.12 mmol) were suspended in a schlenk tube containing solvent (4 ml). Before the reaction, the suspension was degassed and saturated with  $N_2$  to remove any dissolved  $O_2$ . The reaction was performed under irradiation with a LED lamp (65 mW/cm<sup>2</sup>) in room temperature. After the reaction, the products were analyzed by GC (Shimadzu GC-2014) equipped with an HP-5 capillary column and GC-MS.

#### **Results and discussion**

Published on 21 March 2019. Downloaded by University of Western Ontario on 3/21/2019 1:33:28 AM.

ZnIn<sub>2</sub>S<sub>4</sub> was prepared by a solvothermal method from ZnCl<sub>2</sub>, InCl<sub>3</sub>·4H<sub>2</sub>O and thioacetamide (TAA) in a mixture of ethylene glycol (EG) and N,N-dimethyl formamide (DMF). The XRD patterns of the product was indexed to be hexagonal ZnIn<sub>2</sub>S<sub>4</sub> (JCPDS 65-2023), in agreement with our previous report (Fig. 1a).<sup>41</sup> The SEM image shows that the product is composed of flowerlike microspheres with a dimension of ca. 4  $\mu$ m, with the microspheres made up of numerous interweaving nanoflakes (Fig. 1b). The UV/Vis DRS of the product shows that the absorption edge extends to ca. 490 nm, in consistent with its reported band gap of ca. 2.4 eV (Fig. 1c).

To study the performance of ZnIn<sub>2</sub>S<sub>4</sub> for light initiated hydrothiolation reactions, the reaction between phenylacetylene (1a) and benzyl mercaptan (2a) was selected as the model reaction and the reaction was initially carried out in CH<sub>3</sub>CN under visible light. It was found that after irradiated for 15h, 80% of benzyl mercaptane was converted, with a yield of 75% to the desirable product benzyl styryl sulfide (3a) (Table 1, entry 1). An almost undetectable trace amount of H<sub>2</sub> was also produced. On the contrary, no product was detected when the reaction was carried out in absence of either light or  $ZnIn_2S_4$  (Table 1, entries 2-3), indicating that the hydrothiolation between phenylacetylene and benzyl mercaptan to produce benzyl styryl sulfide is actually induced by irradiated ZnIn<sub>2</sub>S<sub>4</sub>. To investigate the effect of solvent on this reaction, the reactions carried out in toluene, ethylacetate, 2-propanol and methanol were also studied. Among all the solvents investigated (Table 1, entries 4-7), methanol showed the highest conversion of benzyl mercaptan (94%) and the best yield to benzyl styryl sulfide (90%) in 15 h (Table 1, entry 7). E-benzyl styryl sulfide was found to be the predominant product and the ratio of E/Z was determined to be 72:28 based on the NMR result (Supporting Fig. S1). Since methanol was found to be 6

#### Green Chemistry

The visible light initiated thiol-yne reaction over ZnIn<sub>2</sub>S<sub>4</sub> was applicable to a wide range of substrate scopes. Aryl alkynes bearing both electron-donating and electron-withdrawing substituents reacted effectively with benzyl mercaptane to produce vinyl sulfides in good to excellent yields (73%-92%, Table 2, entries 1-3). As compared with alkynes containing electron-donating substituent like CH<sub>3</sub>- in their aryl rings, those with electron-withdrawing substituents like Cl- and Br-showed lower reactivity to form vinyl sulfides, indicating the existence of electronic effect in this reaction. Alkyl alkynes like 3-methyl butynol also reacted with benzyl mercaptane to form 2-methyl-4-[(phenylmethyl)thio]-3-buten-2-ol with a moderate yield (58%, Table 2, entry 4). Although varied in the activity, a broad range of thiols, including both aromatic and aliphatic thiols as well as thiophenols also reacted with phenylacetylene, with moderate to excellent yield to their corresponding products (51%-95%). Aromatic thiols like 4-chlorophenethyl mercaptan and 2-phenylethyl mercaptan show high activity, giving a good to excellent yield (82%-93%) to the hydrothiolated products (Table 2, entries 5-6). On the contrary, the reaction on tert-butyl mercaptan was lower, with a yield of 61% to the thiolated product (Table 2, entry 7), probably due to the existence of a steric effect. Aliphatic thiols such as cyclohexyl mercaptan also reacted effectively with phenylacetylene to generate the hydrothiolated product in excellent yield (95%, Table 2, entry 8). Similar to that observed on tert-butyl mercaptan, bulky aliphatic thiols such as 1-dodecanethiol showed moderate yield (56%, Table 2, entry 9) to the hydrothiolated product. Thiophenols such as p-toluenethiol and 2-naphthyl mercaptans also participate smoothly in this process, with moderate to high yields (51%-70%) to the hydrothiolated products (Table 2, entries 10-11).

In addition to alkynes, alkenes like styrene also reacted efficiently with the both aromatic and aliphatic thiols as well as thiophenols to produce the corresponding alkyl sulfides over  $ZnIn_2S_4$  under visible light (Table 3). After irradiated for 15 h, the thiol-ene coupling reactions between styrene and aromatic thiols such as 2-phenylethyl mercaptan, 4-chlorophenethyl mercaptan and tert-butyl mercaptan gave the hydrothiolated products with moderate yields (49%-58%, Table 3, entries 1-3). The reaction between aliphatic thiols such as cyclohexyl mercaptan and 1-dodecanethiol and styrene also generate 2-(cyclohexylthio)ethyl benzene and 7

dodecyl (2-phenylethyl) sulfane in moderate to good yields (50%-63%, Table 3%/C9GC003288 entries 4-5). Thiophenols such as p-toluenethiol was also tolerated in this reaction protocol, with a yield of 61% to 2-phenylethyl 4-methylphenyl sulfide in 15 h (Table 3, entry 6). Aryl alkenes bearing both electron-donating and electron-withdrawing substituents as well as alkyl alkenes like cyclohexene also reacted with benzyl mercaptane to produce corresponding alkyl sulfides, although with lower yields (30%-59%, Table 3, entries 7-9).

Previous studies on light induced hydrothiolation reactions revealed that the formation of thiyl radical is involved.<sup>27-28</sup> Our previous studies on the photocatalytic splitting of thiols over PtS/ZnIn<sub>2</sub>S<sub>4</sub> nanocomposite also suggest the involvement of the photogenerated thiyl radicals. To elucidate the mechanism, the ESR of the reaction system was studied. The ESR of the irradiated reaction system containing ZnIn<sub>2</sub>S<sub>4</sub>, benzyl mercaptan and CH<sub>3</sub>OH in the presence of 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a trapping agent shows four typical signals for the DMPO-thiyl adducts, a confirmation of the formation of thiyl radicals in the reaction system (Figure 2).<sup>42</sup> The addition of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), a radical scavenger, into the reaction system, led to a significantly decreased yield (3%) to the benzyl styryl sulfide, suggesting that the thiyl radicals are indeed involved in the visible light initiated hydrothiolation reactions over ZnIn<sub>2</sub>S<sub>4</sub>.

Based on the above observations, a possible reaction mechanism for visible light initiated hydrothiolation reactions over ZnIn<sub>2</sub>S<sub>4</sub> was proposed (Scheme 1). When irradiated with visible light, electrons and holes are generated over ZnIn<sub>2</sub>S<sub>4</sub>. The photogenerated holes are reductively quenched by the thiols, generating thiyl radical cations (step 1), which followed by deprotonation to give thivl radicals (step 2). The as-formed thiyl radicals initiate the thiol-ene/thiol-yne coupling by addition to the alkynes/alkenes to generate alkene/alkyl radicals (step 3), which abstract protons from the un-reactive thiols to form the hydrothiolated products and produces thiyl radicals to propagate the radical reaction (step 4). A controlled experiment by carrying out the reaction in deuterated methanol under otherwise similar conditions gave the same benzyl styryl sulfide instead of the deuterated product, an evidence to prove that the origin of the proton is indeed from the thiol instead of methanol. As shown in the Scheme 1, although the light initiated hydrothiolation reactions over ZnIn<sub>2</sub>S<sub>4</sub> also contains a photoredox cycle for initiation of the thiyl radicals and the radical propagation cycle to generate the thiolated products, the generation of the thiyl 8

#### Green Chemistry

**Green Chemistry Accepted Manuscript** 

radicals is only required in the beginning of the reaction as evidenced from the almost watche online undetectable trace amount of hydrogen evolved in the system. Therefore, unlike that over TiO<sub>2</sub>-based system, only stoichiometric thiols are required in the thiol-ene and thiol-yne coupling reactions over  $ZnIn_2S_4$ , which not only reduce the cost, but also save the time required for the separation of the products. In addition, since bare TiO<sub>2</sub> only absorb weakly in the visible light, the visible light initiated hydrothiolation reactions over TiO<sub>2</sub> are only applicable to those substrates which can form surface complexes with TiO<sub>2</sub>. On the contrary,  $ZnIn_2S_4$  is well responsive in the visible light region. Therefore, the hydrothiolation reactions realized over  $ZnIn_2S_4$  can be applied to a wider range of substrate scopes.

To study the stability of  $ZnIn_2S_4$  for visible light initiated hydrothiolation reactions, the photocatalyst was centrifuged and filtered for a repeated use. It was found that  $ZnIn_2S_4$  was highly stable in the reaction between phenylacetylene and benzyl mercaptane. No obvious loss of its activity was observed after three cycling tests and the photocatalyst after three runs showed similar XRD patterns (Fig. 3 and Fig. 4).

### Conclusion

In summary, a general and efficient hydrothiolation of alkenes and alkynes can be realized over  $ZnIn_2S_4$  under visible light irradiation. The use of solar light and a semiconductor-based photocatalyst to realize the thiol-ene and thiol-yne coupling reactions in a green solvent (methanol), with only stoichiometric thiols required and applicable to a broad substrate scope, makes this reaction protocol to be a green, sustainable and cost-effectively strategy for the synthesis of thiolated products. This study also highlights the great potential of semiconductor-based photocatalysis for advanced organic syntheses.

#### Acknowledgements

This work was supported by NSFC (21872031, U1705251). Z. Li thanks the Award Program for Minjiang Scholar Professorship for financial support.

## References

Published on 21 March 2019. Downloaded by University of Western Ontario on 3/21/2019 1:33:28 AM

View Article Online DOI: 10.1039/C9GC00328B

- C. Shen, P. Zhang, Q. Sun, S. Bai, T. S. Andy Hor and X. Liu, *Chem. Soc. Rev.*, 2015, 44, 291-314.
- [2] A. D. Rodriguez and A. Nickon, Tetrahedron, 1985, 41, 4443-4448.
- [3] Z. Lian, B. N. Bhawal, P. Yu and B. Morandi, Science, 2017, 356, 1059-1063.
- [4] S. D. Timpa, C. J. Pell and O. V. Ozerov, J. Am. Chem. Soc., 2014, 136, 14772-14779.
- [5] N. Morita and N. Krause, Angew. Chem. Int. Ed., 2006, 45, 1897-1899.
- [6] R. Das and D. Chakraborty, Tetrahedron Lett., 2012, 53, 7023-7027.
- [7] T. Kondo, and T. Mitsudo, Chem. Rev., 2000, 100, 3205-3220.
- [8] C. F. Lee, Y. Liu and S. S. Badsara, Chem. Asian J., 2014, 9, 706-722.
- [9] R. Kumar, Saima, A. Shard, N. H. Andhare, Richa and A. K. Sinha, Angew. Chem. Int. Ed., 2015, 54, 1897-1899.
- [10] J. W. Chan, C. E. Hoyle and A. B. Lowe, J. Am. Chem. Soc., 2009, 131, 5751-5753.
- [11] L. Benati, L. Capella, P. C. Montevecchi and P. Spagnolo, J. Org. Chem., 1995, 60, 7941-7946.
- [12] N. Ten Brummelhuis, C. Diehl and H. Schlaad, *Macromolecules*, 2008, 41, 9946-9947.
- [13] K. Griesbaum, Angew. Chem. Int. Ed., 1970, 9, 273-287.
- [14] C. Cao, L. R. Fraser and J. A. Love, J. Am. Chem. Soc., 2005, 127, 17614-17615.
- [15] Y. Yang and R. M. Rioux, Chem. Commun., 2011, 47, 6557-6559.
- [16] Y. Yang and R. M. Rioux, Green Chem., 2014, 16, 3916-3925.
- [17] T. Bian, L. Shang, H. Yu, M. T. Perez, L.-Z. Wu, C.-H. Tung, Z. Nie, Z. Tang and T. Zhang, *Adv. Mater.*, 2014, 26, 5613-5618.
- [18] Y. Cao, W. Geng, R. Shi, L. Shang, G. I. N. Waterhouse, L.-Z. Wu, C.-H. Tung,
  Y. Yin and T. Zhang, *Angew. Chem., Int. Ed.*, 2016, 55, 14952-14957.
- [19] N. Xue, X. Kong, B. Song, L. Bai, Y. Zhao, C. Lu and W. Shi, *Sol. RRL*, 2017, 1, 1700029.
- [20] Y. Deng, Z. Li and H. Garcia, Chem. Eur. J., 2017, 23, 11189-11209.
- [21] X. Lang, W. Ma, C. Chen, H. Ji and J. Zhao, Acc. Chem. Res., 2014, 47, 355-363.
- [22] G. Zhao, S. Kaur and T. Wang, Org. Lett., 2017, 19, 3291-3294.
- [23] O. O. Fadeyi, J. J. Mousseau, Y. Feng, C. Allais, P. Nuhant, M. Chen, B. Pierce,

R. Robinson, Org. Lett., 2015, 17, 5756-5759.

- [24] A. B. Lowe, C. E. Hoyle and C. N. Bowman, J. Mater. Chem., 2010, 20, 4745-4750.
- [25] E. L. Tyson, M. S. Ament and T. P. Yoon, J. Org. Chem., 2013, 78, 2046-2050.
- [26] M. H. Keylor, J. E. Park, C. J. Wallentin and C. R. Stephenson, *Tetrahedron*, 2014, **70**, 4264-4269.
- [27] S. S. Zalesskiy, N. S. Shlapakov and V. P. Ananikov, Chem. Sci., 2016, 7, 6740-6745.
- [28] V. T. Bhat, P. A. Duspara, S. Seo, N. S. B. Abu Bakar and M. F. Greaney, *Chem. Commun.*, 2015, **51**, 4383-4385.
- [29] F. Parrino, A. Ramakrishnan and H. Kisch, Angew. Chem. Int. Ed., 2008, 47, 7107-7109.
- [30] C. Vila and M. Rueping, Green Chem., 2013, 15, 2056-2059.
- [31] M. Hojamberdiev, Y. Cai, J. J. M. Vequizo, M. M. Khan, R. Vargas, K. Yubuta, A. Yamakata, K. Teshima and M. Hasegawa, *Green Chem.*, 2018, 20, 3845-3856.
- [32] M. Wang, L. Li, J. Lu, N. Luo, X. Zhang and F. Wang, Green Chem., 2017, 19 5172-5177.
- [33] N. S. Chaudhari, A. P. Bhirud, R. S. Sonawane, L. K. Nikam, S. S. Warule, V. H. Rane and B. B. Kale, *Green Chem.*, 2011, 13, 2500-2506.
- [34] L. Ye and Z. Li, ChemCatChem, 2014, 6, 540-2543.
- [35] L. Wei, Y. Chen, Y. Lin, H. Wu, R. Yuan and Z. Li, *Appl. Catal. B: Environ.*, 2014, 144, 521-527.
- [36] B. Wang, Z. Deng, X. Fu, C. Xu and Z. Li, *Appl. Catal. B: Environ.*, 2018, 237, 970-975.
- [37] Q. Li, C. Cui, H. Meng and J. Yu, Chem. Asian J., 2014, 9, 1766-1770.
- [38] L. Shang, C. Zhou, T. Bian, H. Yu, L.-Z. Wu, C.-H. Tung and T. Zhang, J. Mater. Chem. A., 2013, 1, 4552-4558.
- [39] L. Xu, X. Deng and Z. Li, Appl. Catal. B: Environ., 2018, 234, 50-55.
- [40] Y. Gao, H. Lin, S. Zhang and Z. Li, RSC Adv., 2016, 6, 6072-6076.
- [41] L. Ye, J. Fu, Z. Xu, R. Yuan and Z. Li, ACS Appl. Mater. Inter., 2014, 6, 3483-3490.
- [42] S. Pou and G. M. Rosen, J. Chem. Soc., Perkin Trans. 2, 1998, 0, 1507-1512.

# **Captions for Figures**

View Article Online DOI: 10.1039/C9GC00328B

Fig. 1 (a) XRD diffraction pattern, (b) SEM image, (c) UV-visible absorption spectrum of  $ZnIn_2S_4$ .

Fig. 2 DMPO spin-trapping ESR spectra of the reaction system containing  $ZnIn_2S_4$ , benzyl mercaptan and  $CH_3OH$  (a) in the dark; (b) under visible light irradiation.

Fig. 3 Cycling of the hydrothiolation reaction between phenylacetylene and benzyl mercaptane over  $ZnIn_2S_4$  under visible light irradiation.

Fig. 4 XRD diffraction patterns of (a) fresh  $ZnIn_2S_4$ ; (b) used  $ZnIn_2S_4$  (after three cycling reactions).

# **Caption for Scheme**

Scheme 1 Proposed mechanism for visible-light-initiated hydrothiolation of alkenes and alkynes reaction over  $ZnIn_2S_4$ .

# **Captions for Tables**

Published on 21 March 2019. Downloaded by University of Western Ontario on 3/21/2019 1:33:28 AM.

**Table 1** Light initiated reaction between phenylacetylene and benzyl mercaptane over $ZnIn_2S_4$  under different conditions.

**Table 2** Investigation of the substrate scope of visible-light-initiated hydrothiolationof alkynes over  $ZnIn_2S_4$ .

**Table 3** Investigation of the substrate scope of visible-light-initiated hydrothiolationof styrene over  $ZnIn_2S_4$ .



•

**Green Chemistry Accepted Manuscript** 

View Article Online DOI: 10.1039/C9GC00328B



Published on 21 March 2019. Downloaded by University of Western Ontario on 3/21/2019 1:33:28 AM.

•

**Green Chemistry Accepted Manuscript** 



•

**Green Chemistry Accepted Manuscript** 





`

Scheme 1

•

View Article Online DOI: 10.1039/C9GC00328B



**Green Chemistry Accepted Manuscript** 

Table 1								
		+ SH 2a	ZnIn <sub>2</sub> S <sub>4</sub>	3a				
	Entw	Salvant	$C_{onv}(9/)a =$	Yield (%) <sup>b</sup>				
	Entry	Solvent	Conv (76)* —	3a				
	1	CH <sub>3</sub> CN	80	75				
	2 °	CH <sub>3</sub> CN	0	0				
	3 d	CH <sub>3</sub> CN	trace	trace				
	4	Toluene	67	62				
	5	Et <sub>2</sub> O	73	69				
	6	i-PrOH	81	78				
	7	CH <sub>3</sub> OH	94	90				

Conditions: 1a (0.12 mmol), 2a (0.1 mmol),  $ZnIn_2S_4$  (10 mg), solvent (4mL), visible light irradiation for 15h; <sup>a</sup> conv was calculated based on 2a; <sup>b</sup> The amount of the products was calculated based on GC analyses, <sup>c</sup> No catalyst, <sup>d</sup> Without light.

•

Published on 21 March 2019. Downloaded by University of Western Ontario on 3/21/2019 1:33:28 AM.

View Article Online DOI: 10.1039/C9GC00328B

`

View Article Online DOI: 10.1039/C9GC00328B

$R^1 \longrightarrow R^2 - SH \xrightarrow{ZnIn_2S_4} R^1 \xrightarrow{R^2} R^2$							
Entry	Alkenes	Thiols	Vinyl sulfides	Yield (%) <sup>a, b</sup>			
1		2a	s s s	92			
2		2a		81			
3	Br	2a	Br	73			
4	ОН	2a	OH S	58			
5	1a	SH SH		93			
6	1a	CI	S S S C	82			
7	1a	SH		61			
8	1a	⊖SH	© <sup>∞s</sup> ⊖	95			
9	1a	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>11</sub> SH	S (CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub>	56			
10	1a	SH	S S	70			
11	1a	HS		51			

Conditions: alkynes (0.12 mmol), thiols (0.1 mmol),  $ZnIn_2S_4$  (10 mg),  $CH_3OH$  (4mL), visible light irradiation for 15h; <sup>a</sup> conv was calculated based on thiols; <sup>b</sup> The amount of the products was calculated based on GC and GC-MS.

Table 3

Published on 21 March 2019. Downloaded by University of Western Ontario on 3/21/2019 1:33:28 AM.

View Article Online DOI: 10.1039/C9GC00328B



Conditions: styrene (0.12 mmol), thiols (0.1 mmol),  $ZnIn_2S_4$  (10 mg),  $CH_3OH$  (4mL), visible light irradiation for 15h; <sup>a</sup> conv was calculated based on thiols; <sup>b</sup> The amount of the products was calculated based on GC and GC-MS.

**Green Chemistry Accepted Manuscript**