Fluorine Extraction from Organo-fluorine Molecules to Make

Fluorinated Clusters in Yttrium MOFs

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Materials and methods

Chemicals/reagents

N,N-dimethylformamide (DMF) 99.8+%, 2,2'-bicinchoninic acid (98.0+%, TCI America[™]), nitric acid (ACS grade), and, Yttrium(III) nitrate hexahydrate (99.9%), 2-fluorobenzoic acid (99%), 2,6-difluorobenzoic acid (98+%), perfluorohexanoic acid (98+%, MilliporeSigma[™]) and deuterated solvents were purchased from Fisher Scientific. DMF was dried using activated 5A molecular sieves.

Single Crystal XRD (SC-XRD)

Single crystal X-ray diffraction measurements of the single crystal X-ray diffraction datasets were carried out at 110 K employing a three circle Bruker-AXS Quest IµS Mo source for Y-BCA-2D. A Photon III area detector was used in both diffractometers (NSF-CHE-9807975, NSF-CHE-0079822 and NSF-CHE-0215838). In a typical measurement, a crystal was mounted on Kapton[®] loop and cooled in a cold nitrogen stream (OXFORD Crysosystems), to 110(2) K. Bruker AXS APEX 3¹ software was used for data collection and reduction. Absorption corrections were applied using SADABS². Space group assignments were determined by examination of systematic absences, E-statistics, and successive refinement of the structures. Structures were solved using SHELXT³ and refined by least-squares refinement on F² followed by difference Fourier synthesis in the OLEX2 interface⁴ with the SHELXL program⁵. All hydrogen atoms were included in the final structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Thermal parameters were refined anisotropically for all non-hydrogen atoms to convergence. For Y-BCA-3D, a suitable colorless octahedral-like crystal, with dimensions of 0.200 mm × 0.114 mm × 0.085 mm, was mounted in paratone oil onto a nylon loop. All data were collected at 100.0(1) K, using a XtaLAB Synergy/ Dualflex, HyPix fitted with CuK α radiation (λ = 1.54184 Å). Data collection and unit cell refinement were performed using CrysAlisPro software.⁶ The total number of data were measured in the $6.82^{\circ} < 2\theta < 153.4^{\circ}$, using ω scans. Data processing and absorption correction, giving minimum and maximum transmission factors (0.711, 1.000) were accomplished with CrysAlisPro⁶ and SCALE3 ABSPACK,⁷ respectively. The structure, using Olex2,⁴ was solved with the ShelXT³ structure solution program using direct methods and refined (on F²) with the ShelXL⁵ refinement package using full-matrix, least-squares techniques. All non-hydrogen atoms were refined with

anisotropic displacement parameters. All hydrogen atom positions were determined by geometry and refined by a riding model.

Nuclear Magnetic Resonance (NMR)

Bruker Avance IIITM HD 600 MHz spectrometer was used to acquire ¹⁹F NMR data at 298 K. The data was analyzed with TopSpin 4.1.0. for the ¹⁹F NMR spectra. The residual solvent peaks (DMSO-d₆) were used as a reference. A solution of 10% D_2SO_4/D_2O was made and 20 µL of this solution were added to 1 mL of DMSO-d₆. Then, 7 mg of the activated MOFs samples were added to 460 µL of the DMSO-d₆ solution and heated for 6 hours at 60°C. The solution was transferred to the NMR tube.

X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra were collected on a PHI VersaProbe II Scanning XPS Microprobe (Physical Electronics Inc, Chanhassen, Minnesota) equipped with Al K α X-ray source (E_p =1486.7 eV) at a pressure 1.6×10^{-9} Torr. The high-resolution spectra were collected at the pass energy of 23.5 eV with a step size of 0.2 eV. Photoelectron spectra were obtained using a charge compensation of 2 μ A. The sample surface was cleaned by sputtering Gas-Cluster Ion Beam (GCIB) with an energy of 5 kV and cluster size of ~2500 argon atoms. The data was processed with software CasaXPS⁸ and binding energies were doubly calibrated to adventitious C_{1s} at 284.8 eV and Au $4f_{7/2}$ at 83.95 eV.

Powder X-ray diffraction (PXRD)

PXRD patterns were collected on an Ultima IV X-ray diffractometer (Rigaku) equipped with Cu K_{α} radiation, with a scan rate of 2°/min and a step size of 0.04°. The simulated XRD patterns were

generated from the CIF files using a crystal structure visualization tool Mercury⁹ (Cambridge Crystallographic Data Centre).

Gas Adsorption Analysis and Sample Preparation

The adsorption/desorption isotherms were obtained on ASAP 2020 Plus (Micromeritics instrument corporation) at 77 K for N₂ and 273 K for CO₂. For the surface area and porosity analysis, MOFs crystals were washed 3 times with fresh DMF and activated at 170°C under vacuum. The surface area was calculated by built-in Brunauer–Emmett–Teller (BET) model. Ultra-high purity CO₂ and N₂ were used for the analysis.

The scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

SEM and EDX was performed on a Ziess EVO LS SEM and an Aztec Instruments Oxford EDX.

Thermogravimetric analysis (TGA)

The TGA was conducted using a SDT Q600 (TA Instruments). The samples were then heated from room temperature to 800 °C at a rate of 10 °C/min under nitrogen and air.

EXPERIMENTAL

Synthesis of Y-BCA-2D

The yttrium 2D-MOF was synthesized by dissolving 36.8 mg (92.71 μ mol) bicinchoninic acid and 100 mg (0.261 mmol) Y(NO₃)₃.6H₂O in 10 mL dimethyl formamide (DMF). The pH was adjusted to 3 by adding 150 μ L of concentrated nitric acid to slow down the reaction. The solution was

sealed in a 20 mL glass vial and heated isothermally at 80°C for 24 hours. Transparent colorless hexagonal crystals were obtained (**Figure S7(a)**). The crystals were washed 3 times with 10 mL DMF and dried at 80°C for 24 hours.

Synthesis of Y-BCA-3D

Yttrium 3D-MOFs single crystals were synthesized by dissolving 36.8 mg (92.71 μmol) bicinchoninic acid, 100 mg (0.261 mmol) Y(NO₃)₃.6H₂O, and 200 mg (1.29 mmol) of 2,6-difluorobenzoic acid in 10 mL of DMF. The pH was adjusted to 3 by adding a few drops of concentrated nitric acid. The solution was sealed in a 20 mL glass vial and heated isothermally at 120°C for 24 hours. Transparent colorless polyhedral crystals were obtained and washed with 10 mL DMF 3 times and dried at 80°C for 24 hours (**Figure S7b**). Same procedure was followed to synthesize Y-BCA-3D using 2-FBA and PFHxA. In the case of 2-FBA 240 mg (1.71 mmol) and for PFHxA 120 μL (211.08 mg, 0.67 mmol) was used.

Synthesis of YF₃

Yttrium fluoride was synthesized by dissolving 100 mg (0.261 mmol) Y(NO₃)₃.6H₂O and 2-FBA 240 mg (1.71 mmol) in DMF. The solution was sealed in a 20 mL glass vial and heated at 120°C for 24 hours. White precipitates were obtained, washed with 10 mL DMF (×3) and 10 mL water (×3). The white powder was dried in the oven at 80°C for 24 hours. Same procedure was followed to synthesize YF₃ using 2,6-DFBA and PFHxA. In the case of 2,6-DFBA 200 mg (1.29 mmol) and for PFHxA 120 μ L (211.08 mg, 0.67 mmol) was used. The PXRD confirmed that bulk samples were same phase of YF₃. (**Figure S5**).

Table S1. Crystallographic data for Y-BCA-2D and Y-BCA-3D structures
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Compound/MOF	Y-BCA-2D	Y-BCA-3D
CCDC number		
Empirical formula	$C_{75}H_{67}N_{11}O_{18}Y_2$	$C_{30}H_{15}F_2N_3O_{6.62}Y_{1.5}$
Formula weight	1588.21	694.81
Crystal system	Triclinic	Tetragonal
Space group	$P\overline{1}$	14/m
a (Å)	11.851(1)	17.74780 (10)
b (Å)	16.229(2)	17.74780 (10)
c (Ấ)	19.309(2)	25.9278(2)
α (°)	78.447(3)	90
в (°)	75.155(3)	90
(°) γ	89.692(3)	90
Volume (ų)	3512.9(6)	8166.85(11)
Z	2	8
ρ (calc.)	1588.21	1.130
λ	0.71073 Å	1.54184 Å
Temp. (K)	110	100.0(1)
F(000)	1632.0	2764
μ (mm⁻¹)	1.725	3.300

T _{min} , T _{max}	0.7471, 0.5870	0.711, 1.000				
2θ _{range} (°)	3.56 to 73.746	6.82 to 153.4				
Reflections collected	335216	26154				
Independent	32879	4096				
reflections	$[R_{int} = 0.0956,$	[R(int) = 0.0302]				
F	R _{sigma} = 0.0620]					
Completeness	98.9%	97.8%				
Data/restraints/	32879/30/945	4096/0/193				
parameters						
Observed data	32879	4005				
[I > 2σ(I)]						
wR(F ² all data)	0.1439	0.1400				
R(F obsd data)	0.0567	0.0640				
Goodness-of-fit on <i>F</i> ²	1.026	1.05				
Largest diff. peak and	1.95/-1.56	4.6 / -1.6				
hole (e Å-³)						
$wR_2 = \{ \Sigma [w(F_0^2 - F_c^2)^2] / \Sigma [w(F_0^2)^2] \}^{1/2}$						

 $R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|$



Figure S1. Crystal structure of **Y-BCA-2D** showing (a) Type-1 and type-2 BCA linkers in the structure with η^2 and η^3 -carboxylate groups (b) trapped DMF and water molecules between the layers shown in orange and magenta respectively (c) staggered layers of the MOFs shown in different colors



Figure S2. Crystal structure packing (3-by-3) of Y-BCA-2D showing layers arrangements viewed along (a) *a*-axis (b) *b*-axis and, (c) *c*-axis

5-	Map Sum Spectrum		
		Elements	Weight %
4	Wieght % 60 Weight % 60 Powerd by ™u-Q#	с	56.9
Ē		Y	19.8
s/eV		0	11.8
÷ -		F	5.8
		N	5.7
1		Total	100.00
		Y:F ratio	3.41

Figure S3. The EDX spectra of **Y-BCA-3D** synthesized using 2-FBA as a modulator has an experimental Y/F ratio of 3.41 in comparison to the theoretically calculated value of 3.50 within instrumental error range.

5-	Map Sum Spectrum C 1		
	● <mark>●</mark>	Elements	Weight %
1	Weight % 60 Powered by Tru-Q#	с	55.5
3-		Y	18.9
ps/e/		0	12.6
2		F	6.0
		Ν	7.0
1	_P	Total	100.00
		Y:F ratio	3.15

Figure S4. The EDX spectra of **Y-BCA-3D** synthesized using 2,6-DFBA as a modulator has an experimental Y/F ratio of 3.15 in comparison to the theoretically calculated value of 3.50 within instrumental error range.



Figure S5. The EDX spectra of **Y-BCA-3D** synthesized using PFHxA as a modulator has an experimental Y/F ratio of 2.93 in comparison to the theoretically calculated value of 3.50 within instrumental error range.



Figure S6. The PXRD spectra comparison of a) **Y-BCA-2D** as synthesized and simulated pattern from the single crystal b) **Y-BCA-3D** synthesized using 2-FBA, 2,6-DFBA and PFHxA as modulators vs simulated pattern calculated from the single crystal



Figure S7. A comparison of ¹⁹F-NMR of 2-Fluorobenzoic acid δ ppm: -110.61 to -110.65 (q, 1F) and **Y-BCA-3D** digested in D₂SO₄ (synthesized by 2-Fluorobenzoic acid as a modulator).



Figure S8. A comparison of ¹⁹F-NMR of 2,6-difluorobenzoic acid δ ppm: -112.37 to -112.40 (t, 2F) and **Y-BCA-3D** digested in D₂SO₄ (synthesized by 2,6-difluorobenzoic acid as a modulator).



Figure S9. A comparison of $^{19}\text{F-NMR}$ of perfluorohexanoic acid δ ppm: -112.37 to -

112.40 (t, 2F) and **Y-BCA-3D** digested in D₂SO₄ (synthesized by perfluorohexanoic acid as

a modulator).



Figure S10. Reaction scheme for preparing YF_3 from 2-FBA, 2,6-DFBA or PFHxA (YF_3 structure created from CIF file ICSD 26595).¹⁰



Figure S11. Powder XRD pattern of YF_3 prepared from different organofluorine sources in comparison to simulated pattern from (ICSD 26595).¹⁰



Figure S13. TGA analysis of (a) **Y-BCA-2D** and (b) **Y-BCA-3D** in comparison with the linker BCA Change figure



Figure S12. Optical images for crystals of (a) Y-BCA-2D (b) Y-BCA-3D

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