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Metalation of a Thiocatechol-Functionalized Zr(IV)-based Metal-Organic Framework for Selective C-H Functionalization

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Supporting Information Placeholder

ABSTRACT: The incorporation of 2,3-dimercaptoterephthalate (thiocatecholate, tcat) into a highly robust UiO-type metal-organic framework (MOF) has been achieved via postsynthetic exchange (PSE). The anionic, electron-donating thiocatecholato motif provides an excellent platform to obtain site-isolated and coordinatively unsaturated soft metal sites in a robust MOF architecture. Metalation of the thiocatechol group with palladium affords unprecedented Pd-mono(thiocatecholato) moieties within these MOFs. Importantly, Pd-metalated MOFs are efficient, heterogeneous, and recycable catalysts for regioselective functionalization of sp^2 C-H bond. This material is a rare example of chelation-assisted C-H functionalization performed by a MOF catalyst.

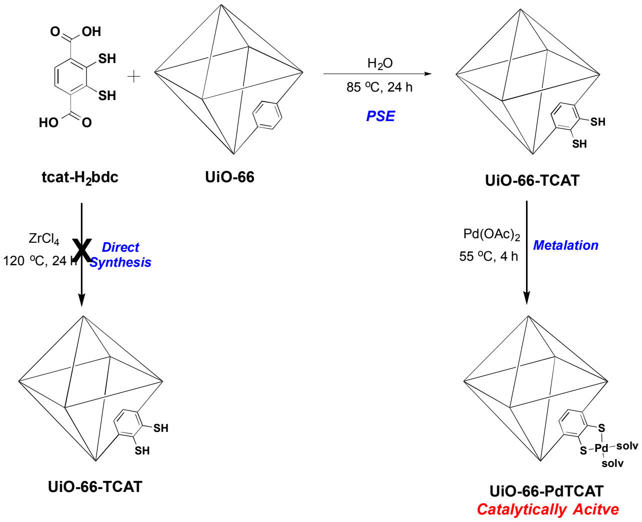
Metal-organic frameworks (MOFs) are a class of microporous crystalline materials gathering increasing attention due to their tunable functionality and high surface area, thus applications in gas storage, separation, molecular sensing, catalysis, and drug delivery.[1] Importantly, MOFs provide a versatile platform to achieve accessible and coordinatively unsaturated metal sites, and metalation of these free open-metal sites give rise to site-isolated catalytically active centers.[2,3] Postsynthetic approaches have proven to be valuable for preparing these single-site solid catalysts, due to their limited accessibility via direct solvothermal synthesis.[4] Recently, postsynthetic exchange (PSE, also known as SALE = solvent-assisted linker exchange) has been developed as a powerful and facile method to synthesize a variety of functionalized MOF materials that otherwise would be inaccessible.[5] In particular, the incorporation of single-site catalytic centers into the Zr(IV)-based UiO (UiO = University of Oslo) series of MOFs has proven attractive, due in part to their excellent chemical stability.[6] Among them, UiO-66 consists of 12-coordinated Zr(IV)-carboxylate clusters $Zr_6(\mu_3\text{-}O)_4(\mu_3\text{-}OH)_4(CO_2)_{12}$ bridged by linear 1,4-benzene dicarboxylate (bdc) ligands. UiO-66 has been extensively studied for gas absorption,[7] catalysis,[8] photochemical reactions,[9] and mercury sequestration.[10]

Catechol, a widely studied chelator in coordination chemistry, has been successfully introduced into a UiO-66 topology.[8b] Subsequent metalation with high-valent, first-row transition metals affords metal-mono(catecholato) species that act as reusable alcohol oxidation catalysis. Herein, the hard Lewis base phenol groups of the catechol were replaced with thiophenols, thereby presenting a soft thiocatechol metal-chelating motif in a highly robust MOF. Although relatively unexplored in the literature,[11] the thiocatechol group should be an excellent ligand for 2nd and 3rd-row transition metals, giving rise to isolated metal-mono(thiocatecholato) sites. Additionally, the dianionic, bidentate thiocatecholato ligands should tightly bind and stabilize active metal sites; thus, generating a stable, but highly unsaturated metal site suitable for catalysis.

The regio- and chemoselective functionalization of aromatic carbon-hydrogen bonds is of tremendous value for the synthesis of natural products and medicinal compounds.[12] Carbon-oxygen and carbon-halogen bond formation are two important fundamental reactions in organic transformations.[13] Ether-containing and halogenated aromatic compounds are widely employed in the synthesis of pharmaceuticals.[13b, 14] The use of chelate-directed functionalization of C-H bonds has attracted widespread attention, thanks to the pioneering work of Sanford and co-workers.[12c, 15]

Herein, we report the synthesis and metalation of a thiocatechol-functionalized UiO-66 material via postsynthetic methods. Though other thiol-containing MOFs have been reported,[16] this is one of the few MOF examples with a sulfur-containing, open metal chelating site. The metalated Pd(thiocatecholato) sites exhibit highly efficient, reusable, and selective catalysis for the oxidative functionalization of aromatic C-H bond. To the best of our knowledge, this is the first example of a

MOF catalyst that performs chelation-assisted C-H functionalization, achieved by a strong metal-sulfur coordination motif.



Scheme 1. Synthesis of UiO-66-TCAT and UiO-66-PdTCAT.

The ligand precursor, 2,3-dimercaptoterephthalic acid (tcat-H_2bdc), was synthesized starting from dimethyl 2,3-dihydroxyterephthalate in three steps and 37% overall yield as described in the Supporting Information. Direct solvothermal synthesis of a DMF solution containing anhydrous $ZrCl_4$ and tcat-H_2bdc did not afford a UiO-66 material, presumably due to the presence of the thiocatechol metal-chelating functionality. Given the high structural analogy of the H_2bdc and tcat-H_2bdc ligands, PSE was employed as a strategy to introduce dimercapto functionality into UiO-66. UiO-66, consisting of Zr(IV)-based secondary building units $[Zr_6O_4(OH)_4]$ and bdc organic linkers, was prepared using solvothermal conditions containing a mixture of $ZrCl_4$, H_2bdc, and acetic acid (as a modulator) at 120 °C in DMF for 24 h, followed by washing with MeOH and activation under dynamic vacuum. PSE was performed by incubating solid UiO-66 in an aqueous solution of tcat-H_2bdc for 24 h at 85 °C. The linker-exchanged material, UiO-66-TCAT, was isolated as a yellow microcrystalline powder using centrifugation, followed by extensive washing with fresh MeOH and activation under vacuum. The presence of tcat-bdc in UiO-66-TCAT was confirmed by ^{1}H NMR of the MOFs digested with dilute HF in CD_3OD (Figure S1). An equimolar reaction between bdc in the UiO-66 solid and tcat-H_2bdc in aqueous solution affords 40% dimercapto-functionalized UiO-66-TCAT. The degree of functionalization was tunable between 40-71%, using 2-5 equivalents of tcat-H_2bdc in the PSE solution (Figure S1). Powder X-ray diffraction (PXRD) patterns and field-emission scanning electron microscopy (FE-SEM) of functionalized UiO-66 confirmed retention of crystallinity with high phase purity (Figure 1 and S2). In addition, activated UiO-66-TCAT exhibited a Brunauer-Emmett-Teller (BET) surface area of 950±5 m^2/g, measured with dinitrogen absorption at 77 K. This value is close to the BET surface area of unmodified UiO-66 (1110±105 m^2/g), suggesting a clean ligand exchange process and not simple inclusion/encapsulation of tcat-H_2bdc within the MOF pores (which would significantly decrease the surface area). Indeed, extensive characterization in our previous studies on PSE of UiO-66 materials confirms a ligand metathesis phenomenon for this functionalization method.[8b, 9a, 17]

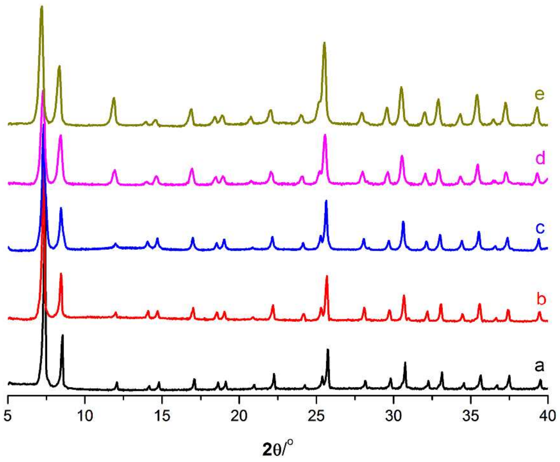
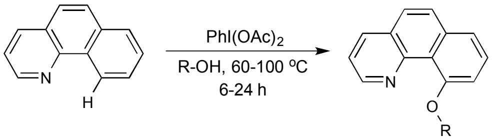


Figure 1. PXRD of UiO-66 (a, black), UiO-66-TCAT (b, red), UiO-66-PdTCAT (c, blue), and recovered UiO-66-PdTCAT after 1 (d, magenta) and 5 (e, gold) catalytic cycles.

Transition metal bis(dithiolene) complexes, especially group 10 metals with square planar coordination geometries, have attracted increasing attention in the field of magnetic and conducting materials because of the strong π-electron donor ability from the involvement of the sulfur donor atoms.[18] Immobilized thiocatechol ligands on the UiO-66-TCAT provide an excellent platform to achieve accessible and unsaturated mono(thiocatecholato) metal centers.[19] The metalation of 40% thiocatechol-functionalized UiO-66-TCAT using Pd(OAc)$_2$ in CH_2Cl_2 afforded dark-brown solids.[20] The crystallinity of UiO-66-PdTCAT was maintained upon metalation, as evidenced by PXRD and FE-SEM (Figure 1 and S2). Inductively coupled plasma-optical emission spectroscopy (ICP-OES) confirmed an atomic ratio of 1:0.18:0.85 (Zr:Pd:S) in the metal-loaded sample, confirming ~42% of thiocatechol sites were metalated. A slight, but expected decrease of the BET surface area was observed after metalation at 865±90 m^2/g for UiO-66-PdTCAT (N_2 at 77 K).

With isolated and coordinatively accessible Pd centers in a robust MOF, we sought to investigate its catalytic activity in regioselective C-H oxidation. Commonly used methods to convert sp^2 C-H bond to C-O or C-X (X=Cl, Br, I) require strong acids/bases, e.g. *n*-BuLi, CF_3SO_3H.[21] Homogeneous Pd(II)-catalyzed methods for chelate-directed oxidative activation has been increasingly studied,[12c, 22] and MOFs can provide a solid-state platform to prepare analogous catalysts that can reuse these precious-metal active sites, achieving recyclable catalysis.

Table 1. Regioselective alkoxy group installment of **1**.[a]

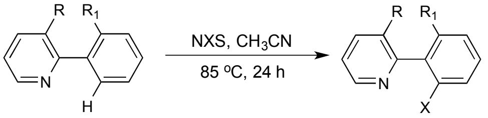


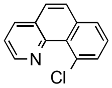
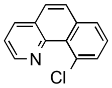
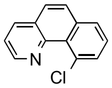
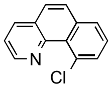
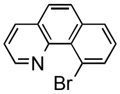
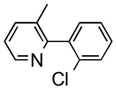
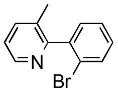
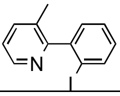
Entry	R (product/solvent	Catalyst	Pd (mol %)	MOF (mol %)	Yield (%)[b]
1[c]	CH_3	blank	0	0	0
2[c]	CH_3	UiO-66	0	25	0
3[c]	CH_3	UiO-66-TCAT	0	25	0
4[c]	CH_3	UiO-66-PdTCAT	5	25	99(1)
5[c]	CH_3	$Pd(OAc)_2$	5	25	99(1)
6[d]	CH_2CH_3	UiO-66-PdTCAT	15	75	95(2)
7[d]	CH_2CF_3	UiO-66-PdTCAT	10	50	99(1)
8[e]	$(CH_2)_2CH_3$	UiO-66-PdTCAT	10	50	21(3)

[a] 0.21 mmol benzoquinoline, 0.42 mmol $PhI(OAc)_2$, 5-15 mol% Pd in 1.75 mL alcohol (R-OH). [b] Determined by GC-MS and ^1H NMR, three independent trials. [c] 6h, 60 °C. [d] 24h, 80 °C. [e] 24h, 100 °C.

The oxidation of benzo[*h*]quinoline (**1**) to install alkoxy groups on a $C-H_{10}$ single bond using iodobenzene diacetate [$PhI(OAc)_2$] as the oxidant was investigated using the metalated MOF. Using UiO-66-PdTCAT (5 mol% in Pd) nearly quantitative yield of methoxy-functionalized **1** was achieved in 6 h at 60 °C (Table 1, entry 4). By comparison, both pristine UiO-66 and UiO-66-TCAT (before Pd metalation) gave no conversion (Table 1, entries 2 and 3). In order to confirm the heterogeneous nature of UiO-66-PdTCAT, a hot filtration experiment was performed, removing the catalyst by filtration after the first hour of the reaction. Time-dependent GC yield indicated no additional conversion to product was observed (up to 5 h) after filtration (Figure S3). No Pd leaching was observed (as evidenced by ICP-OES of the filtrate contained <0.1 ppm Pd), further confirming the heterogeneity of the MOF catalyst. Although the homogeneous Pd(II) catalysts [$Pd(OAc)_2$] completed the reaction in only ~3 h, UiO-66-PdTCAT exhibited excellent recyclability without a significant decrease in yields (92~99%) over five catalytic cycles (Table S2). Between each run, the catalyst could be recovered by centrifugation, washed with MeOH, dried under vacuum, and then directly used for additional reactions. The crystallinity of the MOF was maintained after each cycle, as confirmed by PXRD and FE-SEM (Figure 1 and S2). The alkoxy functional group installation of **1** can be successfully extended to achieve other alkyl-aryl ethers (e.g. OEt, OCH_2CF_3) in nearly quantitative yields, as summarized in Table 1. However, using 1-propanol as solvent only gave 21% conversion, likely due to the weak nucleophilicity of the propoxy group. Nevertheless, the site-isolated Pd-thiocatecholato species in the UiO platform presented here proved that MOFs can achieve efficient and recyclable catalysis for sp^2 C-H activation and installation of alkoxy groups.

Table 2. Pd-catalyzed directed C-H bond halogenation reactions.[a]



Entry	Product	Catalyst	Pd (mol %)	MOF (mol %)	Yield (%)[b]
1		blank	0	0	0
2		UiO-66	0	25	0
3		UiO-66-TCAT	0	25	0
4		UiO-66-PdTCAT	5	25	95(1)
5		UiO-66-PdTCAT	5	25	97(1)
6		UiO-66-PdTCAT	10	50	50(1)
7		UiO-66-PdTCAT	10	50	32(2)
8		UiO-66-PdTCAT	10	50	87(1)

[a] 0.21 mmol substrate, 0.252 mmol NXS, 5 mol% Pd in 1.75 mL CH_3CN. [b] Determined by GC-MS and ^1H NMR, three independent trials.

Chelate-directed oxidation can be extended to halogenations using *N*-halosuccinimides as both oxidants and halogenating reagents. Using the same MOF catalyst (5 mol% in Pd) as well as 1.2 eq. of *N*-chlorosuccinimide achieved 95% yield of mono-chlorinated benzo[*h*]quinoline product (Table 2, entry 4). Again, control reactions, such as using UiO-66-TCAT as catalyst, did not produce the desired product (Table 2, entry 1-3). Recyclability tests were carried out with UiO-66-PdTCAT, showing conversions of 86~95% of **1** to mono-chlorinated products over five successive runs (Table S2). Palladium-catalyzed direct halogenations were also extended to bromination using *N*-bromosuccinimide as a terminal oxidant (Table 2, entry 5). Though iodination was unsuccessful on **1**, perhaps due to steric constraints of the rigid, planar substrate,[15c] *N*-iodosuccinimide could be used to selectively iodinate 3-methyl-2-phenylpyridine (**2**) to give 87% of the mono-iodinated product. Chlorination and bromination of **2** only afforded 50% and 32% yield (Table 2, entry 6, 7), respectively; however, these catalysis results are comparable to homogeneous Pd catalysts (44~56% yield, Table S3).[15c] The lower yield in these cases may be due to the low reactivity of the relatively electron-deficient arene substrate.

In conclusion, PSE is shown to be a facile and mild functionalization approach to synthesize a sulfur-containing thiocatechol site in a robust UiO-66 material. The robust MOF allows for preparation of unprecedented metal-mono(thiocatecholato) species with coordinatively unsaturated soft metal sites. Pd metalation of the thiocatechol functionality affords an efficient and recyclable MOF catalyst for regioselective C-H oxidation. Aromatic substrates are readily oxidized with this metalated MOF converting sp^2 C-H bonds to ethers and arylhalides. The strong covalent metal-thiocatecholato binding allows UiO-66-PdTCAT to act as a recyclable, efficient chelation-assisted catalyst.

ASSOCIATED CONTENT

Supporting Information. Experimental details, additional characterization of MOF catalysts and catalysis reactions. This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

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