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## Metal–organic framework MOF-199-catalyzed direct and one-pot synthesis of thiols, sulfides and disulfides from aryl halides in wet polyethylene glycols (PEG 400)

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#### ABSTRACT

A highly porous metal–organic frame work Cu<sub>3</sub> BTC<sub>2</sub> (copper(II)benzene-1,3,5-tricarboxylate) that is known as MOF-199 was synthesized from the reaction of 1,3,5-benzenetricarboxylic acid and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O by a solvothermal method and characterized by several techniques including FT-IR, XRD, EDX and scanning electron microscopy. The MOF-199 used as an efficient catalyst for one-pot synthesis of thiols by domino reactions of aryl halides and thiourea, and subsequently conversion to aryl alkyl sulfides and diaryl disulfides in polyethylene glycols (PEGs). A variety of aryl alkyl sulfides can be obtained in good to excellent yields in a relatively short reaction time and in the presence of the trace amount of catalyst. Also, the catalyst can be separated from the reaction mixture by decanting, and be reused without significant degradation in catalytic activity.



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Metal–organic framework; 1,3,5-benzenetricarboxylic acid; Cu(OAc)<sub>2</sub>·H<sub>2</sub>O; aryl alkyl sulfides; polyethylene glycols

## Introduction

Organosulfurs are important compounds that exist widely in many biologically and pharmaceutically active molecules [1,2]. Especially, aryl alkyl thioether moieties have been used in the treatment of diseases such as Parkinson's, Alzheimer's, immune and inflammatory, diabetes, and HIV [3,4].

The formation of carbon–sulfur bonds have been widely examined and generally transition-metal-catalyzed coupling have been used for its formation [5–7]. For the first time, Migita et al. [8] reported carbon–sulfur bond formation by reaction between thiol and aryl halide in the presence of Pd (PPh<sub>3</sub>)<sub>4</sub> as a catalyst. In recent years palladium, nickel,

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cobalt, copper and iron salts have been used as catalysts for carbon–sulfur bond formation [9–13]. However, due to some disadvantages such as the use of specially designed ligands, high-temperature, high amount of metal catalyst and harmful organic solvents, a search to find better catalysts has been undertaken [14].

Recently, for the sustainable development of any catalytic process, heterogeneous catalysts have been highly employed for chemical transformations because of their ease of recovery, recycling that decreases undesired toxic wastes, and E-factor [15].

The direct use of volatile thiols is a common synthetic method for synthesis of organosulfur compounds [16]. However, the use of toxic, odorous and volatile thiols is considered a disadvantage of this method. To overcome these difficulties, attention has been directed toward the synthesis of organosulfur compounds using sulfur-transfer reagents instead of thiols [17–19]. Among these reagents, thiourea is used as an inexpensive, non-toxic, odorless, commercial available and eco-friendly *in situ* S-source to produce aryl (alkyl) thiolate in synthetic reactions [20–22].

In continuation of our efforts on the synthesis of organosulfur compounds [23–27], we wish to report the utilization of an efficient heterogeneous copper-based catalyst without the assistance of any ligands for the synthesis of aryl alkyl sulfides.

During the last decade, metal–organic frameworks (MOFs) have been widely investigated as exquisite materials due to their potential applications in several fields [28–31]. Because of the presence of both organic and inorganic parts in these porous materials, MOFs show several benefits such as high surface areas, tuneable pore sizes, processing facility, flexibility and structural diversity [32–35]. In catalysis processes, MOFs have been used as solid catalysts or catalyst support for wide ranges of organic transformations [36]. Specifically, microporous Cu<sub>3</sub>BTC<sub>2</sub> (copper (II)-benzene-1,3,5tricarboxylate) is a copper-based MOF that was first reported in 1999 by Williams and co-workers [37] and also named as HKUST-1. Furthermore, the MOF described herein, namely MOF-199, has been employed widely as heterogeneous catalyst for Friedel–Crafts alkylation and acylation, oxidation, alkene epoxidation, hydrogenation, Suzuki cross-coupling, Knoevenagel condensation, aldol condensation and aza-Michael condensation [38–44].

In this paper, we report, for the first time, the application of a recoverable and reusable nanoporous metal–organic framework (MOF-199) as an efficient heterogeneous catalyst for the synthesis of aryl alkyl sulfides without the need for addition of external ligand other than the effect imparted by PEG (400) as a green solvent and eco-friendly media. High yields were obtained and the MOF-199 catalyst was easily isolated from the reaction mixture by simple filtration and reused without significant degradation in activity (Scheme 1).





### **Results and discussion**

To start to optimize the reaction conditions such as amount of catalyst, temperature, type and amount of base and type of solvent, initially, the reaction between iodobenzene, thiourea and benzyl chloride in the presence MOF-199 as a catalyst, KOH as a base in wet PEG (400) at 130°C under an inert atmosphere was studied as a model reaction for the synthesis of unsymmetrical sulfides (Scheme 2).

The reaction was carried out in two steps: in the first step, potassium benzene thiolate was generated and synthesized by a domino reaction of phenyl iodide (1 mmol) with thiourea (3 mmol) in the presence of 4 mg of MOF-199 and 3 mmol of KOH at 130°C under an N<sub>2</sub> atmosphere. In the second step, benzyl chloride (1.1 mmol) was added into the reaction mixture for the synthesis of benzyl phenyl sulfides. (Scheme 2, Table 1). According to the results shown in Table 1, by employing 3 mg of catalyst, a conversion of 61% was achieved after 13.5 h for both steps. When the amount of MOF was increased to 4 mg, the yield of product (benzyl phenyl sulfide) increased to 96% after 4.5 h for both steps (Table 1, entries 2–4). Then, in studies that screened the effect of solvent on the progress of reaction, wet PEG (400) was found most effective than other examined solvents including dimethyl formamide (DMF), toluene, ethanol and water (Table 1, Entries 3, 5–8).

Temperature effects on the rate of reaction were studied. The reaction was carried out at 100°C, 115°C and 130°C, respectively. It was found the increase in temperature up to 130°C led to an increased yield and rate of the reaction (Table 2, entries 1–4). Also, influence of the base identity and amount on the progress of reaction was examined. KOH with 3 mmol was found to impart a strong effect on the reaction yields (Table 2, entries 5–10). Furthermore, the reaction did not proceed in the absence of a base.

After the optimized reaction conditions were established, a variety of aryl and alkyl halides were examined to explore the scope of this reaction. It can be seen from Table 3 that both bromo and iodo aryl halides could be transformed into corresponding product quite efficiently. Iodo aryl compounds are similarly effective and produced desired products under the optimized reaction conditions (Table 3). Interestingly, good yields were observed

PhI + thiourea 1 2 I) MOF-199, base Solvent, Temp °C, N<sub>2</sub>, 3h II) PhCH<sub>2</sub>Cl (3) II) PhCH<sub>2</sub>Cl (3) II) PhCH<sub>2</sub>Cl (3)

Scheme 2. Reaction for optimization of condition of reaction.

Entry	Solvent	Amount of MOF-199 (mg)	Time (h)	Yield (%)
1	PEG	_	24	N. R
2	PEG	3	13.5	61
3	PEG	4	4.5	96
4	PEG	5	4.5	96
5	DMF	4	16	75
6	Toluene	4	24	30
7	Ethanol	4	24	Trace
8	Water	4	24	Trace

Table 1. Optimization of the reaction conditions.<sup>a</sup>

<sup>a</sup>Reaction conditions: Phl (1.0 mmol), thiourea (3 mmol), KOH (3 mmol), benzyl chloride (1.1 mmol), at 130°C under N<sub>2</sub>.

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Entry	Temp. (°C)	Amount of base (mmol)	Time (h) both step	Yield (%)	
1	25	KOH (3)	24	Trace	
2	80	KOH (3) 24		56	
3	115	KOH (3)	24	75	
4	130	KOH (3)	4.5	96	
5	130	_	24	N. R. <sup>b</sup>	
6	130	KOH (1)	24	Trace	
7	130	KOH (2)	4.5	56	
8	130	KOH (4) 4.5		95	
9	130	$KF/AI_2O_3$ (3)	24	66	
10	130	K <sub>2</sub> CO <sub>3</sub> (3)	24	53	

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<sup>a</sup>Reaction conditions: PhI (1.0 mmol), thiourea (3 mmol), MOF (4 mg), benzyl chloride (1.1 mmol), in 2 ml PEG/H<sub>2</sub>O (20:1) and under N<sub>2</sub>.

<sup>b</sup>No reaction.

 Table 3. MOF-199 catalyzed; the direct synthesis of unsymmetrical sulfides from aryl halides and alkyl halides.

Entry	ArX	RX	Product	Time (h)	Yield (%)
1	PhI	PhCH <sub>2</sub> Cl	5a	1.5	96
2	PhI	Ph(CH <sub>2</sub> ) <sub>2</sub> Br	5b	3	84
3	PhI	Ph(CH <sub>2</sub> ) <sub>3</sub> Br	5c	2	80
4	PhI	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> Br	5d	4	90
5	PhI	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>7</sub> Br	5e	4	87
6	2-MePh-I	PhCH <sub>2</sub> Cl	5f	1.5	90
7	2-MePh-I	Ph(CH <sub>2</sub> ) <sub>2</sub> Br	5g	3	85
8	2-MePh-I	Ph(CH <sub>2</sub> ) <sub>3</sub> Br	5ĥ	4	80
9	4-MePh-I	PhCH <sub>2</sub> Cl	5i	4	86
10	4-MePh-I	$Ph(CH_2)_2Br$	5j	5	82
11	4-MePh-I	Ph(CH <sub>2</sub> ) <sub>3</sub> Br	5k	7	77
12	4-CF <sub>3</sub> Ph-Br	PhCH <sub>2</sub> Cl	51	5.5	91
13	4-CF <sub>3</sub> Ph-Br	$Ph(CH_2)_2Br$	5m	6.5	84
14	4-CF <sub>3</sub> Ph-Br	Ph(CH <sub>2</sub> ) <sub>3</sub> Br	5n	8	80
15	1-Naphthyl-I	PhCH <sub>2</sub> Cl	50	4	93
16	1-Naphthyl-I	Ph(CH <sub>2</sub> ) <sub>3</sub> Br	5р	5	84
17	1-Naphthyl-I	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> Br	5q	5	73

Note: The products were identified by spectroscopic techniques NMR, GC-Mass spectral data and melting points and comparison to authentic samples [45].

ArX + 3 thiourea 
$$\frac{\text{MOF-199, KOH}}{\text{PEG, N}_2, 130 \text{ °C}} \left[ \text{ArS K} \right] \frac{\text{RX (4)}}{1.5 - 8 \text{ h}} \text{ ArSR}$$
1 2 3h 3 5

Scheme 3. Synthesis of asymmetrical sulfides catalyzed by MOF-199.

in the case of *p*-trifluoromethyl bromobenzene reactions with alkyl halides (Table 3, entry 11–13). The first alkyl halides tested worked well with this procedure, however, benzyl chloride was found more reactive than other used alkyl halides (Scheme 3).

As expected, the reaction takes place in two steps via a thiolate  $(ArS^-K^+)$  intermediate. In order to isolate aryl thiols, reaction of aryl iodides with thiourea under optimized reaction conditions were investigated. After completion of reactions (3 h), the reactions mixtures were neutralized with acidic solution (HCl 10%) and thiol derivatives were isolated and characterized (Scheme 4). In this procedure, only aryl thiols were observed and



Scheme 4. Synthesis of aryl thiols, catalyzed by MOF-199.



Scheme 5. Synthesis of symmetrical diaryl disulfides catalyzed by MOF-199.

isolated in PEGs. While, as shown in Table 1, with this procedure benzyl phenyl sulfides were obtained in DMF and Toluene in 75% and 30% yields, respectively; without observation and separation of thiols as intermediates.

This procedure also was successfully examined with regard to synthesis of symmetrical diaryl disulfides from aryl halides under optimized reaction conditions. Symmetrical diaryl disulfides were prepared from aryl halides after self-oxidation of thiolates (intermediates) at long reactions time (20 h; Scheme 5).

## **Catalytic studies**

#### Synthesis and characterization of MOF-199

In this work, the MoF-199 was prepared via a solvothermal method using copper (II) acetate monohydrate and 1,3,5-benzenetricarboxylic acid in DMF [46].

The material was then characterized using a variety of different techniques; results were in good agreement with the literature [47]. The (FT-IR) spectra (Figure 1(a)) exhibited characteristic peak due to the water molecules at wave number  $3446 \text{ cm}^{-1}$ . Carbonyl group of benzenetricarboxylic acid and the double bonds of benzene were resonated at 1625 and 1444 cm<sup>-1</sup>, respectively.

The synthesized MoF-199 were analyzed by using energy-dispersive EDX (Figure 1(b)). As shown in Figure 1(b), the characteristic peak of Cu showed well that the organic framework was successfully incorporation with Cu metal the crystallinity of the MOF-199 was

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Figure 1. (a) FT-IR spectra for the MOF-199, (b) EDX spectrum of the MOF-199, (c) X-ray powder diffractogram for the MOF-199 and (d) SEM micrograph for the MOF-199.

Catalyst	Cul	Cu <sub>2</sub> O	CuCl <sub>2</sub>	Cu(OAc) <sub>2</sub>	MOF-199
Yield (%)	63	48	71	76	96
Time (h)	24	24	24	24	4.5

 Table 4. Comparison of catalysts activity in sulfide synthesis.

examined by powder X-ray diffraction (XRD) (Figure 1(c)). The strong and sharp reflection peaks in XRD pattern prove the crystalline nature of the prepared MoF nanoparticles. Also, the morphology of the MoF-199 was investigated by scanning electron microscopy (SEM, Figure 1(d)).

To confirm the advantage of MoF-199 as heterogeneous catalyst rather than usual copper salts for the synthesis of unsymmetrical sulfides from aryl halides and alkyl halides, to mixture of iodobenzene (1 mmol), thiourea (3 mmol), KOH (3 mmol) and 1.1 mmol of benzyl chloride was added 10 mol% copper salts such as CuI, CuCl<sub>2</sub>, Cu<sub>2</sub>O and Cu (OAc)<sub>2</sub> (Table 4). After the completion of these reactions, we obtained benzyl phenyl sulfide with yields 63%, 48%, 71% and 76% using CuI, Cu<sub>2</sub>O, CuCl<sub>2</sub> and Cu (OAc)<sub>2</sub> in 24 h, respectively. Also, Notably, Firouzabadi and co-workers [20] previously employed CuI as catalyst for the same reaction with K<sub>2</sub>CO<sub>3</sub> and PEG under N<sub>2</sub> and afforded 80 yield of benzyl phenyl sulfide in 24 h. This result shows that MOF-199 is an effective catalyst for the synthesis of unsymmetrical sulfides compared with homogeneous copper catalysts.

The reusability of catalysts is an important advantage in modern catalyst research. Thus we have studied the possibility of recycling of the catalyst in the reaction of iodobenzene with benzyl chloride and thiourea in polyethylene glycol. Figure 2 shows the yield of five consecutive cycles for the preparation of unsymmetrical sulfide. At the end of the process, the catalyst was separated from the reaction mixture by simple decantation, and then washed with copious amounts of *n*-hexane to remove any physisorbed reagents. The sample was dried at 160°C for 3 h. Then, fresh substrate was added to the recovered MoF-199 catalyst without any activation and employed for the next reaction. The catalytic activity was studied for five successive times and it showed a similar activity (Figure 2).



**Figure 2.** Catalyst recycling studies. Reaction conditions: (a) PhI (1.0 mmol), MOF-199 (4 mg), thiouea (3 mmol), KOH (3 mmol), benzylchloride (1.1 mmol), temp. 130°C in 2 ml PEG/H<sub>2</sub>O (20:1) under N<sub>2</sub>.



Figure 3. X-ray powder diffractogram of (a) MoF-199 and (b) recovered MOF-199.



Figure 4. FT-IR spectra of (a) MoF-199 (b) recovered MOF-199.

To confirm the recoverability and reusability of the MOF-199 in the benzyl phenyl sulfide reaction, the nature of the recovered catalyst was investigated by FT-IR and XRD pattern (Figures 3 and 4). FT-IR and XRD pattern of recovered catalyst show that the catalyst can be recycled five times with maintain its crystallinity and structure during the course of the reaction.

## **Conclusions**

In conclusion, in this article we have employed a recyclable, porous catalyst for one-pot synthesis of unsymmetrical sulfides and symmetrical diaryl disulfides. The catalyst was also

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successfully applied for isolation of aryl thiols as an intermediate in the first step in PEG. The use of a small amount of catalyst, easily available reagents, ligand-free reaction conditions, a faint odor procedure, short reaction times and high yields are the main advantages of this procedure.

## **Experimental**

## Synthesis of MOF-199

For the synthesis of MoF-199, Benzenetricarboxylic acid (500 mg, 2.38 mmol) was dissolved in 12 ml of *N*,*N*-dimethylformamide (DMF),  $C_2H_5OH$  and  $H_2O$  (with ratio DMF: $C_2H_5OH$  :  $H_2O = 1:1:1$ ) next a mixture of Cu (OAc)<sub>2</sub>· $H_2O$  (860 mg, 4.31 mmol) in 12 ml of the same solvent was added and the resulting mixture stirred. Then, Triethylamine (0.5 ml) was added to the reaction mixture, which was stirred for 24 h. The product was collected by filtration, washed twice with DMF (25 ml) and finally dried.

## Unsymmetrical sulfides synthesis; typical experimental procedure

MOF-199 (4 mg) were added to solution of iodobenzene (1.0 mmol), thiourea (0.228 g, 3.0 mmol) and KOH (0.168 g, 3 mmol) in 2 ml PEG/H<sub>2</sub>O (20:1). The reaction continued at 130°C under N<sub>2</sub> conditions until production of thiolate salt as intermediate after 3. Then 1.1 mmol benzylchloride was added to mixed reaction and the reaction continued at 130°C under atmospheric conditions. After completion of the reaction [about 10 h; TLC (EtOAc/hexane, 1:20) monitoring. CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added and the mixture was washed with H<sub>2</sub>O (2 × 15 ml). The combined organic fractions dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated under reduced pressure. The residue was purified by preparative chromatography [silica gel, hexane/EtOAc, 20:1] to give the product.

## The synthesis of arylthiols: typical experimental procedure

A mixture of iodobenzene (1.0 mmol), thiourea (0.228 g, 3.0 mmol), KOH (0.168 g, 3 mmol) and MOF-199 (4 mg) was added to a flask containing 2 ml PEG/H<sub>2</sub>O (20:1). The reaction continued at 130°C under N<sub>2</sub> conditions until production of thiolate salt as intermediate after 3 h. After cooling and neutralizing reaction mixture by adding acidic solutions (10 ml, HCl 10%), CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was added to mixture. Then organic layer was removed and evaporated to give the crude product, which was purified by preparative chromatography (silica gel, *n*-hexane–ethyl acetate, 20:1).

## Symmetrical diaryl disulfides synthesis: general experimental procedure

The prepared catalyst (4 mg) was added to a mixture of aryl halide (1.0 mmol), thiourea (0.228 g, 3.0 mmol) KOH (0.168 g, 3.0 mmol) in 2 ml PEG/H<sub>2</sub>O (20:1) at 130°C under atmospheric conditions until completion (20 h). The progress of the reaction was monitored by TLC. After removal of solvent, the residue was purified by chromatography (SiO<sub>2</sub>; hexane/AcOEt 20: 1) to give the crude diaryl disulfides.

## **Disclosure Statement**

No potential conflict of interest was reported by the authors.

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