

Supporting Information

Fabrication of MOF Thin Films at Miscible Liquid-Liquid Interface by Spray Method

Xiao-jue Bai,[†] Dan Chen,[†] Lin-lin Li,[†] Lei Shao,[†] Wen-xiu He,[†] Huan Chen,[†] Yu-nong Li,[†] Xue-min Zhang,[†] Li-ying Zhang,[†] Tie-qiang Wang,[†] Yu Fu^{†} and Wei Qi^{*‡}*

[†]Department of Chemistry, College of Sciences, Northeastern University, Shenyang 110819, P. R. China

[‡]Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, P. R. China

Corresponding Author

* E-mail: fuyu@mail.neu.edu.cn (Y. F.)

* E-mail: wqi@imr.ac.cn (W. Q.)

EXPERIMENTAL SECTION

Materials: Copper acetate ($\text{Cu}(\text{CH}_3\text{COO})_2$), cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), nickel acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), ferric nitrate ($\text{Fe}(\text{NO}_3)_3$), Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), 2-aminoterephthalic acid ($\text{H}_2\text{BDC-NH}_2$), 1,4-benzenedicarboxylic acid (H_2BDC), 1,4-naphthalenedicarboxylic acid ($\text{H}_2(1,4\text{-NDC})$), 2,6-naphthalenedicarboxylic acid ($\text{H}_2(2,6\text{-NDC})$), 2,5-dihydroxyterephthalic acid (H_2DOBDC) and 2-methylimidazole were purchased from Energy Chemical. Sodium borohydride (NaBH_4), 4-nitrophenol (4-NP) were purchased from Sigma-Aldrich. Coomassie Brilliant Blue R-250 was purchased from Biotopped. N, N-Dimethylformamide (DMF), acetonitrile (CH_3CN), methanol (CH_3OH), ethanediol ($\text{C}_2\text{H}_6\text{O}_2$), dimethyl sulfoxide (DMSO) and ethanol ($\text{C}_2\text{H}_6\text{O}$) were purchased from Sinopharm Chemical Reagent Co., Ltd. The water used in this work was deionized water. All chemicals used in this study were of analytical grade and used without further purification.

Experimental procedure:

Fabrication of CuBDC thin film: H_2BDC (13.3 mg, 0.08 mmol) was dissolved in 6 mL of mixture of DMF and CH_3CN (V:V=2:1) in a vial. Then the transparent solution was added into a glass petri dish covered with solid substrates. After that, $\text{Cu}(\text{CH}_3\text{COO})_2$ (5.5 mg, 0.03 mmol) was dissolved in 1.5 mL of mixture of DMF and CH_3CN (V:V=1:2), and the metal precursor solution was uniformly sprayed into the

glass petri dish using the ultraphonic spray nozzle & system on the top of the linker precursor solution with the flow rate of 1 $\mu\text{L}/\text{sec}$. The synthetic process was maintained in static conditions, and the blue thin films floated at the liquid surface as free-standing films. Subsequently, the reaction solution was carefully removed from the glass petri dish, and the resulting blue thin film was deposited onto the solid substrate. Finally, the composite membrane was washed consecutively three times with DMF followed by another three times with CH_3OH and dried at 70°C for 12 h.

Synthesis of bulk-type CuBDC MOF: Bulk-type CuBDC was synthesized following the hydrothermal synthesis. Thus, 1.053 g of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 724 mg of 1,4-benzenedicarboxylic acid and 87 mL of DMF were mixed in a 250 mL round-bottom flask and refluxed at 100°C during 24 h. The resulting powder was collected by centrifugation at 6000 rpm. Finally, the solid was washed consecutively three times with DMF followed by another three times with CH_3OH and dried at 70°C for 12 h.

Forming of miscible liquid-liquid interface: (a) 12 mL DMF/ CH_3CN (V:V=2:1) was added into a vial, and then 2 mL of the Coomassie Brilliant Blue dyed DMF/ CH_3CN (V:V=1:2) was sprayed onto the lower liquid. 12 mL of the Coomassie Brilliant Blue dyed DMF/ CH_3CN (V:V=1:2) was added into the vial, and then 2 mL DMF/ CH_3CN (V:V=2:1) was sprayed onto the lower liquid. 12 mL DMF/ CH_3CN (V:V=2:1) was added into the vial, and then 2 mL of the Coomassie Brilliant Blue dyed DMF/ CH_3CN (V:V=1:2) was added onto the lower liquid along the glass wall. 12 mL DMF was added into the vial, and then 2 mL of the Coomassie Brilliant Blue dyed DMF was

sprayed onto the lower liquid. (b) The miscible liquid-liquid interface consisted of DMF/CH₃CN (V:V=1:2) containing Cu²⁺ as upper layer and DMF/CH₃CN (V:V=2:1) as lower layer by using the above spray method. UV-Vis absorption spectroscopy (the absorbance-time curve at 276 nm) at 0.1 cm below the liquid-liquid interface was detected. (c) 5 mL DMF/methanol (1/2), ethanediol/ methanol (1/2), DMSO/DMF (1/2), acetonitrile/ethanol (1/2) was sprayed onto the DMF/methanol (2/1) containing CuAc₂, ethanediol/ methanol (2/1) containing CoAc₂, DMSO/DMF (2/1) containing NiAc₂, acetonitrile/ethanol (2/1) containing Fe(NO₃)₃, respectively.

Generalization of the MOFs thin film synthesis approach to other MOF structures: (To investigate the scope of the MOFs thin film synthesis strategy, the MLLI method was extended to other MOFs structures by selecting alternative metal nodes and organic linker molecules.)

Cu(1,4-NDC)/Cu(2,6-NDC) thin film was synthesized by using Cu²⁺ as metal cation and 1,4-NDC/2,6-NDC as organic ligand. H₂(1,4-NDC)/H₂(2,6-NDC) (17.3 mg, 0.08 mmol) was dissolved in 6 mL of mixture of DMF and CH₃CN (V:V=2:1) in a vial. Then the transparent solution was added into a glass petri dish covered with solid substrates. After that, Cu(CH₃COO)₂ (5.5 mg, 0.03 mmol) was dissolved in 1.5 mL of mixture of DMF and CH₃CN (V:V=1:2), and the metal precursor solution was uniformly sprayed into the glass petri dish using the ultraphonic spray nozzle & system on the top of the linker precursor solution with the flow rate of 1 μL/sec. Subsequently, the reaction solution was carefully removed from the glass petri dish,

and the resulting thin film was deposited onto the solid substrate. Finally, the composite membrane was washed consecutively three times with DMF followed by another three times with CH₃OH and dried at 70°C for 12 h.

Cu(BDC-NH₂) thin film was synthesized by using Cu²⁺ as metal cation and BDC-NH₂ as organic ligand. H₂BDC-NH₂ (14.5 mg, 0.08 mmol) was dissolved in 6 mL of mixture of DMF and CH₃CN (V:V=2:1) in a vial. Then the light yellow solution was added into a glass petri dish covered with solid substrates. After that, Cu(CH₃COO)₂ (5.5 mg, 0.03 mmol) was dissolved in 1.5 mL of mixture of DMF and CH₃CN (V:V=1:2), and the metal precursor solution was uniformly sprayed into the glass petri dish using the ultraphonic spray nozzle & system on the top of the linker precursor solution with the flow rate of 1 μL/sec. Subsequently, the reaction solution was carefully removed from the glass petri dish, and the resulting thin film was deposited onto the solid substrate. Finally, the composite membrane was washed consecutively three times with DMF followed by another three times with CH₃OH and dried at 70°C for 12 h.

Ni-Co(BDC) thin film was synthesized by using Ni²⁺ and Co²⁺ as metal cation and BDC as organic ligand. H₂(BDC) (13.3 mg, 0.08 mmol) was dissolved in 6 mL of mixture of DMF and CH₃CN (V:V=2:1) in a vial. Then the transparent solution was added into a glass petri dish covered with solid substrates. After that, Ni(CH₃COO)₂•4H₂O (2.5 mg, 0.01 mmol) and Co(CH₃COO)₂•4H₂O (2.5 mg, 0.01 mmol) were dissolved in 1.5 mL of mixture of DMF and CH₃CN (V:V=1:2), and the metal precursor solution was uniformly sprayed into the glass petri dish using the

ultraphonic spray nozzle & system on the top of the linker precursor solution with the flow rate of 1 $\mu\text{L}/\text{sec}$. Subsequently, the reaction solution was carefully removed from the glass petri dish, and the resulting thin film was deposited onto the solid substrate. Finally, the composite membrane was washed consecutively three times with DMF followed by another three times with CH_3OH and dried at 70°C for 12 h.

Cu₂(DOBDC) thin film was synthesized by using Cu^{2+} as metal cation and DOBDC as organic ligand. $\text{H}_2(\text{DOBDC})$ (79.2 mg, 0.40 mmol) was dissolved in 6 mL of mixture of DMF and CH_3CN (V:V=2:1) in a vial. Then the claybank solution was added into a glass petri dish covered with solid substrates. After that, $\text{Cu}(\text{CH}_3\text{COO})_2$ (36.2 mg, 0.20 mmol) were dissolved in 1.5 mL of mixture of DMF and CH_3CN (V:V=1:2), and the metal precursor solution was uniformly sprayed into the glass petri dish using the ultraphonic spray nozzle & system on the top of the linker precursor solution with the flow rate of 0.5 $\mu\text{L}/\text{sec}$. Subsequently, the reaction solution was carefully removed from the glass petri dish, and the resulting thin film was deposited onto the solid substrate. Finally, the composite membrane was washed consecutively three times with DMF followed by another three times with CH_3OH and dried at 70°C for 12 h.

ZIF-8 thin film was synthesized by using Zn^{2+} as metal cation and 2-methylimidazole as organic ligand. 2-methylimidazole (110 mg, 0.60 mmol) was dissolved in 6 mL of mixture of DMF and CH_3OH (V:V=2:1) in a vial. Then the transparent solution was added into a glass petri dish covered with solid substrates. After that, $\text{Zn}(\text{CH}_3\text{COO})_2$ (6.2 mg, 0.075 mmol) were dissolved in 1.5 mL of mixture of DMF and CH_3OH (V:V=1:2), and the metal precursor solution was uniformly sprayed into the glass petri

dish using the ultraphonic spray nozzle & system on the top of the linker precursor solution with the flow rate of 1 $\mu\text{L}/\text{sec}$. Subsequently, the reaction solution was carefully removed from the glass petri dish, and the resulting thin film was deposited onto the solid substrate. Finally, the composite membrane was washed consecutively three times with DMF followed by another three times with CH_3OH and dried at 70°C for 12 h.

Continuous catalytic operation: Typically, an aqueous solution of 4-NP (8×10^{-2} mmol/L) and NaBH_4 (4×10^{-2} mol/L) was pumped through a piece of the CuBDC/hydrophobic filter composite membrane (diameter 25 mm, effective area 314 mm^2) using a peristaltic pump. A flow rate of 6 mL/min was used to realize the continuous catalysis operation of 4-NP. The solution passing through the composite membrane was collected at the outlet and an UV-Vis absorption spectrum was measured with a time interval of 30 min. A reference experiment was also carried out by passing the reactants through the filter membrane without CuBDC under the above same conditions.

In NaBH_4 aqueous solution, the 4-NP has characteristic UV-absorbance peak at 400 nm with bright yellow color. The solution was stable in the absence of the catalyst and no significant change was observed in absorbance intensity or peak position. After the solution cross through the CuBDC/filter composite membrane, the bright yellow color bleached to colorless, indicating that the 4-NP reduction was finished. Meanwhile, the UV-Vis spectra monitoring showed that the absorption of 4-NP at 400 nm significantly reduced. At the same time, a new 4-AP peak appears at 300nm as the

reaction progressed.

Characterization of material: Morphologies of MOFs thin film were characterized by field-emission scanning electron microscopy (FE-SEM, Hitachi SU8010). The elemental mapping was done by energy-dispersive X-ray (EDX, Oxford Instruments). The crystallographic information was analyzed by X-ray diffraction (XRD, Shimadzu XRD-6000) equipped with a Cu K α radiation source ($\lambda=1.5406$ Å). Specific surface areas and pore size of the samples were determined by using nitrogen adsorption-desorption isotherms at 77 K (Micromeritics ASAP 2020 system). The organic groups in the MOF structures were characterized by Fourier transform infrared spectroscopy (FT-IR, Bruker VERTEX 70). The ultraphonic spray nozzle & system was manufactured by Siansonic Technology Co., Ltd. The ultraphonic generator was DP30 and the nozzle is ZPQ-S-95. The catalytic reduction of 4-NP to 4-AP was monitored with an optics spectrometer (Maya2000 Pro). The peristaltic pump (ATP-3200) used in the membrane reactor was produced in Automatic science (Tianjin) Instrument Co., Ltd.

Samples of CuBDC MOFs thin film used for SEM (elemental mapping) and XRD characterization were prepared by depositing free-standing MOFs thin films onto monocrystalline Si and piranha-cleaned monocrystalline Si, respectively. IR and BET of CuBDC thin film samples were obtained by collecting free-standing MOFs film.

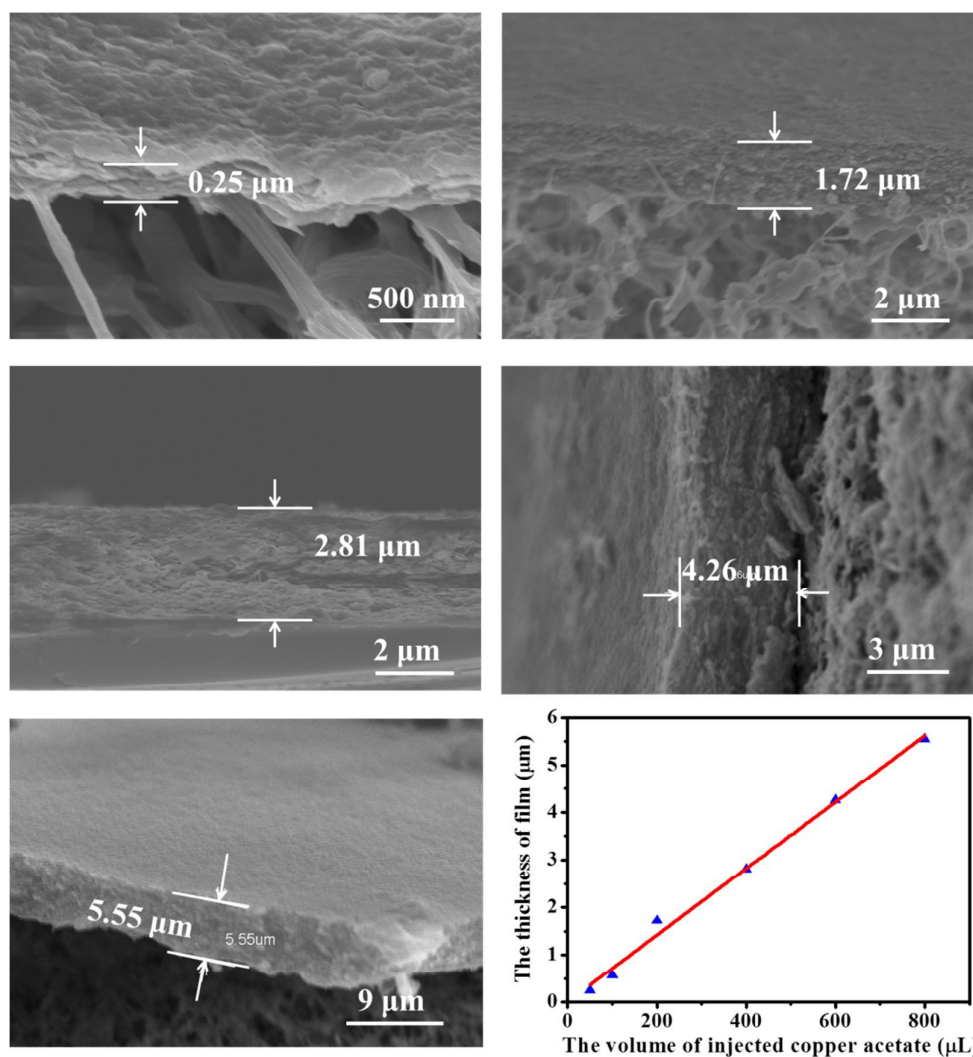


Figure S1. The cross-section SEM images of CuBDC thin films with different thickness and the relationship between CuBDC film thickness and the sprayed Cu ions volume.

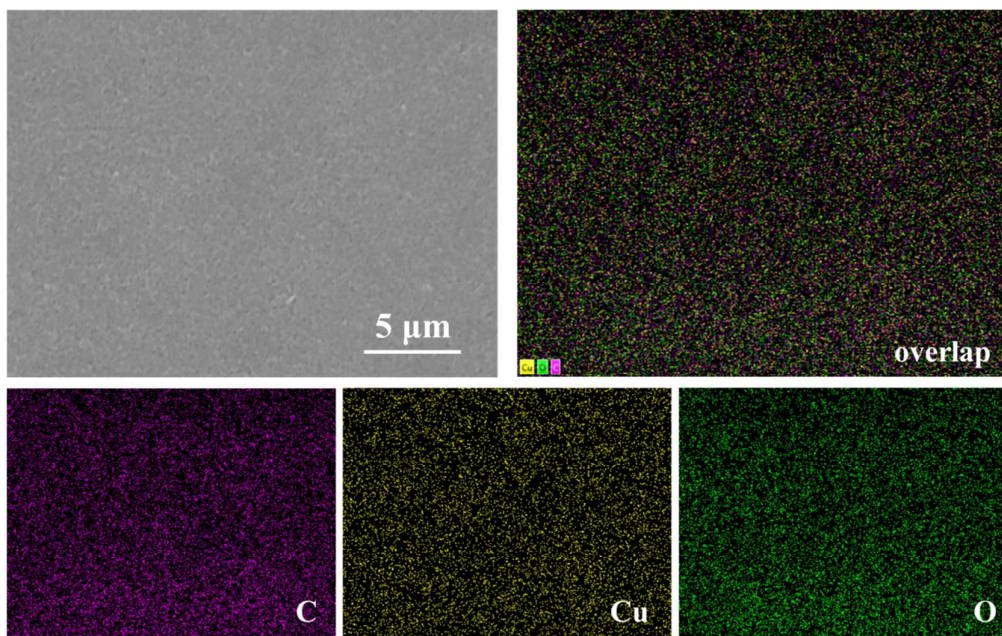


Figure S2. SEM image and EDX elemental map images of CuBDC thin films.

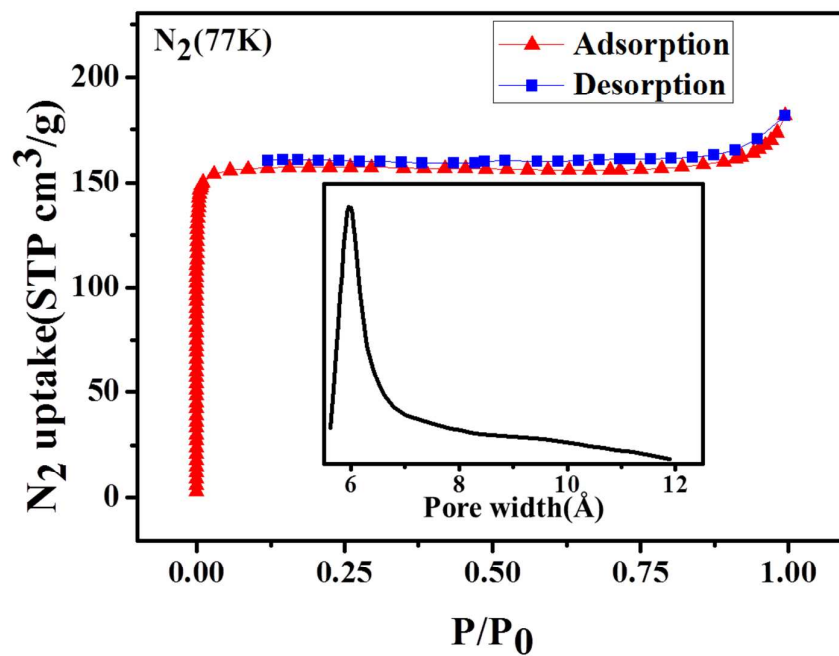


Figure S3. N_2 adsorption/desorption isotherm and the pore-size distribution (inset) of bulk CuBDC

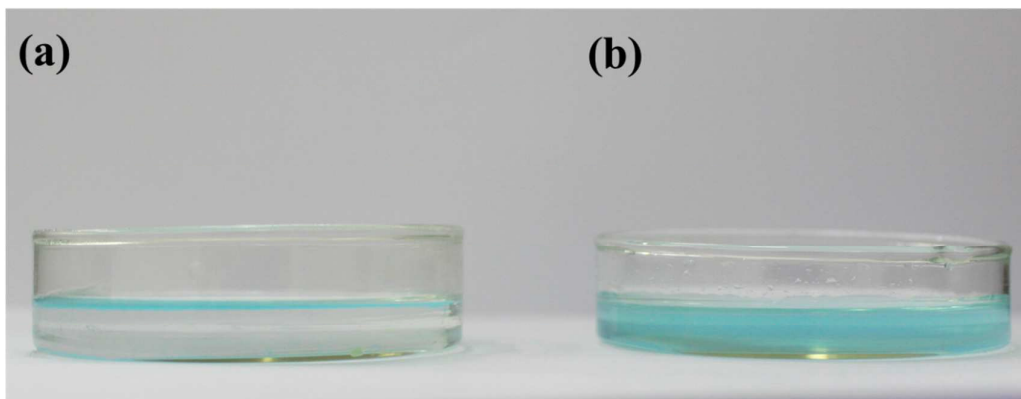


Figure S4. The photographs of (a) floating CuBDC thin film by selecting the solvent of DMF/CH₃CN (1/2) and DMF/CH₃CN (2/1), (b) CuBDC floccule by selecting the solvent of pure DMF.

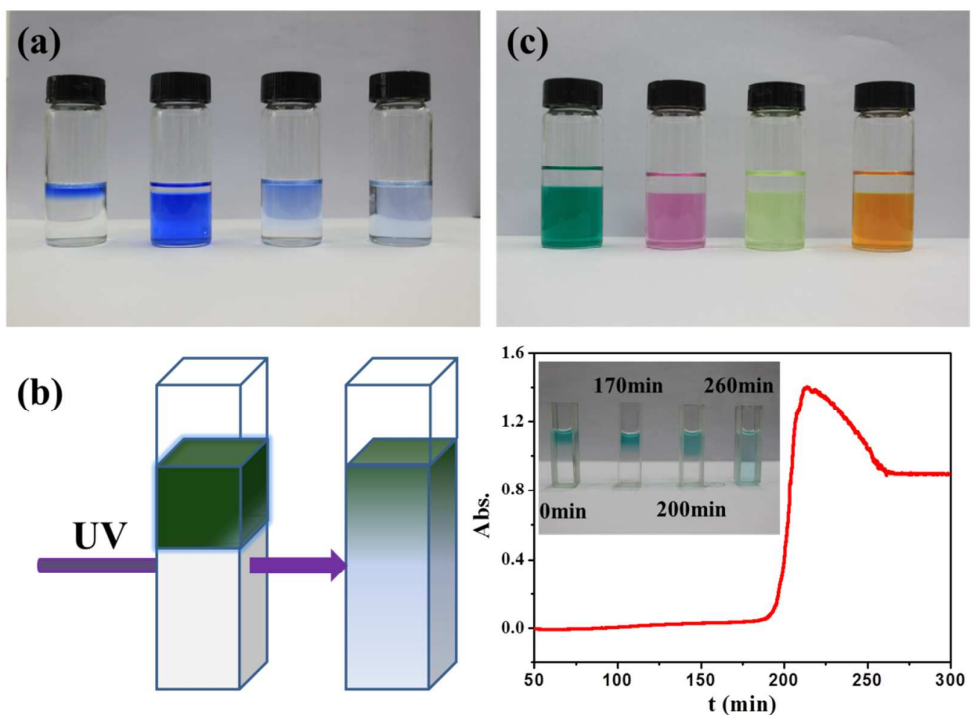


Figure S5. (a) From left to right: the dyed DMF/CH₃CN (V/V=1:2) was sprayed onto DMF/CH₃CN (V/V=2:1), DMF/CH₃CN (V/V=2:1) was sprayed onto dyed DMF/CH₃CN (V/V=1:2), the dyed DMF/CH₃CN (V/V=1:2) was carefully added onto DMF/CH₃CN (V/V=2:1) along the glass wall, the dyed DMF was sprayed onto DMF. (b) The absorbance-time curve at 0.1 cm below the DMF/CH₃CN (V/V=1:2)@Cu²⁺-DMF/CH₃CN (V/V=2:1) interface (right) and the schematic (left). (c) A series of miscible liquid-liquid interfaces. From left to right: DMF/methanol (1/2)-DMF/methanol (2/1) containing CuAc₂, ethanediol/ methanol(1/2)-ethanediol/ methanol (2/1) containing CoAc₂, DMSO/DMF (1/2)-DMSO/DMF(2/1) containing NiAc₂, acetonitrile/ethanol (1/2)-acetonitrile/ethanol (2/1) containing Fe(NO₃)₃.

To quantify this metastable MLLI, DMF/CH₃CN (V/V=1:2) as upper solution containing the copper acetate was sprayed onto pure DMF/CH₃CN (V/V=2:1), and

the downward diffusion rate of Cu ions was detected by UV-Vis absorption spectra at 0.1 cm below the liquid-liquid interface (**Figure S5b**). The absorbance-time curve at 276 nm (the maximum absorbance of Cu ions) shows that Cu ions were almost undetectable below the interface in the first 3 hours which represented few Cu ions across the interface into the lower phase, whereas in the next 20 minutes the absorbance increased rapidly meaning the upper Cu ions quickly broke through the interface, and the solution finally became homogeneous system. Coincidentally, the interface exists not only in DMF/CH₃CN mixing system, but also in other mixing solutions, such as DMF/methanol, ethanediol/methanol, DMSO/DMF, acetonitrile/ethanol (**Figure S5c**).

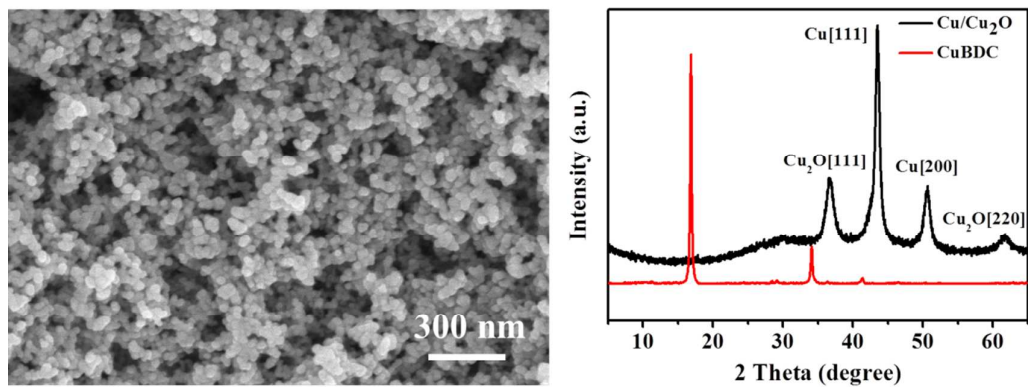


Figure S6. SEM image (left) and XRD pattern (right) of the thin film after catalytic reaction

600 MHz, D₂O

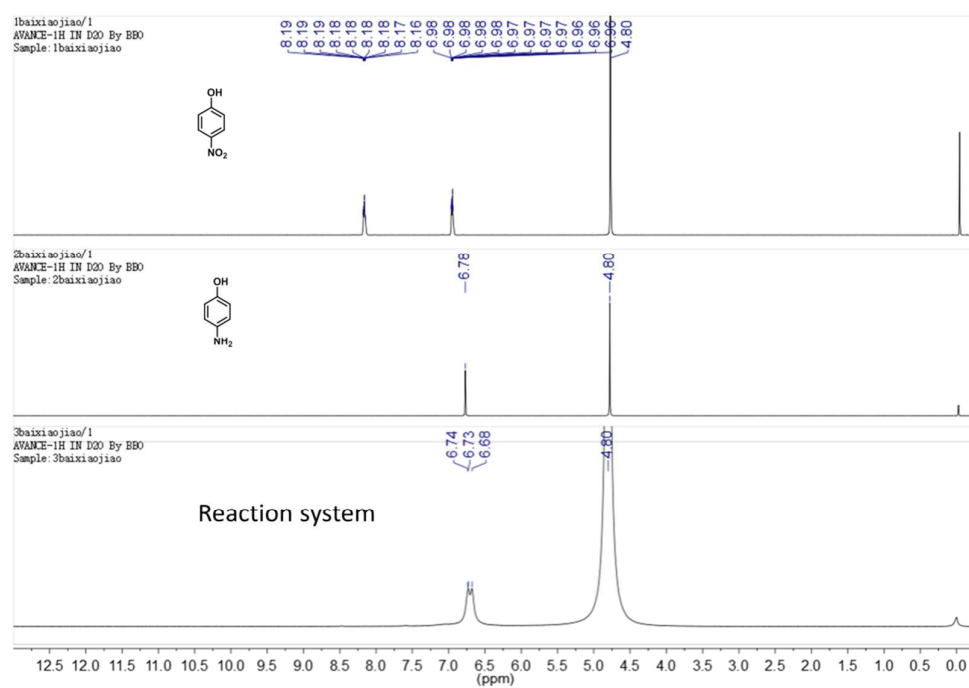


Figure S7. ¹H NMR spectrums of reactant (4-NP) and product (4-AP)

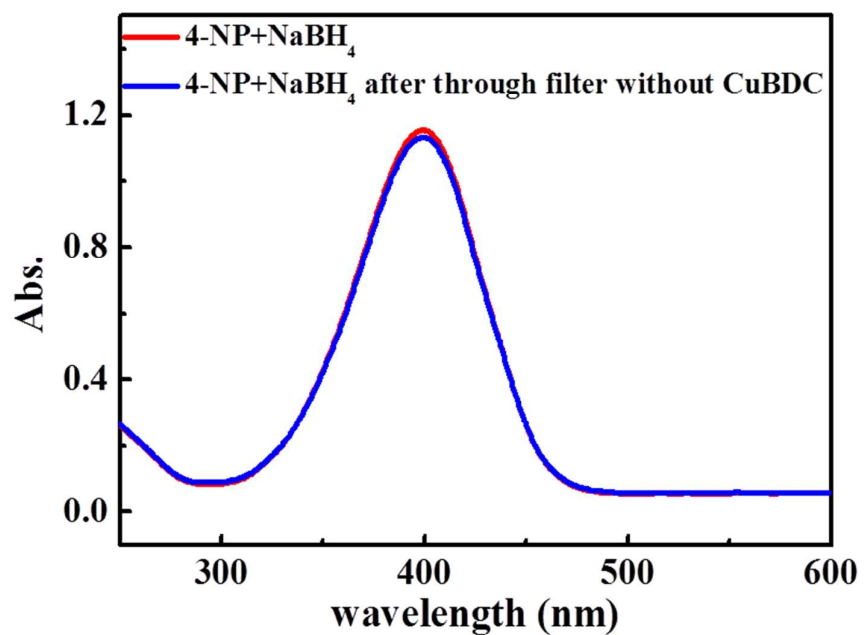


Figure S8. UV-Vis absorption spectra of the outlet solution by passing the reactants through the filter membrane without CuBDC

To demonstrate the catalysis of CuBDC thin film, a reference experiment was also carried out by passing the reactants (4-NP+NaBH₄) through the filter membrane without CuBDC, and in that case, 4-NP was hardly degraded.