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Article

Upcycling of Dyed Polyester Fabrics into Copper-1,4-Benzenedicarboxylate (CuBDC) Metal−Organic Frameworks

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ABSTRACT: We report on a pathway to synthesize metal−organic frameworks (MOFs) using discarded textiles as a raw material. Discarded objects made of poly(ethylene terephthalate) (PET) could be an inexpensive and globally available source for 1,4-benzenedicarboxylic acid (H2BDC), also known as terephthalic acid, a building block of carboxylate-based MOFs. Previous studies on using discarded PET to synthesize MOFs have mainly focused on PET bottles. In contrast, we demonstrate the use of dyed polyester fabrics as a raw material. Specifically, we report on a synthesis path for copper-1,4-benzenedicarboxylate (CuBDC) utilizing disodium terephthalate (Na2BDC) as a linker and on how we obtained the linker from depolymerized polyester fabrics.

To facilitate coordination between the copper ions and Na2BDC and create a localized acidic environment that favors the synthesis of CuBDC MOFs rather than metal oxide byproducts, we added acetic acid to the copper precursor solution. The drop-sized pH-controlled domain enabled the formation of CuBDC MOF crystals at room temperature and at a fraction of time shorter than traditional solvothermal methods. We confirmed the resulting MOF structures using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Fourier transform infrared (FTIR) spectroscopy, and our results were in quantitative agreement with previous reports. Furthermore, we used different copper salts as metal sources and different color-dyed polyester fabrics as linker sources, demonstrating the versatility of the proposed synthesis path. These results may open an avenue for using discarded textiles as a raw material and offer a more circular approach for managing textile waste.

INTRODUCTION

Textiles industries generate over 5% of the total global solid waste.[1] A report by U.S. Environmental Protection Agency in 2015 estimated that the average amount of discarded textile waste per person in the United States is approximately 32 kg per year. More than 85% of textile waste ends up in landfills, raising serious environmental concerns and highlighting the need for effective and sustainable strategies to handle it.[2] Polyester fibers account for 50% of the fiber market. Since the 1990s, the consumption of polyester fibers has grown at a rate of nearly 7% per year.[3] Several chemical recycling pathways available for polyester include methanolysis,[4] glycolysis,[5] aminolysis,[6] and hydrolysis.[7] Hydrolysis decomposes polyester into 1,4-benzenedicarboxylic acid (H_2BDC) and ethylene glycol. H_2BDC is a main building block for the preparation of high-value compounds.[8,9]

One attractive upcycling target for H_2BDC are carboxylate-based metal−organic frameworks (MOFs). MOFs have a wide range of applications including catalysis,[10] gas separation,[11] oil/water separation,[12] gas storage,[13] sensing,[14] and drug delivery.[15] MOF synthesis often requires expensive raw materials, toxic organic solvents such as *N*,*N*-dimethylformamide (DMF), and harsh reaction conditions.[16] H_2BDC obtained from depolymerizing poly(ethylene terephthalate) (PET) can be obtained at high purity levels[7,17] and used as an organic linker in MOF assembly. Some researchers have demonstrated PET-to-MOF upcycling using PET bottles. For instance, Doan et al. synthesized copper-1,4-benzenedicarboxylate (CuBDC) utilizing H_2BDC recovered from PET bottles and used the resulting MOF to remove dyes from an aqueous solution.[18] Dyosiba et al. and Dyosiba et al. demonstrated that various sources of PET waste, including PET bottles,[19] food trays, colored bottles, and recycled PET beads,[20] could be used as a source for H_2BDC and in the synthesis of UiO-66 (UiO: Universitetet i Osl). Lo et al. used PET bottles as a starting material for the synthesis of MIL-47 (MIL: Materials Institute Lavoisier), MIL-53(Cr, Al, Ga), and MIL-101(Cr) frameworks using a one-pot strategy.[21]

However, previous attempts to employ H_2BDC obtained from PET as a linker for MOF synthesis have suffered from several limitations. For example, most methods require

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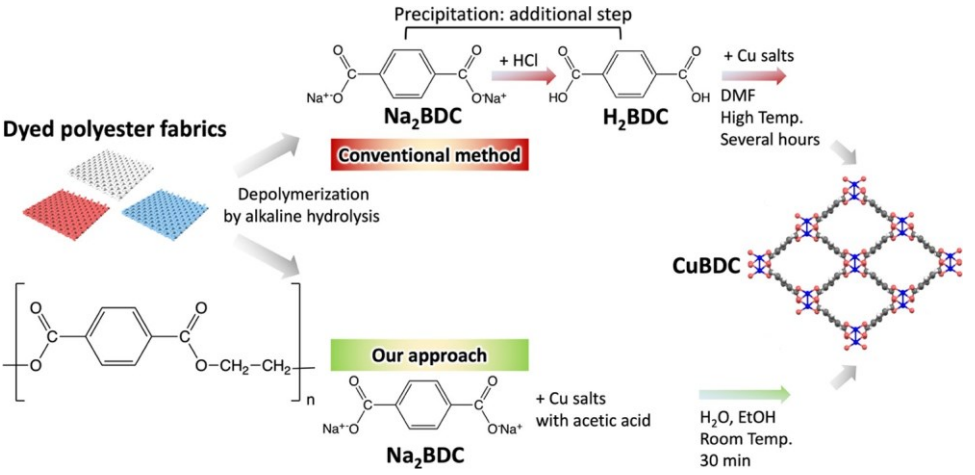
Scheme 1. Methods to Synthesize CuBDC MOFs from Dyed Polyester Fabrics[a]



[a]Top: A conventional pathway requiring protonation to isolate H2BDC. Bottom: Our proposed approach which directly utilizes Na2BDC available after depolymerization of polyester fabrics.

Table 1. Initial pH and Final pH of Copper Precursor Solutions after Adding Acetic Acid

copper salts	initial pH	amount of acetic acid added (mL)	final pH
$Cu(NO_3)_2{\cdot}3H_2O$	3.02 ± 0.02	0.015	1.97 ± 0.02 (pH 2.0 condition)
		0.115	1.53 ± 0.03 (pH 1.5 condition)
		0.300	1.23 ± 0.01 (pH 1.2 condition)
$Cu(CH_3COO)_2{\cdot}H_2O$	6.65 ± 0.03	0.015	6.03 ± 0.02 (pH 6.0 condition)
		0.115	5.04 ± 0.03 (pH 5.0 condition)
		0.300	4.51 ± 0.04 (pH 4.5 condition)
$CuSO_4{\cdot}5H_2O$	4.31 ± 0.04	0.015	3.19 ± 0.02 (pH 3.2 condition)
		0.115	2.67 ± 0.03 (pH 2.7 condition)
		0.300	2.49 ± 0.01 (pH 2.5 condition)

deprotonation of H_2BDC, which necessitates the inclusion of at least one of the following steps: (1) isolation of H_2BDC, involving a series of subsequent steps such as precipitation, filtration, and drying; (2) use of a toxic organic solvent such as DMF to dissolve H_2BDC; or (3) use of solvothermal method requiring high reaction temperature.

An approach that utilizes an already-deprotonated linker (BDC^{2-}) instead of the linker conjugated acid (H_2BDC), as a MOF precursor, could potentially overcome these restrictions. However, although several reports have partially demonstrated the feasibility of this approach for the preparation of MOF structures,[22,23] direct conversion of a BDC^{2-} salt obtained from depolymerized PET into a MOF has not yet been explored. We propose that as alkaline hydrolysis decomposes PET into Na_2BDC, using the deprotonated linker available after PET depolymerization would eliminate the need for additional protonation/precipitation steps (Scheme 1).

To prevent copper ions from coordinating with a hydroxide ion and forming insoluble impurities such as $Cu(OH)_2$ or CuO under alkaline reaction conditions,[24] we added acetic acid (AcOH) to the copper precursor solutions. This approach allowed for the localized adjustment of the pH value of the copper precursor drops inside the alkaline depolymerization solution, creating localized conditions that favored MOF assembly. Our approach uses ethanol and water as solvents and requires a reaction time of 30 min at room temperature, which is significantly faster than previous reports in which toxic solvents and higher reaction temperatures have been used.[25]

We used no-dye polyester, blue-dye polyester, and a 50/50 mixture (by weight) of red- and blue-dye polyester fabrics as raw materials and characterized the purity of the H_2BDC obtained from each source. We also determined the optimal pH values for MOF formation using several copper salts such as $Cu(NO_3)_2{\cdot}3H_2O$, $Cu(CH_3COO)_2{\cdot}H_2O$, and $CuSO_4{\cdot}5H_2O$. These experiments provided insights into the role of the copper precursor solution's pH on the properties of resulting MOF structures.

EXPERIMENTAL SECTION

Materials. Polyester fabrics without any dyes (100% polyester knit, lot 2926), with blue dye (100% polyester knit, disperse dye blue, lot 6554), and with red dye (100% polyester knit, disperse dye rust, lot 3044) were purchased from Testfabrics, Inc. $Cu(NO_3)_2{\cdot}3H_2O$ (Sigma-Aldrich, 99%), $Cu(CH_3COO)_2{\cdot}H_2O$ (Sigma-Aldrich, 99%), $CuSO_4{\cdot}5H_2O$ (Sigma-Aldrich, 98%), terephthalic acid (Sigma-Aldrich, 98%), hydrochloric acid (EMD Millipore, 36.5−38.0%), acetic acid (Macron Fine Chemicals, 99.7%), sodium hydroxide (Macron Fine Chemicals), and ethanol (Koptec, 100%) were used as received without further purification.

Depolymerization of Polyester Fabrics. Polyester fabrics weighing 0.2 g were placed into a round-bottom flask containing 7 mL of 0.7 M sodium hydroxide solution (6 mL of ethanol and 1 mL of deionized water, DI water). Each flask was heated in a silicone oil bath at 80 °C for 3 h under magnetic stirring. A water-cooled reflux condenser was placed on top of the reaction flask. In a separate experiment, to determine the maximum amount of recoverable H_2BDC, hydrochloric acid was added

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into the depolymerization mixture until the pH of the mixture reached 2.0. The resulting crystalline solid was filtered and dried in an oven at 100 °C for 4 h.

Room-Temperature Synthesis of CuBDC MOFs. To increase the solubility of the Na_2BDC linker, 5 mL of DI water was added to the solution containing the depolymerized polyester fabrics. Separately, a metal precursor solution was prepared by dissolving each of the copper salts ($Cu(NO_3)_2 \cdot 3H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, and $CuSO_4 \cdot 5H_2O$) in 12 mL of a solvent. Ethanol was used as the solvent for $Cu(NO_3)_2 \cdot 3H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$, and DI water was used as the solvent for $CuSO_4 \cdot 5H_2O$. Acetic acid was added to each copper salt solution in the following amounts: 0.015, 0.115, and 0.300 mL. The values for the initial pH of the copper precursor solutions and their final pH after the addition of acetic acid are shown in Table 1.

Table 2. % Yield of H_2BDC Recovered from Depolymerized Polyester Fabrics

	polyester fabric (g)	H_2BDC recovered (g)	H_2BDC yield (%)
no-dye polyester	0.2	0.1689 ± 0.001	99.35
blue-dye polyester	0.2	0.1610 ± 0.001	94.73
50/50 mixture of red and blue-dye polyester	0.2	0.1600 ± 0.001	94.12

The acidic copper precursor solution was added dropwise to the depolymerization solution under magnetic stirring at room temperature leading to the immediate precipitation of a blue solid. After adding the total amount of the copper solution for each experiment into the depolymerization mixture, the contents were stirred for an additional 30 min before collecting the solids via centrifugation.

The solids were transferred to a tube and washed with 5 mL of DI water using an ultrasonic bath sonicator. After adding 9 mL of ethanol, the tube was placed in a 900 rpm vortexer. The resulting solids were redispersed in ethanol and dried in an oven at 75 °C overnight prior to their characterization.

Characterization of the Resulting H_2BDC Linker and CuBDC MOF Structures. Powder X-ray diffraction (PXRD) patterns of CuBDC MOFs were collected using a Bruker D8 Advance ECO powder diffractometer equipped with Cu Kα radiation (40 kV, 25 mA, wavelength λ = 1.5606 Å) at a scan speed of 0.03°·s^{-1}. Nuclear magnetic resonance (NMR) spectra of H_2BDC were obtained at 500.03 MHz (^{1}H) and at 125.75 MHz (^{13}C) on a Bruker AVIII spectrometer equipped with a broadband Prodigy cryoprobe. The spectra were processed using MNova (v. 14.3, Mestrelab Research S. L.) software. Thermogravimetric analysis (TGA) of H_2BDC and CuBDC MOFs was carried out in a TGA analyzer (Q500, TA Instruments) by heating the samples from 25 to 600 °C in a N_2 atmosphere at a heating rate of 10 °C·min^{-1}. Differential scanning calorimetry (DSC) of H_2BDC was performed using a TA Instruments Q2000 system heated from 40 to 400 °C at a rate of 5 °C·min^{-1}. Fourier transform infrared (FTIR) spectra of H_2BDC and CuBDC MOFs were obtained by a PerkinElmer FTIR spectrophotometer on a range of 4000−600 cm^{-1}. Scanning electron microscopy (SEM) images of CuBDC MOFs coated with a thin carbon layer were collected at a voltage of 2.0 kV using a Zeiss Gemini 500 Scanning Electron Microscope. Surface area measurements of CuBDC MOFs were obtained on a Micromeritics ASAP 2460 gas sorption analyzer using ultrapure N_2 (99.999%) and a liquid N_2 bath. The Brunauer−Emmett−Teller (BET) surface areas of CuBDC MOFs were determined by a linear least squares regression analysis using the linearized form of the BET equation. The Barrett−Joyner−Halenda model (BJH) was used to determine the average pore diameter and pore size distribution.

RESULTS AND DISCUSSION

Purity of Terephthalic Acid Obtained after Polyester Depolymerization. The obtained H_2BDC powders were white, purple-gray, and pink when no-dye polyester, blue-dye polyester, and the 50/50 mixture of red and blue-dye polyester fabrics were used as precursors, respectively (Figure S1). The yield for obtaining H_2BDC was calculated using eq 1, where m_{H_2BDC} is the mass of the H_2BDC after the depolymerization reaction[26] and m_{PET} is the mass of polyester fabrics used (Table 2). The coefficient of 0.85 represents the theoretical ratio of the molecular weight of BDC units ($C_8H_4O_4$, 164.11 g·mol^{-1}) to that of ethylene terephthalate repeating units ($C_{10}H_8O_4$, 192.17 g·mol^{-1}).[9]

$$H_2BDC\ \text{yield}\ (\%) = \frac{m_{H_2BDC}}{m_{PET} \times 0.85} \times 100 \quad (1)$$

The ^{1}H and ^{13}C NMR spectra of the H_2BDC obtained from the depolymerized polyester fabrics were recorded and compared to the spectra of commercial H_2BDC. The NMR

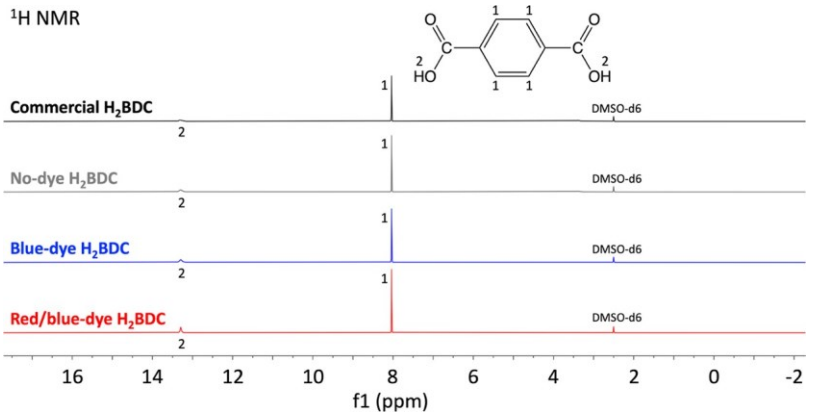

Figure 1. ^{1}H NMR spectra of commercial H_2BDC, H_2BDC recovered from no-dye polyester, H_2BDC recovered from blue-dye polyester, H_2BDC recovered from the 50/50 mixture of red and blue-dye polyester fabrics.

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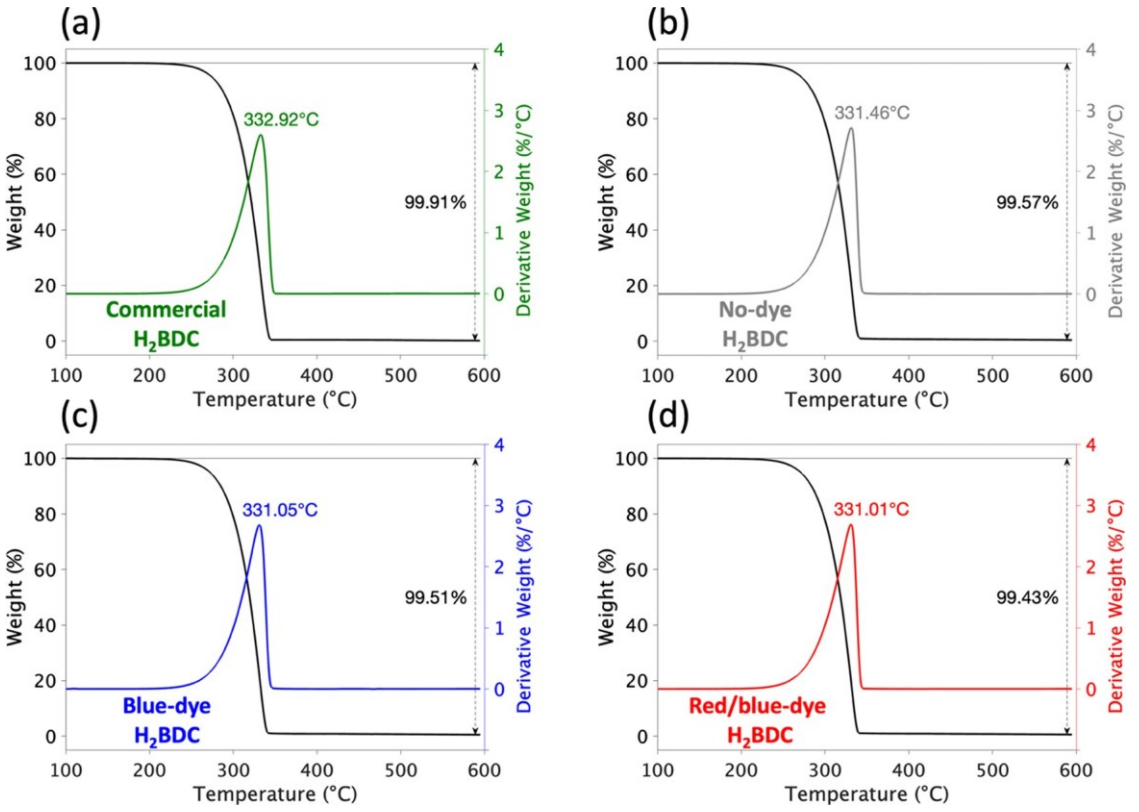

Figure 2. TGA curves of H_2BDC: (a) commercial H_2BDC, (b) H_2BDC from no-dye polyester, (c) H_2BDC from blue-dye polyester, and (d) H_2BDC from the 50/50 mixture of red and blue-dye polyester fabrics.

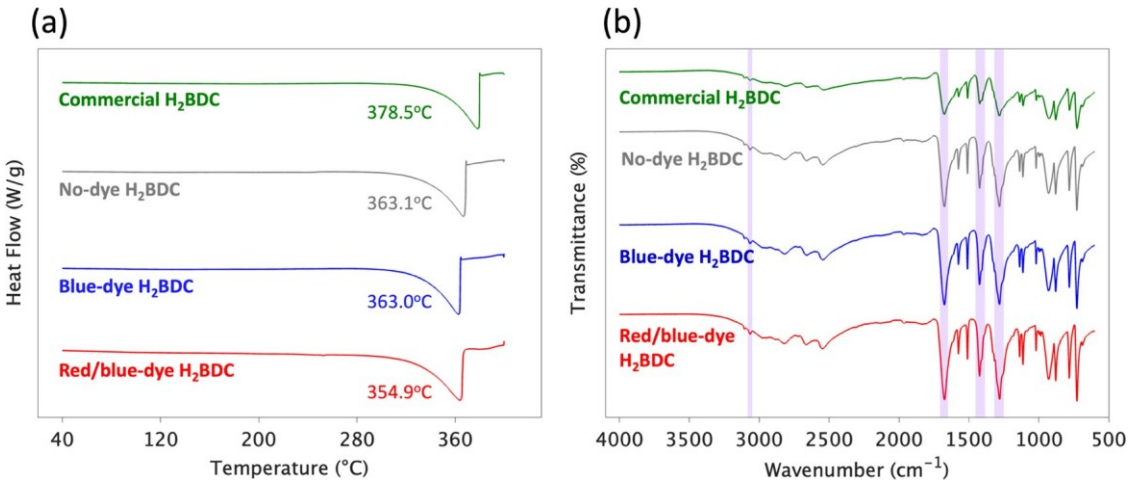

Figure 3. (a) DSC thermogram and (b) FTIR spectra of commercial H_2BDC and H_2BDC recovered from no-dye polyester, blue-dye polyester, and the 50/50 mixture of red and blue-dye polyester fabrics.

spectra for both ^1H and ^{13}C were identical (Figures 1 and S2). The signals at 8.04 and 13.29 ppm in ^1H NMR (Figure 1) spectra correspond to the protons of the benzene ring and the carboxylic acid group.[27] Based on the ^1H NMR analysis, the purity of H_2BDC recovered from the no-dye polyester, blue-dye polyester, and the 50/50 mixture of red and blue-dye polyester fabrics was 99.6, 99.5, and 98.7%, respectively. These results indicate that the presence of dyes had a negligible effect on the chemical structure of the recovered H_2BDC.

TGA thermograms are presented in Figure 2. The H_2BDC recovered from the depolymerized no-dye polyester, blue-dye polyester, and the 50/50 mixture of red and blue-dye polyester fabrics, as well as the commercially available H_2BDC, exhibited a similar single-step decomposition pattern with a large peak around 332 °C, which is in quantitative agreement with previously reported values for the sublimation of H_2BDC.[26] Both the H_2BDC recovered from the polyester fabrics and the commercial H_2BDC completely decomposed when heated up to 600 °C. Similarly, the DSC curves of the recovered H_2BDC obtained from the depolymerized polyester fabrics and the commercial H_2BDC showed the absence of any melting transition, as shown in Figure 3a.[17,28] The intense endothermic peak of the H_2BDC obtained from the polyester depolymerization appeared at slightly lower temperatures compared to that of

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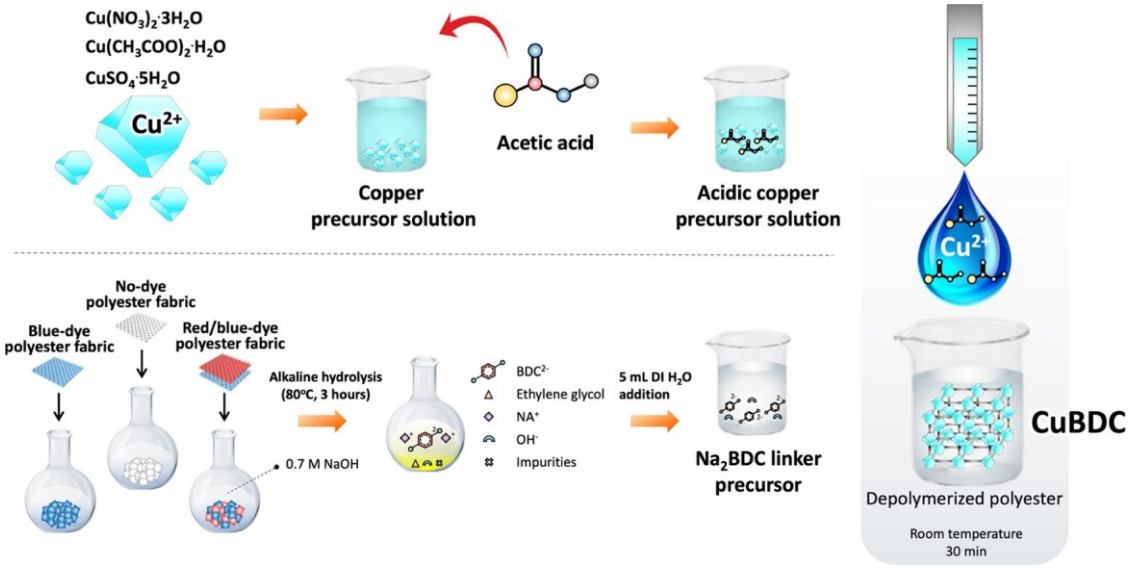
Scheme 2. Schematic Illustration of Our Approach to Synthesize CuBDC MOFs Using Polyester Fabrics



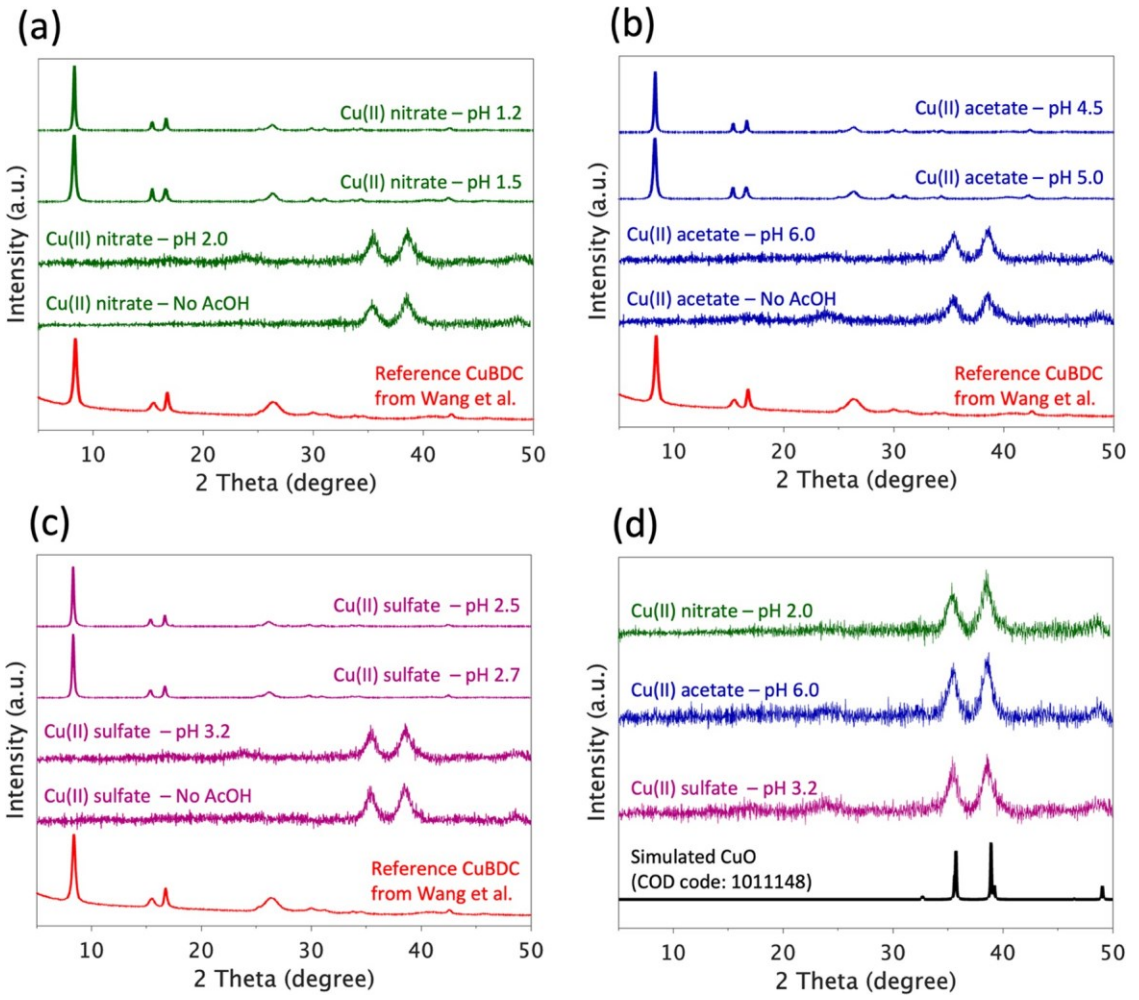


Figure 4. PXRD patterns of samples obtained using different copper precursor solutions at different pH values: (a) $Cu(NO_3)_2{\cdot}3H_2O$, (b) $Cu(CH_3COO)_2{\cdot}H_2O$, (c) $CuSO_4{\cdot}5H_2O$, and (d) comparison between simulated CuO and byproduct compounds obtained at higher pH values.

the commercial H_2BDC (Figure 3a), but the difference falls within reported ranges.[29,30] The thermogravimetric and DSC analyses are in agreement with the NMR data and confirm the high purity of the recovered H_2BDC from the colored polyester fabrics.

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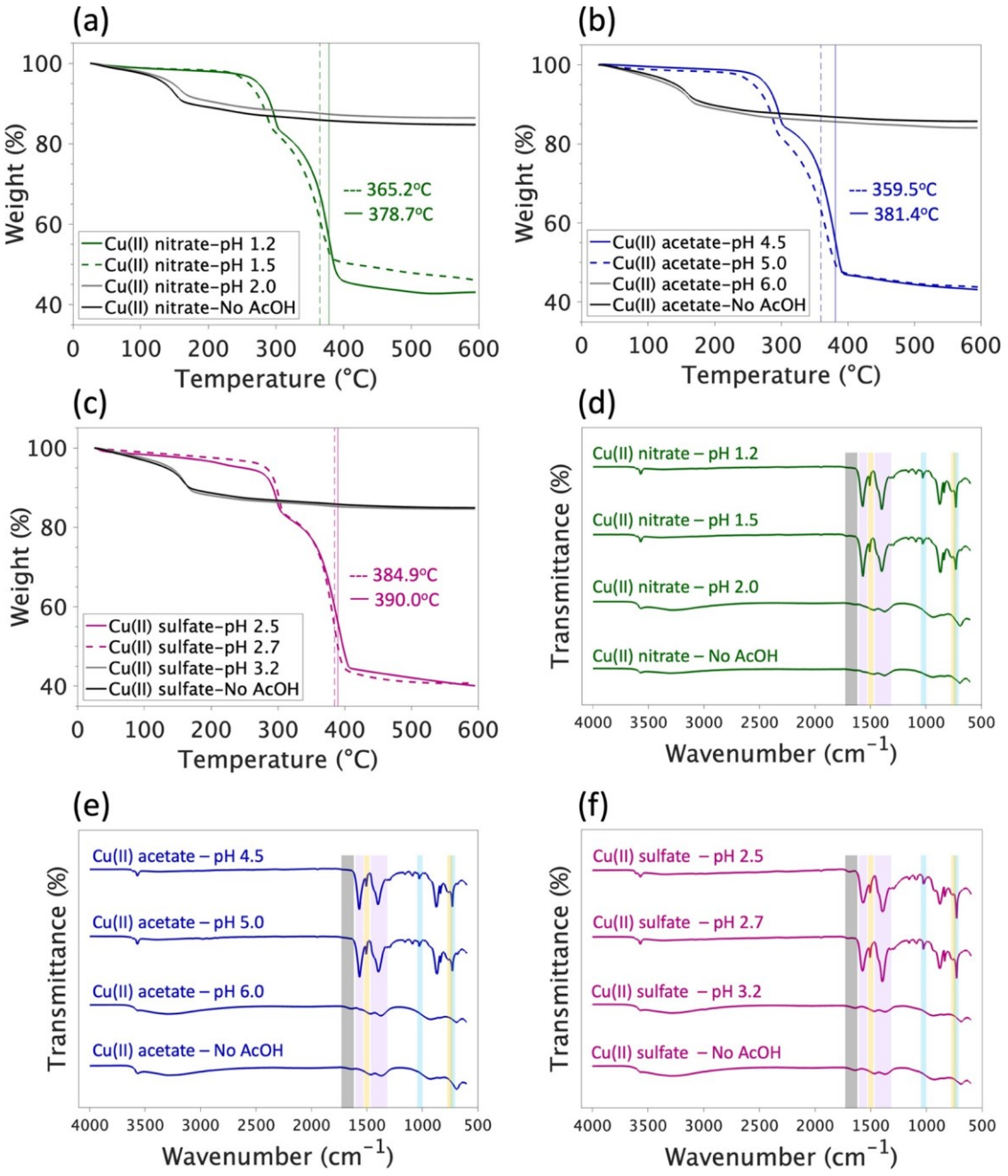

Figure 5. TGA curves (a−c) and FTIR spectra (d−f) of samples synthesized using Na_2BDC obtained from no-dye polyester fabrics and different copper salts: (a, d) $Cu(NO_3)_2{\cdot}3H_2O$, (b, e) $Cu(CH_3COO)_2{\cdot}H_2O$, and (c, f) $CuSO_4{\cdot}5H_2O$.

The FTIR characteristic peaks of the H_2BDC obtained from the depolymerized polyester fabrics also matched those of the commercial H_2BDC and those reported in the literature,[31] as shown in Figure 3b. The peak at 3064 cm^{-1} is attributed to the C−H stretching of the benzene ring, while the peak at 1685 cm^{-1} indicates the presence of C=O stretching. The peaks at 1424 and 1285 cm^{-1} correspond to OH in-plane deformation and ether C−O stretching.

Synthesis of CuBDC Using Polyester Fabrics as a Linker Source. The approach we used to synthesize CuBDC MOFs from depolymerized polyester fabrics is described in Scheme 2. Different copper salts were considered as metal precursors, and to prevent copper ions from forming impurities, acetic acid was added to the copper precursor solution before it was added dropwise to the alkaline depolymerization solution.

Experiments with No-Dye Polyester Fabrics. Before conducting synthesis experiments with dyed polyester fabrics, baseline experiments were performed using no-dye polyester fabrics to investigate the effect of the copper precursor solutions' pH on the formation of CuBDC MOF structures. The PXRD patterns shown in Figure 4 indicate that the precipitates formed using copper solutions with no acetic acid or with lower amounts of acetic acid (pH 2.0 for $Cu(NO_3)_2{\cdot}3H_2O$, pH 6.0 for $Cu(CH_3COO)_2{\cdot}H_2O$, and pH 3.2 for $CuSO_4{\cdot}5H_2O$ solution) contained Cu-based byproducts such as CuO (Code of Crystallography Open Database, COD: 1011148) (Figure 4d). These impurities can be attributed to the hindered

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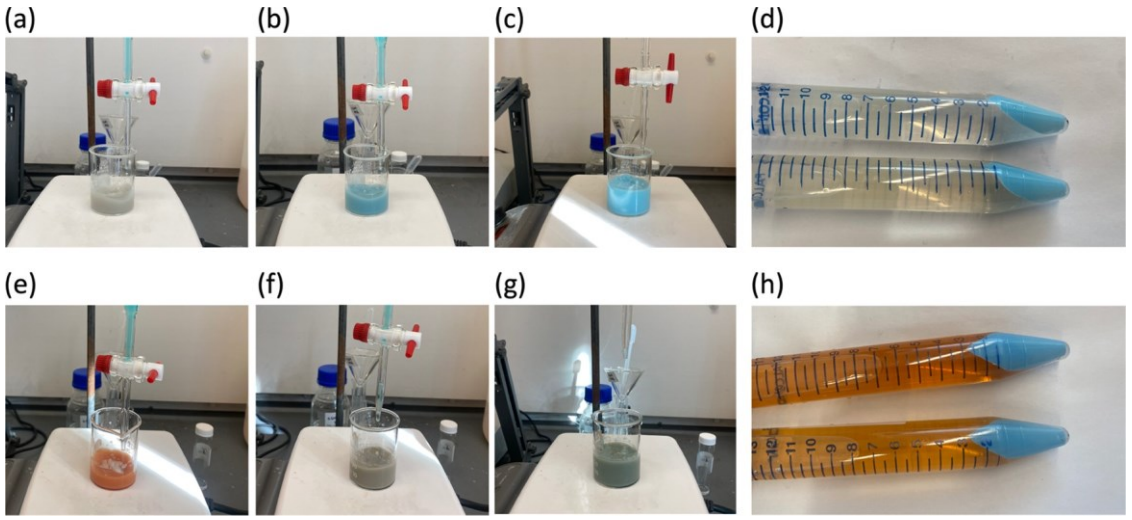

Figure 6. Digital photos of the room-temperature CuBDC MOFs synthesis using Na_2BDC from depolymerized blue-dye polyester (top) and a 50/50 mixture of red and blue-dye polyester fabrics (bottom): (a, e) before adding the Cu/AcOH solution at pH 4.5, (b, f) while adding the Cu/AcOH solution, (c, g) after completion of the reaction, (d, h) blue solids and colored supernatant obtained after centrifugation.

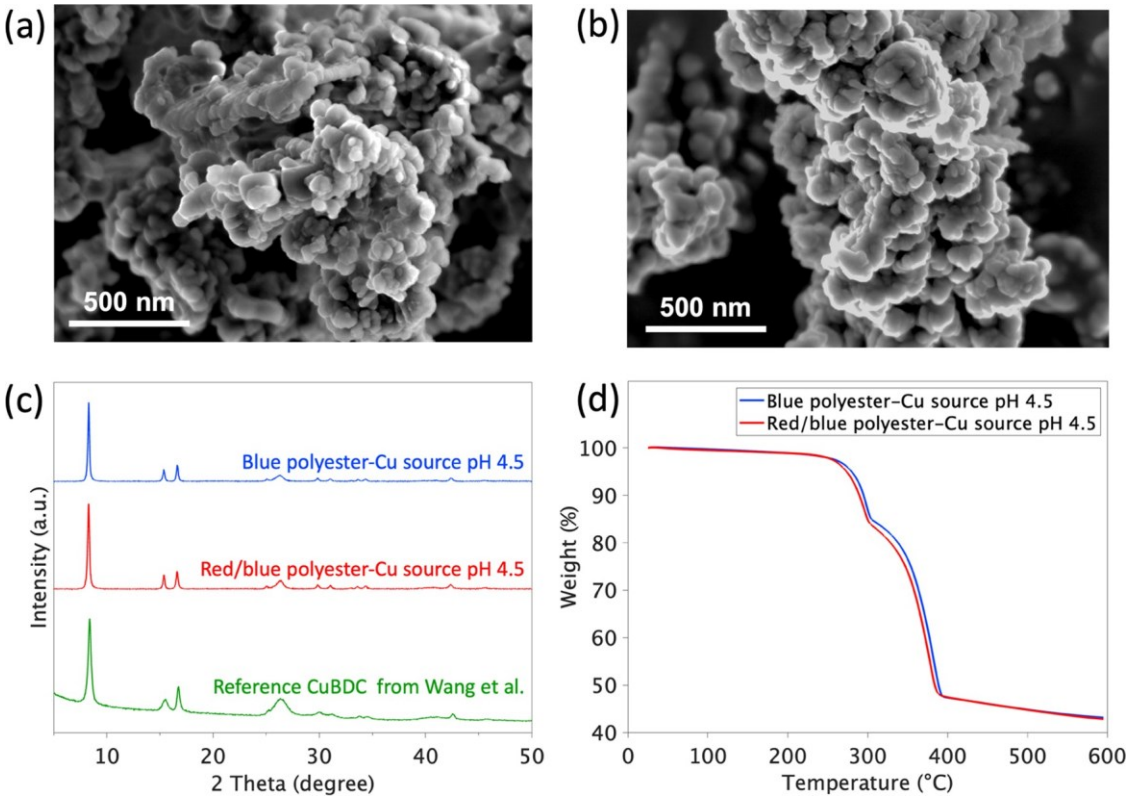

Figure 7. Characterization of CuBDC MOFs synthesized using Na_2BDC from depolymerized blue-dye polyester and the 50/50 mixture of red and blue-dye polyester fabrics and the copper acetate solutions at pH 4.5: (a) SEM image of CuBDC MOFs obtained from blue-dye polyester fabrics, (b) SEM image of CuBDC MOFs obtained from the 50/50 mixture of red and blue-dye polyester fabrics, (c) PXRD patterns, and (d) TGA curves.

formation of dimeric copper centers in the copper paddlewheel clusters—the most critical step in CuBDC MOF crystallization—leading to Cu-based byproducts known to occur under basic conditions.[24] In contrast, all structures formed at lower pH values produced phase-pure CuBDC MOFs (Figure 4a–c), and their PXRD patterns were in quantitative agreement with those reported by Wang et al.[32] and others.[33−36]

The thermal stability of the samples synthesized using Na_2BDC obtained from no-dye polyester fabrics and three different copper salts was evaluated using TGA, as shown in Figure 5a–c. Similar to their corresponding PXRD patterns, f5 samples synthesized using larger amounts of acetic acid (below pH 1.5 for $Cu(NO_3)_2{\cdot}3H_2O$ solution, pH 5.0 for $(CH_3COO)_2{\cdot}H_2O$ solution, pH 2.7 for $CuSO_4{\cdot}5H_2O$ solution) exhibited a two-stage weight loss, which is common for CuBDC MOFs.[18,22] The first stage of weight loss (16–17%) is likely due to the removal of the water and ethanol solvent. The second stage of weight loss appeared between approximately 300 and

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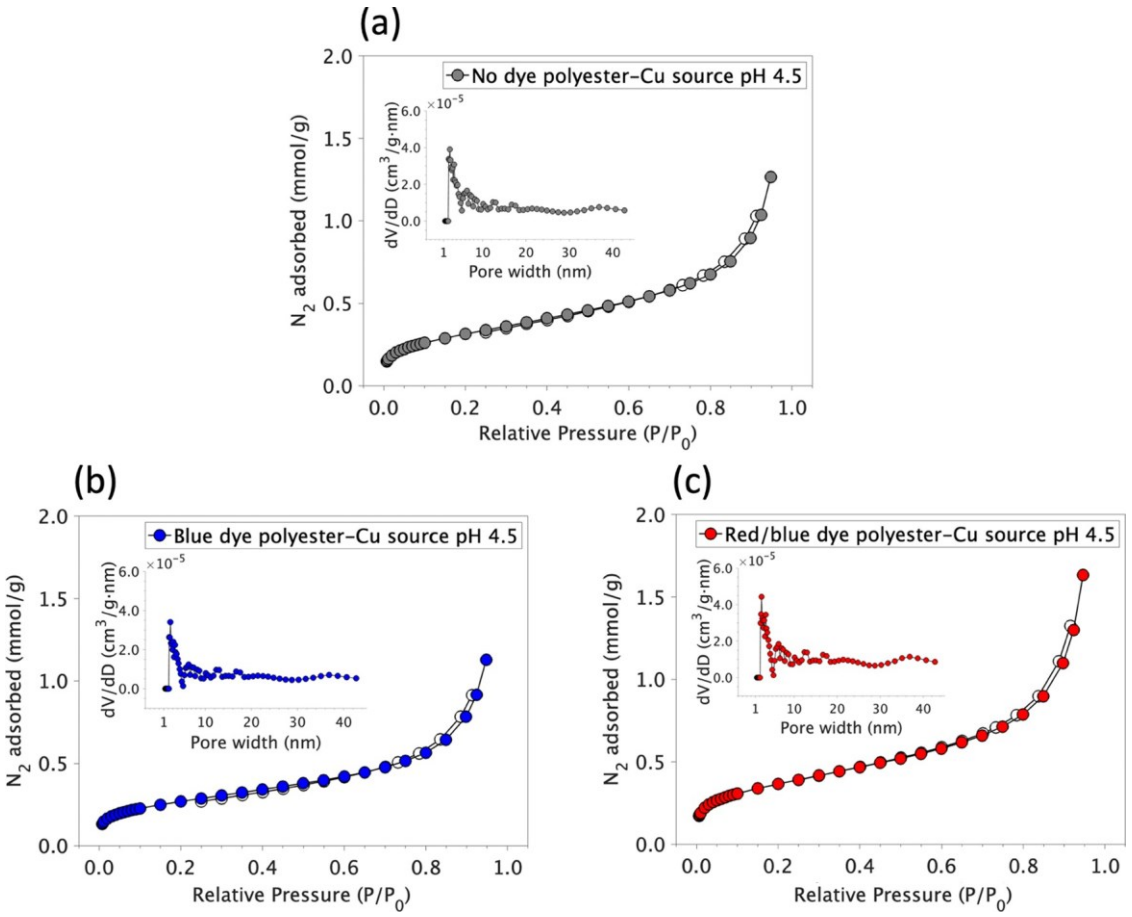

Figure 8. Nitrogen sorption (closed circles) and desorption (open circles) isotherms for CuBDC MOFs synthesized using Na_2BDC from depolymerized polyester fabrics and copper acetate solutions at pH 4.5. The inset corresponds to pore diameter distributions: (a) no-dye polyester, (b) blue-dye polyester, and (c) the 50/50 mixture of blue and red-dye polyester fabrics.

400 °C, accounting for 34−39% of the initial weight. This loss is attributable to the decomposition of the organic linker.[38] The residue after 400 °C corresponds to CuO, which is thermally stable up to 600 °C. According to the literature, CuBDC MOF structures at high temperatures collapse into CuO.[39]

The chemical composition of the samples synthesized using Na_2BDC recovered from no-dye polyester fabrics and three different copper salts was also evaluated using FTIR, as shown in Figure 5d−f. The FTIR spectra are in quantitative agreement with previously reported spectra for CuBDC MOFs.[25,37] The characteristic peaks at 1566 and 1394 cm^{-1} correspond to COO^- antisymmetric and symmetric stretching vibrations. The peaks at 1500 and 775 cm^{-1} match the vibrations specific to the phenyl ring, while the C−H vibrations in the aromatic ring are evident at 1025 and 738 cm^{-1}.[25,37] The carbonyl peaks related to the protonated carboxyl group are assigned to 1710−1760 cm^{-1}.

After demonstrating the synthesis of pure CuBDC MOFs using depolymerized undyed polyester fabrics, we turned our attention to exploring the potential scale-up of the synthesis reaction using dyed polyester fabrics. To this end, we chose to use $Cu(CH_3COO)_2{\cdot}H_2O$ as the copper source. Water can react with metal oxide clusters, causing ligand displacement[40] and slowly hydrolyzing the symmetrical bidentate carboxylate ligands bonded to the copper cations.[41] Therefore, we did not use $CuSO_4{\cdot}5H_2O$, which is soluble in water but not in ethanol. We also decided against using $Cu(NO_3)_2{\cdot}3H_2O$ due to its higher cost and the need for extra safety precautions when it is used in large amounts.[42]

Experiments with Dyed Polyester Fabrics. We used polyester fabrics containing blue and red dyes to assess the robustness of the crystallization during the assembly of MOF structures using a pH 4.5 copper acetate solution. As shown in Figure 6a−c, blue-dye polyester fabrics depolymerized into a gray-purple solution that eventually turned blue after the addition of the acidic copper acetate solution. The depolymerized solution obtained from the 50/50 mixture of red and blue-dye polyester fabrics changed from orange to cloudy khaki after adding the copper acetate solution, as shown in Figure 6e−g. After centrifugation, we observed that a dye-containing liquid remained in the supernatant while the blue solids precipitated (Figure 6d,h).

The isolated blue solids were characterized by SEM, PXRD, TGA, and FTIR spectra, as shown in Figures 7 and S3. The morphology of the CuBDC MOFs samples synthesized from blue-dye polyester (Figure 7a) and the 50/50 mixture of red and blue-dye polyester fabrics (Figure 7b) appeared similar in the SEM images and exhibited a granular structure that qualitatively agrees with those of the reported literature.[14,25] All tested samples exhibited the same CuBDC crystal structure as reported by Wang et al.[32] and others (Figure 7c).[33−36] The TGA thermograms indicated that the CuBDC MOF structures synthesized with dyed polyester fabrics showed a two-step weight loss pattern, similar to those of the CuBDC MOF

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samples synthesized with no-dye polyester fabrics (Figure 7d). The rapid weight loss appeared at 382.1 and at 377.2 °C for the CuBDC MOF samples prepared with blue-dye polyester and with the 50/50 mixture of red and blue-dye polyester fabrics, respectively. These values are comparable to those obtained using no-dye polyester fabrics. (Figure 5b). The FTIR spectra of both samples confirmed the presence of the characteristic peaks of CuBDC MOFs (Figure S3), which agree with those observed in the CuBDC MOFs structures obtained using no-dye polyester fabrics (Figure 5e) and with those reported in the literature.[25,37]

Figure 8 shows nitrogen isotherms measured at 77 K to study the porosity of the CuBDC MOF samples prepared using no-dye and dyed polyester fabrics and a pH 4.5 copper acetate solution. The average pore diameters determined by the BJH method and total pore volumes are presented in Table 3. All

Table 3. Porous Properties of the As-Synthesized CuBDC MOFs Prepared Using Na_2BDC from No-Dye and Dyed Polyester Fabrics

CuBDC MOFs	BET surface area ($m^2 \cdot g^{-1}$)	average pore diameter (nm)	total pore volume ($cm^3 \cdot g^{-1}$)
no-dye/Cu source at pH 4.5	25 ± 0.21	7.66	0.044
blue-dye/Cu source at pH 4.5	21 ± 0.12	8.87	0.039
red/blue-dye/Cu source at pH 4.5	29 ± 0.17	8.90	0.057
CuBDC synthesized at RT by Li et al.[22]	49.6		
CuBDC synthesized at RT by Zhang et al.[25]	46.78		0.223
CuBDC synthesized at RT by Wang et al.[32]	87	1.4	
CuBDC synthesized at RT by Chen et al.[33]	33.27		

samples tested exhibited a type II isotherm (Figure 8a−c),[43,44] which is in agreement with previously reported data for CuBDC MOFs.[22] The BET surface area values are also comparable with previously reported data for CuBDC MOFs synthesized using Na_2BDC at room temperature (Table 3).[22,25,32,33] The N_2 isotherm (Figure 8a−c) and porous properties (Table 3) of the CuBDC MOF samples synthesized using Na_2BDC from blue-dye polyester and the 50/50 mixture of red and blue-dye polyester fabrics were similar to those of CuBDC MOFs made using no-dye polyester fabrics. These findings further demonstrate the suitability of this pathway to synthesize CuBDC MOFs directly from a depolymerization mixture without the need for isolating H_2BDC.

CONCLUSIONS

We demonstrated the direct upcycling of dyed polyester fabrics into CuBDC MOFs. The reported approach directly utilizes Na_2BDC from a depolymerized solution without the need to precipitate and purify the H_2BDC linker. This approach avoids the use of toxic solvents and high reaction temperatures for crystallization and does not require additional steps for linker isolation, hence making it amenable to scale-up. We also determined that the reported approach allows for the use of different copper salts ($Cu(NO_3)_2 \cdot 3H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$, and $CuSO_4 \cdot 5H_2O$), as well as dye-colored polyester fabrics, without affecting the structure of the resulting CuBDC MOFs. These findings suggest that discarded textiles could be used as raw materials for MOF synthesis and highlight the selective crystallization properties of metal−organic frameworks. These results also demonstrate that MOF assembly provides an effective means to reject dye molecules and other impurities, enabling simplified separation of terephthalate from polyester fabric digestion mixtures.

As CuBDC MOF structures have already shown antibacterial and other functional properties, MOFs synthesized from discarded textiles could be incorporated as functional finishes for other substrates, potentially enabling a more circular approach for the textile industry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.iecr.3c00226.

Digital photos and ^{13}C NMR spectra of commercial H_2BDC, H_2BDC from no-dye polyester, blue-dye polyester, and the 50/50 mixture of red and blue-dye polyester fabrics; FTIR spectra of CuBDC MOFs synthesized using Na_2BDC from blue-dye polyester and the 50/50 mixture of red and blue-dye polyester fabrics and copper acetate solutions at pH 4.5 (PDF)

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Author Contributions

Y.K. performed most experiments and wrote the initial drafts. T.J.A. performed BET experiments and analysis of the data. P.M. provided guidance on the experimental setup and MOF synthesis strategies, as well as edited and reviewed the manuscript. J.H. performed initial planning of the experiments and analysis of the experimental data, as well as reviewed and edited the manuscript. The manuscript could not have been written without the contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

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ABBREVIATIONS

AcOH	acetic acid
BET	Brunauer−Emmett−Teller
BJH	Barrett−Joyner−Halenda
COD	crystallography open database
CuBDC	copper-1,4-benzenedicarboxylate
DI water	deionized water
DMF	*N*,*N*-dimethylformamide
DSC	differential scanning calorimetry
FTIR	Fourier transform infrared spectroscopy
H_2BDC	1,4-benzenedicarboxylic acid
MOFs	metal−organic frameworks
MIL	Materials Institute Lavoisier
Na_2BDC	disodium terephthalate
NMR	nuclear magnetic resonance
PET	poly(ethylene terephthalate)
PXRD	powder X-ray diffraction
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
TPA	terephthalic acid
UiO	Universitetet i Osl

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