Inorganic Chemistry
Article
Cite This: Inorg. Chem. XXXX, XXX, XXX−XXX
pubs.acs.org/IC

A Strategic High Yield Synthesis of 2,5-Dihydroxy-1,4-benzoquinone Based MOFs

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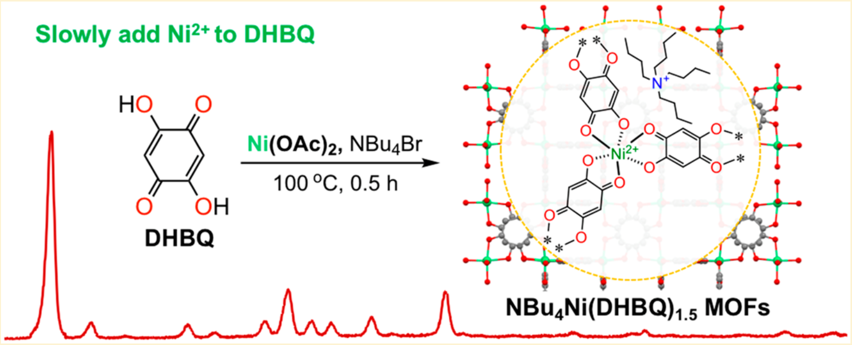
Supporting Information



ABSTRACT: Metal organic frameworks (MOFs) of the type $NBu_4M(DHBQ)_{1.5}$ (M = Ni^{2+}, Fe^{2+}, and Co^{2+}; DHBQ = 2,5-dihydroxy-1,4-benzoquinone) were prepared with improved yield up to 100% via a simple benchtop aqueous addition reaction. For the first time, the crystalline phase of this formula polymer was synthesized without in situ generation of the DHBQ ligand from 2, 5-diamino-1,4-benzoquinone (DABQ). Powder X-ray diffraction and elemental analysis confirm the crystalline phase and composition of products. Infrared and electron dispersive spectroscopy further confirm that the materials are homologous to the reported single crystalline polymers. The present MOF synthesis can be extended to halide-substituted ligands, i.e., 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone (chloranilic acid, CAN) and 3,6-difluoro-2,5-dihydroxy-1,4-benzoquinone (fluoranilic acid, FAN).

INTRODUCTION

Electrically conductive metal organic frameworks (MOFs)[1−4] represent an important extension of the applications of MOF materials beyond their current applications in gas sorption/separation, sensors, and catalysis.[5] Indeed, over the past ten years, conductive MOFs have found use in a variety of applications including, but not limited to, electrocatalysis, thermoelectrics, field effect transistors, and supercapacitors.[4,6−8] In 2011 Abrahams et al. reported on the synthesis of single crystals for a family of coordination polymers with formula $NBu_4M(DHBQ)_{1.5}$ (M = Mn, Fe, Co, Ni, Zn, and Cd).[9] This pioneering research inspired others, including Long's research group, to more closely examine this family of MOF polymers.[10−12] Long's group analyzed $NBu_4Fe(DHBQ)$-1.5 by studying its electrical and magnetic properties.[10,11] Their results concluded that this material had a very high electrical conductivity (10^{-2} S cm^{-1}) and high ferromagnetic ordering temperature (130 K), making this a desirable material for applications requiring high charge mobility. Recently, our group has also become interested in this class of MOF materials specifically to exploit their non-innocent DHBQ ligand-based redox properties for energy storage/conversion applications.

However, the synthesis of these materials is not straightforward. Both research groups and following publications employed an indirect synthetic method whereby the DHBQ ligand was not used in the synthesis in favor of 2,5-diamino-1,4-benzoquinone (DABQ) which undergoes in situ hydrolysis to become the DHBQ ligand (see Figure 1A and Scheme S1).[9] The reported reactions were typically done on a milligram scale in sealed glass vial reactors above the boiling point of the solvent. These conditions led to low yields (<43%), requiring up to 48 h of reaction time. To further study these polymers or produce them on a large enough scale for materials utilization, a straightforward, high-yield synthesis needs to be demonstrated. In addition, it is important to mention that for a scaled-up synthesis of $NBu_4M(DHBQ)_{1.5}$ crystalline polymers, the direct use of the DHBQ ligand is intuitively desired rather than DABQ. This is due in part to the much lower cost of DHBQ compared to DABQ (see Table S1 for price comparison of several major vendors). However, no study has been reported on the direct use of this ligand in making $NBu_4M(DHBQ)_{1.5}$ MOF materials. Herein, we report the highly efficient, selective synthesis of $NBu_4M(DHBQ)_{1.5}$ MOFs (M = Ni and Fe) using

Received: March 29, 2019

DOI: 10.1021/acs.inorgchem.9b00903

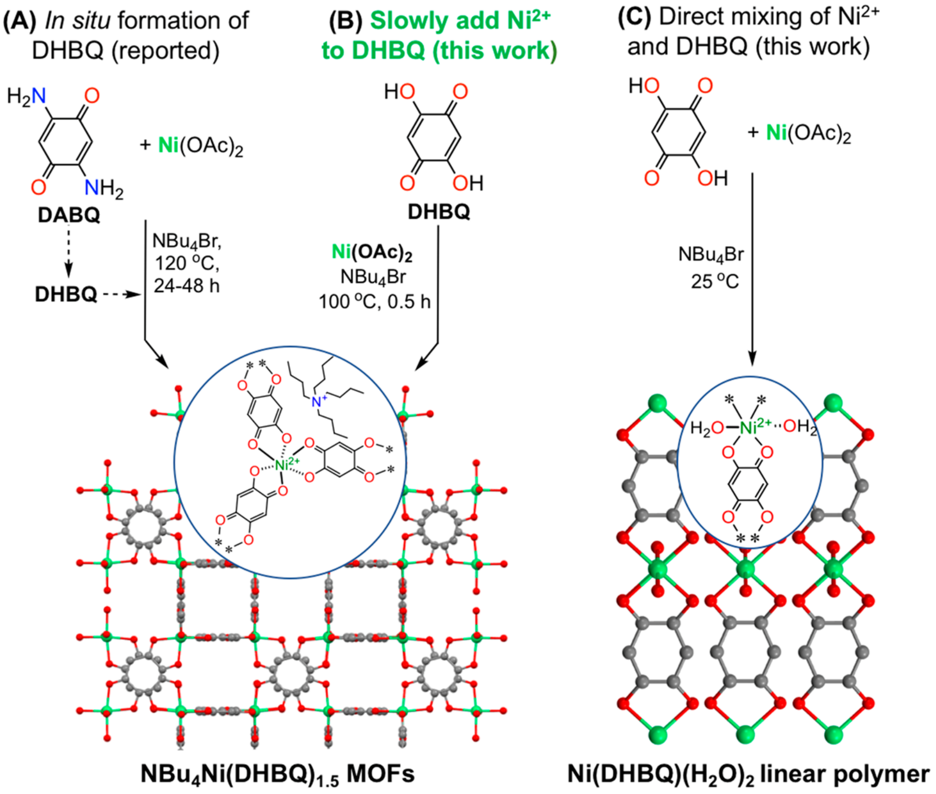


Figure 1. (A) Literature reported $NBu_4Ni(DHBQ)_{1.5}$ by in situ hydrolysis of DABQ to DHBQ. (B) Synthesis of $NBu_4Ni(DHBQ)_{1.5}$ reported here by direct use of the DHBQ ligand. (C) Generation of $Ni(DHBQ)(H_2O)_2$ one-dimensional polymer by direct mixing Ni^{2+} and DHBQ at room temperature.

the DHBQ ligand under strategically controlled reaction conditions.

■ EXPERIMENTAL SECTION

Chemicals and Instruments. All chemicals were purchased from TCI, stored in an Ar glovebox, and used directly. Elemental analysis was performed by Atlantic Microlabs. SEM was performed on a FEI Quanta FEG 650. PXRD results were obtained from a Rigaku MiniFlex II table-top X-ray diffractometer with a silicon wafer sample holder. FT-IR was performed on a PerkinElmer Spectrum 100 FT-IR spectrometer with a universal ATR sampling accessory. NMR analysis was performed on a Jeol 300 MHz spectrometer. All reagents and prepared samples were dried at 100 °C in a vacuum oven before masses were taken.

SEM Sample Preparation. First, 1.0 mg of sample powder was dispersed in 1.0 mL of new degassed absolute ethanol. The sample was sonicated for 30 min. Under Ar atmosphere glovebox conditions (< 1.0 ppm of O_2, < 0.1 ppm of H_2O), several drops of suspension were layered onto an Al SEM sample stub and left to dry. The samples were then sealed in air-free SEM sample holders for transportation. The sample stubs were loaded into the FEI Quanta FEG 650 under a cool stream of nitrogen and then tested under reduced pressures (< 5.0×10^{-5} mm Hg).

Literature Synthesis of $NBu_4Ni(DHBQ)_{1.5}$. The exact conditions reported by Abrahams et al.[13] were utilized to prepare this sample. In brief, 2,5-diamino-1,4-hydroquinone dihydrochloride (38.14 mg, 0.1803 mmol) was dissolved in 30 mL of D.I. H_2O and bubbled with oxygen to generate 2,5-diamino-1,4-benzoquine. The solution was then cleared of oxygen by freeze pump thaw. Tetra butyl ammonium bromide (excess, 300 mg) was dissolved, followed by dissolution of $Ni(OAc)_2{\cdot}4H_2O$ (44.86 mg, 0.1803 mmol). This suspension was loaded into a thick-walled glass vial and flame-sealed. The vial was placed in a preheated 120 °C oven for 48 h and then removed all at once. A black precipitate lined the walls of the vial, and some small crystals were observed above the solvent line. The solid components were extracted by vacuum filtration with rinsing by degassed water. The solids were dried in a vacuum oven at 100 °C for 1 h. Yield: < 20 mg, 47%. Anal. calcd for $C_{25}H_{39}NiNO_6$: C, 59.07; H, 7.73; N, 2.75. Found: C, 55.01; H, 6.36; N, 5.54. ^1H NMR (300 MHz, 4 drops conc. HCl in 1 mL of DMSO-d_6, TMS): δ 7.27 (acid), 5.63 (3H; aromatic CH), 2.88 (6.92 H; NBu_4 CH_2), 1.27 (6.91 H; NBu_4 CH_2), 1.00 (6.90 H; NBu_4 CH_2), 0.61 (10.44 H; NBu_4 CH_3) (see the XRD spectra in Figure S2).

Literature Synthesis of $NBu_4Fe(DHBQ)_{1.5}$. The exact conditions reported by Long et al.[7] were utilized to prepare this sample. The conditions were the same as the above synthesis for $NBu_4Ni(DHBQ)_{1.5}$ except that $Fe(SO_4)_2{\cdot}7H_2O$ (150.4 mg, 0.5409 mmol) was used in place of $Ni(OAc)_2{\cdot}4H_2O$. Yield: < 15 mg, 63%. Anal. calcd for $C_{25}H_{39}FeNO_6$: C, 59.41; H, 7.78; N, 2.77. Found: C, 55.14; H, 6.50; N, 5.58.

$Ni(DHBQ)(H_2O)_2$. The conditions reported by Abrahams and Long for the Ni and Fe polymers, respectively, were followed, excepting the direct use of 2,5-dihydroxy-1,4-benzoquinone. Gray (Ni) or Black (Fe) powders were collected by filtration. These reactions did not produce the correct phase of material, so reporting a percent yield is not meaningful. Additionally, it was found that low crystallinity one-dimensional polymers formulated as M(DHBQ)-(H_2O) were generated at room temperature with or without the presence of NBu_4^+ salts. Highly crystalline $NiDHBQ(H_2O)_2$ could be prepared by combining aqueous metal solution to ligand solution at 100 °C, cooling the solution to room temperature, and rinsing it with water and ethanol on the filter.

New Synthesis of $NBu_4Ni(DHBQ)_{1.5}$. DHBQ (1.5 mmol, 210 mg) and NBu_4Br (excess, 2.0 g) were dissolved in 50 mL of degassed H_2O under N_2 reflux. $Ni(OAc)_2{\cdot}4H_2O$ (248.84 mg, 1.0 mmol) was dissolved separately in 10 mL of degassed H_2O, added dropwise over 15 min, and then was left to reflux for an additional 30 min. A carrot-orange precipitate was extracted by vacuum filtration and rinsing with water. Yield: 510.0 mg, 100%. Anal. calcd for $C_{25}H_{39}NiNO_6$: C, 59.07;

H, 7.73; N, 2.75. Found: C, 58.92; H, 7.67; N, 2.73. ^{1}H NMR (300 MHz, 4 drops HCl in 1 mL of DMSO-d_6, TMS): δ 6.93 (acid), 5.54 (3H; aromatic CH), 2.73 (7.97 H; NBu$_4$ CH$_2$), 1.13 (7.99 H; NBu$_4$ CH$_2$), 0.86 (7.98 H; NBu$_4$ CH$_2$), 0.47 (12.0 H; NBu$_4$ CH$_3$) (see the NMR spectrum of acid digested NiBu$_4$Ni(DHBQ) in Figure S6).

New Synthesis of NBu$_4$Fe(DHBQ)$_{1.5}$. The conditions were the same as the previous synthesis with minor modifications. FeSO$_4$·7H$_2$O (278 mg, 1.0 mmol) was used as the metal source, and a greater excess of NBu$_4$Br (3.0−4.0 g) was found to improve the yield. Also, air sensitivity was observed for this material by loss of crystallinity after air exposure. As such, air-free Schlenck filtration under N$_2$ was utilized to extract a black-purple microcrystalline precipitate that was then stored in an inert atmosphere. Yield: 434.6 mg, 86%. Anal. calcd for C$_{25}$H$_{39}$FeNO$_6$: C, 59.41; H, 7.78; N, 2.77. Found: C, 59.95; H, 7.86; N, 2.76.

Synthesis of NBu$_4$Ni(CAN)$_{1.5}$. 3,6-Dichloro-2,5-dihydroxy-1,4-benzoquinone (chloranilic acid, CAN) (0.3 mmol, 60.0 mg) and NBu$_4$Br (1.0 mmol, 322 mg) were dissolved in 100 mL of degassed H$_2$O under N$_2$ reflux. Ni(NO$_3$)$_2$·6H$_2$O (58.0 mg, 0.2 mmol) was dissolved separately in 10 mL of degassed H$_2$O, added dropwise over 15 min, and then was left to reflux for an additional 30 min. A brown precipitate was extracted by vacuum filtration and rinsing with water. Yield: 175.0 mg, 96.4%. Anal. calcd for C$_{25}$H$_{36}$FNiNO$_6$Cl$_3$: C, 49.0; H, 5.88; N, 2.29; Cl, 17.39. Found: C, 49.95; H, 6.71; N, 2.40; Cl, 16.76. PXRD results can be seen in Figure S4.

Synthesis of NBu$_4$Ni(FAN)$_{1.5}$. 3,6-Difluoro-2,5-dihydroxy-1,4-benzoquinone (fluoranilic acid, FAN) (0.3 mmol, 53.4 mg) and NBu$_4$Br (1.0 mmol, 322 mg) were dissolved in 100 mL of degassed H$_2$O under N$_2$ reflux. Ni(NO$_3$)$_2$·6H$_2$O (58.0 mg, 0.2 mmol) was dissolved separately in 10 mL of degassed H$_2$O, added dropwise over 15 min, and then was left to reflux for an additional 30 min. A brown precipitate was extracted by vacuum filtration and rinsing with water. Yield: 120.0 mg, 96.2%. Anal. calcd for C$_{25}$H$_{36}$FNiNO$_6$F$_3$: C, 53.40; H, 6.45; N, 2.49; F, 10.13. Found: C, 53.66; H, 6.76; N, 2.50; F, 9.75. PXRD results can be seen in Figure S5.

■ RESULTS AND DISCUSSION

To prepare the as-mentioned MOFs, first, the exact synthetic procedures were followed from Abrahams et al. for the NBu$_4$Ni(DHBQ)$_{1.5}$ MOFs using Ni(OAc)$_2$·4H$_2$O and DABQ in the presence of excess NBu$_4$Br. The X-ray diffraction pattern obtained was in close agreement to the simulated pattern obtained from the reported NBu$_4$Ni(DHBQ)$_{1.5}$ MOF crystal structure where the NBu$_4$$^+$ cation was squeezed because of disorder.[9] The location of all peaks was a good match, confirming the presence of the reported crystalline phase for NBu$_4$Ni(DHBQ)$_{1.5}$ (Figure 2). The relative intensities of some peaks are not in close agreement, which is explained as there is no NBu$_4$$^+$ cation in the simulated PXRD pattern. In the ^{1}H NMR spectrum of ^{1}H NMR studies of HCl-digested MOF samples (Figure S7), the proton resonances for the in-situ formed DHBQ from the hydrolysis of DABQ and the ^{n}Bu$_4$N$^+$ cation were confirmed. The elemental analysis performed on these samples indicated a 2-fold excess of nitrogen for both samples, suggesting incomplete hydrolysis of the amine or incorporation of NH$_4$$^+$ cations into the product. The presence of NH$_4$$^+$ in the product can be explained by the in-situ hydrolysis of DABQ to produce NH$_3$ and subsequent solvation to NH$_4$OH (Scheme S1). It is reasonable to believe that NH$_4$$^+$ can be incorporated as counter cations into the Ni-MOF. NH$_4$$^+$ in the product is also corroborated by low C and H percentages from elemental analysis (Scheme S1). In the ^{1}H NMR studies of the acid-digested MOFs (Figure S7), the observed ratio (3:7) of the aromatic protons in DHBQ versus the protons of one methylene group in the ^{n}Bu$_4$N$^+$ cation is lower than the formula ratio (3:8), 1.5:1, further suggesting the present of the NH$_4$$^+$ cation.

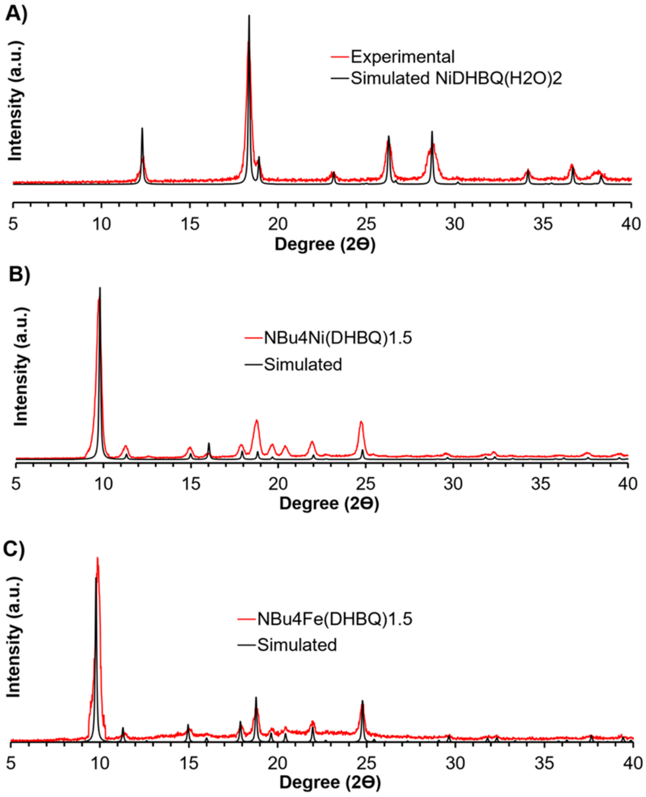


Figure 2. X-ray diffraction data obtained from samples prepared by facile synthesis compared to simulated patterns for (A) Ni(DHBQ)-(H$_2$O)$_2$ prepared by room temperature reagent combination. Hot addition reactions presented for (B) NBu$_4$Ni(DHBQ)$_{1.5}$ and (C) NBu$_4$Fe(DHBQ)$_{1.5}$.

Initial attempts to synthesize NBu$_4$Ni(DHBQ)$_{1.5}$ followed the synthetic method reported by Abrahams exactly, excepting the direct use of DHBQ over 2,5-amino-*p*-quinone. However, it was observed every time that the metal and ligand, with or without the NBu$_4$Br salt, was combined, precipitates immediately began to fall out of solution at room temperature. There was no indication of the correct phase of material by PXRD (Figure 2A). According to the literature,[13,14] the obtained PXRD pattern indicates only the formation of the one-dimensional polymer, Ni(DHBQ)(H$_2$O)$_2$. Even after heating at 120 °C for 2 days, the linear polymer diffraction pattern was still observed without the formation of NBu$_4$Ni-(DHBQ)$_{1.5}$. In the case of Fe, only amorphous or unknown phases could be observed by PXRD under the same conditions.

The precipitation of the linear polymer Ni(DHBQ)(H$_2$O)$_2$ dominated the reaction chemistry when Ni(OAc)$_2$·4H$_2$O, tetrabutylammonium salts, and DHBQ were directly mixed at room temperature. This phenomenon was attributed to the low solubility (<3 mM) of DHBQ in water at ambient temperatures and high solubility of the metal salt. We envisioned that slow addition of the Ni salt into a refluxing aqueous solution of DHBQ (20 mM) would instead maintain a high ligand-to-metal ratio and favor the desired three-ligand-coordinated NBu$_4$Ni(DHBQ)$_{1.5}$ over the two-ligand-coordinated linear polymer. We believe NBu$_4$Ni(DHBQ)$_{1.5}$ is a thermodynamic product formed at the reflux temperature, while the formation of the Ni(DHBQ)(H$_2$O)$_2$ is kinetically

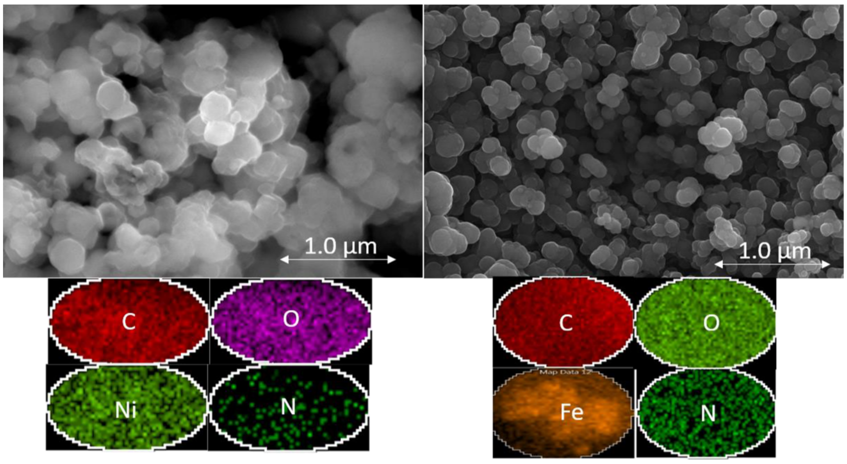


Figure 3. SEM and EDS analysis of $NBu_4Ni(DHBQ)_{1.5}$ (left) and $NBu_4Fe(DHBQ)_{1.5}$ (right).

driven by precipitation at a lower temperature. By refluxing 50 mL of degassed water with the oil bath temperature set to 120 °C, we dissolved DHBQ and excess NBu_4Br. $Ni(OAc)_2 \cdot 4H_2O$ dissolved in H_2O was added dropwise with vigorous stirring over 20−30 min while making sure that the water was boiling before subsequent drops were added. After the metal solution was added, the reaction was kept under reflux for an additional 30 min. The vial was removed from the oil bath and left until the boiling dissipated. The contents of the flask were then filtered hot using an air-free Schlenck filtration device under Ar. The carrot-orange powder was then rinsed with degassed H_2O and dried on the filter. The PXRD pattern of the synthesized $NBu_4Ni(DHBQ)_{1.5}$ MOFs matched the reported phase (Figure 2B). The Ni sample remained stable after several days exposed to ambient atmospheric conditions and showed no loss of crystallinity by PXRD analysis. To further confirm the generality of the synthesis route using the DHBQ ligand, $NBu_4Fe(DHBQ)_{1.5}$ was also prepared as purple (Fe) powders using $Fe(SO_4)_2 \cdot 7H_2O$, which was confirmed by the match of the experimental and simulated PXRD results (Figure 2C). The Fe sample, on the other hand, was highly sensitive to the atmosphere and lost its crystallinity within 3 h of ambience. Thus, it is very important to utilize air-free conditions when handling the Fe MOFs.

The elemental analysis for the Ni and Fe MOF samples agreed quite well with their chemical formula. Indeed, by direct use of DHBQ, the possibility of incomplete hydrolysis of DABQ or NH_4^+ incorporation is eliminated (Scheme S1). The ^1H NMR studies of acid-digested Ni-MOF samples consistently determine the organic composition (Figure S6). Qualitatively, only DHBQ molecules and NBu_4^+ cations were observed for all samples digested by concentrated HCl. The integration ratio (ca. 3:7.98) of peaks of the aromatic protons in the DHBQ versus the protons of one methylene group in the $^nBu_4N^+$ cation of the sample (Figure S6) prepared by the slow addition method agreed better with the expected chemical formula of $NBu_4Ni(DHBQ)_{1.5}$ (3:8) than did the integrations for the sample prepared by the hydrothermal method (Figure S7).

The IR spectra of the Ni and Fe MOFs agreed with the results reported in the literature (Figure S1).[10,11] Most notably from the IR spectra, it was observed that the $C=O$ stretching frequency for the Fe polymer was located 30 cm^{-1} lower than the Ni polymer. This result is consistent with the conclusion made by Long and co-workers concerning the increased $C=O$ bond length in the DHBQ (3-) radical ligands.[10,11] SEM indicated uniform morphology for both samples (Figure 3). The Ni MOFs appeared to lack a noticeable micrometer-sized morphology; instead, they appear to be polycrystalline nanoparticles. This observation is consistent with the broader Bragg diffraction peaks (full width at half maximum at 18.84°; 2θ: c.a. 0.42°; 2θ: c.a. 20.2 nm) when compared to the simulated spectra (Figure 2). The Fe polymer had a similar morphology of submicrometer nanoparticle aggregates (full width at half maximum at 18.84°; 2θ: c.a 0.40°; 2θ: c.a. 21.02 nm).

We also conducted another reaction using $Co(OAc)_2 \cdot 4H_2O$ and observed the formation of the $NBu_4Co(DHBQ)_{1.5}$ phase by PXRD analysis (Figure S3). Moreover, the scope and modularity of this synthetic method was briefly extended further, beyond the DHBQ ligand, by substitution of 3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone (chloranilic acid, CAN) and 3,6-difluoro-2,5-dihydroxy-1,4-benzoquinone (fluoranilic acid, FAN) as bridging ligands. Under more dilute conditions, $NBu_4Ni(CAN)_{1.5}$ and $NBu_4Ni(FAN)_{1.5}$ were prepared as brown powders with PXRD spectra matching their simulated PXRD patterns (Figures S4 and S5).[9,12] Small impurity peaks observed in the PXRD spectra of $NBu_4Ni(CAN)_{1.5}$ are likely attributed to a small unknown impurity (97%) in the chloroanilic acid reagent.

■ CONCLUSIONS

In summary, $NBu_4MDHBQ_{1.5}$ (M = Fe, Ni, Co) crystalline powders were prepared via a simple addition reaction of a metal to ligand in boiling water. Via temperature regulation of addition, the products were uniform and pure according to XRD, FT-IR, SEM, EDS, ^1H NMR, and EA analyses. Most importantly, the straightforward synthesis utilizing the DHBQ ligand rather than in situ generation of DHBQ was demonstrated with a greater than 10-fold scale up of product with improved yield up to 100% and with better elemental and PXRD agreement than that produced by the sealed glass vial reactor using DABQ. This synthesis was successfuly demonstrated for Ni, Fe, and Co and can reasonably be extended to other divalent metals. By substituting chloranilate or fluoranilate ligands for the DHBQ-based Ni-MOFs, materials matching simulated PXRD were prepared. The present convenience of DHBQ ligand-based (and its

DOI: 10.1021/acs.inorgchem.9b00903
Inorg. Chem. XXXX, XXX, XXX−XXX

derivatives) MOFs will further promote their applications, such as conductive MOFs and magnetic materials. Currently investigations into MOF syntheses extending to other metals, ligands, and ions are under way while exploiting the redox chemistry of $NBu_4M_2DHBQ_3$ (M = Fe and Ni) for potential energy storage applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.9b00903.

> Reaction schemes, FT-IR results, additional PXRD results, NMR results of digested samples, and price comparison of starting reagents (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Utah State University for providing faculty startup funds to the PI (T.L.L.) and the Utah Energy Triangle Faculty Award sponsored by Utah State Governor's Office of Energy Development for supporting this study. Q.Z. acknowledges the funding support by Washington State University.

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