Synthesis, Structural and Computational Comparisons, of Five New Fluorinated Metal Organic Frameworks (*F*-MOFs)

(Supporting Information: 33 pages including this page)

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Section S1: Detailed synthesis procedures for *F*-MOFs including multi-gram scale products, experimental and simulated PXRD patterns and elemental microanalyses.

4,4′-Hexafluoroisopropylidene-bis-benzoic acid (Hbba), 2,2′-Bipyridyl (Bp), 4,4′-dimethyl-2,2′-Bipyridyl (dmBp) and neocuproine (Ncp) were purchased from the Aldrich Chemical Co. 1,10-Phenanthroline (Phen), 3-Picolin (Pico), Cupric nitrate trihydrate were purchased from the Loba chemical co. *N*,*N*-dimethylformamide (DMF) was purchased from Rankem chemicals. All starting materials were used without further purification. All experimental operations were performed in air

Synthesis of [Cu(hfbba)(phen)$_2$]•2(H$_2$hfbba)(H$_2$O)(HCO$_2$) (*F*-MOF-1) : Hydrothermal reaction of $Cu(NO_3)_2{\cdot}3H_2O$ (0.029 g, 0.12 mmol) with 1,10-Phenanthroline(0.024 g, 0.12 mmol) and excess 4,4′-Hexafluoroisopropylidene-bis-benzoic acid (0.196 g, 0.50 mmol) in a 23 ml acid-digestion bomb using de-ionized water (7 mL) at 120 ^{0}C for 3 days produced blue colored crystals of *F*-MOF-1 in quantitative yield. Crystals were collected by filtration and dried in air (10 min).

***FT-IR* :** (KBr 4000-400cm^{-1}): 3655(s), 3093(w), 1942(w), 1701(s), 1598(s), 1554(s), 1395(s), 1326(w), 1250(m), 1211(w), 1177(w), 1019(w), 1291(w), 929(w), 843(m), 778(m), 744(m), 723(m).

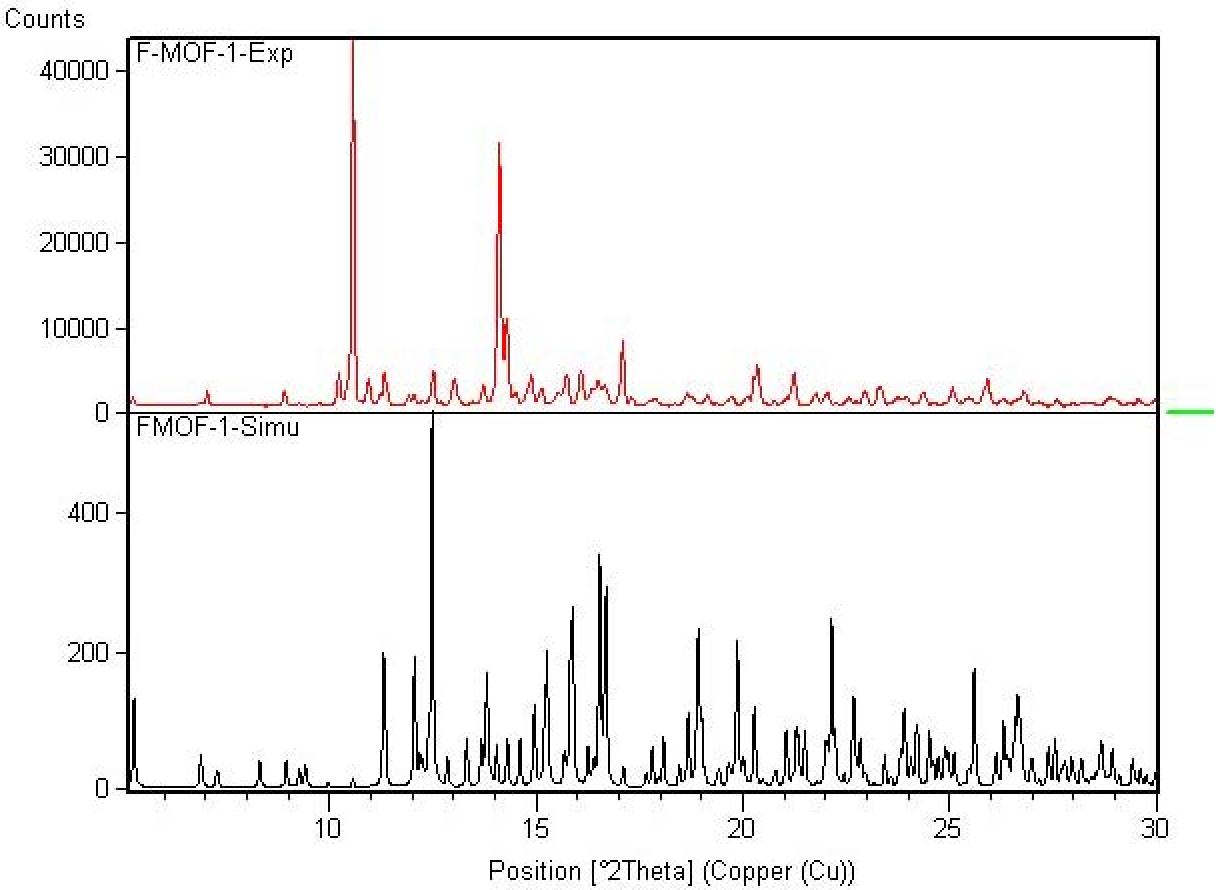

Figure S1. Comparison of the experimental PXRD pattern of as-synthesized *F*-MOF-1 (top) with the one simulated from its single crystal structure (bottom).

Synthesis of [Cu(hfbba)$_2$(2,2′-bipy)$_2$(H$_2$O)] (*F*-MOF-2) : 0.5 mL 2,2′-Bipyridyl stock solution (0.20 M) and 1.5 mL 4,4′-Hexafluoroisopropylidene-bis-benzoic acid stock solution (0.20 M) were mixed in a 5 mL vial. To this solution was added 0.5 mL $Cu(NO_3)_2{\cdot}3H_2O$ stock solution (0.20 M). The vial was capped and heated to 85 ºC for 96 h. The mother liquor was decanted and the products were washed with DMF (15 mL) three times. Blue colored crystals of *F*-MOF-2 were collected by filtration and dried in air (10 min) (yield: 68%).

***FT-IR* :** (KBr 4000-400cm^{-1}): 3040(s), 2554(w), 1945(w), 1817(w), 1689(s), 1626(s), 1557(m), 1515(w), 1482(w), 1390(m), 1289(w), 1213(w), 1175(m), 1140(s), 1068(w), 1020(m), 946(w), 846(w), 779(m), 749(m), 727(s), 589(w), 541(w), 496 (w).

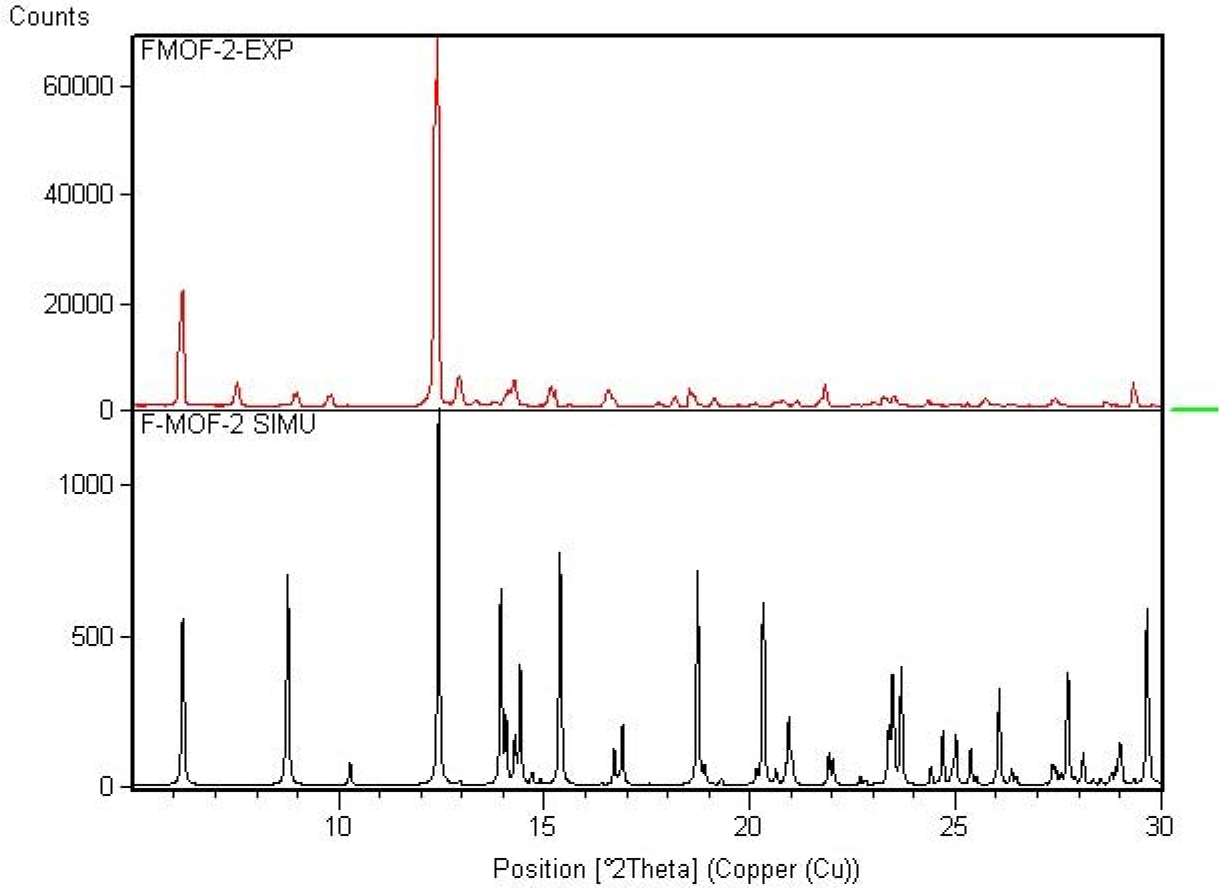

Figure S2. Comparison of the experimental PXRD pattern of as-prepared *F*-MOF-2 (top) with the one simulated from its single crystal structure (bottom).

Synthesis of [Cu(hfbba)(4,4′dime-2,2′-bipy)(HCO$_2$)]•(hfbba)(H$_2$O) (*F*-MOF-3):

Hydrothermal reaction of Cu(NO$_3$)$_2$·3H$_2$O (0.029 g, 0.12 mmol) with 4,4′-dimethyl-2,2′-Dipyridyl (0.022 g, 0.12 mmol) and excess 4,4′-Hexafluoroisopropylidene-bis-benzoic acid (0.196 g, 0.50 mmol) in a 25 ml acid-digestion bomb using de-ionized water (7 mL) at 120 ^{0}C for 3 days produced blue colored crystals of *F*-MOF-3 in quantitative yield. Crystals were collected by filtration and dried in air (10 min).

FT-IR **:** (KBr 4000-400cm^{-1}): 3695(br), 3557(m), 3090(w), 2496(w), 2094(w), 1942(w), 1824(w), 1698(m), 1681(m), 1591(w), 1543(m), 1399(s), 11326(w), 1290(s), 1257(w), 1172(w), 1021(w), 960(w), 860(w), 779(m), 745(w), 723(m), 519(w).

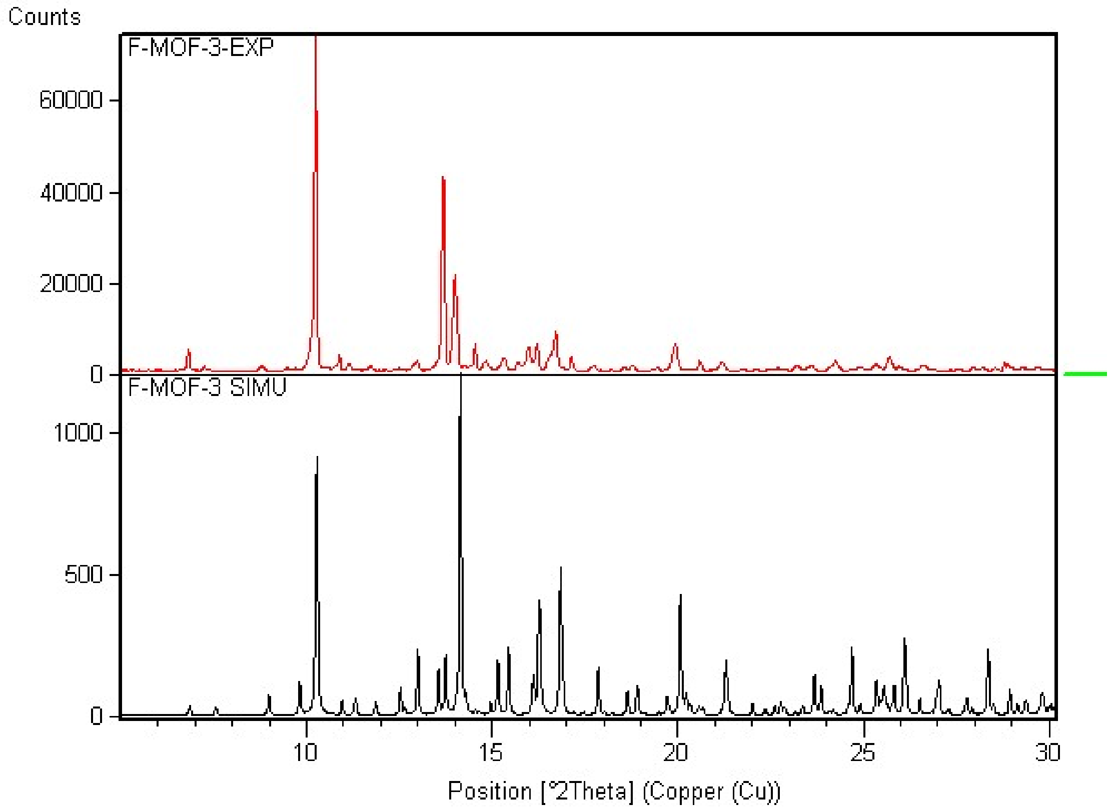

Figure S3. Comparison of the experimental PXRD pattern of as-prepared *F*-MOF-3 (top) with the one simulated from its single crystal structure (bottom).

Synthesis of [Cu$_2$(hfbba)$_2$(3-mepy)$_2$]•(DMF)$_2$(3-mepy) (*F*-MOF-4) : 0.5 mL 3-Picolin stock solution (0.20 M) and 1.5 mL 4,4′-Hexafluoroisopropylidene-bis-benzoic acid stock solution (0.20 M) were mixed in a 5 mL vial. To this solution was added 0.5 mL Cu(NO$_3$)$_2$·3H$_2$O stock solution (0.20 M). The vial was capped and heated to 85 ºC for 96 h. The mother liquor was decanted and the products were washed with DMF (15 mL) three times. Blue colored crystals of *F*-MOF-4 were collected by filtration and dried in air (10 min) (yield: 68%).

***FT-IR* :** (KBr 4000-400cm^{-1}): 3676(br), 3068(w), 3935(m), 2657(w), 2548(w), 2331(s), 1944(m), 1816(w), 1683(m), 1632(w), 1561(w), 1410(s), 1291(w), 1239(s), 1174(w), 1090(w), 1020(w), 971(w), 929(w), 846(m), 780(s), 748(w), 706(w), 514(m), 494(w).

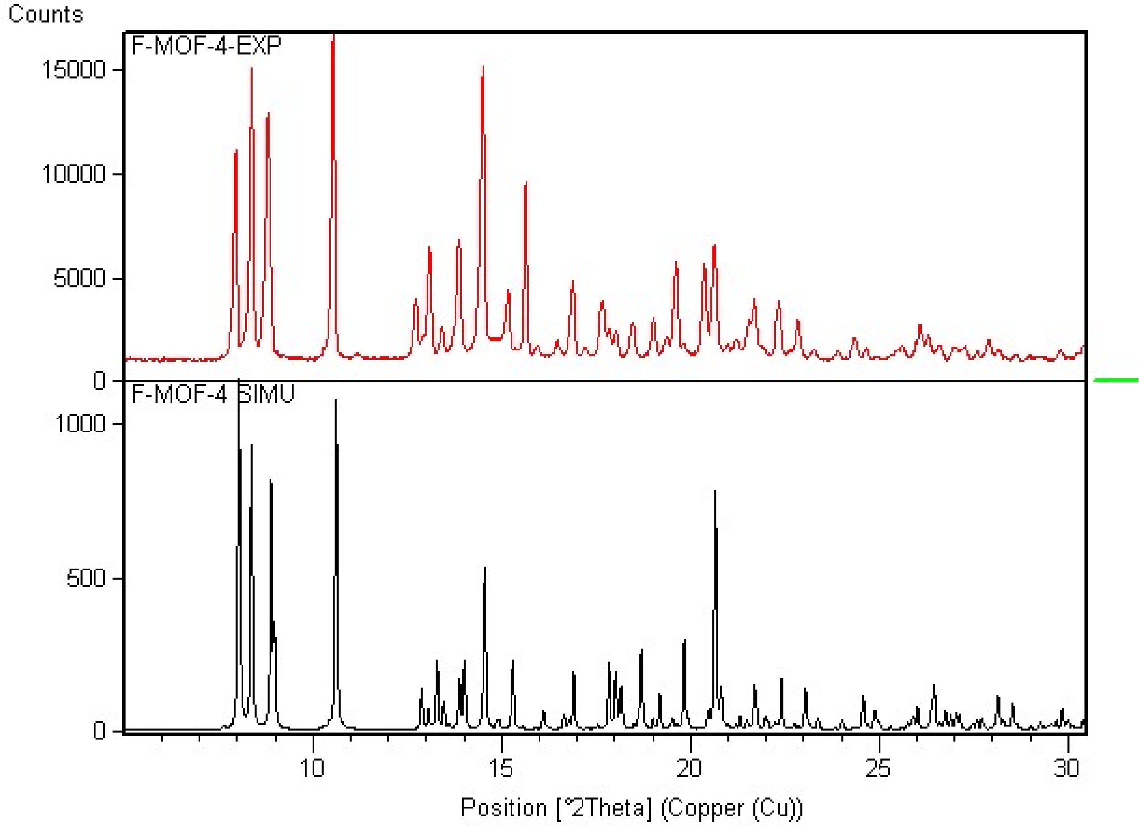

Figure S4. Comparison of the experimental PXRD pattern of as-prepared *F*-MOF-4 (top) with the one simulated from its single crystal structure (bottom).

Synthesis of (*F*-MOF-5): Cu(Hbba) (Phen). 0.5 mL 1,10-Phenanthroline stock solution (0.20 M) and 1.5 mL 4,4′-Hexafluoroisopropylidene-bis-benzoic acid stock solution (0.20 M) were mixed in a 5 mL vial. To this solution was added 0.5 mL $Cu(NO_3)_2{\cdot}3H_2O$ stock solution (0.20 M). The vial was capped and heated to 85 ºC for 96 h. The mother liquor was decanted and the products were washed with DMF (15 mL) three times. Blue colored crystals of *F*-MOF-4 were collected by filtration and dried in air (10 min) (yield: 68%).

***FT-IR* :** (KBr 4000-400cm^{-1}): 3680(br), 3056(s), 2937(m), 2510(w), 1941(m), 1813(w), 1683(s), 1599(m), 1557(w), 1519(w), 1411(s), 1253(w), 1211(w), 1172(w), 1138(w), 1019(m), 971(w), 845(s), 778(s), 748(w), 725(m), 557(w), 515(w), 495(w).

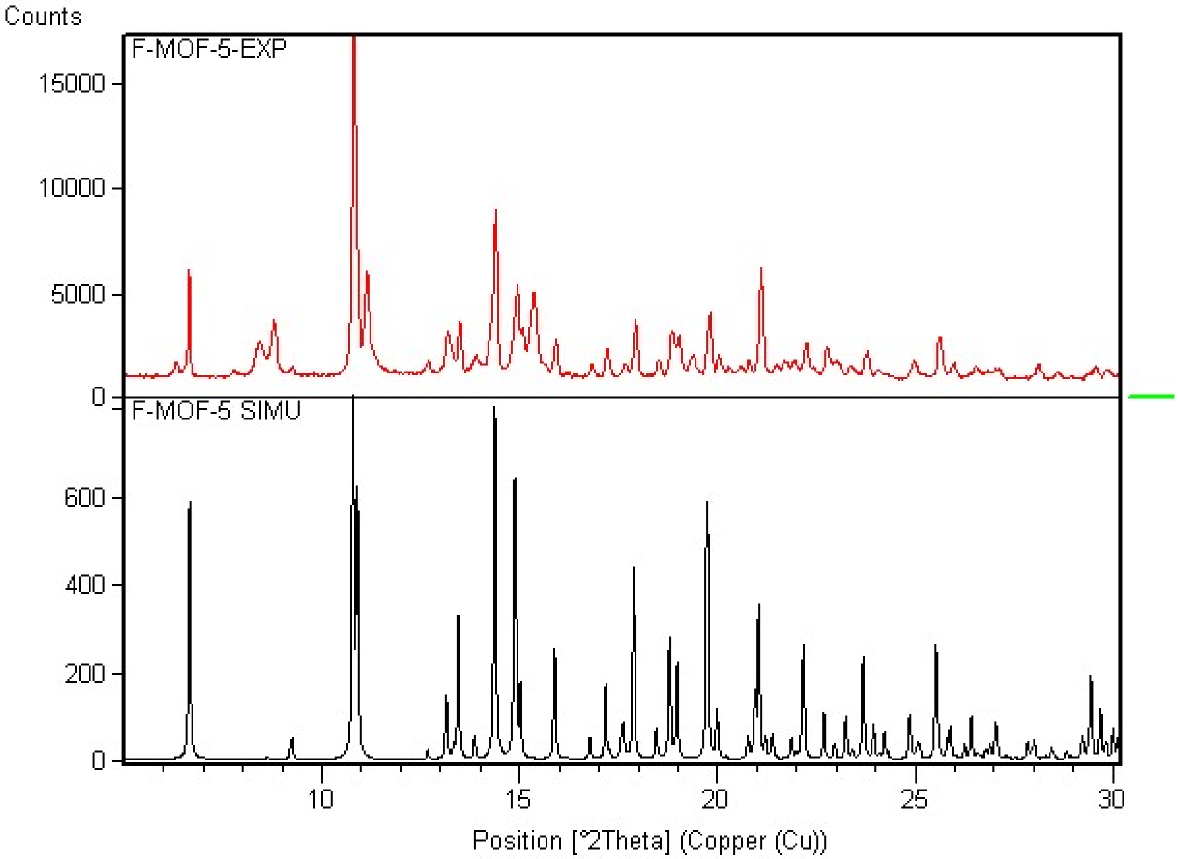

Figure S5. Comparison of the experimental PXRD pattern of as-prepared *F*-MOF-5 (top) with the one simulated from its single crystal structure (bottom).

Section S2. Single crystal X-ray diffraction data collection, structure solution and refinement procedures.

General Data Collection and Refinement Procedures:

All single crystal data were collected on a Bruker SMART APEX three circle diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo Kα radiation (λ=0.71073 Å). The incident X-ray beam was focused and monochromated using Bruker Excalibur Gobel mirror optics. Crystals of the *F*-MOFs reported in the paper were mounted on nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). Crystals were flash frozen to 100(2) K in a liquid nitrogen cooled stream of nitrogen.

Initial scans of each specimen were performed to obtain preliminary unit cell parameters and to assess the mosaicity (breadth of spots between frames) of the crystal to select the required frame width for data collection. In every case frame widths of 0.5° were judged to be appropriate and full hemispheres of data were collected using the *Bruker SMART*[1] software suite. Following data collection, reflections were sampled from all regions of the Ewald sphere to redetermine unit cell parameters for data integration and to check for rotational twinning using CELL_NOW[2]. In no data collection was evidence for crystal decay encountered. Following exhaustive review of the collected frames the resolution of the dataset was judged. Data were integrated using Bruker SAINT [3] software with a narrow frame algorithm and a 0.400 fractional lower limit of average intensity. Data were subsequently corrected for absorption by the program SADABS[4]. The absorption coefficient (μ) ranges between 1 and 2 for all of the *F*-MOFs reported in this paper. However, it is should be noted that μ is based on the atomic contents and these contents are uncertain for most of these structures. In some cases the precise guest molecule (solvent) content is not known because the small solvent molecules neither fit tightly nor reproducibly into the voids of these framework structures. The space group determinations and tests for merohedral twinning were carried out using *XPREP*[3]. In all cases, the highest possible space group was chosen.

All structures were solved by direct methods and refined using the *SHELXTL 97*[5] software suite. Atoms were located from iterative examination of difference F-maps following least squares refinements of the earlier models. Final models were refined anisotropically (if the number of data permitted) until full convergence was achieved. Hydrogen atoms were placed in calculated positions (C-H = 0.93 Å) and included as riding atoms with isotropic displacement parameters 1.2-1.5 times U_{eq} of the attached C atoms. In some cases modeling of electron density within the voids of the frameworks did not lead to identification of recognizable solvent molecules in these structures, probably due to the highly disordered contents of the large pores in the frameworks. Highly porous crystals that contain solvent-filled pores often yield raw data where observed strong (high intensity) scattering becomes limited to ~1.0 Å at best, with higher resolution data present at low intensity. A common strategy for improving X-ray data, increasing the exposure time of the crystal to X-rays, did not improve the quality of the high angle data in these cases, as the intensity from low angle data saturated the detector and minimal improvement in the high angle data was achieved. Additionally, diffuse scattering from the highly disordered solvent within the void spaces of the framework and from the capillary to mount the crystal contributes to the background and the 'washing out' of the weaker data. The only optimal crystals suitable for analysis were generally small and weakly diffracting. Unfortunately, larger crystals, which would usually improve the quality of the data, presented a lowered degree of crystallinity and attempts to optimize the crystal growing conditions for large high-quality specimens have not yet been fruitful. Data were collected at 298(2) K for *F*-MOF-5. For the other four *F*-MOFs presented in this paper data collection took place at 100(2) K. This lower temperature was considered to be optimal for obtaining the best data. Electron density within void spaces has not been assigned to any guest entity but has been modeled as isolated oxygen and/or carbon atoms. The foremost errors in all the models are thought to lie in the assignment of guest electron density. All structures were examined using the *Adsym* subroutine of PLATON[7] to assure that no additional symmetry could be applied to the models. All ellipsoids in ORTEP diagrams are displayed at the 30% probability level unless noted otherwise. For all structures we note that elevated R-values are commonly encountered in MOF crystallography for the reasons expressed above by us and by other research groups.[8-17] Table S1 contains crystallographic data for the five *F*-MOFs.

1. Bruker (2005). *APEX2*. Version 5.053. Bruker AXS Inc., Madison,Wisconsin, USA.
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7. A. L. Spek (2005) PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands.
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F-MOF-1 (Monoclinic)

Experimental and Refinement Details for *F*-MOF-1

A green colored prismatic crystal (0.12 × 0.10 × 0.08 mm^3) of *F*-MOF-1was placed in a 0.7 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 51721 reflections were collected of which 13429 were unique and 11209 of these were greater than $2\sigma(I)$. The range of θ was from 1.22 to 26.02º. All non-hydrogen atoms were refined anisotropically. *F*-MOF-1 contains three 4,4′-hexafluoroisopropylidene-bis-benzoic acid and two 1,10-phenanthroline in the asymmetric unit. *F*-MOF-1 has a higher R_{int} (0.1197) which could possibly be due to a deformed or irregular shaped crystal. It should be noted that other supporting characterization data (*vide infra* Section S1) are consistent with the crystal structure. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0424$ ($F > 2\sigma F$)) and $wR_2 =$ 0.1186 (all data) with GOF = 1.037.

Table S1. Crystal data and structure refinement for ***F*-MOF-1**.

Empirical formula	C76 H47 F18 N4 O15 Cu
Formula weight	1661.73
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 19.358(5) Å α = 90°
	b = 13.756(4) Å β = 99.951°
	c = 26.012(7) Å γ = 90°
Volume	6822.0(3)
Z	4
Density (calculated)	1.618
Absorption coefficient	0.444
F(000)	3368
Crystal size	0.12 × 0.10 × 0.08 mm^3
Theta range for data collection	1.22- 26.02
Index ranges	-23 <= h <= 23, -16 <= k <= 16, -32 <= l <= 32
Reflections collected	51721
Independent reflections	11209 [Rint= 0.12]
Completeness to theta = 26.02°	100%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11209/5/ 1026
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R_1 = 0.0424, wR_2 = 0.1186
R indices (all data)	R_1 = 0.0533, wR_2 = 0.1283
Largest diff. peak and hole	0.078 and -0.822 e.$Å^{-3}$

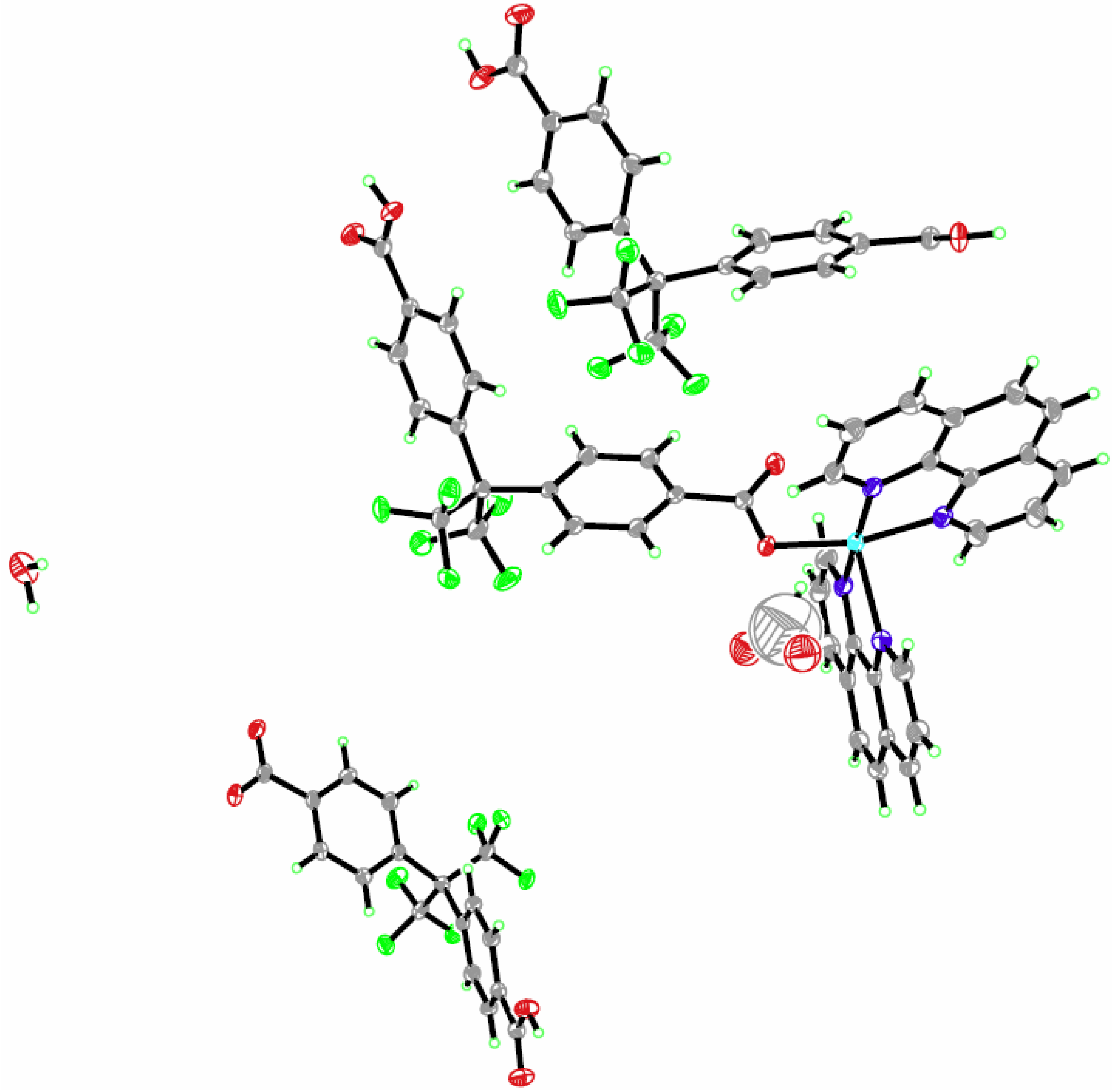


Figure S6. ORTEP drawing of a Cu atom surrounded by Hbba and Phen linkers of *F*-MOF-1 including the guest atoms.

F-MOF-2 (Monoclinic)

Experimental and Refinement Details for *F*-MOF-2

A colorless prismatic crystal (0.18 × 0.12 × 0.10 mm^3) of *F*-MOF-2 was placed in a 0.4 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 24548 reflections were collected of which 4722 were unique and 4009 of these were greater than $2\sigma(I)$. The range of θ was from 1.43 to 26.02°. All non-hydrogen atoms were refined anisotropically. *F*-MOF-2 is composed of one 4,4′-hexafluoroisopropylidene-bis-benzoic acid one 2,2′-bipyridyl and one lattice water per Cu. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0348$, and $wR_2 = 0.0889$ (all data) with GOF = 1.045.

Table S2. Crystal data and structure refinement for ***F*-MOF-2**.

Empirical formula	C27 H18 F6 N2 O5Cu
Formula weight	1661.73
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	*a* = 7.7882(11) Å α = 90°
	b = 28.449(4) Å β = 90.520°
	c = 10.7928(15) Å γ = 90°
Volume	2391.2(6)
Z	4
Density (calculated)	1.744
Absorption coefficient	1.006
F(000)	1268
Crystal size	0.18 × 0.12 × 0.10 mm^3
Theta range for data collection	1.43- 26.02
Index ranges	-9 <= h <= 9, -35 <= k <= 35, -13 <= l <= 13
Reflections collected	24548
Independent reflections	4009 [Rint= 0.0860]
Completeness to theta = 26.02°	100%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4722/1/ 371
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	$R_1 = 0.0348$, $wR_2 = 0.0889$
R indices (all data)	$R_1 = 0.0439$, $wR_2 = 0.1007$
Largest diff. peak and hole	0.097 and -0.375 e.$Å^{-3}$

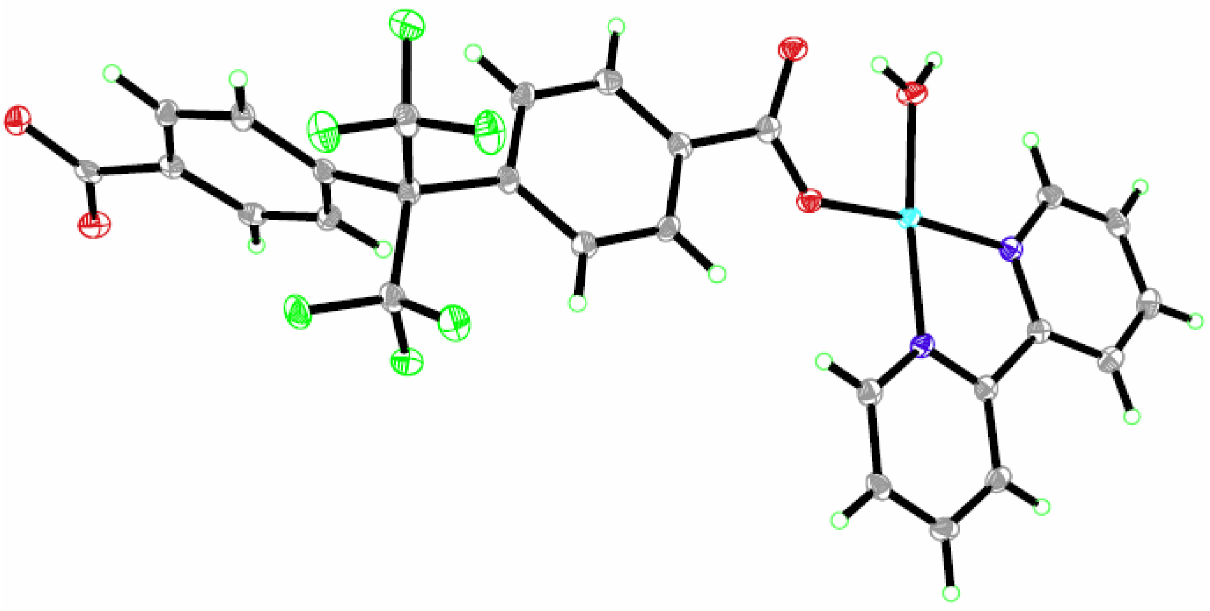


Figure S7. ORTEP drawing of a Cu atom surrounded by Hbba and Bp linkers of *F*-MOF-2.

F-MOF-3 (Orthorhombic)

Experimental and Refinement Details for *F*-MOF-3

A colorless prismatic crystal (0.18 × 0.12 × 0.10 mm^3) of *F*-MOF-3 was placed in a 0.4 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 92999 reflections were collected of which 9518 were unique and 8080 of these were greater than $2\sigma(I)$. The range of θ was from 1.58 to 27.0º. All non-hydrogen atoms were refined anisotropically. *F*-MOF-3 is composed of one 4,4′-hexafluoroisopropylidene-bis-benzoic acid and one 4,4′dimethyl 2,2′-bipyridine per Cu. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0552$, and $wR_2 = 0.1254$ (all data) with GOF = 1.151.

Table S3. Crystal data and structure refinement for ***F*-MOF-3**.

Empirical formula	C46 H29 F12 N2 O9 Cu
Formula weight	1045.26
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*P*ccn
Unit cell dimensions	*a* = 51.500(14) Å α = 90°
	b = 11.992(3) Å β = 90°
	c = 14.114(4)Å γ = 90°
Volume	8717.0(4)
Z	4
Density (calculated)	1.593
Absorption coefficient	0.613
F(000)	4224
Crystal size	0.20 × 0.16 × 0.12 mm^3
Theta range for data collection	1.58 - 27.00
Index ranges	-65 <= h <= 65, -15 <= k <= 15, -17 <= l <= 17
Reflections collected	92999
Independent reflections	8080 [Rint= 0.0926]
Completeness to theta = 64.75°	99.9%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8080/0/635
Goodness-of-fit on F^2	1.151
Final R indices [I>2sigma(I)]	R_1 = 0.0552, wR_2 = 0.1254
R indices (all data)	R_1 = 0.0681, wR_2 = 0.1308
Largest diff. peak and hole	0.708 and -0.683e.$Å^{-3}$

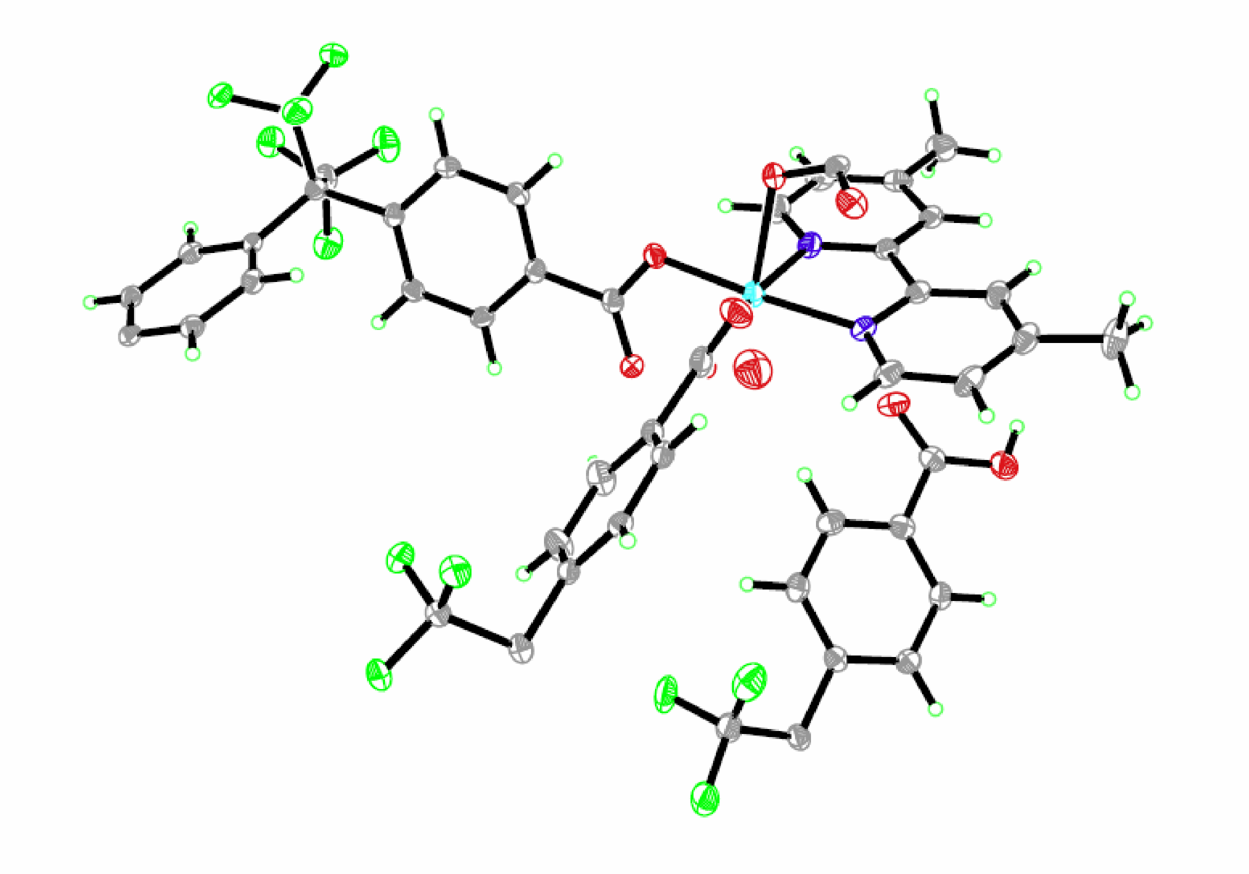


Figure S8. ORTEP drawing of *F*-MOF-3.

F-MOF-4 (Monoclinic)

Experimental and Refinement Details for *F*-MOF-4

A colorless prismatic crystal (0.18 × 0.12 × 0.10 mm^3) of *F*-MOF-2 was placed in a 0.4 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 44864 reflections were collected of which 12226 were unique and 7364 of these were greater than $2\sigma(I)$. The range of θ was from 0.88 to 26.06º. All non-hydrogen atoms were refined anisotropically. *F*-MOF-4 is composed of one 4,4′-hexafluoroisopropylidene-bis-benzoic acid and one 3-methyl-pyridine per Cu. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0557$, and $wR_2 = 0.1278$ (all data) with GOF = 0.968.

Table S4. Crystal data and structure refinement for ***F*-MOF-4**.

Empirical formula	C29.97 H27.97 F6 N2.91 O5.5 Cu
Formula weight	694.51
Temperature	100(2) K
Wavelength	0.71073
Crystal system	Monoclinic
Space group	*P*2(1)/c
Unit cell dimensions	*a* = 25.643(8)Å α = 90°
	b = 11.004(3)Å β =115.518°
	c = 24.351(7)Å γ = 90°
Volume	6201.0(3)
Z	4
Density (calculated)	1.488
Absorption coefficient	0.785
F(000)	2842
Crystal size	0.20 × 0.19 × 0.18 mm^3
Theta range for data collection	0.88- 26.06
Index ranges	-31= h <= 31,-13<= k <= 13,-29<= l <= 30
Reflections collected	44864
Independent reflections	7364 [Rint= 0.0926]
Completeness to theta = 64.75°	99.7%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7364/3/804
Goodness-of-fit on F^2	0.986
Final R indices [I>2sigma(I)]	R_1 = 0.0557, wR_2 = 0.1278
R indices (all data)	R_1 = 0.0990, wR_2 = 0.1439
Largest diff. peak and hole	0.762and -0.575eÅ^{-3}

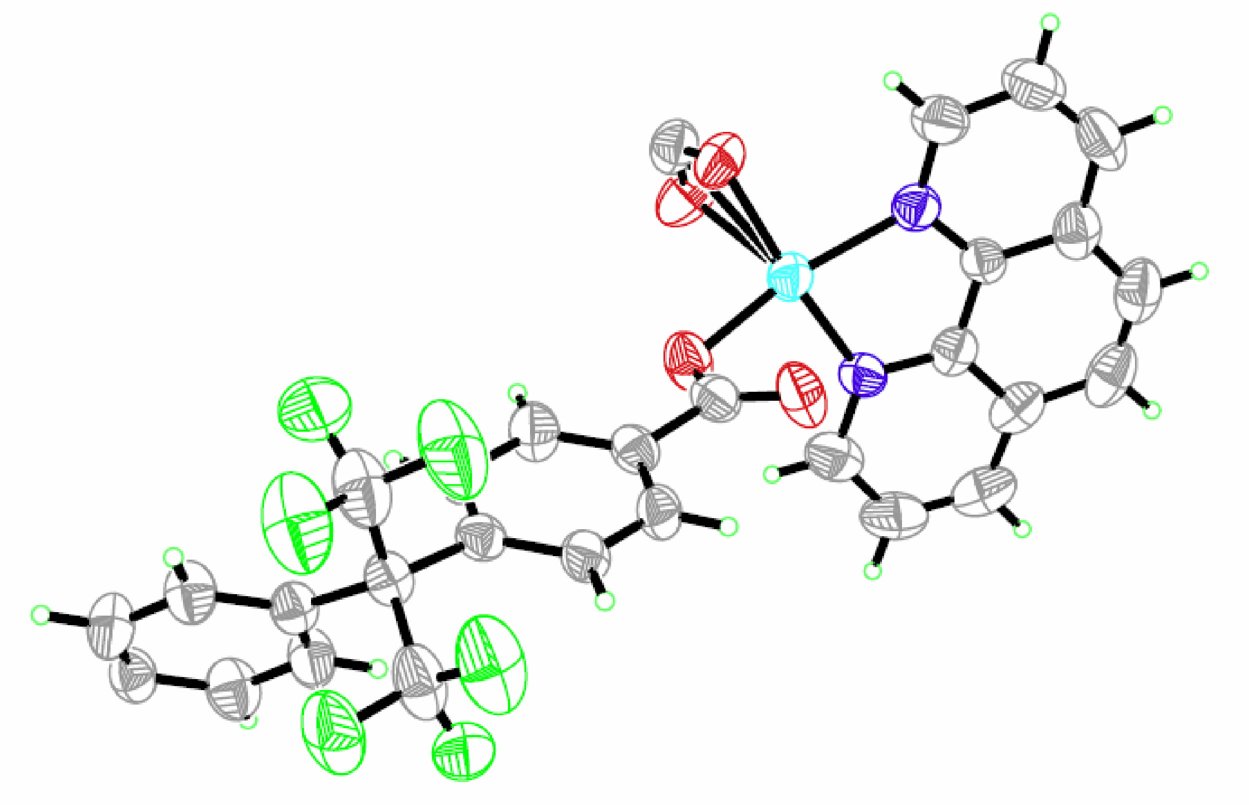


Figure S9. ORTEP drawing of *F*-MOF-4.

***F*-MOF-5 (Orthorhombic)**

Experimental and Refinement Details for *F*-MOF-5

A colorless prismatic crystal (0.18 × 0.12 × 0.10 mm^3) of *F*-MOF-5 was placed in a 0.4 mm diameter nylon CryoLoops (Hampton Research) with Paraton-N (Hampton Research). The loop was mounted on a SMART APEX three circle diffractometer. A total of 24548 reflections were collected of which 4722 were unique and 4009 of these were greater than $2\sigma(I)$. The range of θ was from 1.43 to 26.02°. All non-hydrogen atoms were refined anisotropically. *F*-MOF-5 is composed of one 4,4′-hexafluoroisopropylidene-bis-benzoic acid and one 1,10-phenanthroline per Cu. Final full matrix least-squares refinement on F^2 converged to $R_1 = 0.0562$, and $wR_2 = 0.1512$ (all data) with GOF = 0.908.

Table S5. Crystal data and structure refinement for ***F*-MOF-5**.

Empirical formula	C31 H16 F6 N2.5 O5 Cu
Formula weight	681.015
Temperature	100(2) K
Wavelength	0.71073Å
Crystal system	Orthorhombic
Space group	*P*bcn
Unit cell dimensions	*a* = 16.389(7)Å α = 90°
	b = 13.157(6)Å β = 90°
	c = 26.553(12)Å γ = 90°
Volume	5726.0(4)
Z	4
Density (calculated)	1.580
Absorption coefficient	0.848
F(000)	2740
Crystal size	0.22× 0.20× 0.18mm^3
Theta range for data collection	1.53- 27.00
Index ranges	-20 <= h <= 20, -16 <= k <= 16, -33<= l <= 33
Reflections collected	60708
Independent reflections	3032 [Rint= 0.0926]
Completeness to theta = 64.75°	100%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3032/0/393
Goodness-of-fit on F^2	0.908
Final R indices [I>2sigma(I)]	$R_1 = 0.0562$, $wR_2 = 0.1512$
R indices (all data)	$R_1 = 0.1255$, $wR_2 = 0.1862$
Largest diff. peak and hole	0.749and -0.352$eÅ^{-3}$

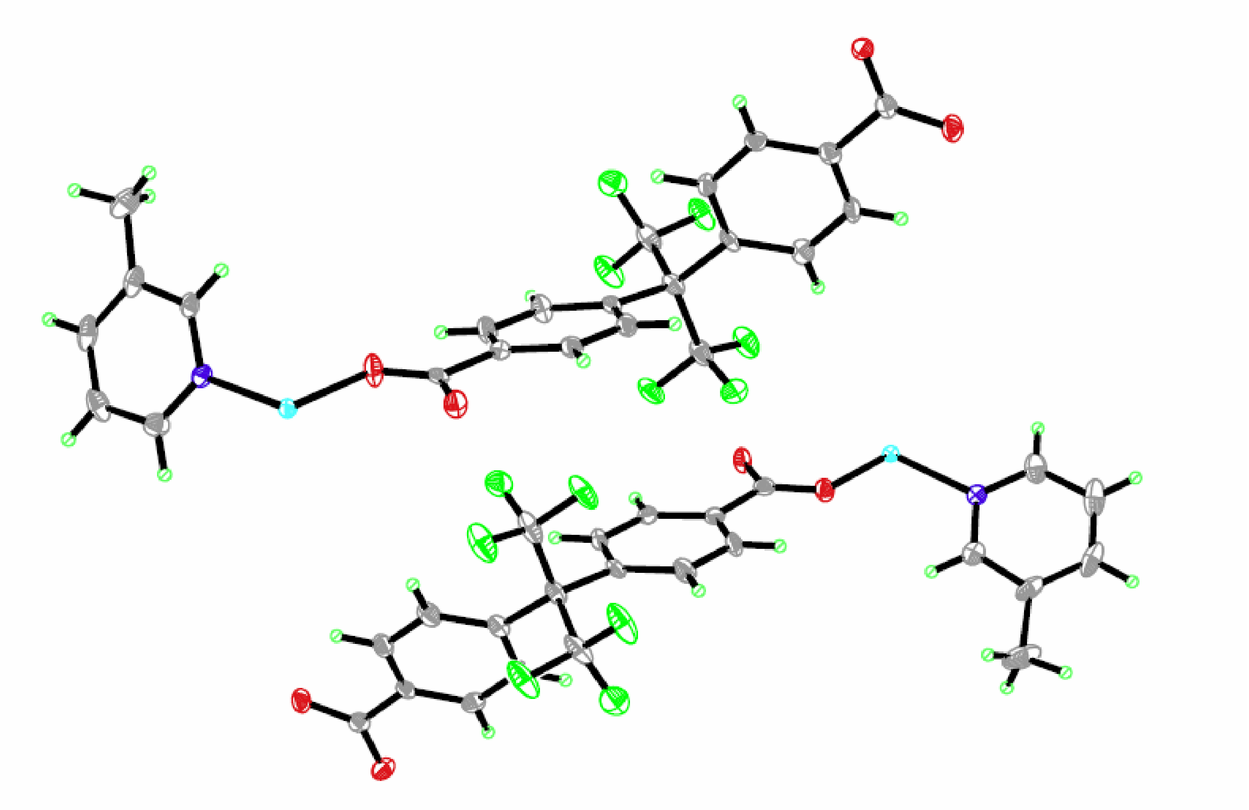
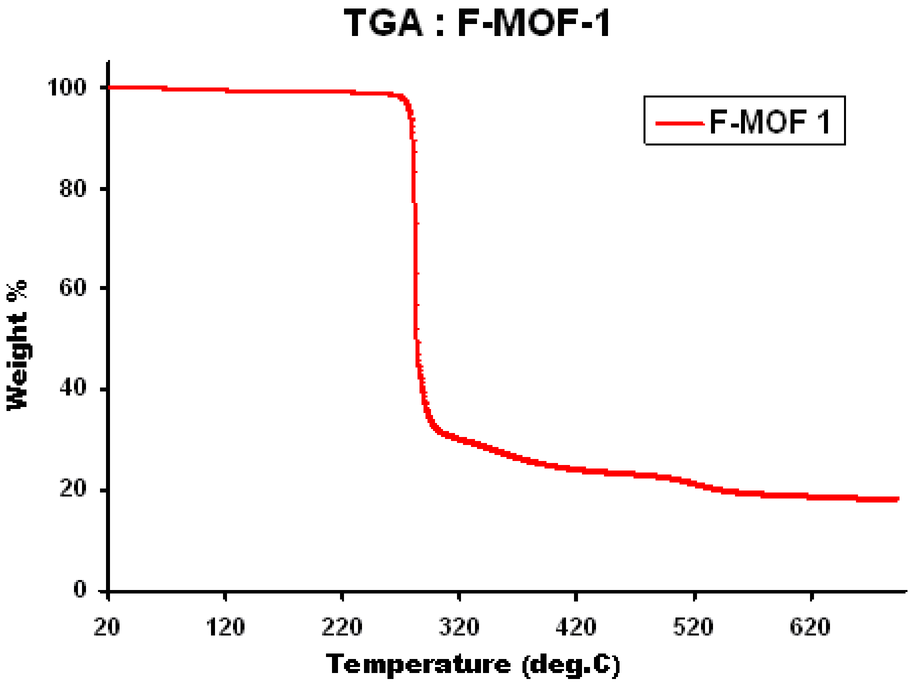
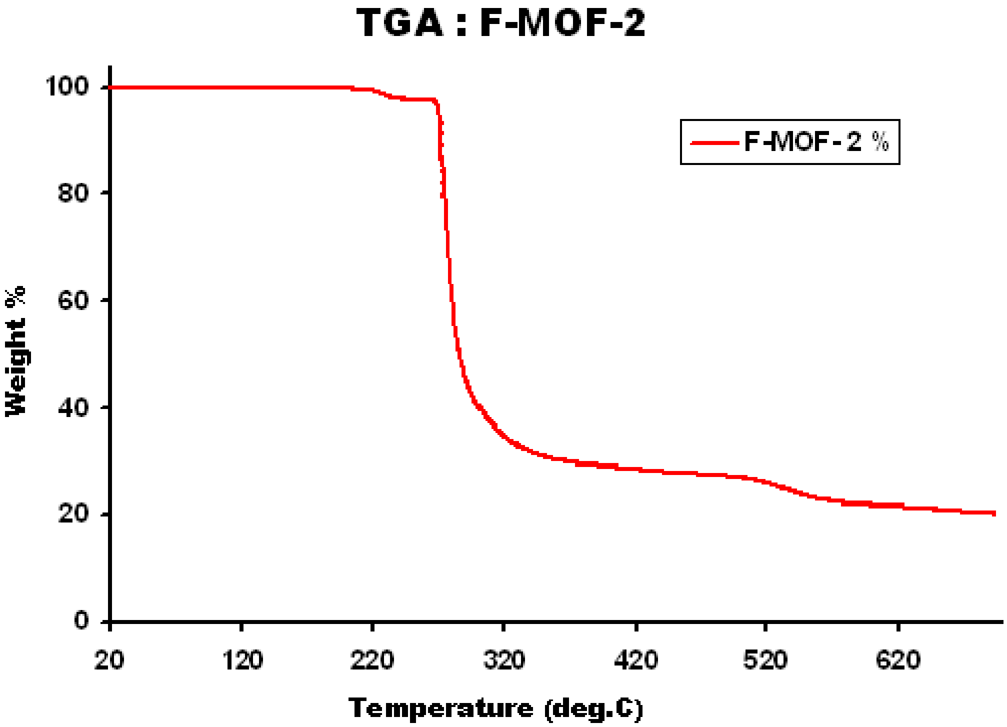
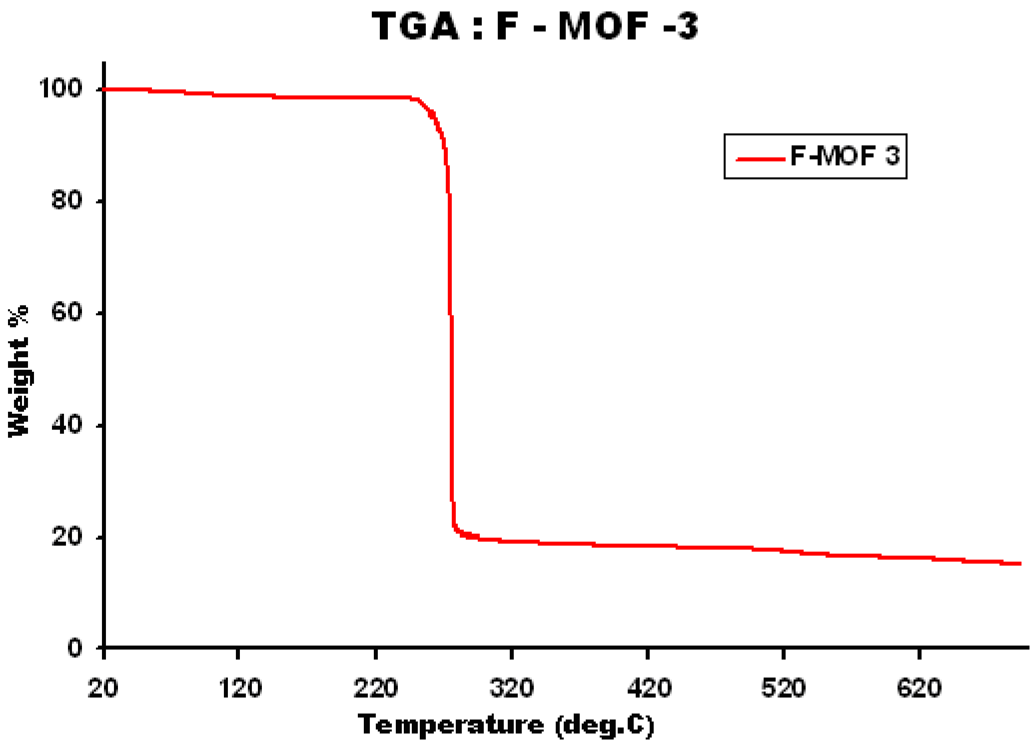


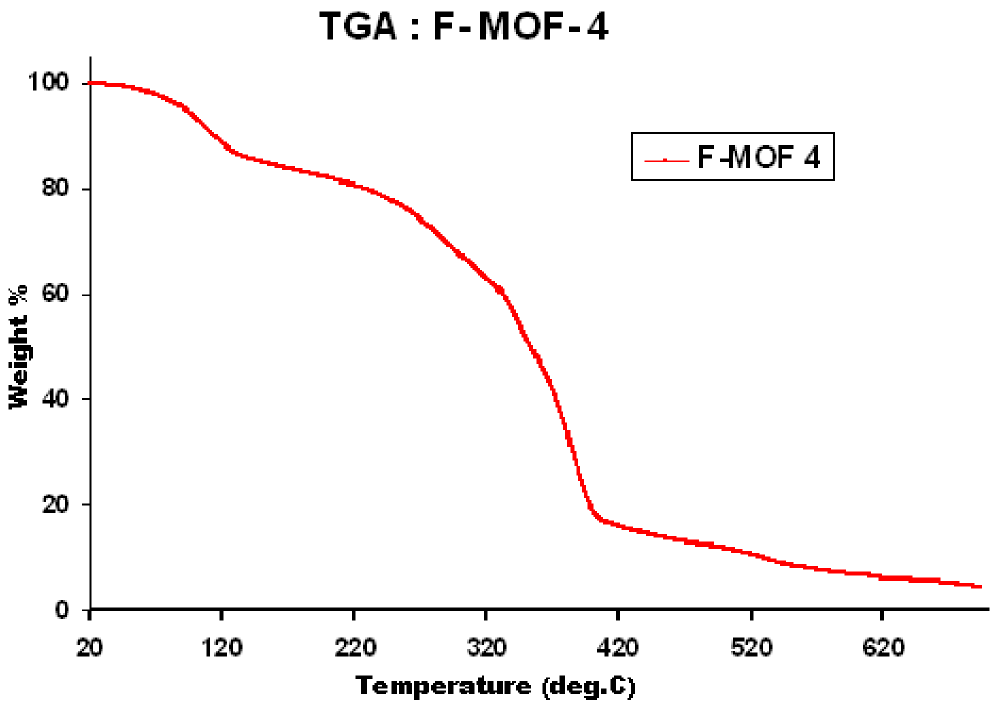
Figure S10. ORTEP drawing of *F*-MOF-5.

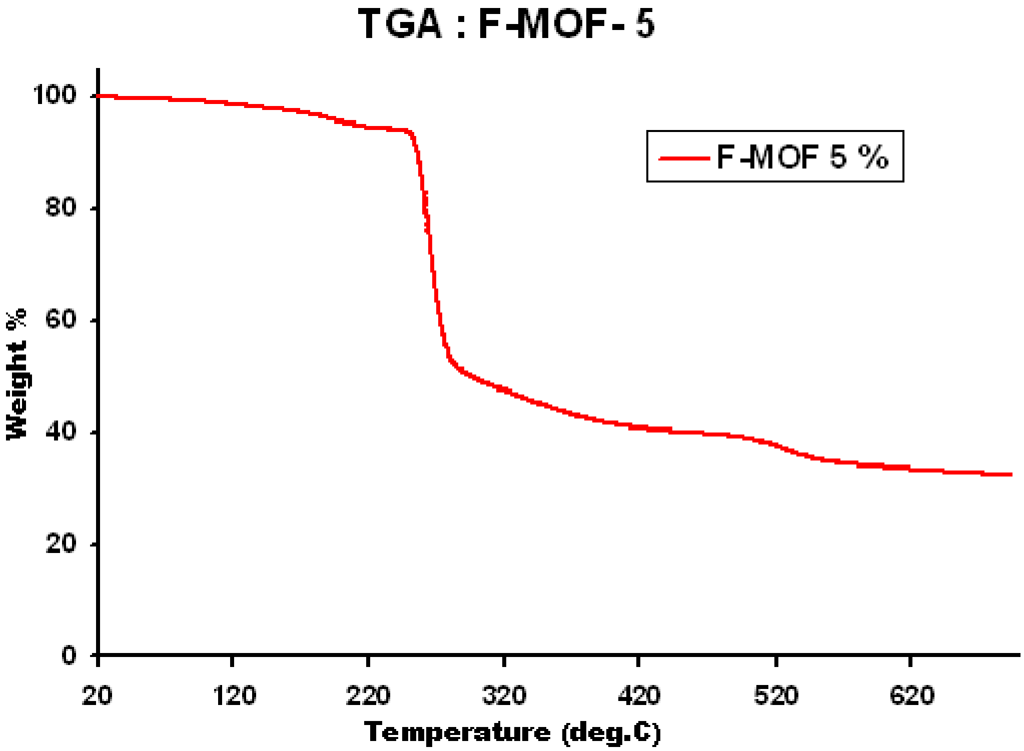
Section S3. Thermal stability of FMOFs and the thermal gravimetric analysis (TGA) data.





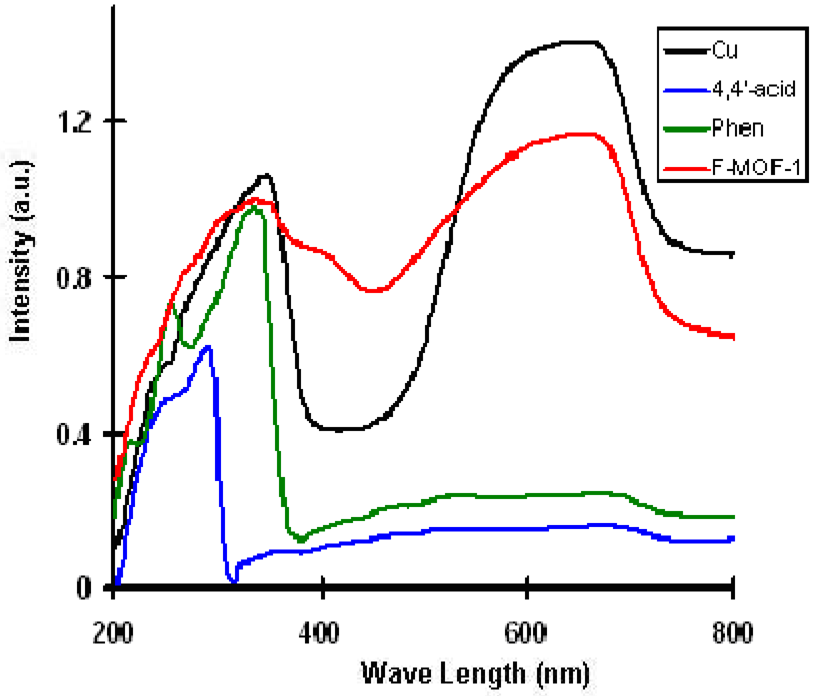

TGA : F - MOF -3
F-MOF 3
Weight %
100
80
60
40
20
0
20
120
220
320
420
520
620
Temperature (deg.C)


TGA : F-MOF-4
F-MOF 4
Weight %
100
80
60
40
20
0
20
120
220
320
420
520
620
Temperature (deg.C)

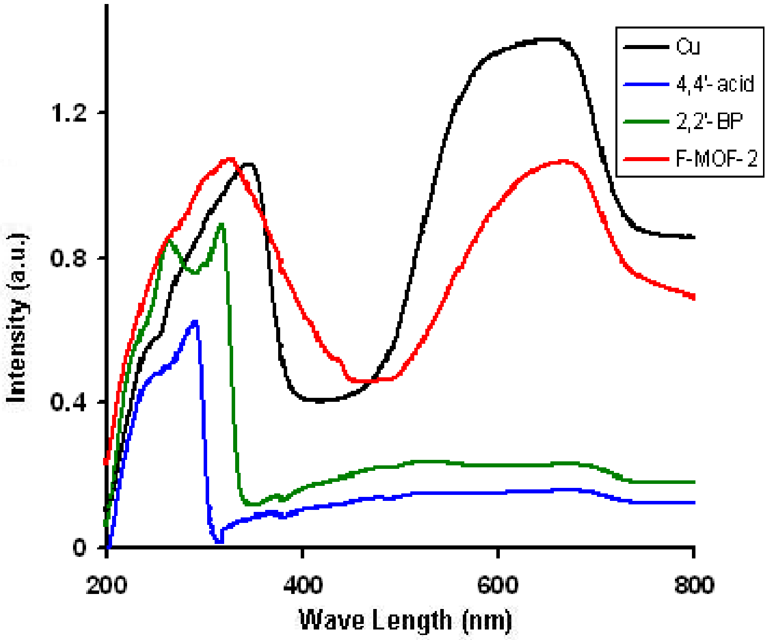

TGA : F-MOF- 5
F-MOF 5 %
Weight %
100
80
60
40
20
0
20
120
220
320
420
520
620
Temperature (deg.C)

Section S4. UV Data.

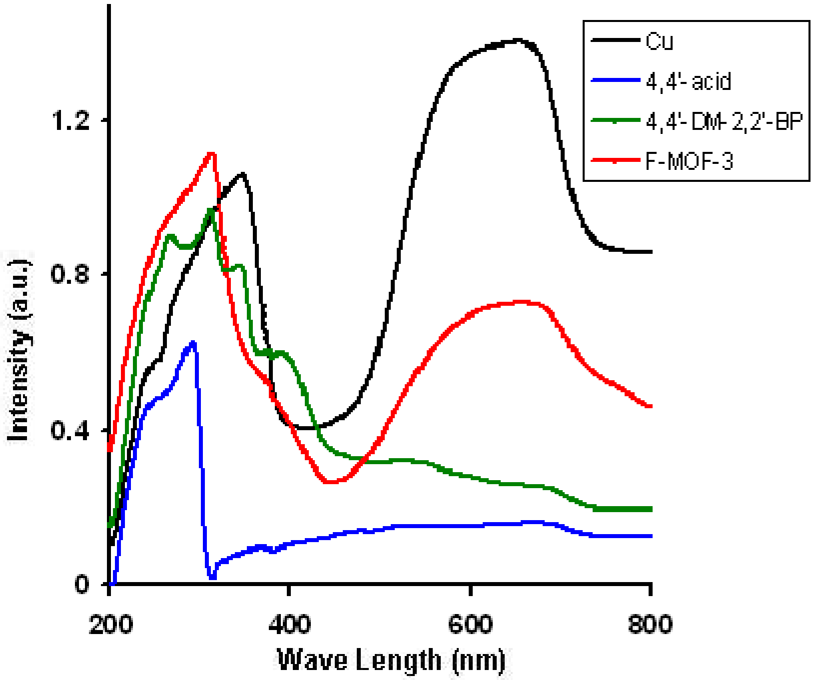
F-MOF-1 : UV-VIS SPECTRUM



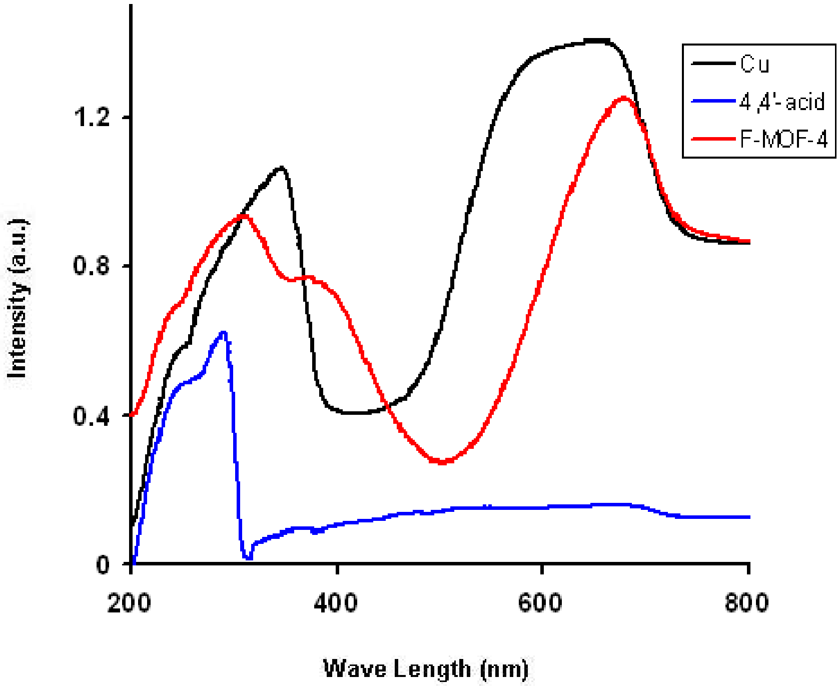
F-MOF-2 : UV-VIS SPECTRUM



F-MOF-3 : UV-VIS SPECTRUM



F-MOF-4 : UV-VIS SPECTRUM



F-MOF-5 : UV-VIS SPECTRUM.