

Microwave-Assisted Cyanation of an Aryl Bromide Directly on a Metal-Organic Framework

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SUPPORTING INFORMATION

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General Methods.

Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Solutions were concentrated by using a rotary evaporator, and generally followed by removal of residual solvents on a vacuum line. Flash column chromatography was performed on silica gel (400-630 mesh). Nuclear magnetic resonance spectra (^1H NMR and ^{13}C NMR) were recorded Varian FT-NMR spectrometer (400 or 500 MHz for ^1H / 100 or 125 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) referenced to the appropriate solvent peak or 0 ppm for TMS. The following abbreviations were used to describe peak patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Coupling constants, J , were reported in Hertz unit (Hz). Microwave reactions were performed in a 10 mL microwave tube using a CEM Discover S microwave reactor. UiO-66-Br was prepared and activated as previously described in the literature (Garibay, S. J.; Cohen, S. M. *Chem. Commun.* **2010**, 46, 7700-7702.).

Experimental Procedures for Ligands Synthesis.

Dimethyl 2-bromoterephthalate (1). To an oven-dried round-bottom flask, 2-bromo-1,4-benzenedicarboxylic acid (2.45 g, 10 mmol) was dissolved in 200 mL of methanol and 5 mL of conc. H_2SO_4 was added by dropwise. The mixture was heated to reflux for 48 h. After cooling to room temperature, MeOH was removed by evaporation and then 100 mL of CH_2Cl_2 was added. The solution was washed with 5% NaHCO_3 . After drying with MgSO_4 , the desired compound was obtained after removal of solvent in 99% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.27 (1H, s), 7.96 (1H, d, $J = 8.1$ Hz), 7.78 (1H, d, $J = 8.1$ Hz), 3.93 (3H, s), 3.92 (3H, s); ^{13}C NMR (125 MHz, CDCl_3) δ 166.0, 164.9, 136.0, 135.1, 133.6,

131.0, 128.1, 121.4, 52.8, 52.7. HR-EI-MS m/z calcd. for $C_{10}H_9BrO_4$ $[M]^+$: 271.9679, found $[M]^+$: 271.9680.

Dimethyl 2-cyanoterephthalate (2). To an oven-dried 20 mL dram vial, dimethyl 2-bromoterephthalate (0.246 g, 0.9 mmol) was dissolved in 1 mL of DMF and copper cyanide (98 mg, 1.1 mmol) was added. The mixture was heated to 140 °C in an oil bath for 30 min. After cooling to room temperature, 2 mL of cold water was added, and the mixture was stirred at room temperature for 1 h. The solids were filtered and transferred to new vials with 2 mL of water. Potassium cyanide (175 mg, 2.7 mmol) was added, and the solution was heated to 50 °C in an oil bath for 1 h. After cooling to room temperature, the solid was filtered and washed twice with water. The solid was dissolved in 5 mL of $CHCl_3$ and dried with $MgSO_4$. The desired compound was obtained after removal of solvent in 70% yield. 1H NMR (400 MHz, CD_3OD) δ 8.43 (1H, s), 8.33 (1H, d, $J = 8.2$ Hz), 8.24 (1H, d, $J = 8.2$ Hz), 4.00 (3H, s), 3.97 (3H, s); ^{13}C NMR (125 MHz, $CHCl_3$) δ 164.3, 163.8, 135.7, 135.6, 134.1, 133.3, 131.4, 113.3 ($C\equiv N$), 53.2, 53.0. HR-ESI-FT-MS m/z calcd. for $C_{11}H_{10}NO_4$ $[M+H]^+$: 220.0604, found $[M+H]^+$: 220.0603.

2-Cyano-1,4-benzenedicarboxylic acid (3). To an oven-dried round bottom flask, dimethyl 2-cyanoterephthalate (88 mg, 0.4 mmol) was dissolved in 3 mL of MeOH and 1.1 mL of 1.0 M NaOH aqueous solution was added by dropwise. The mixture was stirred at room temperature for 24 h. Once conversion was complete (by TLC), the MeOH was removed by evaporation and the mixture was diluted with 3 mL of water and 3 mL of $CHCl_3$. The mixture was acidified with ca. 2 mL of 1.0 M HCl aqueous solution. The precipitate was collected by filtration, and washed with water and hexane. The desired compound was air dried giving a 45% yield. 1H NMR (400 MHz, CD_3OD) δ 8.41 (1H, s), 8.33 (1H, d, $J = 8.2$

Hz), 8.25 (1H, d, $J = 8.2$ Hz). HR-MS m/z calcd. for $C_9H_5NO_4$ $[M+H]^+$: 192.0219, found $[M+H]^+$: 192.0290.

Experimental Procedures for Metal-Organic Frameworks.

UiO-66-CN. UiO-66-Br (ca. 70 mg, 0.2 mmol equiv. in bromide) and copper cyanide (23 mg, 0.26 mmol) were suspended in 2 mL of NMP in a microwave tube. The mixture was heated in a microwave reactor at 170 °C for 10 min without stirring (Maximum power = 200 W). After cooling to room temperature, the suspension was diluted with 10 mL of DMF and the solids were isolated by centrifugation. After centrifugation, 10 mL of 0.01 M KCN was added to remove remaining copper and the solids were isolated by centrifugation again. Then, the solids were washed three times with 10 mL of MeOH, and after the last wash, the material was transferred to a clean vial containing 10 mL of MeOH and was left to soak in MeOH overnight. The solid material was then rinsed with 10 mL of MeOH and left to soak for 3 days with fresh MeOH exchanged every 24 h. After 3 days of soaking, the solid was isolated by centrifugation, air dried, and then dried at 120 °C in an oven. Yield: ca. 90% (based on three independent samples).

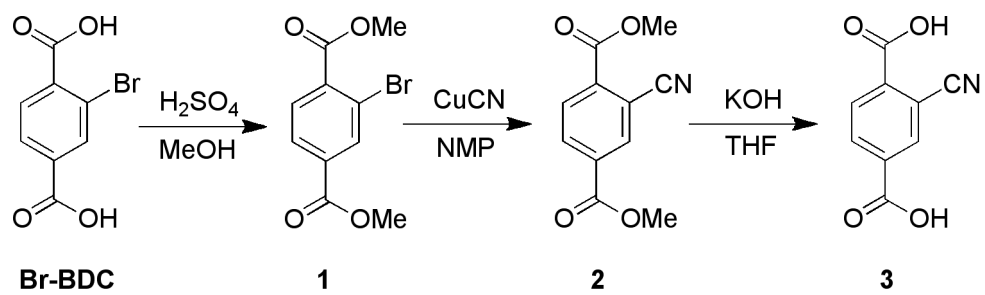
Digestion and Analysis by 1H NMR. Approximately 10 mg of UiO-66-Br or UiO-66-CN materials were dried under vacuum at 100 °C and digested with sonication in 580 mL of CD_3OD and 20 mL of HF (48% aqueous solution).

Mass Spectrometry Analysis. Electrospray ionization mass spectrometry (ESI-MS) was performed using a ThermoFinnigan LCQ-DECA mass spectrometer and the data was analyzed using the Xcalibur software suite. Approximately 5 mg of the sample was digested with sonication in 1 mL of MeOH and 10 μ L of HF (48% aqueous solution).

Thermal Analysis. Approximately 10-15 mg of UiO-66-Br or UiO-66-CN was dried at 100 °C under vacuum line for 2 h before TGA measurements. Samples were analyzed under a stream of dinitrogen using a TA Instrument Q600 SDT running from room temperature to 800 °C with a scan rate of 5 °C/min.

PXRD Analysis. vApproximately 20-30 mg of UiO-66-Br or UiO-66-CN was dried at 120 °C before powder X-ray diffraction (PXRD) analysis. vPXRD data were collected at ambient temperature on a Bruker D8 Advance diffractometer at 40 kV, 40 mA for Cu Ka ($\lambda = 1.5418$ Å), with a scan speed of 3 sec/step, a step size of 0.02° in 2 θ , and a 2 θ range of 5-45°.

BET Surface Area Analysis. Approximately 100 mg of UiO-66-Br or UiO-66-CN was evacuated on a vacuum line for 2 h at 100 °C. The sample was then transferred to a preweighed sample tube and degassed at 105 °C on an Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 mmHg. The sample tube was re-weighed to obtain a consistent mass for the degassed UiO-66-Br or UiO-66-CN. BET surface area (m²/g) measurements were collected at 77 K using N₂ on a Micromeritics ASAP 2020 Adsorption Analyzer using a volumetric technique.



Scheme S1. Synthesis of the ligand CN-BDC (**3**).

Table S1. Atomic absorption analysis of UiO-66-Br and UiO-66-CN (analyses performed in duplicate as indicated).

		UiO-66-Br		UiO-66-CN	
		1 st	2 nd	1 st	2 nd
Theoretical ^a	Zr	24.91%		34.61%	
	Cu	n.d.		(33.64%) ^b	n.d.
Experimental	Zr	24.02%	23.82%	32.44%	32.02%
	Cu	0.0277%	0.0272%	0.2813% ^c	0.2757%

^a Determined from a formula unit of ZrO₂(BDC). ^b Based on 90% conversion. ^c Remaining Cu ratio per 1g of material is 0.000039 mol/g and molar ratio of remaining Cu to CN-BDC ligand is 0.014:1.

Table S2. Reaction conditions explored for the direct synthesis of UiO-66-CN.^a

Entry	Ratio (Zr:BDC)	Solvent	Temp	Time	Vessel	Outcome
1	1 : 1	DMF	120 °C	24 h	Bomb	No product
2	1 : 1	DMF	85 °C	24 h	Bomb	UiO-66-CN ^b
3	1 : 1	DMF	150 °C	24 h	Bomb	No product
4	1 : 1	DEF ^c	120 °C	24 h	Bomb	No product
5	1 : 1	DMF	120 °C	48 h	Bomb	No product
6	2 : 1 ^d	DMF	120 °C	24 h	Bomb	No product
7	1 : 2 ^e	DMF	120 °C	24 h	Bomb	No product
8	1 : 1	DMF	120 °C	24 h	Pressure Tube ^f	No product
9	1 : 1	DMF	120 °C	24 h	Vial	No product
10	1 : 1	DMF	85 °C	24 h	Vial	No product
11	1 : 1	DMF	150 °C	24 h	Vial	No product

^a Zr (0.35 mmol), CN-BDC (0.35 mmol), and DMF (4 mL) were used. ^b PXRD pattern: see Figure S7. ^c DEF = *N,N*-Diethylformamide, 4 mL was used. ^d Zr (0.7 mmol) and CN-BDC (0.35 mmol) were used. ^e Zr (0.35 mmol) and CN-BDC (0.7 mmol) were used. ^f Teflon-capped screwed tube was used.

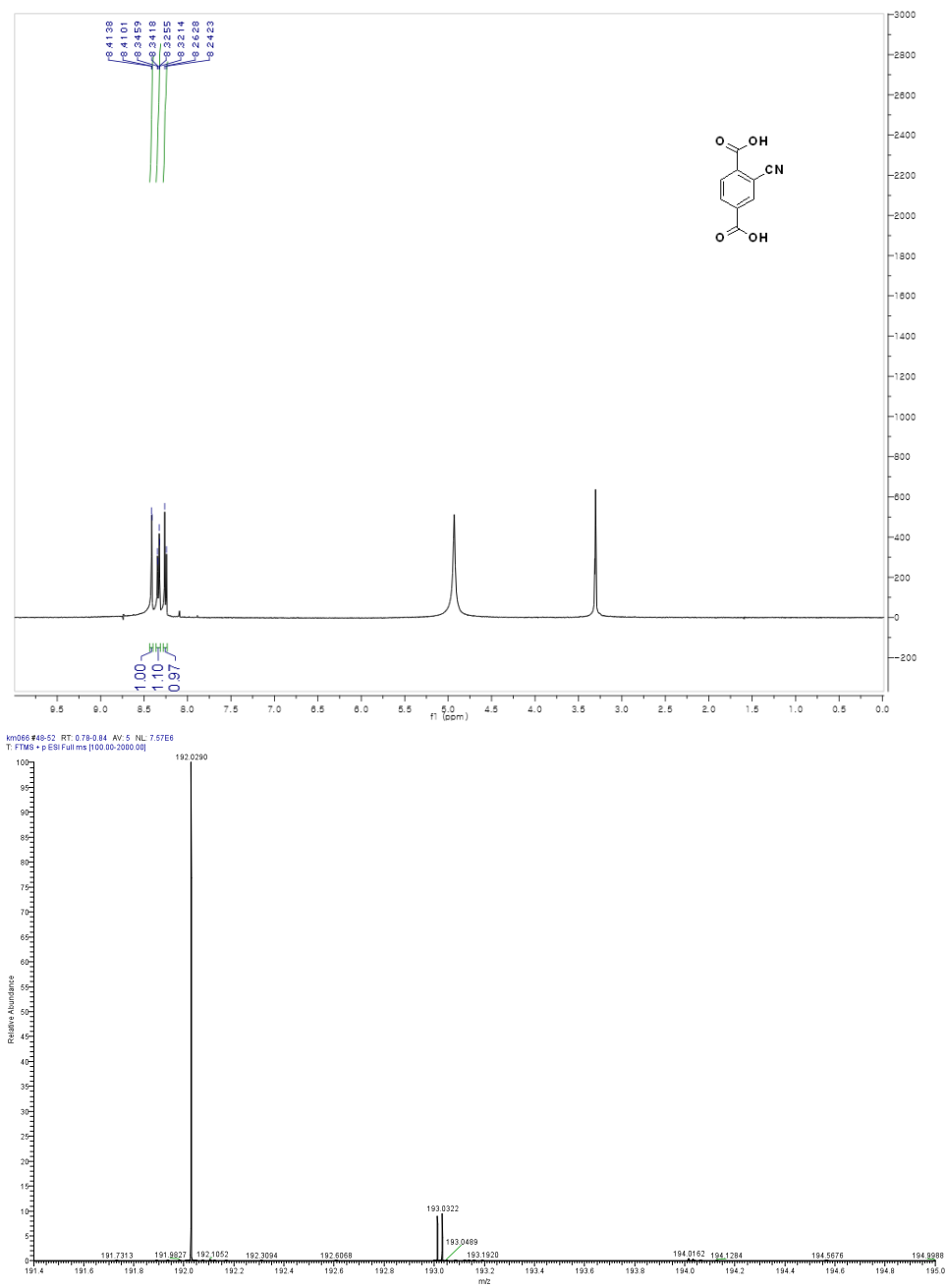


Figure S1. ¹H NMR spectrum (top) and ESI-MS (bottom) analysis of 2-cyano-1,4-benzenedicarboxylic acid (CN-BDC, **3**).

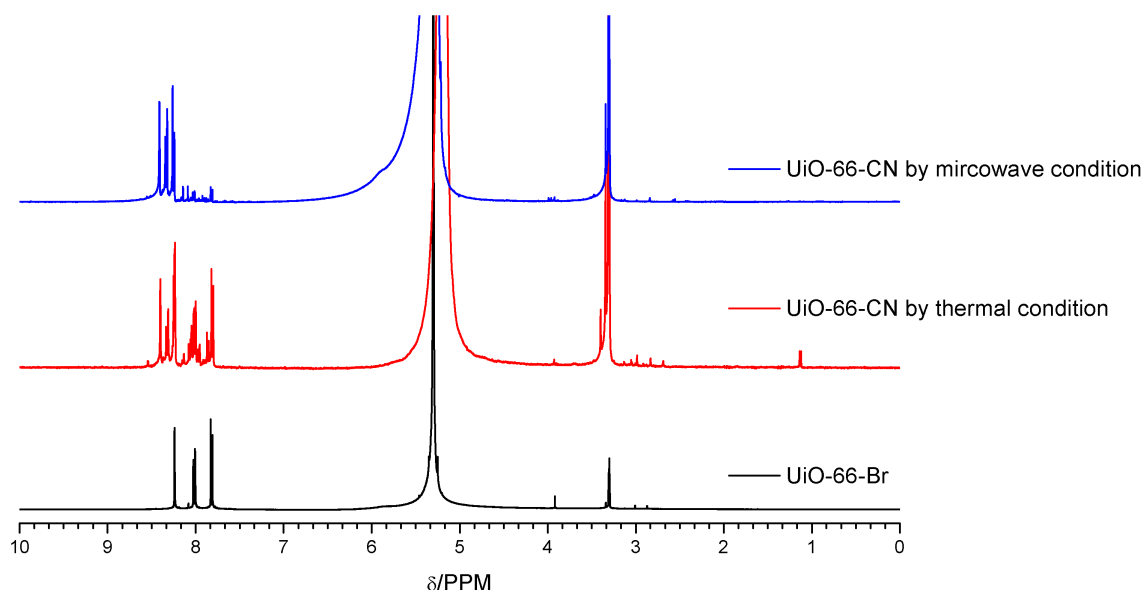


Figure S2. Complete ^1H NMR spectra of digested UiO-66-Br, UiO-66-CN via thermal synthesis, and UiO-66-CN via microwave synthesis.

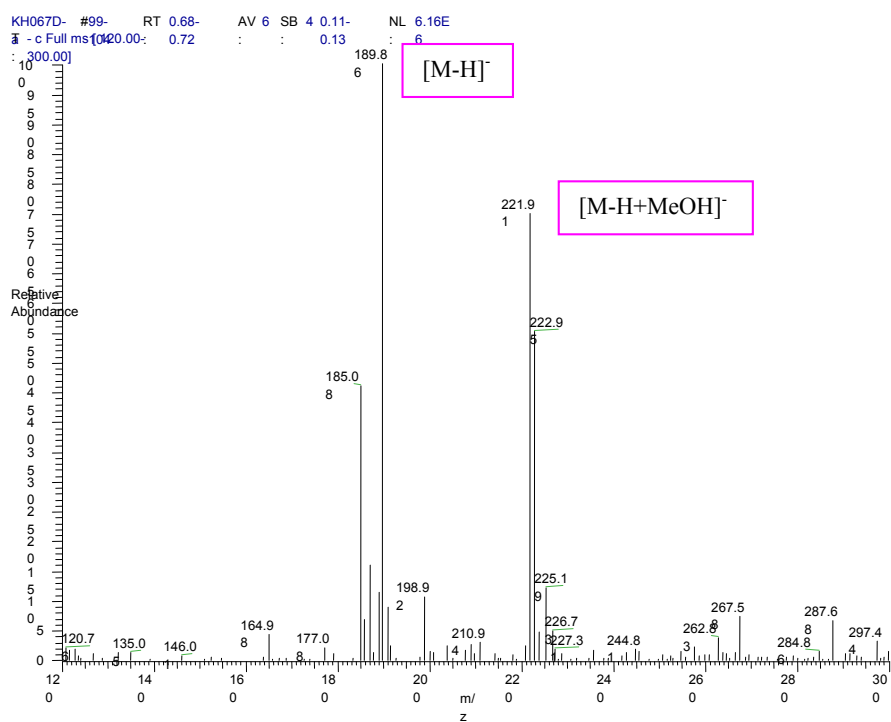
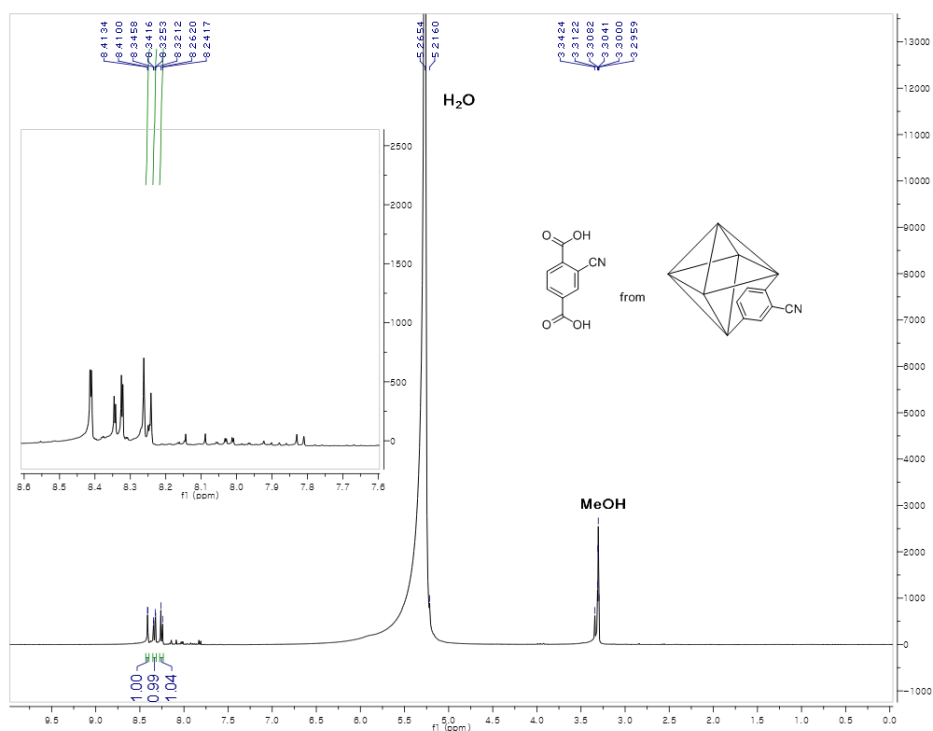


Figure S3. ^1H NMR spectrum (top) and ESI-MS analysis (bottom) of digested UiO-66-CN.

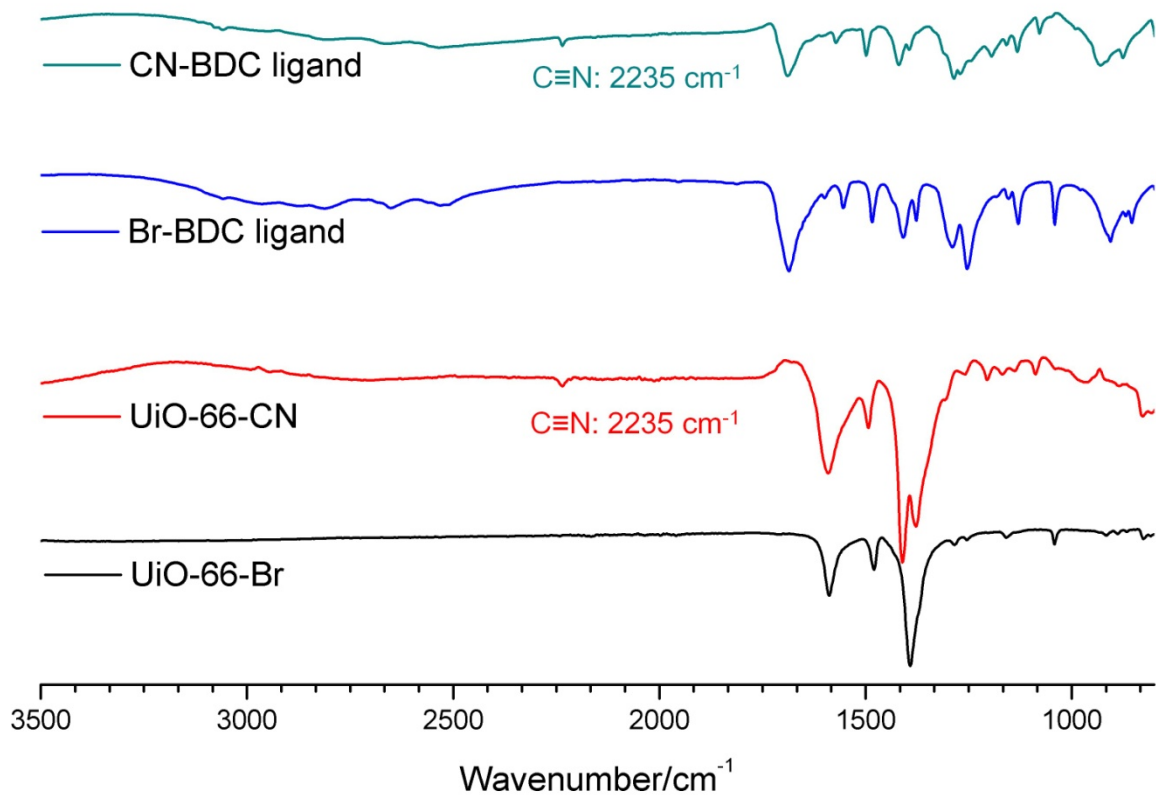


Figure S4. Infrared spectrum (ATR-FTIR) of CN-BDC, Br-BDC, UiO-66-Br, and UiO-66-CN.

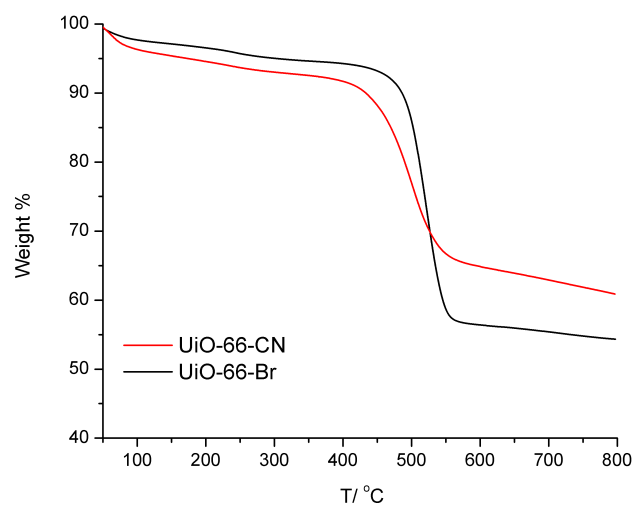


Figure S5. Thermogravimetric analysis of activated (100 °C for 2 h under vacuum line) UiO-66-Br and UiO-66-CN.

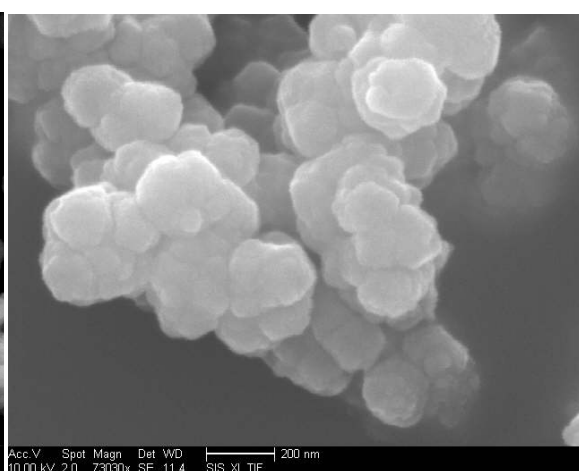
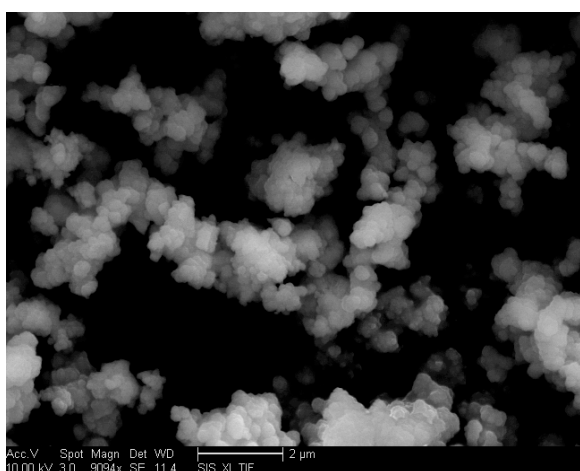
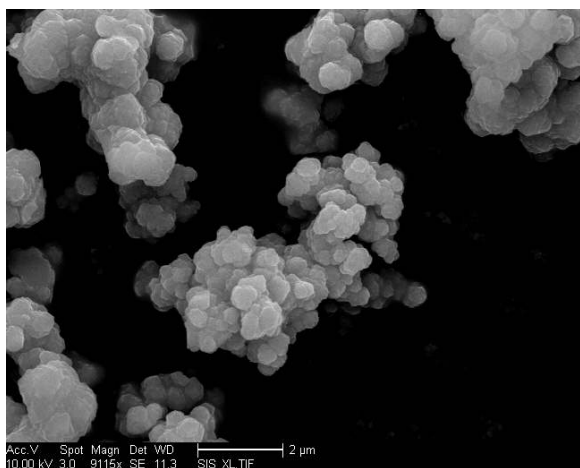


Figure S6. Scanning electron microscopy images (SEM) of UiO-66-Br (top) and UiO-66-CN (bottom, produced by microwave-assisted PSM, two different magnifications).

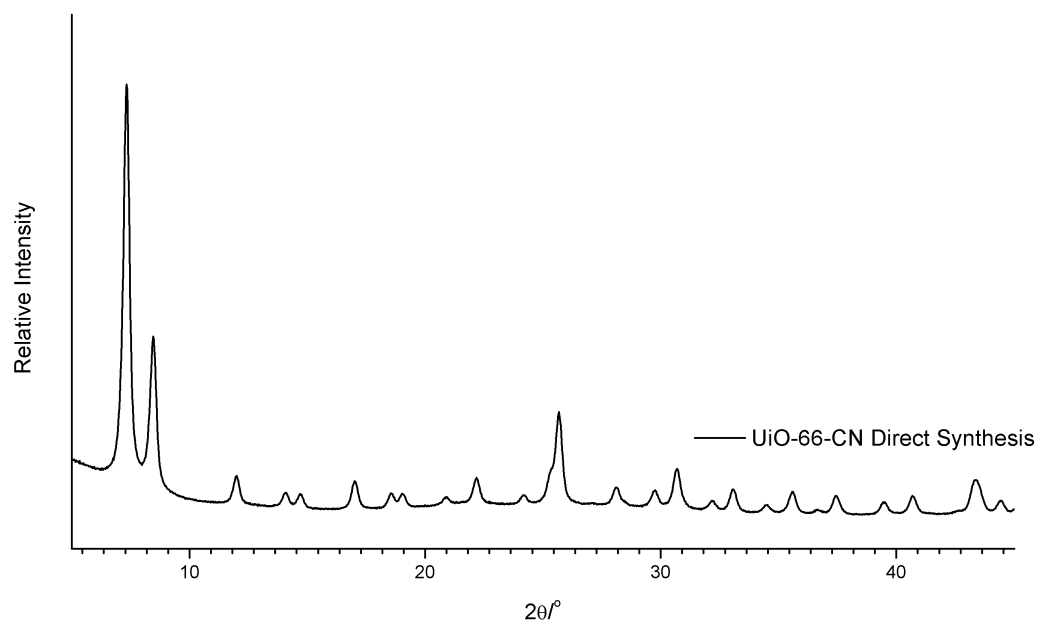


Figure S7. PXRD pattern of UiO-66-CN direct synthesized from CN-BDC at 85 °C (reactions conditions are those from entry 2, Table S2).