Electronic Supplementary Material (ESI) for Dalton Transactions

Functional Tolerance in an Isoreticular Series of Highly Porous Metal-Organic Frameworks

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SUPPORTING INFORMATION

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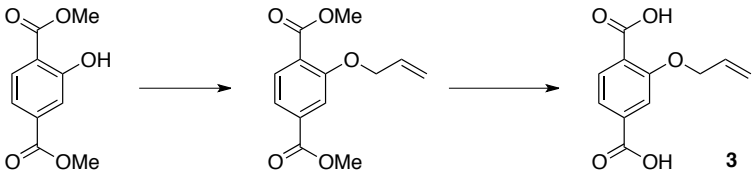
General Methods for Metal-Organic Frameworks Experiments.

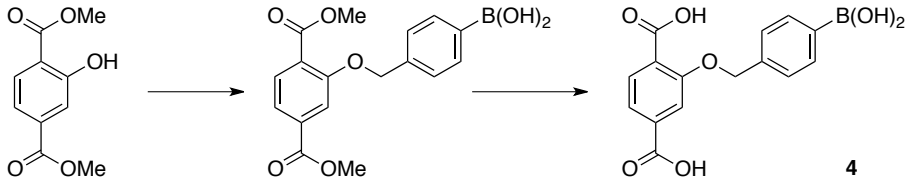
Starting materials and solvents were purchased and used without further purification from commercial suppliers (Sigma-Aldrich, Alfa Aesar, EMD, TCI, Cambridge Isotope Laboratories, Inc., and others). Proton nuclear magnetic resonance spectra (^{1}H NMR and ^{13}C NMR) were recorded by a Varian FT-NMR spectrometer (400 MHz for ^{1}H/ 100 MHz for ^{13}C). Carbon nuclear magnetic resonance spectroscopy was fully decoupled by broad band decoupling. Chemical shifts were quoted 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).

Ligand Synthesis



*AllylO BDC-(**3**) synthesis.* Dimethyl 2-hydroxyterephthalate (2 g, 9.5 mmol) and K_2CO_3 (2.6 g, 19 mmol) were dissolved in *N,N*-dimethylformaldehyde (DMF, 85 mL). Allyl bromide (1.4 g, 11.4 mmol) was added and the reaction was heated at 85 °C for 1 h. The mixture was cooled to room temperature, the K_2CO_3 was filtered off and water was added until a white solid precipitated. This was isolated by filtration, and obtained dimethyl 2-(allyloxy)terephthalate (1.8 g, 77%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 3.92 (d, 6H; CO_2CH_3), 4.68 (s, 2H, CH_2), 5.32 (d, 1H; CH), 5.53 (d, 1H; CH), 6.06 (m, 1H; Allyl CH), 7.63 (m, 2H; ArH) 7.82 (d, 1H; ArH). ESI-MS(+): m/z 250.88 $[M+H]^+$, 272.91 $[M+NH_4]^+$. Dimethyl 2-(allyloxy)terephthalate (1.8 g, 7.4 mmol) was dissolved in THF (30 mL) and a 4% KOH solution (30 mL) was added. This was stirred at room temperature for 1 h. Water (50 mL) was added and the mixture was washed twice with ether (2x30 mL). The aqueous layer was acidified to around pH 1 with conc. HCl to precipitate a white solid. After filtration the solid was dried under vacuum with heat. (1.5 g, 93%). ^{1}H NMR (*d*$_6$-DMSO, 400 MHz, 25 °C): δ 4.71 (s, 2H; CH_2), 5.27 (d, 1H; CH), 5.47 (d, 1H;

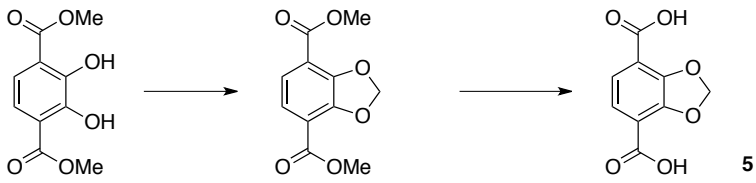
CH), 6.04 (m, 1H; Allyl CH), 7.55 (m, 2H; ArH), 7.69 (d, 1H, ArH). ESI-MS(+): m/z 222.80 $[M-H]^+$.



4

*OBnB(OH)$_2$ BDC (**4**) synthesis.* Dimethyl 2-hydroxyterephthalate (0.293 g, 1.4 mmol) and Cs_2CO_3 (2.28 g, 7 mmol) were dissolved in THF (30 mL). (4-(bromomethyl)phenyl)boronic acid (0.350 g, 164 mmol) was added and the reaction was heated to reflux at 70 °C overnight. The mixture was cooled to room temperature, and solvent was removed by evaporation. H_2O (20 mL) was added to mixture and extracted with CH_2Cl_2 (20 mL) three times. The combined organic layer was dried with $MgSO_4$, after filtration and evaporation, the white solid ((4-((2,5-bis(methoxycarbonyl)phenoxy)methyl)phenyl)boronic acid) was isolated by column chromatography (0.420 g, 88%). ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 3.92 (d, 6H; CO_2CH_3), 5.18 (s, 2H, OCH_2), 7.39 (d, 2H; ArH) 7.52 (d, 2H; ArH), 7.65 (m, 2H; ArH), 7.85 (d, 1H; ArH).

(4-((2,5-Bis(methoxycarbonyl)phenoxy)methyl)phenyl)boronic acid (0.420 g, 1.2 mmol) was dissolved in THF (30 mL) and a 4% KOH solution (30 mL) was added. This was stirred at room temperature overnight. The organic layer was separated, and the aqueous layer was acidified to around pH 1 with 1M aqueous HCl solution to precipitate a white solid. After filtration the solid was dried under vacuum with heat (0.280 g, 89%). ^{1}H NMR (d_6-DMSO, 400 MHz, 25 °C): δ 5.23 (s, 2H; OCH_2), 7.44 (d, 2H; ArH), 7.55 (m, 2H; ArH), 7.59 (d, 2H; ArH), 7.70 (d, 1H; ArH). ^{13}C NMR (d_6-DMSO, 100 MHz, 25 °C): δ 167.6, 157.0, 137.0, 135.1, 132.0, 129.9, 129.1, 127.7, 127.7, 126.8, 122.1, 121.5, 114.7, 69.6.



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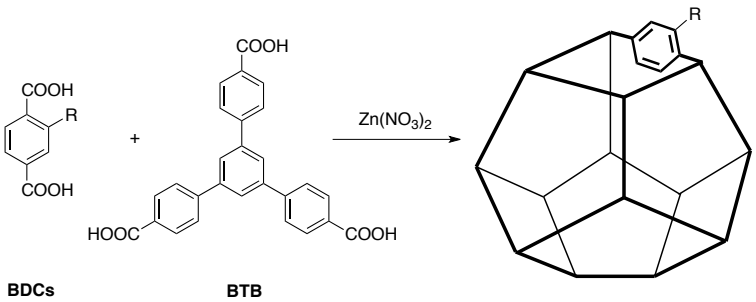
*Dioxole BDC (**5**) synthesis.* Dimethyl 2,3-dihydroxyterephthalate (1 g, 4.4 mmol) and CsF (2.98 g, 19.6

mmol) were dissolved in DMF (20 mL). CH_2Cl_2 (3 mL, excess) was added and the reaction was heated to reflux at 110 °C overnight. The mixture was cooled to room temperature, and water (50 mL) was added and then extracted with ethyl acetate (50 mL) three times. The organic layer was collected and dried with $MgSO_4$. The beige solid (dimethyl benzo[1,3]dioxole-4,7-dicarboxylate) was obtained by evaporation (0.9 g, 97%). ^{1}H NMR (d_6-DMSO, 400 MHz, 25 °C): δ 3.82 (s, 6H; CO_2CH_3), 6.28 (s, 2H, OCH_2O), 7.32 (s, 2H; ArH). ESI-MS(+): m/z 239.01 $[M+H]^+$, 255.85 $[M+NH_4]^+$.

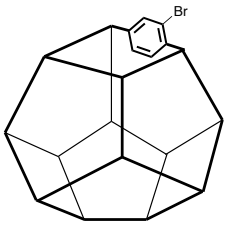
Dimethyl benzo[1,3]dioxole-4,7-dicarboxylate (0.85 g, 3.6 mmol) was dissolved in THF (50 mL) and a 4% KOH solution (50 mL) was added. This was stirred at room temperature overnight. The organic layer was separated, and the aqueous layer was acidified to around pH 1 with conc. HCl to precipitate a white solid. After filtration the solid was dried under vacuum with heat (0.605 g, 80%). ^{1}H NMR (d_6-DMSO, 400 MHz, 25 °C): δ 6.25 (s, 2H; OCH_2O), 7.27 (s, 2H; ArH). ^{13}C NMR (d_6-DMSO, 100 MHz, 25 °C): δ 165.3, 150.2, 122.3, 116.3, 103.6. ESI-MS(-): m/z 209.44 $[M-H]^-$.

NH_2X BDC derivatives. 2-Amino-3-chloro-1,4-benzenedicarboxlyic acid, 2-Amino-5-chloro-1,4-benzenedicarboxlyic acid, 2-Amino-3-bromo-1,4-benzenedicarboxlyic acid, 2-Amino-5-bromo-1,4-benzenedicarboxlyic acid, and 2-Amino-5-iodo-1,4-benzenedicarboxlyic acid were prepared using a method previously described.[1]

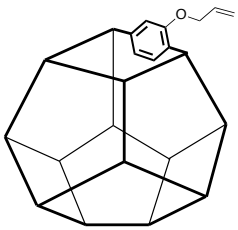
UMCM Synthesis



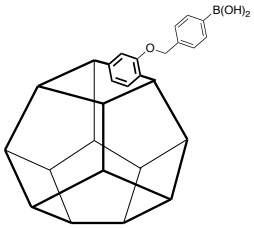
The UMCM-1 series was prepared and activated using a modified method from what has been previously described.[2]



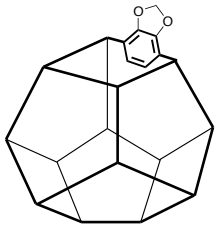
UMCM-1-Br. Bromo-1,4-benzene dicarboxylic acid (Br-BDC, 66 mg, 0.27 mmol), 4,4′,4″-benzene-1,3,5-triyl-tribenzoic acid (BTB, 39 mg, 0.09 mmol), and $Zn(NO_3)_2 \bullet 6H_2O$ (321 mg, 1.08 mmol) were dissolved in 10 mL of *N,N*-diethylformamide (DEF) in a scintillation vial. This was placed in a sand bath and placed into an isothermal oven at 85 °C. After 48 h, the vial was removed from the oven and left to cool to room temperature. Crystalline needle clusters formed in the vial. The mother liquid was decanted, and crystals were washed with 10 mL DMF (three times) and soaked with 10 mL $CHCl_3$ for 24 h. The crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 days of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.



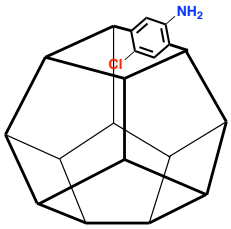
UMCM-1-OAllyl. 2-(Allyloxy)-1,4-benzene dicarboxylic acid (**3**, 60 mg, 0.3 mmol), BTB (39 mg, 0.09 mmol), and $Zn(NO_3)_2 \bullet 6H_2O$ (321 mg, 1.08 mmol) were dissolved in *N,N*-dimethylformamide (DMF, 10 mL) in a scintillation vial. This was placed in a sand bath and placed into an isothermal oven at 85 °C. After 48 h, the vial was removed from the oven and left to cool to room temperature. Crystalline needle clusters formed in the vial. The mother liquid was decanted, and crystals were washed with 10 mL DMF (three times) and soaked with 10 mL $CHCl_3$ for 24 h. The crystal left to soak for 3 days with fresh $CHCl_3$ added every 24 h. After 3 d of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.



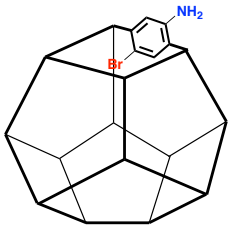
UMCM-1-OBnB(OH)$_2$. 2-((4-boronobenzyl)oxy)terephthalic acid (**4**, 85 mg, 0.27 mmol), BTB (39 mg, 0.09 mmol), and $Zn(NO_3)_2$•$6H_2O$ (321 mg, 1.08 mmol) were dissolved in DMF (10 mL) in a scintillation vial. This was placed in a sand bath and placed into an isothermal oven at 85 °C. After 48 h, the vial was removed from the oven and left to cool to room temperature. Crystalline needle clusters formed in the vial. The mother liquid was decanted, and crystals were washed with 10 mL DMF (three times) and soaked with 10 mL $CHCl_3$ for 24 h. The crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 days of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.



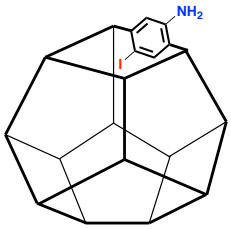
UMCM-1-Dioxole. Benzo[d][1,3]dioxole-4,7-dicarboxylic acid (**5**, 57 mg, 0.27 mmol), BTB (39 mg, 0.09 mmol), and $Zn(NO_3)_2$•$6H_2O$ (321 mg, 1.08 mmol) were dissolved in DMF (10 mL) in a scintillation vial. This was placed in a sand bath and placed into an isothermal oven at 85 °C. After 48 h, the vial was removed from the oven and left to cool to room temperature. Crystalline needle clusters formed in the vial. The mother liquid was decanted, and crystals were washed with 10 mL DMF (three times) and soaked with 10 mL $CHCl_3$ for 24 h. The crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 days of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.



UMCM-1-[2,5-NH_2Cl]. 2-Amino-5-chloro-1,4-benzenedicarboxlyic acid (42 mg, 0.194 mmol), BTB (28 mg, 0.065 mmol), and $Zn(NO_3)_2$•$6H_2O$ (230 mg, 0.776 mmol) were dissolved in DMF (10 mL). The vial was placed in a sand bath, and the sand bath was transferred to an isothermal oven heated at 85 °C. After 48 h, the vial was removed from the oven and left to cool to room temperature. Crystalline needle clusters formed in the vial. The mother liquid was decanted, and crystals were washed with 10 mL DMF (three times) and soaked with 10 mL $CHCl_3$ for 24 h. The crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 days of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.

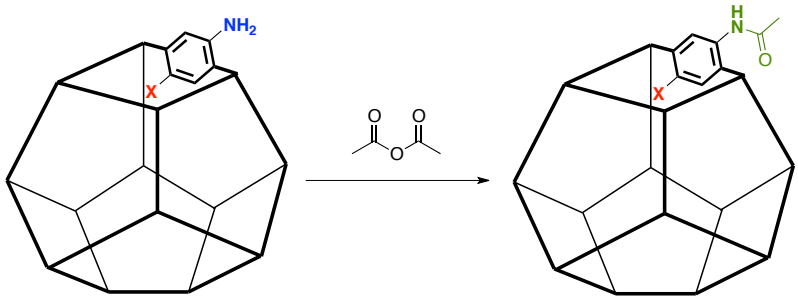


UMCM-1-[2,5-NH_2Br]. 2-Amino-5-bromo-1,4-benzenedicarboxlyic acid (50 mg, 0.194 mmol), BTB (28 mg, 0.065 mmol), and $Zn(NO_3)_2$•$6H_2O$ (230 mg, 0.776 mmol) were dissolved in DMF (10 mL). The vial was placed in a sand bath, and the sand bath was transferred to an isothermal oven heated at 85 °C. After 48 h, the vial was removed from the oven and left to cool to room temperature. Crystalline needle clusters formed in the vial. The mother liquid was decanted, and crystals were washed with 10 mL DMF (three times) and soaked with 10 mL $CHCl_3$ for 24 h. The crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 days of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.

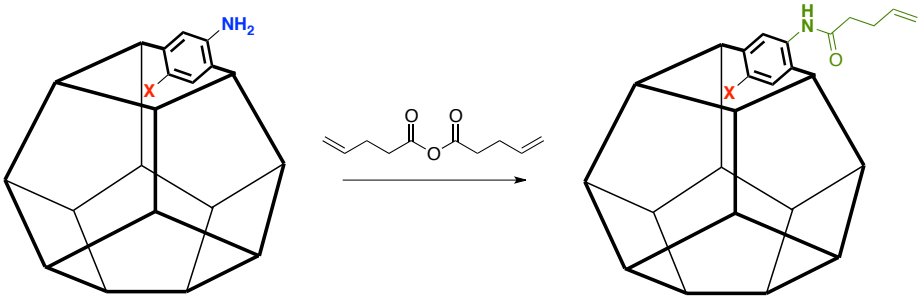


UMCM-1-[2,5-NH_2I]. 2-Amino-5-iodo-1,4-benzenedicarboxlyic acid (60 mg, 0.194 mmol), BTB (28 mg, 0.065 mmol), and $Zn(NO_3)_2$•$6H_2O$ (230 mg, 0.776 mmol) were dissolved in DMF (10 mL). The vial was placed in a sand bath, and the sand bath was transferred to an isothermal oven heated at 85 °C. After 48 h, the vial was removed from the oven and left to cool to room temperature. Crystalline needle clusters formed in the vial. The mother liquid was decanted, and crystals were washed with 10 mL DMF (three times) and soaked with 10 mL $CHCl_3$ for 24 h. The crystal left to soak for 3 days with fresh $CHCl_3$ added every 24 h. After 3 d of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.

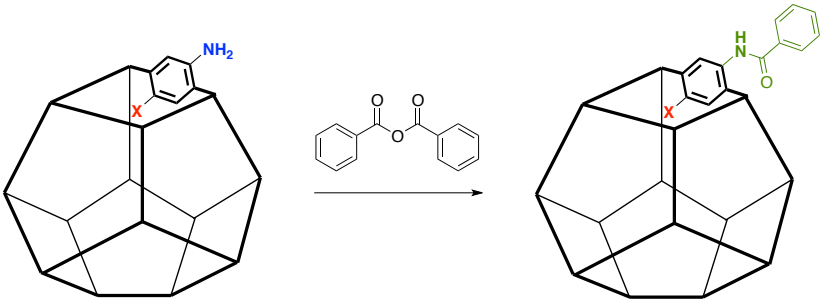
Postsynthetic modification of *UMCM-1-[2,5-NH_2X]*



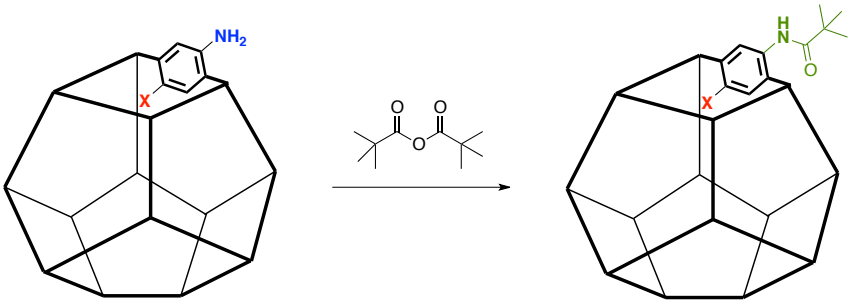
UMCM-1-[2,5-AM1X]. Approximately 0.04 mmol of UMCM-1-[2,5-NH_2X] was placed in a vial with 4 equiv. of acetic anhydride (16 mg, 0.16 mmol) in 2 mL of $CHCl_3$. The mixture was heated in an oven at 55 °C for 24 h, after which the solution was decanted, and a fresh solution of acid anhydride (in 2 mL of $CHCl_3$) was added to the vial again and heated for an additional 24 h. The product was washed with 10 mL of $CHCl_3$ three times and the crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 d of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.



UMCM-1-[2,5-AMButeneX]. Approximately 0.04 mmol of UMCM-1-[2,5-NH_2X] was placed in a vial with 4 equiv. of 4-pentenoic anhydride (29 mg, 0.16 mmol) in 2 mL of $CHCl_3$. The mixture was heated in an oven at 55 °C for 24 h, after which the solution was decanted, and a fresh solution of acid anhydride (in 2 mL of $CHCl_3$) was added to the vial again and heated for an additional 24 h. The product was washed with 10 mL of $CHCl_3$ three times and the crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 d of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.



UMCM-1-[2,5-AMPhX]. Approximately 0.04 mmol of UMCM-1-[2,5-NH_2X]was placed in a vial with 4 equiv. of benzoic anhydride (36 mg, 0.16 mmol) in 2 mL of $CHCl_3$. The mixture was heated in an oven at 55 °C for 24 h, after which the solution was decanted, and a fresh solution of acid anhydride (in 2 mL of $CHCl_3$) was added to the vial again and heated for an additional 24 h. The product was washed with 10 mL of $CHCl_3$ three times and the crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 d of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.



UMCM-1-[2,5-AMtBuX]. Approximately 0.04 mmol of UMCM-1-[2,5-NH_2X]was placed in a vial with 4 equiv. of trimethylacetic anhydride (30 mg, 0.16 mmol) in 2 mL of $CHCl_3$. The mixture was heated in an oven at 55 °C for 24 h, after which the solution was decanted, and a fresh solution of acid anhydride (in 2 mL of $CHCl_3$) was added to the vial again and heated for an additional 24 h. The product was washed with 10 mL of $CHCl_3$ three times and the crystal left to soak for 3 d with fresh $CHCl_3$ added every 24 h. After 3 d of soaking, the crystals were stored in the last $CHCl_3$ solution until needed.

Postsynthetic Deprotection (PSD) trials

UMCM-1-OAlly, UMCM-1-OBnB$(OH)_2$, and UMCM-1-Dioxole were used in an attempt to generate a phenol group in the UMCM pore by chemical postsynthetic deprotection. The OAllyl group deprotection was performed using a previously reported procedure with LiCl/$NaBH_4$ condition.[3] The OBnB$(OH)_2$ group deprotection was performed using a previously reported procedure with H_2O_2 condition.[4] Lastly, deprotection of the dioxole group was performed with $Pb(OAc)_4$.[5] However, the PXRD pattern of all UMCM materials after treatment changed completely to amorphous patterns indicating the collapse or destruction of the frameworks. In addition, the ^{1}H NMR spectra of digested samples showed no conversion to HO-BDC from protected BDCs.

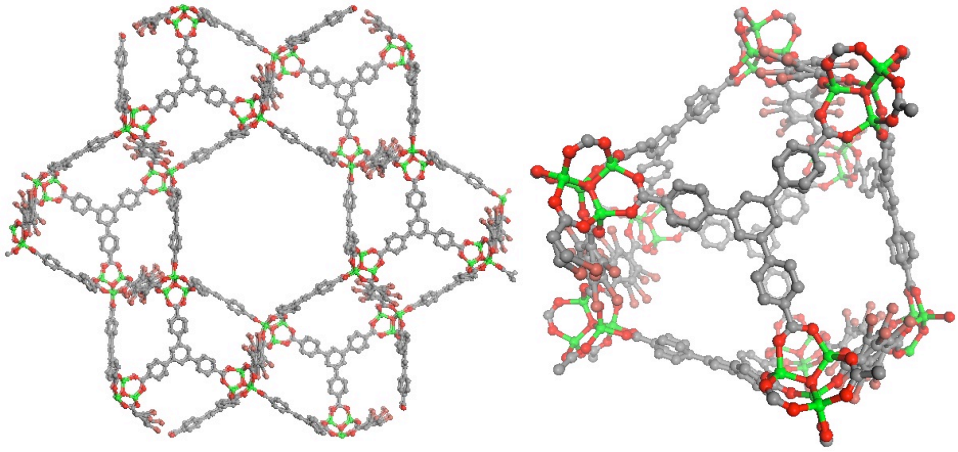


Fig. S1 The X-ray crystal structure of UMCM-1-Br; framework (left) and small cage (right). Color scheme: Zn (green), O (red), C (gray), Br (brown).

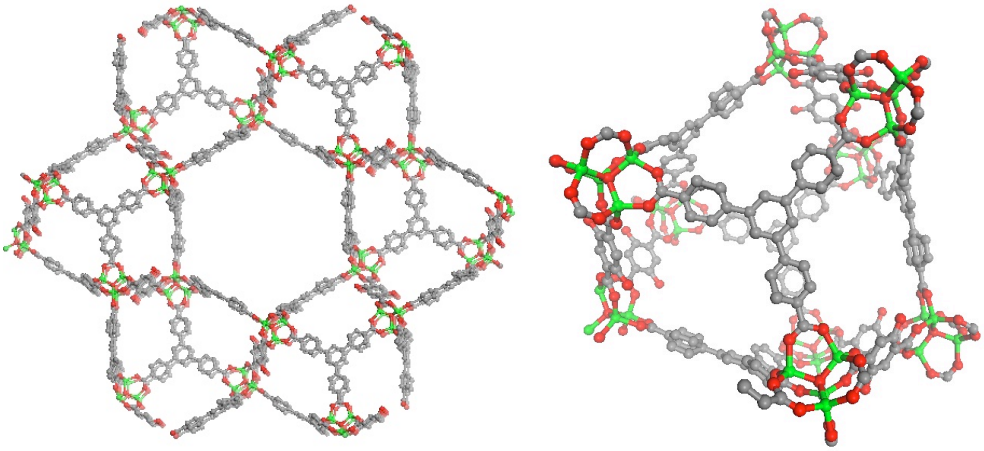


Fig. S2 The X-ray crystal structure of UMCM-1-OAllyl; framework (left) and small cage (right). Color scheme: Zn (green), O (red), C (gray).

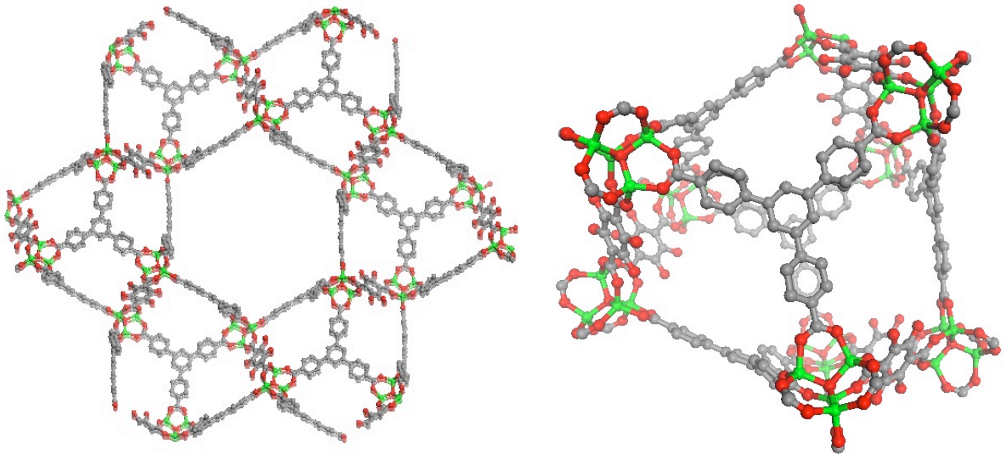


Fig. S3 The X-ray crystal structure of UMCM-1-OBnB$(OH)_2$; framework (left) and small cage (right). Color scheme: Zn (green), O (red), C (gray).

Table S1 Crystal data and structure refinement for UMCM-1-Br, OAlly, and OBnB(OH)$_2$.

Identification code	UMCM-1-Br	UMCM-1-OAllyl	UMCM-1-OBnB(OH)$_2$
Empirical formula	C_{44} H0 $Br_{0.50}$ O_{13} Zn_4	C_{46} H_0 O_{15} Zn_4	C_{46} H_0 O_{14} Zn_4
Formula weight	1037.88	1053.94	1037.94
Temperature	200(2) K	200(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Hexagonal	Hexagonal	Hexagonal
Space group	P63/m	P63/m	P63/m
Unit cell dimensions	a = b = 41.336(3) Å c = 17.554(3) Å α = β = 90° γ = 120°	a = b = 41.351(4) Å c = 17.5266(16) Å α = β = 90° γ = 120°	a = b = 41.283(3) Å c = 17.5145(11) Å α = β = 90° γ = 120°
Volume	25976(5) Å^3	25953(4) Å^3	25850(3) Å^3
Z	6	6	6
Density (calculated)	0.398 Mg/m^3	0.405 Mg/m^3	0.400 Mg/m^3
Absorption coefficient	0.678 mm^{-1}	0.565 mm^{-1}	0.567 mm^{-1}
F(000)	3033	3096	3048
Crystal size	0.15 x 0.10 x 0.10 mm^3	0.15 x 0.10 x 0.10 mm^3	0.15 x 0.10 x 0.10 mm^3
Theta range for data collection	0.99 to 25.44°.	1.14 to 25.37°.	0.99 to 25.39°.
Index ranges	-44<=h<=47, -49<=k<=41, -21<=l<=21	-49<=h<=37, -34<=k<=49, -21<=l<=21	-46<=h<=49, -48<=k<=49, -21<=l<=21
Reflections collected	306780	170316	118540
Independent reflections	16515 [R(int) = 0.1426]	16412 [R(int) = 0.0000]	16408 [R(int) = 0.0944]
Completeness to theta = 25.44°	99.5 %	99.7 %	100.0 %
Data / restraints / parameters	16515 / 0 / 348	16412 / 0 / 338	16417 / 0 / 152
Goodness-of-fit on F^2	1.050	0.624	0.709
Final R indices [I>2sigma(I)]	R1 = 0.0716, wR2 = 0.1895	R1 = 0.0621, wR2 = 0.1790	R1 = 0.0653, wR2 = 0.1933
R indices (all data)	R1 = 0.1190, wR2 = 0.2129	R1 = 0.0819, wR2 = 0.1960	R1 = 0.1072, wR2 = 0.2193
Largest diff peak and hole	1.094 and -0.573 e.Å^{-3}	0.869 and -0.519 e.Å^{-3}	1.161 and -0.555 e.Å^{-3}

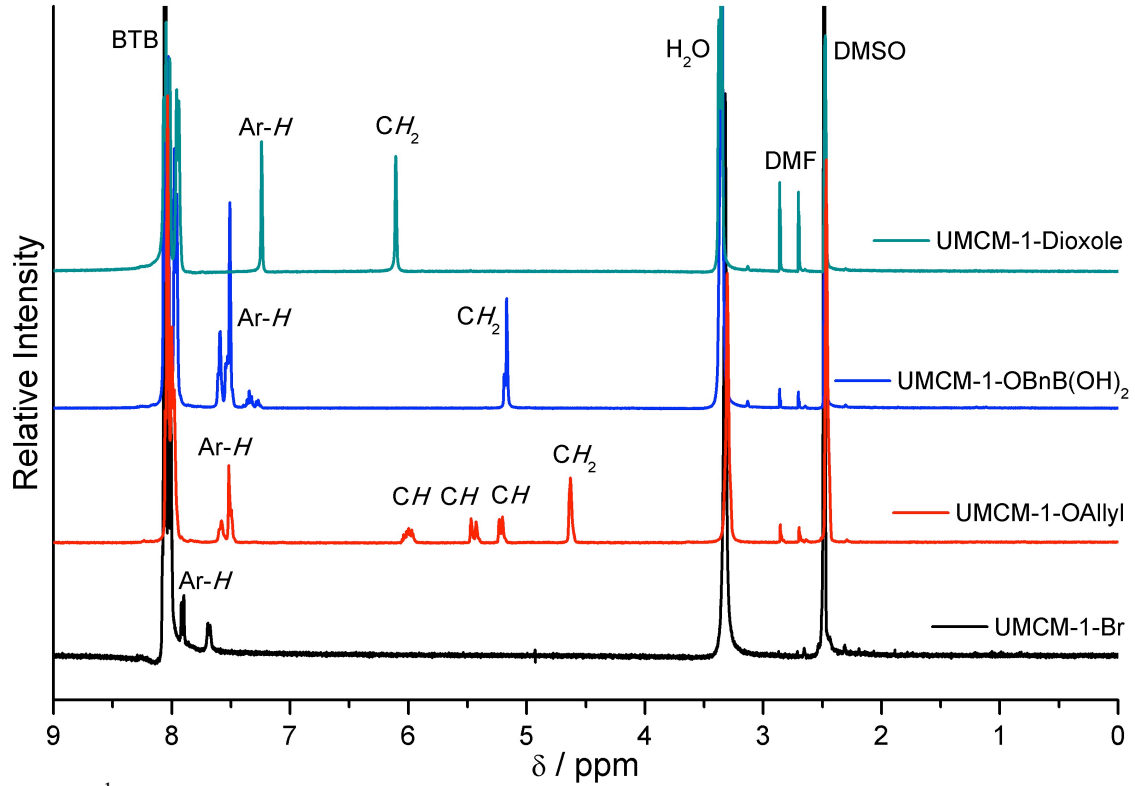


Fig. S4 ^{1}H NMR analysis of UMCM-1-Br, OAllyl, OBnB(OH)$_2$, and Dioxole materials.

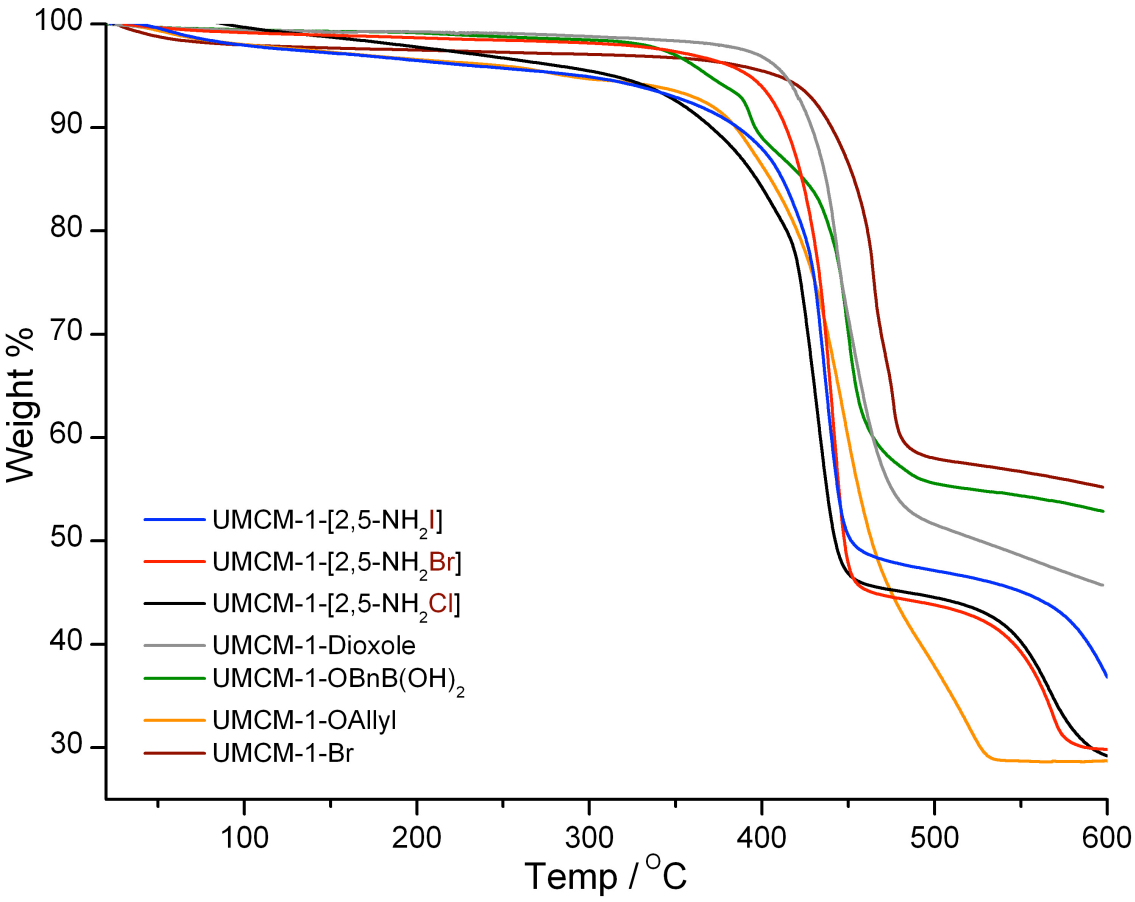


Fig. S5 Thermogravimetric analysis (TGA) of mono- and bi- functionalized UMCM-1 materials.

Table S2 Brunauer-Emmett-Teller (BET) surface area of pre-functionalized UMCM materials.[a]

UMCM	BET Surface Area (m^2/g)
UMCM-1-Br	3782
UMCM-1-OAllyl	3513
UMCM-1-OBnB$(OH)_2$	3351

[a] The average surface area number was determined from two independent samples.

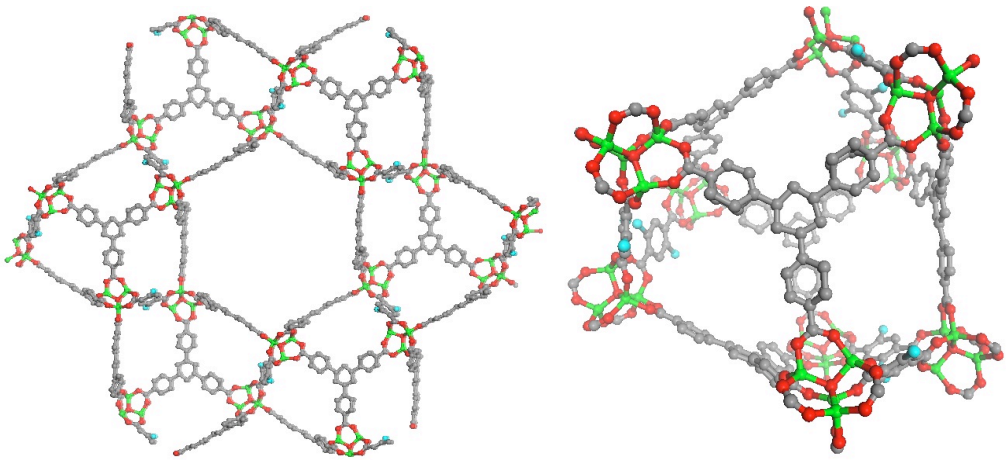


Fig. S6 The X-ray crystal structure of UMCM-1-[2,5-NH_2Cl]; framework (left) and small cage (right). Due to the disorder of the Cl atom on the functionalized benzene dicarboxylate ligands, the amino cannot be determined. Color scheme: Zn (green), O (red), C (gray), Cl (cyan).

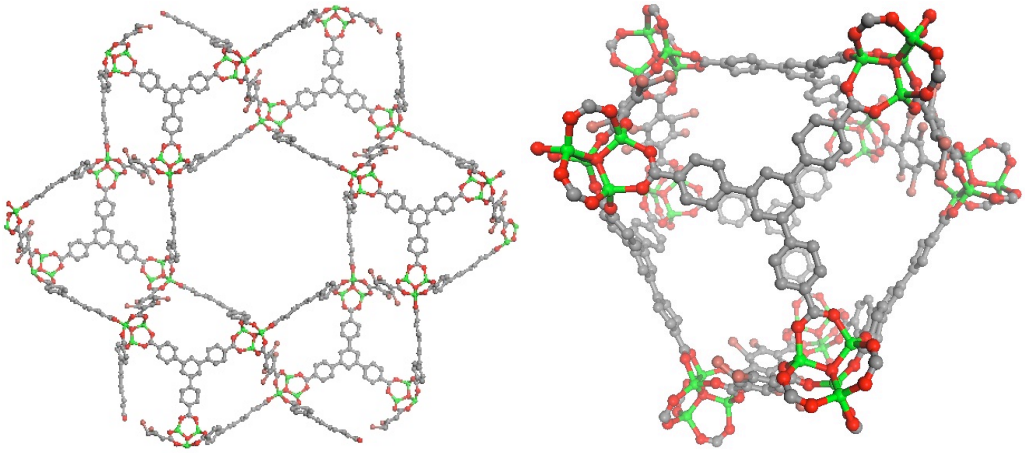


Fig. S7 The X-ray crystal structure of UMCM-1-[2,5-NH_2Br]; framework (left) and small cage (right). Due to the disorder of the Br atom on the functionalized benzene dicarboxylate ligands, the amino cannot be determined. Color scheme: Zn (green), O (red), C (gray), Br (brown).

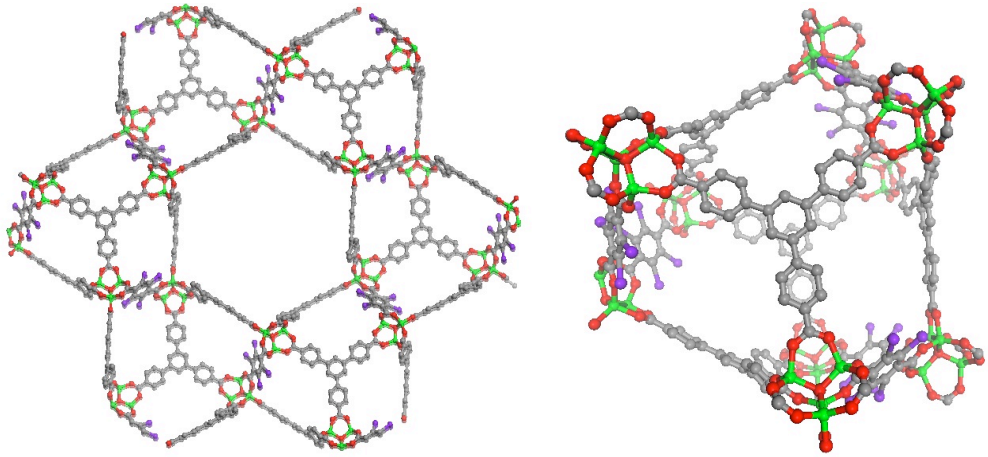


Fig. S8 The X-ray crystal structure of UMCM-1-[2,5-NH_2I]; framework (left) and small cage (right). Due to the disorder of the I atom on the functionalized benzene dicarboxylate ligands, the amino cannot be determined. Color scheme: Zn (green), O (red), C (gray), I (purple).

Table S3 Crystal data and structure refinement for UMCM-1-[2,5-NH_2X] and UMCM-1-Dioxole.

Identification code	UMCM-1-[2,5-NH_2Cl]	UMCM-1-[2,5-NH_2Br]	UMCM-1-[2,5-NH_2I]	UMCM-1-Dioxole
Empirical formula	C_{42} H_{17} Cl N_0 O_{13} Zn_4	C_{44} H_0 Br N_0 O_{13} Zn_4	$C_{43.50}$ H_{18} I N_0 O_{13} Zn_4	C_{44} H_0 O_{13} Zn_4
Formula weight	1026.49	1077.83	1136.96	997.92
Temperature	200(2) K	200(2) K	200(2) K	200(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Hexagonal	Hexagonal	Hexagonal	Hexagonal
Space group	*P63/m*	*P63/m*	*P63/m*	P63/m
Unit cell dimensions	a = b = 41.247(7) Å c = 17.447(3) Å α = β = 90° γ = 120°	a = b = 41.285(8) Å c = 17.489(3) Å α = β = 90° γ = 120°	a = b = 41.345(2) Å c = 17.5177(9) Å α = β = 90° γ = 120°	a = b =41.367(4) Å c = 17.5389(17) Å α = β = 90° γ = 120°
Volume	25706(8) $Å^3$	25815(8) $Å^3$	25932(2) $Å^3$	25992(4) $Å^3$
Z	6	6	6	6
Density (calculated)	0.398 Mg/m^3	0.416 Mg/m^3	0.437 Mg/m^3	0.383 Mg/m^3
Absorption coefficient	0.584 mm^{-1}	0.799 mm^{-1}	0.743 mm^{-1}	0.563 mm^{-1}
F(000)	3060	3138	3336	2928
Crystal size	0.15 x 0.10 x 0.10 mm^3	0.15 x 0.10 x 0.10 mm^3	0.15 x 0.10 x 0.10 mm^3	0.15 x 0.10 x 0.10 mm^3
Theta range for data collection	1.30 to 17.25°.	1.30 to 20.84°.	1.29 to 25.37°.	1.50 to 25.37°.
Index ranges	-34<=h<=26, -21<=k<=34, -10<=l<=14	-41<=h<=29, -41<=k<=38, -17<=l<=17	-48<=h<=46, -35<=k<=49, -11<=l<=21	-49<=h<=49, -49<=k<=49, -21<=l<=21
Reflections collected	63917	67885	119356	239558
Independent reflections	5485 [R(int) = 0.1453]	9420 [R(int) = 0.1998]	16412 [R(int) = 0.1495]	16465 [R(int) = 0.1256]
Completeness to theta = 25.44°	99.7 %	99.8 %	99.9 %	99.9 %
Data / restraints / parameters	5485 / 3 / 148	9420 / 0 / 166	16412 / 4 / 150	16467 / 4 / 142
Goodness-of-fit on F^2	1.038	0.861	0.775	0.780
Final R indices [I>2sigma(I)]	R1 = 0.0966, wR2 = 0.2456	R1 = 0.0713, wR2 = 0.1746	R1 = 0.0819, wR2 = 0.2308	R1 = 0.0683, wR2 = 0.1981
R indices (all data)	R1 = 0.1271, wR2 = 0.2671	R1 = 0.1430, wR2 = 0.1993	R1 = 0.1266, wR2 = 0.2640	R1 = 0.1220, wR2 = 0.2385
Largest diff. peak and hole	1.182 and -0.904 $e.Å^{-3}$	0.983 and -0.462 $e.Å^{-3}$	2.293 and -0.810 $e.Å^{-3}$	1.007 and -0.757 $e.Å^{-3}$

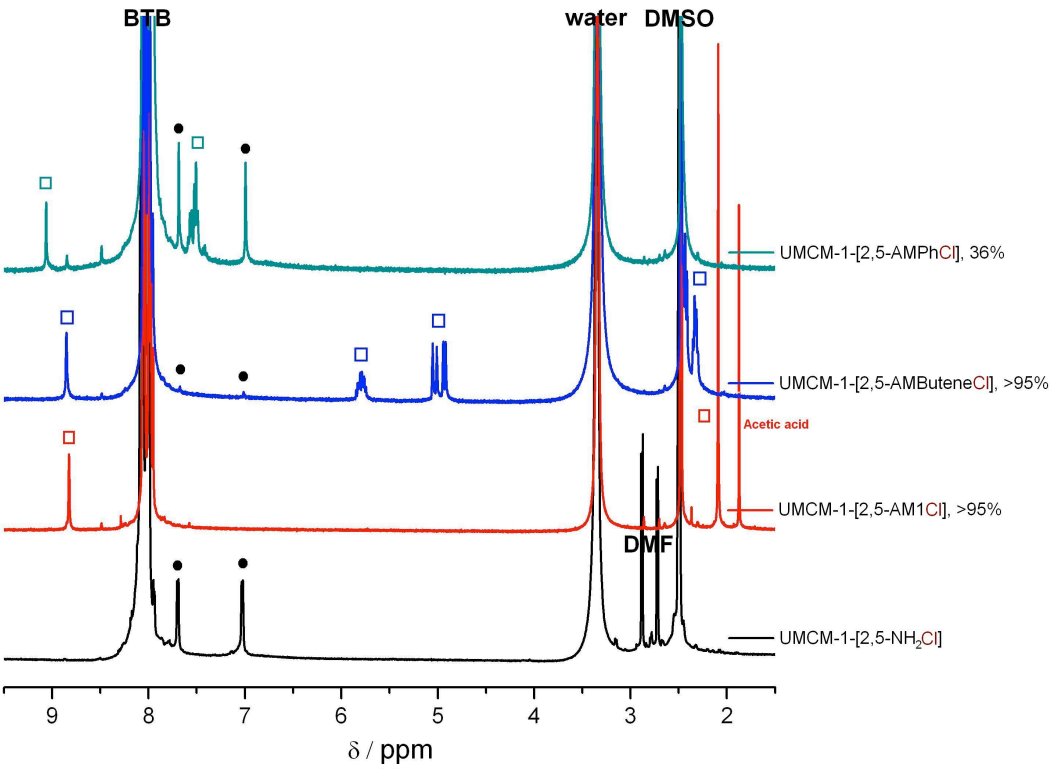


Fig. S9 ^{1}H NMR spectra of UMCM-1-[2,5-NH_2Cl] and postsynthetic modified UMCM-1-[2,5-AMCl] after acid digestion. Filled circles indicate 2,5-NH_2Cl-BDC, and open squares indicate modified ligands.

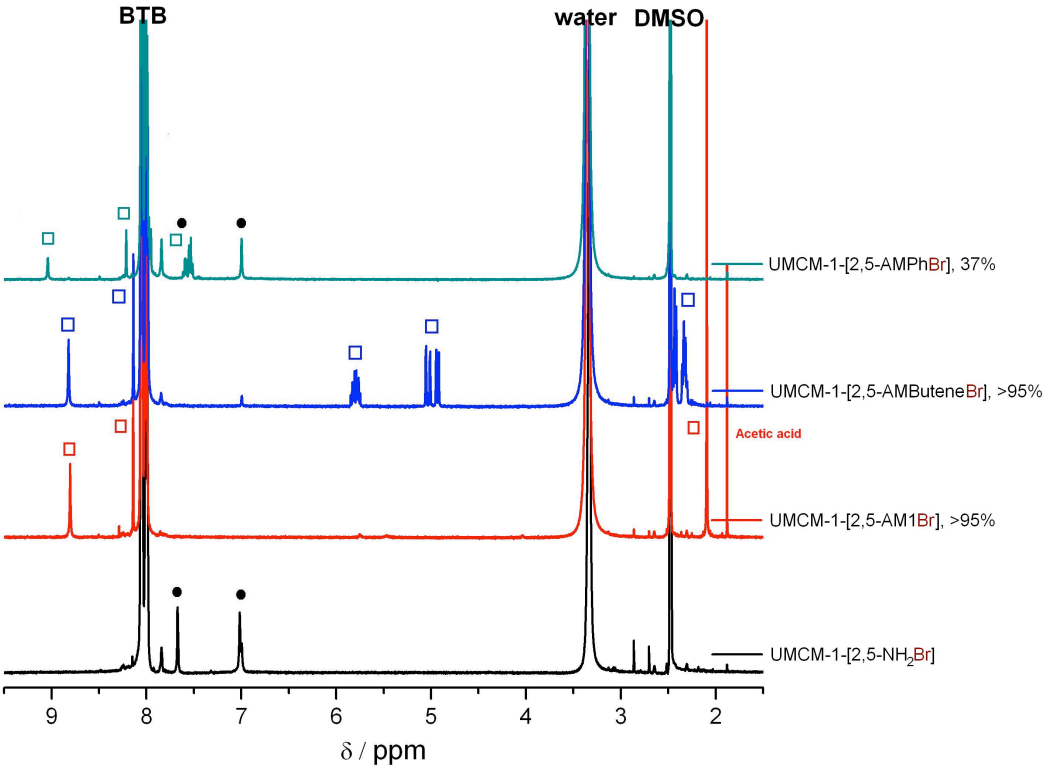


Fig. S10 ^{1}H NMR spectra of UMCM-1-[2,5-NH_2Br] and postsynthetic modified UMCM-1-[2,5-AMBr]after acid digestion. Filled circles indicate 2,5-NH_2Br-BDC, and open squares indicate modified ligands.

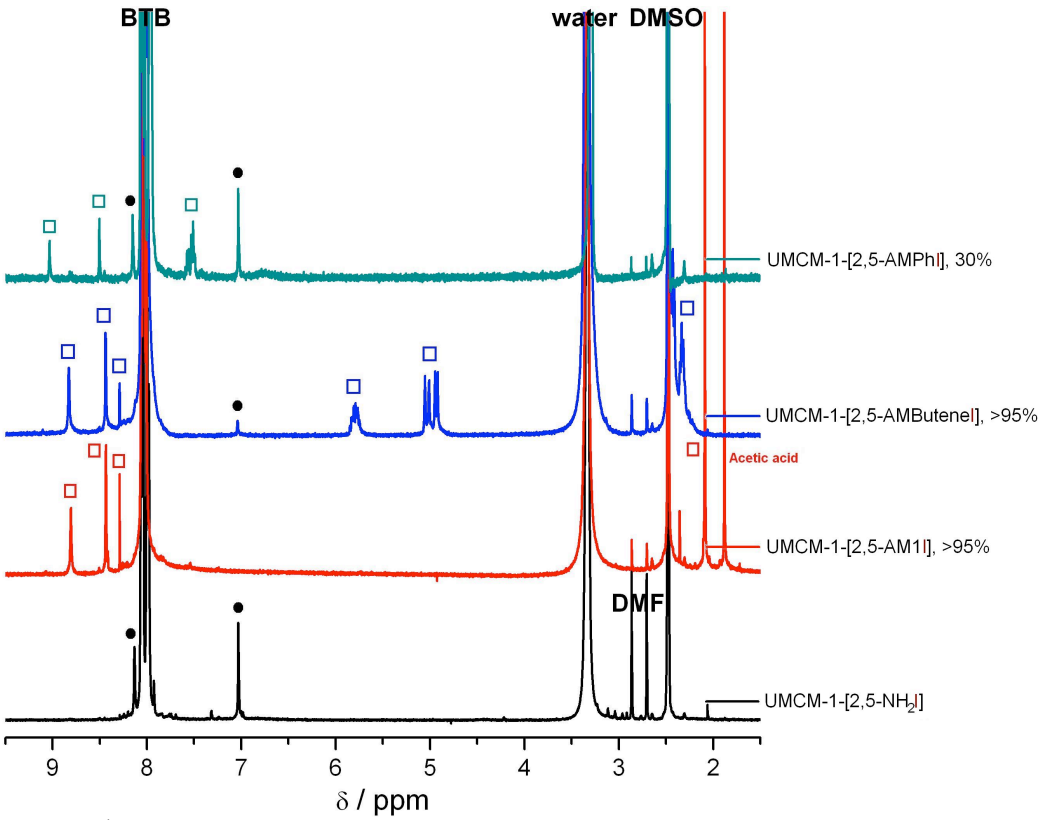


Fig. S11 ^{1}H NMR spectra of UMCM-1-[2,5-NH_2I]and postsynthetic modified UMCM-1-[2,5-AMI]after acid digestion. Filled circles indicate 2,5-NH_2I-BDC, and open squares indicate modified ligands.

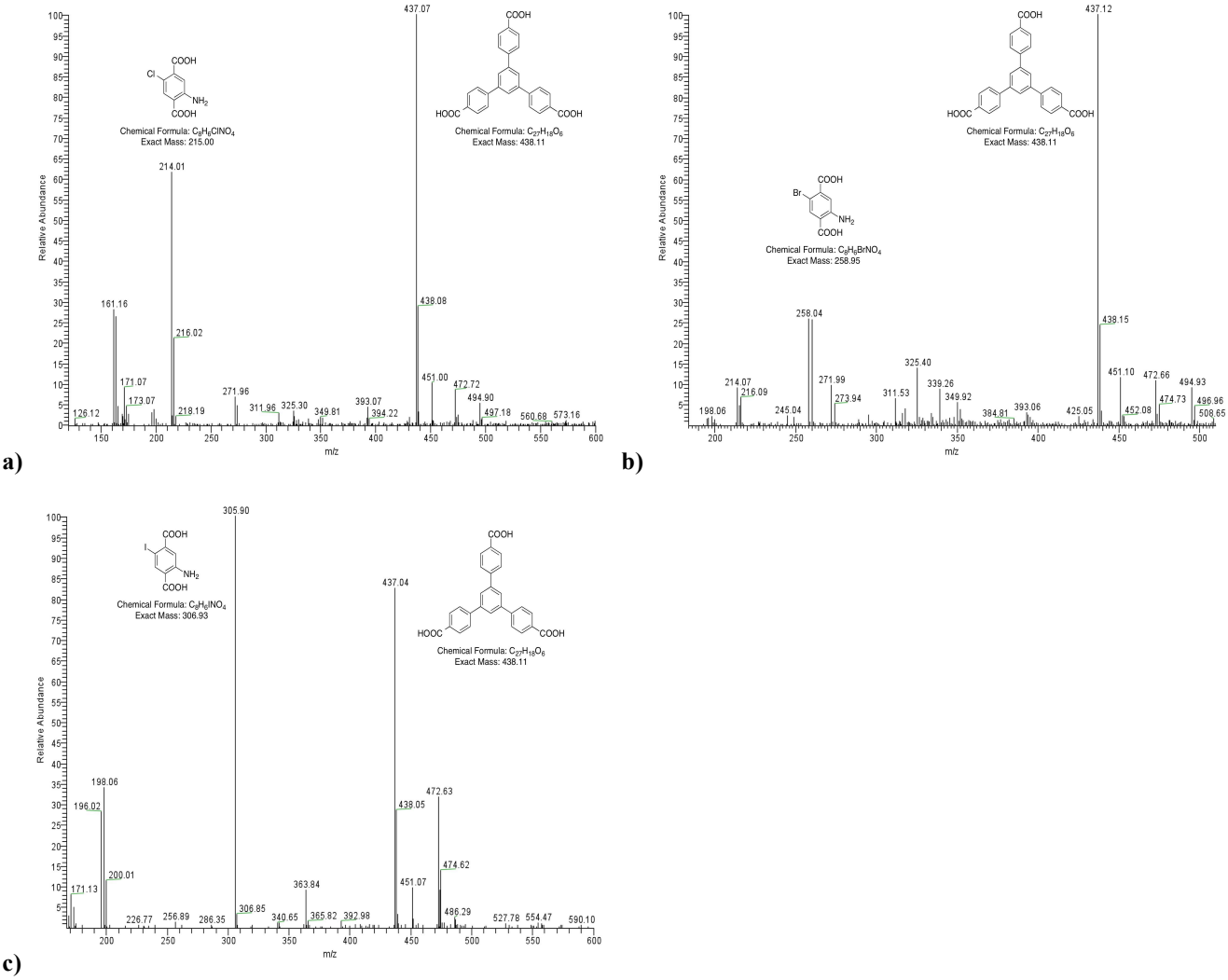


Fig. S12 ESI-MS spectra of UMCM-1-[2,5-NH_2X] after acid digestion; a) X = Cl, b) X = Br, c) X = I.

Table S4 Brunauer-Emmett-Teller (BET) surface area of bifunctional UMCM-1 materials.[a]

UMCM	BET Surface Area (m^2/g)
UMCM-1-Dioxole	3858
UMCM-1-[2,5-NH_2Cl]	3596
UMCM-1-[2,5-NH_2Br]	3599
UMCM-1-[2,5-NH_2I]	3270

[a] The average surface area number was determined from two independent samples.

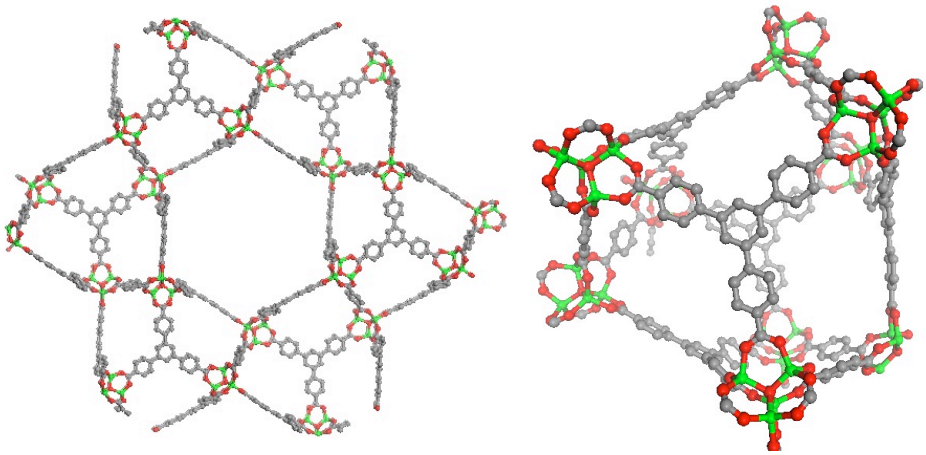
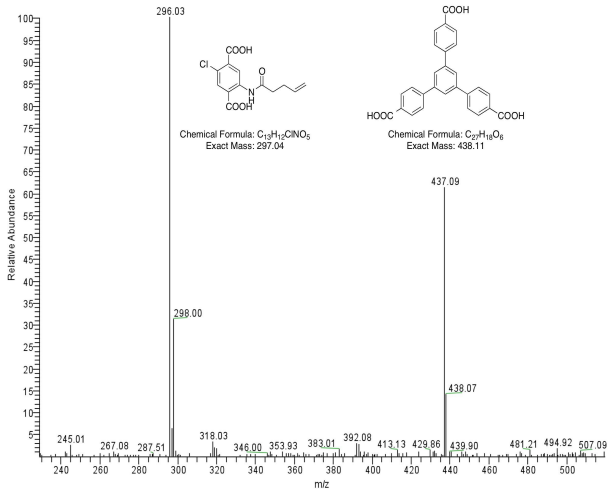
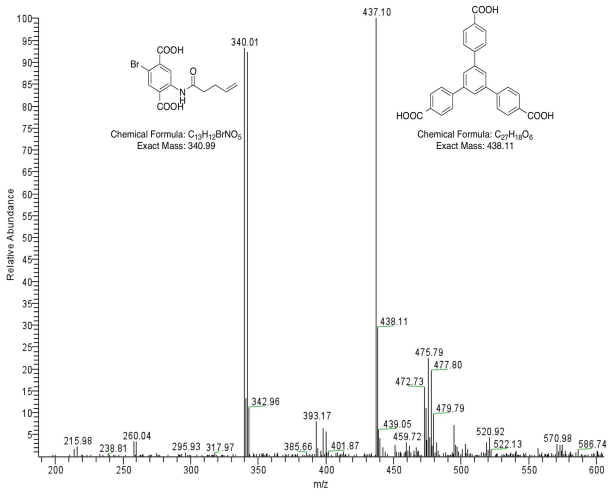


Fig. S13 The X-ray crystal structure of UMCM-1-Dioxole framework (left) and small cage (right). Color scheme: Zn (green), O (red), C (gray).

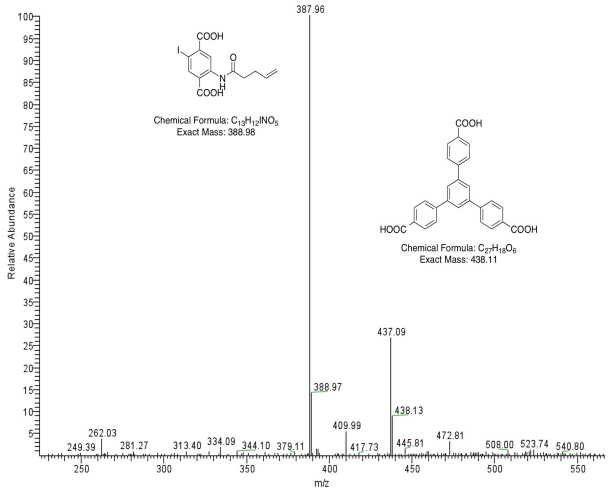
Fig. S14 ESI-MS spectra of UMCM-1-[2,5-AM1X] after acid digestion; a) X = Cl, b) X = Br, c) X = I.



a)



b)



c)

Fig. S15 ESI-MS spectra of UMCM-1-[2,5-AMButeneX] after acid digestion; a) X = Cl, b) X = Br, c) X = I.

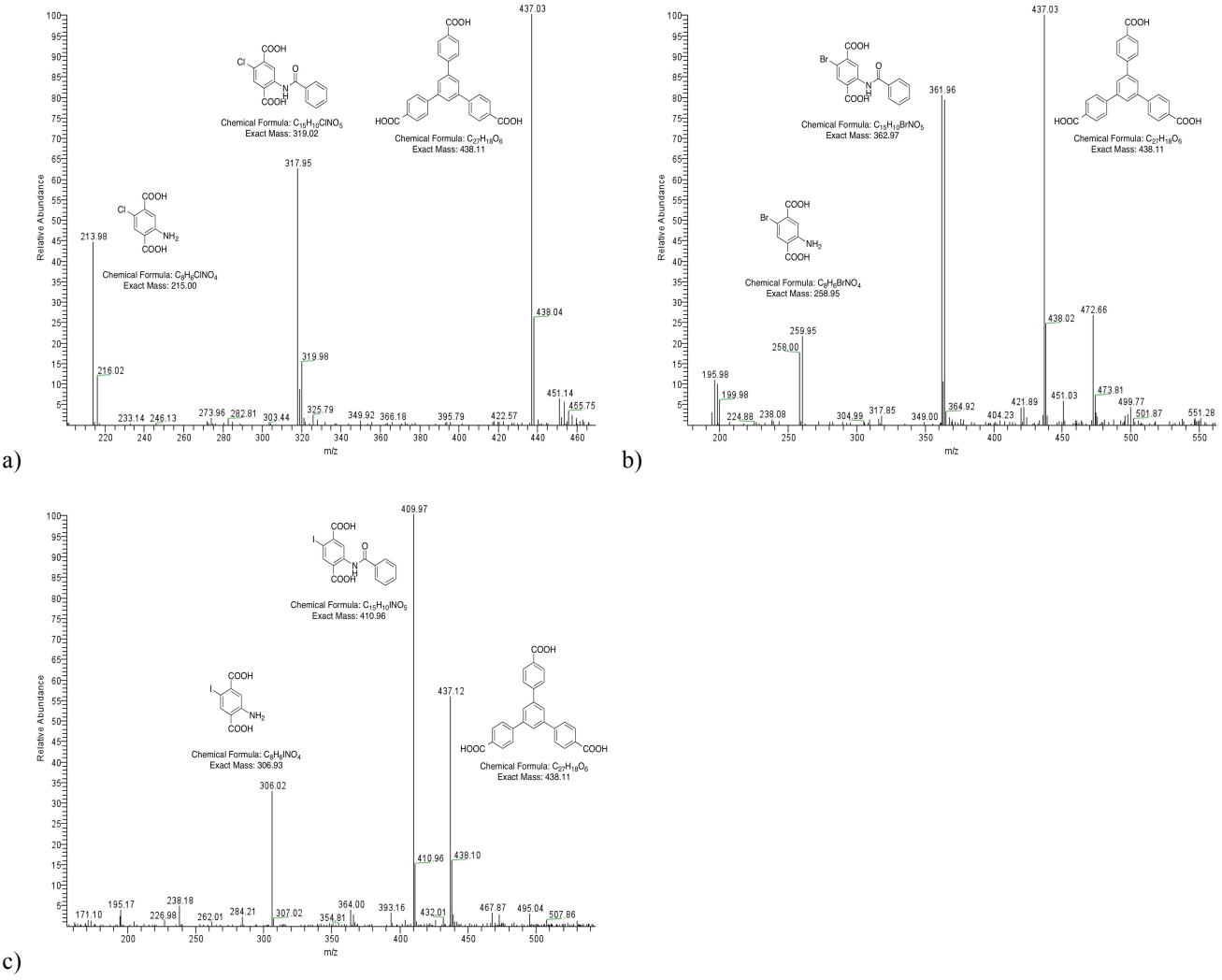


Fig. S16 ESI-MS spectra of UMCM-1-[2,5-AMPhX] after acid digestion; a) X = Cl, b) X = Br, c) X = I.

Table S5 Brunauer-Emmett-Teller (BET) surface area of postsynthetically modified UMCM-1-[2,5-AMX] materials.[a]

UMCM	BET Surface Area (m^2/g)
UMCM-1-[2,5-AM1Cl]	3051
UMCM-1-[2,5-AM1Br]	3528
UMCM-1-[2,5-AM1I]	2810
UMCM-1-[2,5-AMButeneCl]	3221
UMCM-1-[2,5-AMButeneBr]	3196
UMCM-1-[2,5-AMButeneI]	3517
UMCM-1-[2,5-AMPhCl]	2756
UMCM-1-[2,5-AMPhBr]	2872
UMCM-1-[2,5-AMPhI]	2830

[a] The average surface area number was determined from two independent samples.

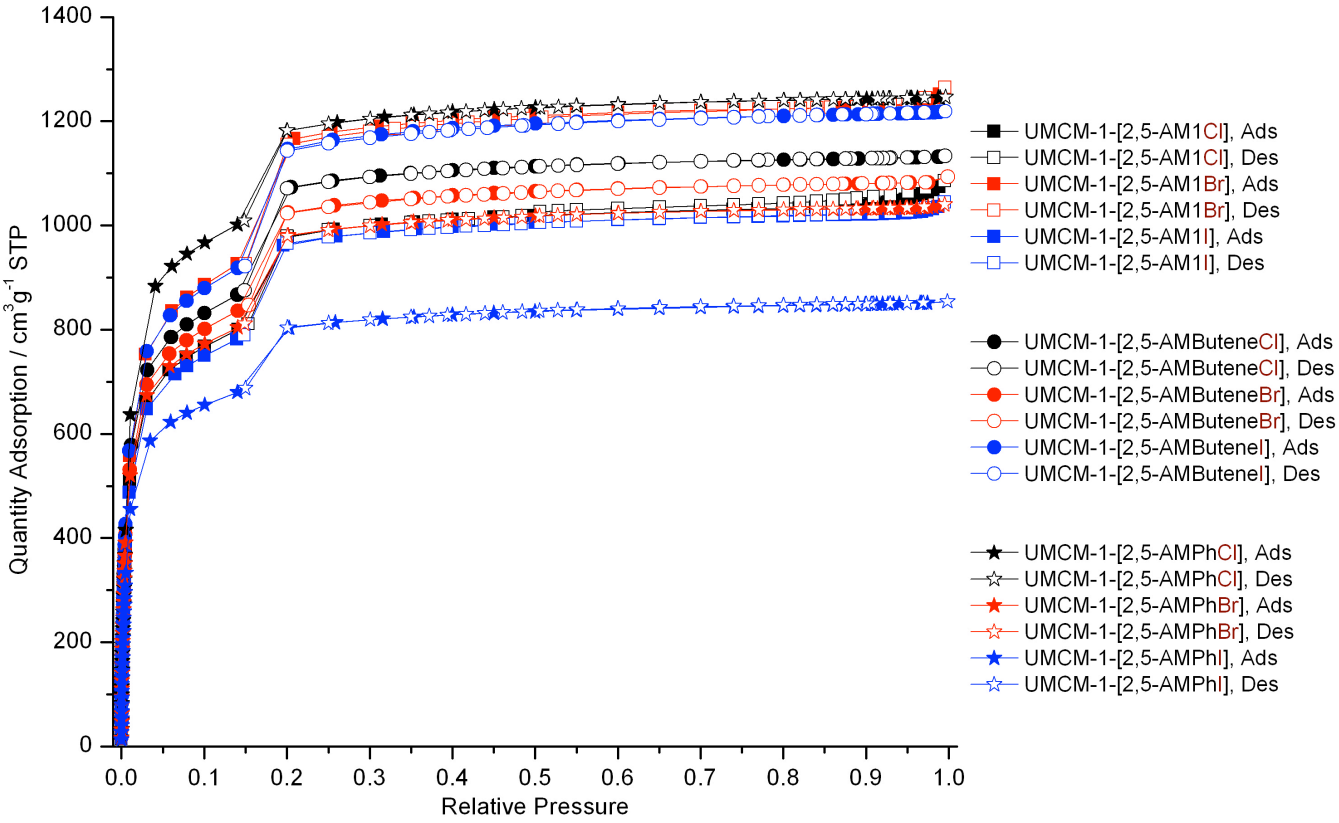


Fig. S17 N_2 isotherm (77 K) of postsynthetically modified UMCM-1-[2,5-AMX].

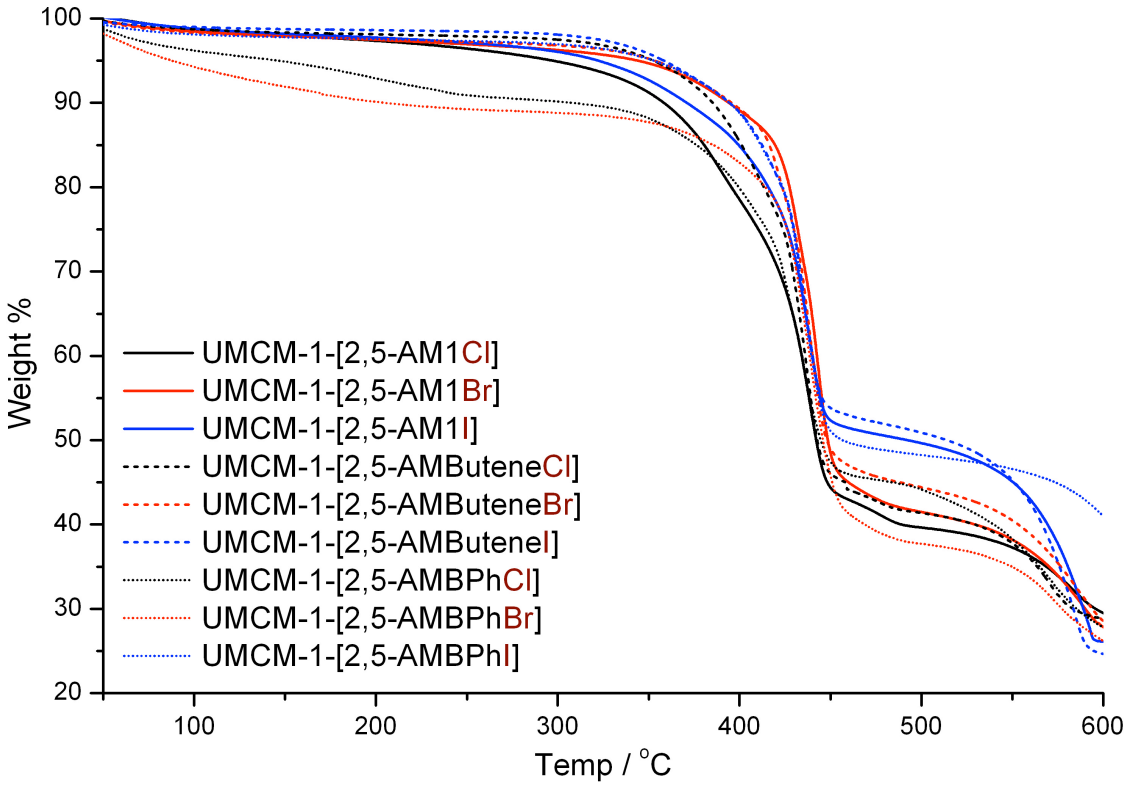
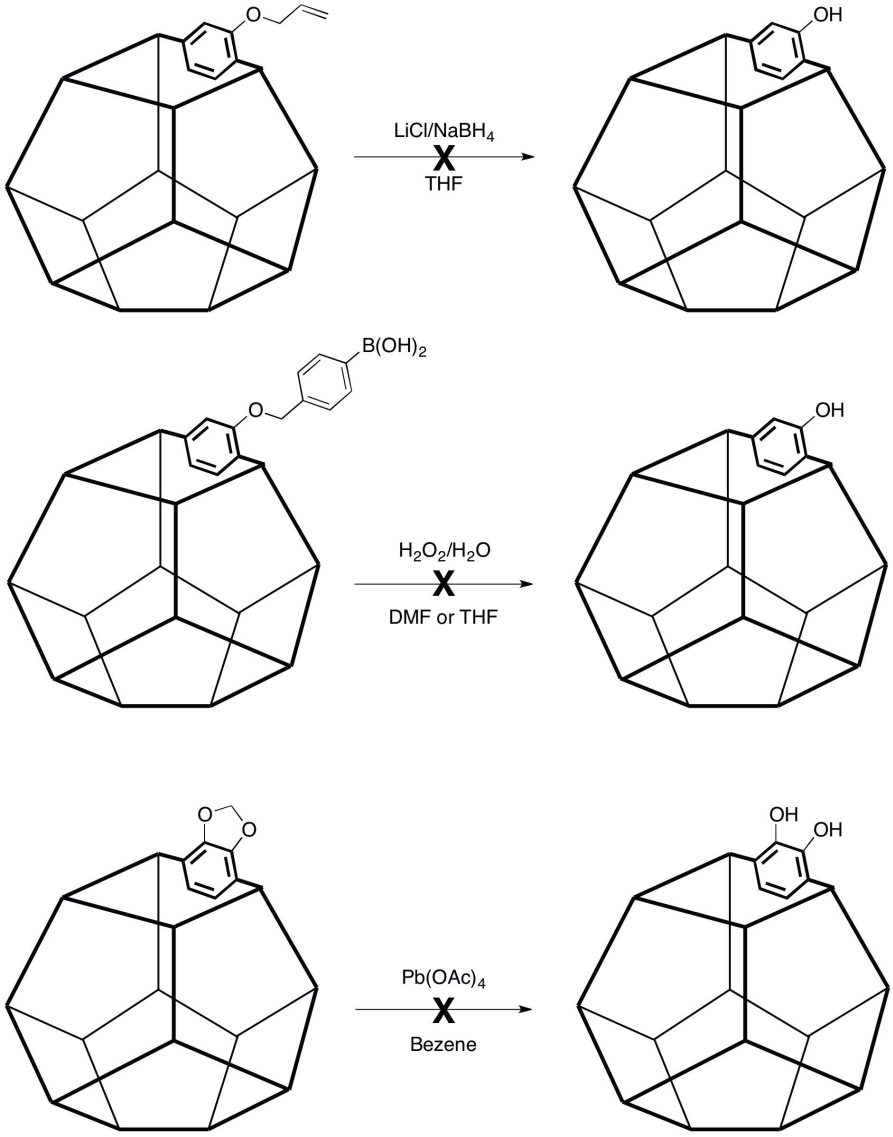


Fig. S18 TGA of the modified UMCM-1-[2,5-AMX].

Scheme S1 Chemical postsynthetic deprotection trials from protected UMCMs.



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