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Communication

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A Nickel-Doped Dehydrobenzoannulene-Based Two-Dimensional Covalent Organic Framework for the Reductive Cleavage of Inert Aryl C-S Bonds

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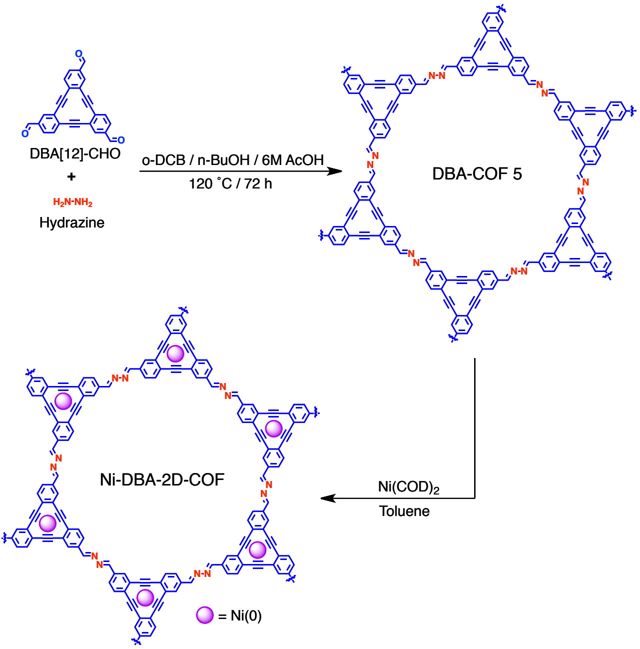
Supporting Information Placeholder

ABSTRACT The development of metalated covalent organic frameworks (COFs) is useful for generating recyclable catalytic systems for practical applications. Herein, we report the synthesis, characterization, and catalytic properties of an azine-linked two-dimensional (2D) COF containing nickel-doped dehydrobenzoannulene (DBA) units. We demonstrate that Ni-DBA-2D-COF can be used to reductively cleave the aryl C-S bonds of several organosulfur compounds utilizing dimethylethylsilane as the reducing agent. The Ni-DBA-2D-COF catalytic system displays excellent recyclability and good yields. This work highlights a rare example of utilizing metalated DBA complexes to perform catalytic transformations.

The reductive cleavage of C-S bonds (i.e., hydrodesulfurization (HDS)) plays a pivotal role in removing sulfur impurities from petroleum feedstocks to produce clean chemical fuels.[1] The C-S bonds of organosulfur compounds can also be utilized as cleavable directing groups to help produce synthetic precursors.[2] While both chemical transformations are often accomplished using expensive transition metals (i.e., Pd,[3] Rh,[4] etc.), it is much more desirable to use cheap earth abundant metals like Ni, which are less toxic and more environmentally friendly. Interestingly, Vicic and Jones have shown[5] that the HDS of thiophene can be achieved by using a $[(\text{dippe})\text{NiH}]_2$ nickel hydride dimer and hydrogen gas as the reducing agent. Alternatively, Martin and coworkers have demonstrated[6] that unactivated aryl C-S bonds can be reductively cleaved using a bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)_2) complex and hydrosilanes as the reducing agents. While both reactions are effective under homogenous conditions, complications associated with catalyst stability, recyclability, and catalyst separation are still a challenge. Although Raney nickel has been utilized for many decades as an effective heterogeneous catalyst for the reductive cleavage of C-S bonds,[7,8] the efficiency of the catalyst significantly decreases after the first reduction. Thus, it is advantageous to develop novel heterogeneous catalytic systems to help improve the efficiency and recyclability of the catalysts.

Scheme 1. Synthesis of DBA-COF-5 using DBA[12]-CHO and Hydrazine Monomer Units Followed by Metalation with Ni(COD)_2 to Produce Ni-DBA-2D-COF.



Covalent organic frameworks (COFs),[9-11] an advanced class of crystalline porous polymers, have emerged as an excellent platform to address these issues due to their high chemical stability, tunable pore sizes, and high internal surface areas. These characteristics make COFs useful for applications related to gas storage,[12,13] proton conduction,[14,15] catalysis,[16,17] optoelectronics,[18,19] and energy storage.[20-22] The modular nature of COFs permits the integration of suitable monomer units that can be metalated and utilized to complete any desirable catalytic transformation. For instance, Liu, Cui, and coworkers have shown[23] that salen-based two-dimensional (2D) chiral COF systems metalated with Fe or Mn are effective at catalyzing the epoxidation of alkenes. Fang and coworkers have also demonstrated[24] that three-dimensional (3D) salphen-based COF systems metalated with Cu(II) are useful for removing superoxide radicals from antioxidants. While both of the systems highlight the utility of

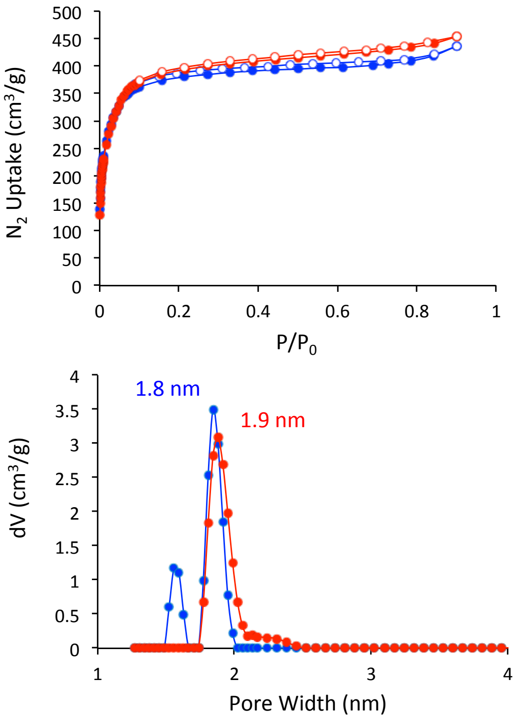


Figure 1. Nitrogen adsorption/desorption isotherms (top) and NLDFT pore size distributions (bottom) for DBA-COF 5 (red) and Ni-DBA-2D-COF (blue) measured at 77 K.

COFs as heterogeneous catalysts, examples of using COF-based systems to reductively cleave C-S bonds have not been reported.

Herein, we report the synthesis, characterization, and catalytic properties of an azine-linked 2D COF containing nickel-doped dehydrobenzoannulene (DBA)[25] units. DBAs are planar triangular-shaped macrocycles that have the ability to use their soft alkynyl ligands to form complexes with low oxidation state transition metals.[26,27] However, to the best of our knowledge, the catalytic activity of metalated DBA complexes has not been reported. We demonstrate that the DBA[12] monomer units of DBA-COF 5 can be metalated with Ni(COD)$_2$ to generate Ni-DBA-2D-COF, and used to reductively cleave the inert aryl C-S bonds of several organosulfur compounds using dimethylethylsilane as the reducing agent. Ni-DBA-2D-COF exhibits great recyclability with yields that are comparable to other Ni-based homogeneous catalytic systems.

DBA-COF 5 was synthesized by reacting DBA[12]-CHO with hydrazine in *o*-dichlorobenzene (*o*-DCB), n-butanol (n-BuOH), and 6M acetic acid (AcOH) in a flame-sealed ampule at 120 °C for 72 h (Scheme 1). DBA-COF 5 was obtained by filtration and washed with methanol to produce a bright yellow crystalline powder. Thermogravimetric analysis revealed that DBA-COF 5 maintains ~ 95% of it's weight up to 430 °C (Figure S10, SI). Scanning electron microscopy (SEM) images revealed the formation of fluffy-like crystallites (Figure S11, SI). Metalation was achieved by combining 67 mg of DBA-COF 5 with 49 mg of Ni(COD)$_2$ in 6.5 ml of dry toluene. The mixture was then stirred at room temperature in an argon-purged glovebox for 16 h to produce Ni-DBA-2D-COF as a dark green crystalline powder. Ni-DBA-2D-COF was obtained by filtration and washed with dry hexanes to remove excess Ni(COD)$_2$. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis revealed that ~ 8.56 wt % of Ni was incorporated into Ni-DBA-2D-COF, which corresponds to ~ 64% of DBA[12] units being metalated.

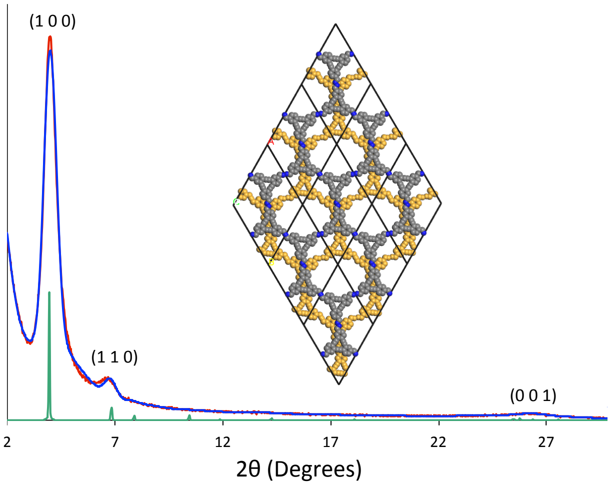


Figure 2. Indexed experimental (red) and Pawley refined (blue) PXRD patterns of DBA-COF 5 compared to the simulated hexagonal unit cell (green) with an offset of 9 Å, and views along the x and y directions.

The porosity of DBA-COF 5 and Ni-DBA-2D-COF were determined by nitrogen gas adsorption measurements at 77 K. DBA-COF 5 exhibited a type-I isotherm displaying a sharp uptake at low pressure ($P/P_0 < 0.1$), which is indicative of a microporous material (Figure 1). The Brunauer-Emmett-Teller (BET) model was applied over the low-pressure region ($0.03 < P/P_0 < 0.07$) of the isotherm to afford a surface area of 1643 $m^2\ g^{-1}$. The total pore volume calculated at $P/P_0 = 0.899$ provided a value of 0.70 $cm^3\ g^{-1}$. The pore size distribution of DBA-COF 5 was estimated using the nonlocal density functional theory method (NLDFT) yielding an average pore size of 1.9 nm. The experimental pore size is lower than the theoretical value of 2.8 nm, which suggests that the adjacent layers are significantly offset. In contrast, Ni-DBA-2D-COF also exhibited a type-I isotherm. Application of the BET model over the low-pressure region ($0.03 < P/P_0 < 0.07$) provided a surface area of 1565 $m^2\ g^{-1}$. The NLDFT pore size of Ni-DBA-2D-COF revealed a slight reduction to 1.8 nm, which is very close to the experimental pore size of the DBA-COF 5. The total pore volume calculated at $P/P_0 = 0.899$ provided a value of 0.68 $cm^3\ g^{-1}$.

The crystallinity of DBA-COF 5 and Ni-DBA-2D-COF were evaluated using powder X-ray diffraction (PXRD). Considering the differences between the experimental and theoretical pore sizes, DBA-COF 5 was modeled using a *P6* hexagonal unit cell in which the adjacent layers were offset by 9 Å (Figure 2). DBA-COF 5 exhibits an intense peak at 3.89° followed by smaller peaks at 6.73° and 26.5°, which correspond to the (100), (110), and (001) planes, respectively. Pawley refinement of the experimental data provided unit cell parameters

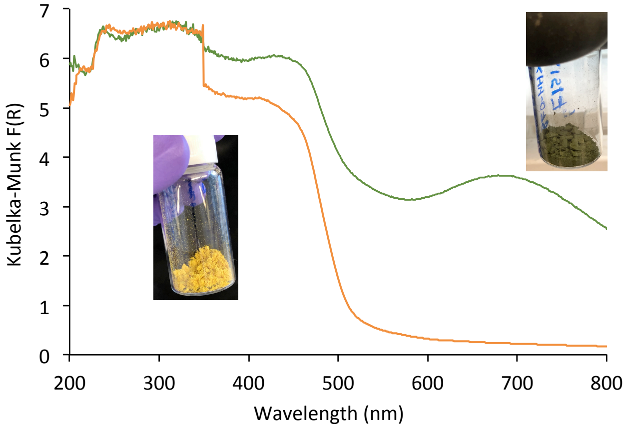
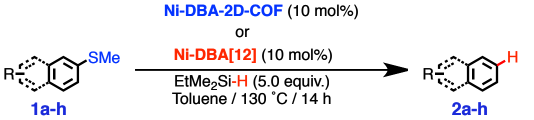


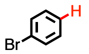
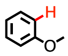
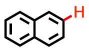
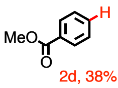
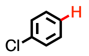
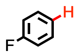
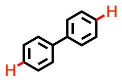
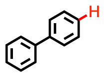
Figure 3. Kubelka-Munk diffuse reflectance spectra and photographs of DBA-COF 5 (orange) and Ni-DBA-2D-COF (green).

of a = b = 26.222 Å and c = 3.4 Å (residuals R_p = 3.81%, R_{wp} = 5.12%) The simulated patterns were almost identical to the experimental plot. It should be noted that the crystallinity of DBA-COF 5 is maintained after soaking the material in aqueous, acidic, and basic solutions for 24 h (Figure S5, SI). The PXRD profile of Ni-DBA-2D-COF also revealed retention of crystallinity following metalation with $Ni(COD)_2$ (Figure S4, SI). Surprisingly, Fourier transform infrared (FT-IR) spectra of DBA-COF 5 and Ni-DBA-2D-COF both exhibited identical –C=N- and –N-N- stretching modes at 1620 and 1081 cm^{-1}, respectively, which suggests that the metal is predominantly bound within the cavity of DBA[12] to produce a Ni(0) 16 electron complex[28] with virtually no interaction at the azine linkage (Figure S1, SI).

The presence of the DBA-Ni(0) complex was confirmed by characterizing DBA-COF 5 and Ni-DBA-2D-COF using ^{13}C cross-polarization magic angle spinning (CP-MAS) NMR and UV-Vis diffuse reflectance spectroscopies. The alkynyl units for DBA-COF 5 were confirmed by ^{13}C CP-MAS NMR displaying a

Table 1. Catalytic performance of Ni-DBA[12][a] and Ni-DBA-2D-COF[b] for the reductive cleavage of aryl C-S bonds.



				
Ni-DBA[12]	2a, 26%[d]	2b, 45%	2c, 99%	2d, 38%[d]
Ni-DBA-2D-COF	2a, 22%[c,d]	2b, 76%[c]	2c,87%[c]	2d, 45%[c,d]
				
Ni-DBA[12]	2e, 79%	2f, 72%	2g, 5%	2h, 9%
Ni-DBA-2D-COF	2e, 46%[c]	2f, 44%[c]	2g, 2%	2h,18%[c]

[a] Reaction conditions: 4.6 mg (0.011 mmol) of Ni-DBA[12] was added to 2.0 mL of toluene containing $EtMe_2SiH$ (5 equiv., 0.55 mmol) and the aryl thioethers (0.11 mmol). [b] Performed with 5.0 mg (0.011 mmol) of Ni-DBA-2D-COF. [c] Yields are based on an average of three trials. [d] Reaction was performed at 90 °C.

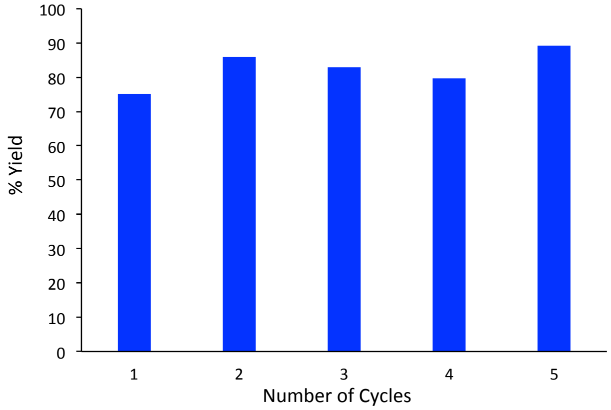


Figure 4. Recyclability of Ni-DBA-2D-COF after reductively cleaving 2-(methylthio)naphthalene (**1c**) at 130 °C using dimethylethylsilane as the reducing agent.

distinct resonance at ~ 93 ppm (Figure S6, SI). After metalation, the alkynyl peak of DBA-COF 5 shifts downfield to ~109 ppm, which is indicative of forming the DBA-Ni(0) complex (Figure S7, SI).[27,28] The UV-Vis diffuse reflectance spectrum of DBA-COF 5 exhibits broad absorbance bands ranging from 200 to 500 nm (Figure 3). After metalation, a noticeable charge transfer band surfaces at ~ 690 nm for Ni-DBA-2D-COF, which further suggests the formation of the DBA-Ni(0) complex. Lastly, the X-ray photoelectron spectroscopy (XPS) spectrum of Ni-DBA-2D-COF revealed the presence of two broad peaks at 855.89 and 852.89 eV, which correspond to the core energy levels of $Ni(II)2p_{3/2}$ and $Ni(0)2p_{3/2}$ (Figure S14, SI). The peak at 855.89 eV results from residual Ni(II) that is carried over after metalation with $Ni(COD)_2$.[28] XPS also confirmed the presence of the carbon, nitrogen, and oxygen atoms of Ni-DBA-2D-COF (Figure S13, SI).

Since the catalytic activity of metalated DBA complexes has not been experimentally evaluated or reported, we first assessed the reactivity of various aryl thioether substrates in the presence of dimethylethylsilane at temperatures ranging from 90-130 °C using 10 mol% Ni-DBA[12] (Scheme S1, SI) as a homogeneous catalyst (Table 1). Interestingly, the Ni-DBA[12] catalyst demonstrated great functional group tolerance and produced yields ranging from 26-99 % for substrates **2a-2f**. Substrate **2g** produced the lowest yield (5 %), which indicates that this system might not be capable of efficiently cleaving aryl substrates containing two thioether functionalities. In contrast, Ni-DBA-2D-COF also exhibited a low yield for **2g**, but much higher yields for **2a-2f** (22-87%) and **2h** (18%). It should be noted that these yields are higher than or comparable to other homogeneous Ni-based catalysts that have been utilized for the desulfurization of organosulfur compounds.[6,29] Surprisingly, Ni-DBA-2D-COF exhibited excellent recyclability up to five cycles and no reduction in catalytic activity providing yields ranging from 75-89% after reductively cleaving 2-(methylthio)naphthalene (**1c**) to produce **2c** (Figure 4). XPS and PXRD data taken after catalysis revealed preservation of the DBA-Ni(0) complex and retention of crystallinity, respectively (Figures S15 & S16, SI). The lack of additional peaks in the PXRD also suggests that no Ni-based nanoparticles are formed after catalysis. However, a nitrogen adsorption isotherm of Ni-DBA-2D-COF taken after catalysis revealed a slight reduction in the surface area of the material (Figure S17 & S18, SI). This reduction could be attributed to minor amounts of desulfurized product trapped within the pores of Ni-DBA-2D-COF. In addition, a mercury poisoning experiment and leaching test has confirmed that the heterogeneity of Ni-DBA-2D-COF remains intact (see Section N in the SI). ICP-MS analysis of the filtrate after catalysis also revealed minimal leaching of Ni ions (~ 0.02%).

Mechanistically, we believe that the DBA-Ni(0) catalytic system proceeds through a classical Ni(0)/Ni(II) catalytic pathway.[30] However, DFT calculations reveal that the aryl thioether substrates do not bind to the center of the DBA-Ni(0) complex due to the Ni center being coordinately saturated with all three alkynyl units (Figure S20, SI). As a consequence the DFT calculations suggest that the Ni has to pop out of the DBA[12] cavity and bind with only one alkynyl unit to form a three-coordinate complex before it can oxidatively add the C(aryl)-SMe bond. This initial oxidative addition step is estimated to be thermodynamically ~ 30 kcal/mol uphill, but accessible since the reaction is performed at high temperature. Afterwards, σ-bond metathesis with dimethylethylsilane, followed by reductive elimination regenerates the DBA-Ni(0) complex (Figure S23, SI). The σ-bond metathesis step is supported by the isolation and characterization of dimethylethyl(methylthio)silane, which is a common byproduct from this particular σ-bond metathesis reaction (Figure S22, SI).

In conclusion, we have demonstrated that a DBA-COF metalated with Ni can be used to reductively cleave inert aryl C-S bonds. The Ni-DBA-2D-COF catalytic system exhibited great recyclability and provided good yields. This work highlights a rare example of utilizing a Ni-doped DBA-COF as a platform for the desulfurization of organosulfur compounds. Since DBAs can be doped with other earth abundant metals (i.e. Fe, Co, etc.),[31] the proof-of-principle is important as metalated DBA-COFs could also be utilized to perform many other sustainable catalytic transformations.

ASSOCIATED CONTENT

Supporting Information

Synthetic procedures, FT-IR, solid-state ^{13}C NMR, XPS, TGA PXRD, and SEM. This material is available free of charge via the internet at http://pubs.acs.org.

The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interests.

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