



The Direct Synthesis of Organic Disulfides/ Diselenide from Aryl Halides; Catalysed by Metal-Organic Framework MOF-199

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Complete List of Authors:	Soleiman Beigi, Mohammad; Ilam University, chemistry Yavari, Issa; Tarbiat Modares university, chemistry sadeghizadeh, fatemeh; ilam university, chemistry
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ARTICLE

The Direct Synthesis of Symmetrical Disulfides and Diselenides by Metal-Organic Framework MOF-199 as an Efficient Heterogenous Catalyst

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Mohammad Soleiman-Beigi,^{* a} Issa Yavari,^b Fatemeh Sadeghizadeh^a

A highly crystalline porous copper-based metal-organic framework MOF-199 was synthesized, and characterized by several techniques, including (XRD), (EDX), (SEM), (FT-IR). The MOF-199 was used as an efficient catalyst for the one-pot and efficient synthesis of organic dichalcogenides from aryl halides (-OTs) and elemental sulfur and selenium in Polyethylene glycols (PEGs). A variety of disulfides and diselenides can be obtained in good to excellent up to 98% in relatively short time reaction.

INTRODUCTION

disulfides and diselenides are important synthetic intermediates¹ and have been studied as essential moieties of Pharmaceutically and biologically active compounds.² For example disulfide bonds have been employed in stabilization of peptides in proteins,³ DNA cleaving⁴ and design of drug delivery systems.⁵ also diselenides have been applied as antioxidant,⁶ anti-ulcer⁷ and anti-inflammatory.⁸ Traditional methods for preparation of organic diselenide include oxidation of selenoles,⁹ reaction of alkali metal diselenide with different electrophiles¹⁰ and reduction of selenocyanates.¹¹ recently, the copper-catalyzed and iron catalyzed reactions of aryl halides with selenium have been introduced as new methods for synthesis of this material.¹² However, some disadvantages such as the use of particularly designed ligands, expensive reagents and long reaction time, limited the scope of their applications.¹³ classical method of disulfide bonds formation is the oxidative coupling of thiols.¹⁴ Although these method is very efficient, employment of thiols for the synthesis is often very annoying, because thiols are toxic, odorous, and volatile. To overcoming these difficulties, the direct synthesis of disulfides by coupling reaction of different sulfur transfer reagent with arylhalide have been increased,¹⁵ but among these sulfur transfers, S-arylation from sulfur powder, due to its only faint odor and inexpensive price, shows especial promise.¹⁶ In continuation of our efforts on the synthesis of organosulfur compounds and for the development simple and safe processes for direct synthesis of symmetric diary disulfides and diaryl diselenide.¹⁷

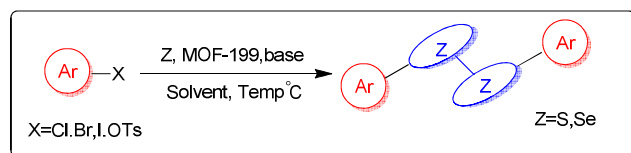
We wish to report the utilization of efficient heterogeneous copper-based catalyst without the assistance of any ligands for the preparation of disulfides and diselenides.

Metal-organic frameworks (MOFs) have recently aroused much attention as a new category of nanoporous material that can be built by metal node with copolymerization of organic molecules as linkers.¹⁸ Due to the unique properties of such as extraordinary high surface, well-defined structure, tunable pore size, high absorption capacity and structural diversity, MOFs have a wide range of potential uses in several fields.¹⁹ among the applications of MOFs, using MOFs as solid catalysts or catalyst supports for a variety of chemical conversions is very attractive.²⁰ Specifically, Microporous CuBTC (copper(II)-benzene-1,3,5-tricarboxylate) is one of the best-studied MOFs whose the first sample has been reported in 1999.²¹ then this MOF that namely MOF-199 has been employed widely as heterogenous catalyst for the the aza-Michael reaction,^{22a} quinoline synthesis^{22b} the oxidation of the esterification reaction,^{22c} ring opening of epoxides with methanol,^{22d} α -pinene oxide rearrangement,^{22e} and the three-component couplings of amines, aldehydes and alkynes to propargylamines.^{22f} In this work, we describe for the first time a method for the direct, efficient and highly chemoselective synthesis of symmetric diary disulfides and diaryl diselenide from their corresponding aryl halides with elemental S or Se by the use of a few amount of a highly porous MOF-199 and without need to ligand, High activity was observed, and the MOF-199 catalyst was easily isolated from the reaction mixture by simple filtration and reused without significant degradation in activity. also for the development of greener processes, we use of Polyethylene glycols (PEGs) as solvent reaction that have negligible vapour pressure, are cheap, nontoxic, thermally stable, eco-friendly (scheme 1).

^a Conclusions Chemistry Departement, Ilam University, PO Box 69315-516, Ilam, Iran. E-mail: SoleimanBeigi@yahoo.com

^b Chemistry Department, Tarbiat Modares University, PO Box 14115-175, Tehran, Iran Address here. Fax +98(21)82883455; E-mail: yavarisa@modares.ac.i

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scheme 1

As shown in Table 2, selenium is more reactive than sulphur under the mentioned conditions so this reaction proceeded with 1:1 ratio of arylhalide and selenide.

RESULTS AND DISCUSSION

To find the optimal reaction conditions in terms of temperature, type of base, amount of base, amount of catalyst, time and solvent ratio, initially, the reaction between iodobenzene and elemental sulphur powder in the presence MOF-199 as a catalyst, NaOH as a base in DMF at 130 was selected as a model for the synthesis of symmetrical disulfides (Table 1, entry 1).

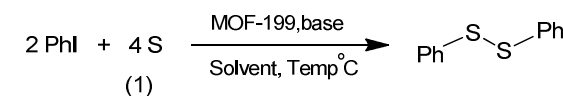
Changing the solvent to PEG led to good yields and short time, but the use of other solvents including Toluene, EtOH, H₂O, resulted in significantly reduced yields (Table 1, Entries 2-5). Then the amount of MOF-199 was controlled; diphenyl disulphide was obtained in 98% yield with 10 mg of catalyst, but increasing amount of catalyst more than 10 mg has not been perceptible alteration in the progress of reaction (Table 1, Entries 6-10). The reaction did not proceed in the absence of a base, also among the bases tested, KOH with amount of 4 mmol showed a superior effect on the reaction yields (Table 1, Entries 11-17), finally, different temperatures were evaluated and it was found that increase of temperature up to 130 led to increase yield and rate of the reaction (Table 1, Entries 18-21).

After the optimized reaction conditions were established, a large number of aryl halides (Ar-X) was examined to explore the scope of this reaction. As summarized in Table 2, aryl iodides and aryl bromides were converted into the corresponding diaryl disulfides in higher yields than their chloro and tosylate analogues. The results show that the aryl halide derivatives with different functional groups, such as CH₃, OCH₃, NO₂, Br, Cl provide good to excellent yields, although in most cases, yields in the presence of electron-withdrawing substituents were higher than electron-donating substituents. For instance, 4-nitro-bromobenzene afforded disulfide **3m** in 64% yield and 3 hours, while 84% and 67% yields were obtained in the case of 4-methoxyiodobenzene and 2-methoxyiodobenzene after 24 hours, respectively (Table 2, Entries 11 and 12). Symmetrical diheteroaryl disulfides were well synthesized from the corresponding heteroaryl iodides, bromides and chlorides (Table 2, Entries 8-10). In addition, the reaction was carried out with high chemoselectivity and single products were selectively obtained from reaction substrates with two halide groups (Table 2, Entries 15,16).

Also, this protocol efficiently generated symmetric diaryl diselenides in the optimal conditions, a range of these materials were obtained with aryl halide (2 mmol), elemental selenide (2 mmol) in the presence of MOF-199 (10 mg), NaOH (4 mmol) and in PEG at 130 °C under normal atmospheric conditions (Table 2).

The results show that the aryl halide derivatives with different functional groups were converted into the corresponding diselenides (**4a-4p**) in 67% to 98% yields, and it indicated functional group tolerance in the reaction conditions (Table 2, Entry 17-32).

Table 1. Optimization of the reaction conditions^a.



Entry	solvent	Time(h)	Yield(%)
1	DMF	10	94
2	PEG	6	98
3	Toluene	24	trace
4	etanol	24	trace
5	H ₂ O	24	trace

^aReaction conditions: PhI (2.0 mmol), MOF-199 (8 mg), S (1) (4 mmol), KOH (4 mmol), temp 130 °C, in 2 mL solvent. and under air

Entry	MOF-199(mg)	Time(h)	Yield(%)
6	4	16	92
7	6	10	96
8	8	8	95
9	10	6	98
10	12	6	97

^aReaction conditions: PhI (2.0 mmol), S (1) (4 mmol), KOH (4 mmol), temp 130 °C, in 2 mL PEG/H₂O (20:1) and under air

Entry	Base	Amount of base (mmol)	Yield(%)
11	-	-	NO
12	KOH	1	trace
13	KOH	2	56
14	KOH	4	98
15	KOH	8	98
16	KF/Al ₂ O ₄	4	45
17	K ₂ CO ₃	4	22

^aReaction conditions: PhI (2.0 mmol), MOF-199 (10 mg), S (1) (4 mmol), temp 130 °C, in 2 mL PEG/H₂O (20:1), under air and 6h

Entry	temp °C	Time(h)	Yield(%)
18	25	24	trace
19	80	24	67
20	110	24	84
21	130	6	98

^aReaction conditions: PhI (2.0 mmol), MOF-199 (10 mg), S (1) (4 mmol), KOH (4 mmol), in 2 mL PEG/H₂O (20:1) and under air

Table 2. Screening of different substrates

Entry	Ar-X	Z	Product	Time(h)	Yield(%)
1	PhI	S	3a	6	98
2	PhBr	S	3b	7.5	95
3	PhOTs	S	3c	18	92
4	PhCl	S	3d	22	87
5	<i>o</i> -MePh-I	S	3e	5.5	96
6	1-Iodonaphthalene	S	3f	6.5	97
7	1-Bromonaphthalene	S	3g	11	90
8	2-Iodothiophene	S	3h	8	86
9	2-Bromothiophene	S	3i	9	80
10	2-Chlorothiophene	S	3j	10.5	73
11	<i>p</i> -MeOPh-I	S	3k	24	84
12	<i>o</i> -MeOPh-I	S	3l	24	67
13	<i>p</i> -NO ₂ Ph-Br	S	3m	3.5	64
14	<i>p</i> -MePh-Br	S	3n	10	85
15	<i>p</i> -BrPh-I	S	3o	5	96
16	<i>p</i> -ClPh-Br	S	3p	8.5	83
17	PhI	Se	4a	5	98
18	PhBr	Se	4b	6.5	96
19	PhCl	Se	4c	16	94
20	PhOTs	Se	4d	19	85
21	<i>o</i> -MePh-I	Se	4e	5	96
22	1-Iodonaphthalene	Se	4f	4.5	97
23	1-Bromonaphthalene	Se	4g	9.5	90

Continue of Table 2.

Entry	Ar-X	Z	Product	Time (h)	Yield(%)
24	2-Iodothiophene	Se	4h	7.5	88
25	2-Bromothiophene	Se	4i	9.5	82
26	2-Chlorothiophene	Se	4j	11	67
27	<i>p</i> -MeOPh-I	Se	4k	24	92
28	<i>o</i> -MeOPh-I	Se	4l	24	78
29	<i>p</i> -NO ₂ Ph-Br	Se	4m	4	93
30	<i>p</i> -MePh-Br	Se	4n	10	80
31	<i>p</i> -BrPh-I	Se	4o	5.5	92
32	<i>p</i> -ClPh-Br	Se	4p	7	85

^aAll the products are known compounds and were characterized by comparison of NMR, GC-Mass spectral data and melting points with those reported in the literature. ^bIsolated yield.

Synthesis and characterization of MOF-199

the MOF-199 was synthesized in a yield of 87% using the reaction of Benzenetricarboxylic acid and Cu(OAc)₂·H₂O in a mixture of DMF/EtOH/H₂O according to a literature procedure.²³ The structures of MOF-199 were deduced from their (FT-IR), EDX, X-ray and SEM spectral data. The (FT-IR) spectra (Fig 1a) displayed absorptions at about 3440, for water molecule, 1642 and 1446 cm⁻¹ for carbonyl group of benzenetricarboxylic acid and double bonds of benzene in order. It also shows the incorporation of Cu metal inside the framework organic and a uniform distribution of the particles throughout the framework, confirmed by EDX analysis (Fig 1b). The X-ray powder diffraction patterns (Fig 1c) exhibited the presence of the main diffraction peak in the 2θ=11. Scanning electron microscopy (Fig 1d) shows the existence of crystals in nano-size. All data are similar to that of other MOF-199 samples previously mentioned in the literature.²⁴

Catalytic studies

When a solid catalyst is used for a liquid-phase organic transformation, an important problem to be seriously addressed is the possibility that some of the active sites can dissolve into the reaction solution during the course of the reaction. The soluble species may exhibit catalytic activity, and therefore, the transformation will not proceed under real heterogeneous catalysis conditions.²⁵

In order to determine if active copper species leached from the solid MOF-199 catalyst can contribute to the total conversion of the coupling reaction between aryl halides (-OTs) and elemental sulfur and selenium for the synthesis of organic disulfides and diselenides, an experiment was carried out using a simple centrifugation during the course of the reaction.

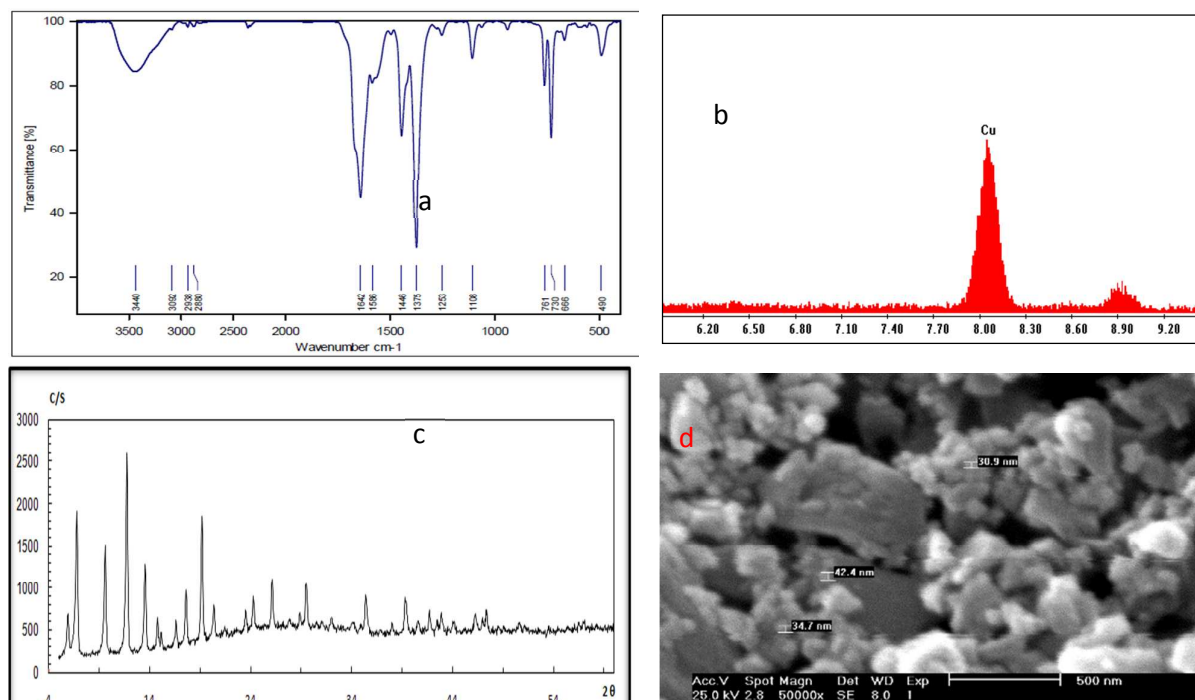


Fig. 1. (a) FT-IR spectra ;(b) Energy-dispersive X-ray spectroscopy ;(c) X-ray powder diffractogram and (d) SEM micrograph of the MOF 199.

The coupling reaction was performed in optimized condition using 10 mg MOF-199 as catalyst for synthesis of disulfides and diselenides, then the solid catalyst was removed from the reaction mixture after 1 hour of reaction time by simple filtration. The reaction solution was then transferred to a new reactor vessel, stirred for an additional 7 h at 130 °C with aliquots being sampled at different time intervals, and analysed by GC. The experimental results clearly confirmed that almost no further conversion was observed for the synthesis of disulfides and diselenides and the preparation of these compounds can only proceed in the presence of the solid MOF-199 catalyst, and the contribution of leached active copper species soluble in the solution, if any, was negligible (Figure 2).

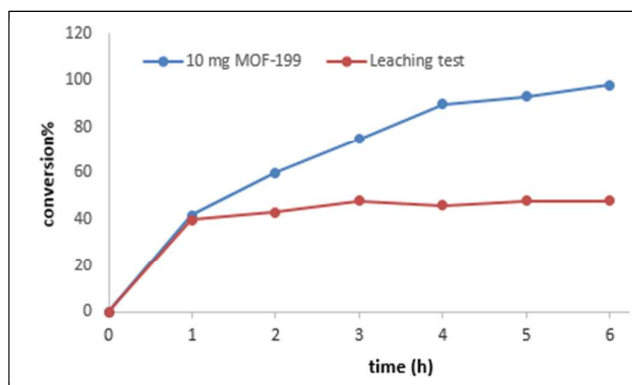


Figure 2. Leaching test indicated no contribution from homogeneous catalysis of active copper species leaching into reaction solution for the synthesis of disulfides

To emphasize the necessity of using the solid MOF-199 as catalyst for synthesis of disulfides and diselenides from aryl halides (-OTs), The catalytic activity of the MOF-199 was also compared with other copper salts including CuI, CuCl₂, Cu₂O and Cu(OAc)₂. The reaction was carried out in PEG at 130 °C in the presence of 10 mol% copper catalyst, 4 mmol of KOH and 2 mmol of iodobenzene with 4 mmol of S powder, it was found that the synthesis of dialkyldisulfides using the MOF-199 catalyst can proceed with comparable rate to the reaction using homogeneous copper catalysts. A conversion of 72% was obtained after 6 h in the presence of 10 mol% CuI as catalyst.. Notably, Chen and co-workers previously employed CuI as catalyst for the same reaction with weak base and DMF under N₂ and afforded 63% yield of ditolyldisulfane in 5 h.^{16b} also was observed that preparation of disulfides using Cu₂O as catalyst proceeded with difficulty, obtaining 58% conversion after 6 h. CuCl₂ and Cu(OAc)₂ exhibited higher activity than Cu₂O, With 80% and 75% conversions obtained after 6 h, respectively. This reaction was performed with 10 mg of MOF-177 in mentioned condition and observed only 40% yield after 24h. The similar results was obtained for synthesis of diaryldiselenides.

In the view of green chemistry, the use of homogeneous catalysis is important, because the solid catalyst offers several advantages, including easy catalyst separation, recovery and recycling. In the best case the solid catalyst can be recovered and reused several times before it eventually deactivates completely. therefore we decided to investigate the recoverability and reusability of the MOF-199 catalyst in the synthesis disulfides and diselenides over five successive runs, by repeatedly separating the MOF-199

from the reaction mixture, washing it and then reusing it. The reaction was performed in PEG at 130 °C, using the 2 mmol iodobenzene in the presence of 4 mmol of KOH and 10 mg MOF-199 catalyst. After each run, 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. And was dried under vacuum at 160 °C for 3 h, The recovered MOF-199 catalyst was then reused in further reaction under identical conditions to those of the first run. It was found that the MOF-199 could be reused several times without a significant degradation in catalytic activity. It was observed that a conversion of 92% for diaryldisulfide and 91% for diaryldiselenide is still achieved in the 5th run. (Figure 3).

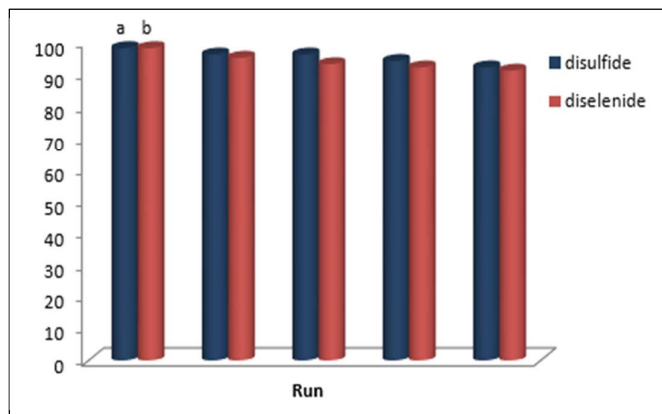


Figure 3. Catalyst recycling studies. Reaction conditions: (a) PhI (2.0 mmol), MOF-199 (10 mg), S (4 mmol), KOH (4mmol), temp 130 °C, in 2 mL PEG/H₂O (20:1), (b) PhI (2.0 mmol), MOF-199 (10 mg), Se (2 mmol), KOH (4mmol), temp 130 °C, in 2 mL PEG/H₂O (20:1).

To confirm the recoverability and reusability of the MOF-199 in the preparation of dichalcogenides reaction, the recovered MOF-199 catalyst was also characterized by XRD, FT-IR, and SEM. The FT-IR spectra of the reused MOF-199 after the fifth run revealed a similar absorption as compared to that of the fresh catalyst (Figure 4).

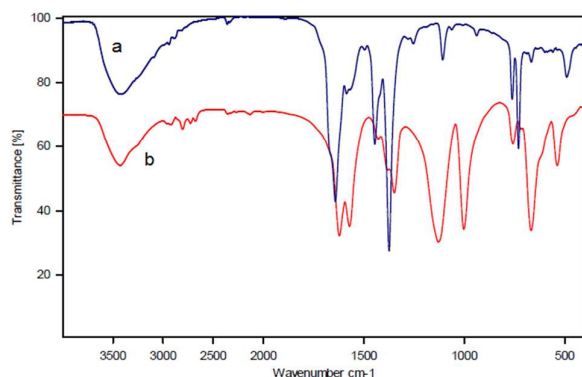


Figure 4. FT-IR spectra of the fresh (a) and reused (b) MOF-199.

Moreover, XRD result of the reused catalyst after the fifth run exhibited that the MOF-199 could maintain its crystallinity during the course of the reaction (Figure 5). Scanning electron microscopy shows existence of crystals in nano-size for the reused MOF-199. (Figure 6). These results indicated that the MOF-199 exhibited excellent reusability in the synthesis of disulfides and diselenides from alkylhalides, thus offering a route to green chemistry for this reaction.

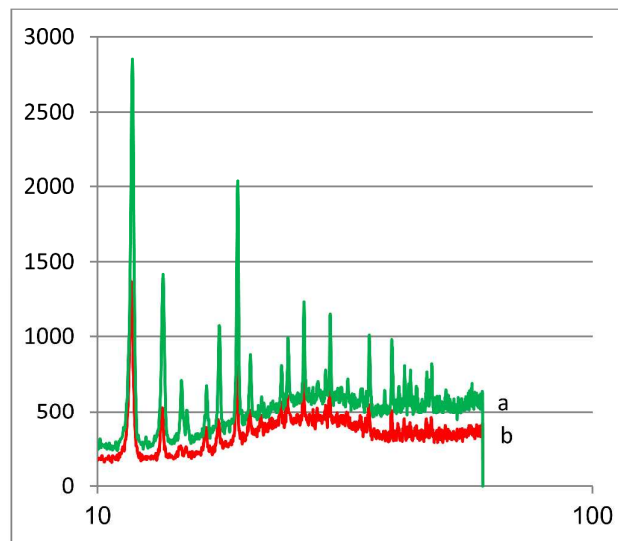


Figure 5. X-ray powder diffractogram of the fresh (a) and reused (b) MOF-199.

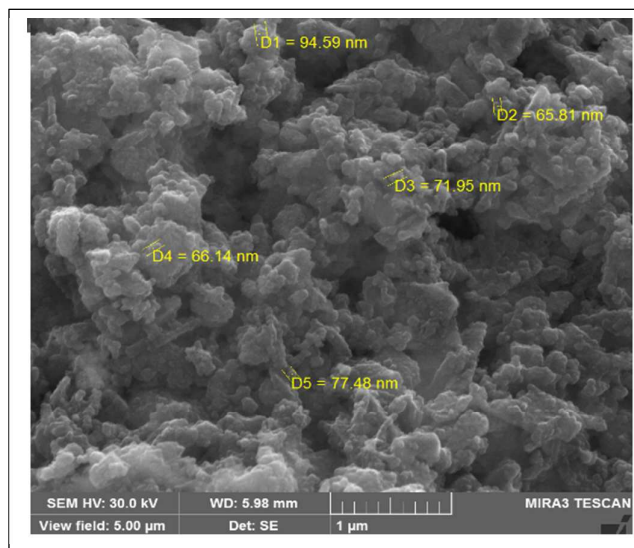


Figure 6. Scanning electron microscopy of the reused MOF-199.

EXPERIMENTAL SECTION

the MOF-199 was synthesis in a yield of 87% using the reaction of Benzenetricarboxylic acid and $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ in a 1:1:1 mixture of DMF/EtOH/ H_2O according to a literature procedure.²³ Initially, Benzenetricarboxylic acid (500 mg, 2.38 mmol) was mixed in 12 mL of a 1:1:1 mixture of DMF/EtOH/ H_2O . $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (860 mg, 4.31 mmol) was mixed with 12 mL of the same solvent and the mixtures were combined with stirring. Then triethylamine (0.5) was added to the reaction mixture and this mixture was stirred for 24h.. The product was collected by filtration, washed twice with DMF (25 ml), and finally dried

Symmetrical organic dichalcogenides synthesis; typical experimental procedure:

To a stirred mixture of aryl halide (-OTs) (2.0 mmol), sulphur (0.128 g, 4.0 mmol) for synthesis of disulfides and selenide (0.158 g, 2mmol) for synthesis diselenides in PEG/ H_2O (20:1) was added MOF-199 (10 mg) followed by KOH (0.224 g) and heated at 130 °C under atmospheric conditions until completion. The progress of reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature and then filtered. The filtrate was evaporated under vacuum, CH_2Cl_2 (20 ml) was added and the mixture was washed with H_2O (2×15 ml). The combined organic layer was dried over Na_2SO_4 , and filtered to afford the crude diaryl disulphide, which was purified by plate chromatography (silica gel, n-hexane–ethyl acetate, 20:1).

Diphenyl disulfide (Table 2, Entry1)

The product was obtained (ethyl acetate/ n-hexane, 1:20) as a White solid in 98% yield. mp = 53-56 °C. ^1H NMR (400 MHz, CDCl_3): δ = 7.24–7.36 (m, 6H), 7.54 (m, 4H). ^{13}C NMR (100MHz, CDCl_3): δ = 137.0, 129.1, 127.5, 127.2. Elemental analysis calculated for $\text{C}_{12}\text{H}_{10}\text{S}_2$: % = C, 66.01; H, 4.62; S, 29.37. Found: C, 66.49; H, 4.47; S, 29.96. GC-Mass (EI): m/z = 218.0 [M+].

Bis (1-naphthalene) disulfide (Table 2, entry 6)

The product was obtained (ethyl acetate/ n-hexane, 1:20) as a yellow solid in 75% yield. mp = 92-95 °C. ^1H NMR (400 MHz, CDCl_3) δ = 8.41-8.50(d, 2H, $J=8.4\text{Hz}$), 7.82-7.95(m, 4H), 7.34-7.7(m, 8H). ^{13}C NMR (100 MHz, CDCl_3) δ = 134.1, 132.6, 130.3, 129.9, 128.6, 128.0, 126.8, 126.6, 125.9, 125.1. MS (EI, m/z): 318 [M+].

Bis(4-mathoxyphenyl) disulfide (Table 2, entry 16)

The product was obtained (ethyl acetate/ n-hexane, 1:5) as a White solid in 55% yield. mp = 40–42 °C. ^1H NMR (CDCl_3 , 400 MHz): δ = 3.82 (s, 6H), 6.87 (d, J = 8.8 Hz, 4H), 7.32 (d, J = 8.8 Hz, 4H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 55.4, 114.7, 127.4, 132.8, 159.0.

Bis(thiophen-2-yl) Diselenide (Table 2, entry 24)

The product was obtained (ethyl acetate/ n-hexane, 1:10) as a Dark orange oil in 88% yield.

^1H NMR (CDCl_3 , 300MHz): δ = 7.03 (m, 2H), 7.26 (m, 2H), 7.5 (m, 2H). MS (EI, m/z): 326 [M+].

Bis(4-mathoxyphenyl) disulfide (Table 2, Entry 31)

The product was obtained (ethyl acetate/ n-hexane, 1:5) as a Dark orange oil in 92% yield..

^1H NMR (CDCl_3 , 300 MHz): δ = 7.27-7.47 (m, 8H).

MS (EI, m/z): 470 [M+].

Diphenyl disulfide (Table 2, Entry17)

The product was obtained (ethyl acetate/ n-hexane, 1:20) as a Yellow solid in 98% yield. mp = 58-61 °C. GC-Mass (EI): m/z = 314.0 [M+].

Conclusions

In summary, a novel, effective and one-pot procedure was developed for the direct synthesis of dichalcogenides from various aryl halides (and-OTs) and sulphur or selenium in PEG. The important feature of this method is using MOF-199 as a recyclable, porous and chemoselective catalyst. This protocol has several advantages: normal atmospheric conditions, the use of a few amount of catalyst, ligand-free systems, an easily available and low cost reagents, faint order procedure and the reactions can be carried out in PEG as green solvent instead of the usually used organic solvents.

Acknowledgements

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