Supporting Information

Charged Functional Group Effects on Metal-Organic Framework for Selective Organic Dye Adsorptions

Hyungwoo Hahm,[a,b,‡] Sungjune Kim,[c,‡] Hyeonbin Ha,[a,b] Suyeon Jung,[a] Youngjo Kim,[a,b] Minyoung Yoon,[c,*] Min Kim[a.b,*]

[a] Department of Chemistry, Chungbuk National University, Cheongju, Chungbuk 362-763, Republic of Korea
[b] Research Team for Syntheses and Physical Properties of Various Molecules (BK21Plus), Chungbuk National University
[c] Department of Nanochemistry, College of Bionano, Gachon University, Sungnam, 461-701, Republic of Korea

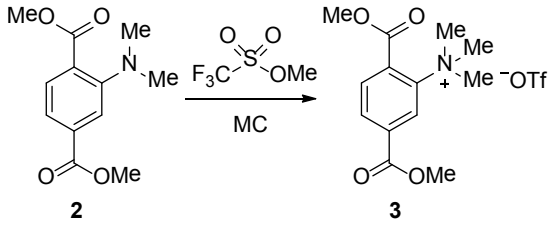
E-mail: myyoon@gachon.ac.kr & minkim@chungbuk.ac.kr; phone: +82-43-261-2283; fax: +82-43-267-2279

I. General Methods for Experiments.

Concentration of solution was carried out by using a rotary evaporator with a water aspirator, and generally followed by removal of residual solvents on a vacuum line held at 0.1–1 torr. Unless otherwise stated, all commercial reagents and solvents were used without additional purification. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F_{254} plates. Visualization on TLC was achieved by the use of UV light (254 nm). Flash column chromatography was undertaken on silica gel (400-630 mesh). Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on FT AM 400 (400 MHz). 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). Carbon 13 nuclear magnetic resonance spectroscopy (^{13}C NMR) was recorded on FT AM 400 (100 MHz) and was fully decoupled by broad band decoupling. Chemical shifts were reported in ppm referenced to the center line of a septet at 39.52 ppm of DMSO-d_6. High resolution mass spectra (HR-MS) were obtained from the Korea Basic Science Institute (Daegu) by using FAB method and from the Chungbuk National University Center for Research Facilities using ESI method.

II. Ligand Synthesis

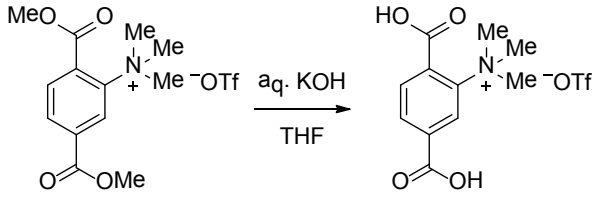
*2-(Dimethylamino)terephthalic acid (**1**)* and *Dimethyl-2-(dimethylamino)terephthalate (**2**)* prepared as previously described.[S1]



2 **3**

*2,5-bis(methoxycarbonyl)-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**3**)* [S2]

2 (390 mg, 1.64 mmol) was dissolved in CH_2Cl_2 (10 mL). Methyl trifluoromethanesulfonate (350 μL, 3.28 mmol) was added by dropwise to the mixture at room temperature. The solution was stirred at room temperature for overnight. Once conversion was complete (monitored by TLC), the solvent was evaporated. The solid mixture was separated by silica gel column chromatography (10% MeOH/CH_2Cl_2) and the desired compound, 2,5-bis(methoxycarbonyl)-*N*,*N*,*N*-trimethyl benzenaminium trifluoromethanesulfonate (**3**, 496 mg, 75%) were obtained as a colorless solid.
^{1}H NMR (DMSO, 400 MHz, ppm.): δ 8.45 (1H, d, *J* = 1.2 Hz), 8.25 (1H, dd, *J* = 8, 1.3 Hz), 7.98 (1H, d, *J* = 8.0 Hz), 3.80 (s, 9H); ^{13}C NMR (DMSO, 100 MHz, ppm): δ 167.7, 164.3, 143.2, 133.0, 132.5, 130.9, 130.7, 123.0, 57.2, 54.6, 53.1. ESI-HR-MS(+) *m/z* calcd. For $C_{13}H_{18}NO_4^+$ $[M]^+$: 252.1230, found $[M]^+$: 252.1230.



3 **4**

*2,5-dicarboxy-N,N,N-trimethylbenzenaminium trifluoromethanesulfonate (**4**)*

3 (200 mg, 0.5 mmol) was dissolved in 2.5 mL of 4% aqueous KOH solution. The mixture was stirred at 70 ^{o}C for overnight. Once conversion was complete (monitored by TLC), water was removed by evaporation and the mixture was acidified with a 1.0 M HCl aqueous solution. Then methanol was added to dissolve desired compound. The solution was filtered, and evaporated of methanol. The desired compound, 2,5-dicarboxy-*N*,*N*,*N*-trimethyl benzenaminium trifluoromethanesulfonate (**4**, 140 mg, 74%) was obtained as a colorless solid.
^{1}H NMR (DMSO-d_6, 400MHz, ppm.): δ 8.42 (1H, d, J = 1.0 Hz), 8.18 (1H, dd, J = 7.9, 1.1 Hz), 7.88 (1H, d, J = 7.9 Hz), 2.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 169.5, 165.4, 142.6, 133.7, 132.6, 131.9, 131.0, 122.8, 56.9. ESI-HR-MS(+) *m/z* calcd. For $C_{11}H_{14}NO_4^+$ $[M]^+$: 224.0917, found $[M]^+$: 224.0917.

III. MOF Synthesis

UiO-66 Synthesis

The UiO-66 series were prepared and activated using a modified method from what has been previously described.[S3]

UiO-66-NH_2: 2-aminoterephthalic acid (63.4 mg, 0.35 mmol) and $ZrCl_4$ (82 mg, 0.35 mmol) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 120 ^{o}C for 24 h. The microcrystalline powders were then isolated by centrifugation and residual DMF and ligand precursors were removed from the material by washing with 10 mL DMF three times. Then the solid was soaked with fresh 10 mL methanol. This process was repeated for three days.

UiO-66-$NMe_3^+OTf^-$: **4** (131 mg, 0.35 mmol) and $ZrCl_4$ (82 mg, 0.35 mmol), acetic acid (600 μL) and DMF (4 mL) were placed in a Teflon lined autoclave and heated at 150 ^{o}C for 24 h. The microcrystalline powders were then isolated by centrifugation and residual DMF and ligand precursors were removed from the material by washing with 10 mL DMF three times. Then the solid was soaked with fresh 10 mL methanol. This process was repeated for three days.

DMOF Synthesis

The DMOF-1 series was prepared and activated using a modified method from what has been previously described.[S4]

DMOF-1-NMe_2: **1** (105 mg, 0.5 mmol) and $Zn(NO_3)_2{\cdot}6H_2O$ (149 mg, 0.5 mmol) were dissolved in 12.5 mL of DMF. To this mixture, dabco (90 mg, 0.8 mmol) was added. Upon adding, a white

precipitate formed. This precipitate was filtered using a filter with a fritted disc of fine porosity. The solution was then transferred to a scintillation vial and heated at a rate of 2.5 ^{o}C/min from room temperature to 100 ^{o}C. The temperature was then held for 12 h and then cooled to temperature at a rate of 2.5 ^{o}C/min. The resulting crystals were then washed three times with 5 mL of DMF. The solvent was then exchanged with chloroform (5 mL) over three days, replacing the old chloroform with fresh chloroform every 24 h.

DMOF-1-$NMe_3^+OTf^-$: approximately 50 mg of DMOF-1-NMe_2 (0.15 mmol, equiv of –NMe_2) was placed in a vial with 3 equiv. (0.45 mmol) of methyl trifluoromethanesulfonate dissolved in 4.5 mL of $CHCl_3$. The sample was heated at 40 ^{o}C for 24 h, after which the solution was decanted and the crystals were washed with 2 × 5 mL of $CHCl_3$. A fresh solution of the methyl trifluoromethanesulfonate was added to the vial, and the mixture was heated for an additional 24 h. The aforementioned procedure was repeated three more times, giving a total reaction time of 5 days. After the reaction was complete, the $CHCl_3$ solution was decanted, and the crystals were washed with 3 × 5 mL of $CHCl_3$ before soaking in 5 mL of pure $CHCl_3$ for 3 days of soaking the crystals were stored in the last $CHCl_3$ solution until analyzed. After acid digestion of MOF, the material was analyzed by ^{1}H NMR, IR and HR-MS. FAB-HR-MS(+) *m/z* calcd. For $C_{11}H_{14}NO_4$ $[M]^+$: 224.0923, found $[M]^+$: 224.0924.

IV. MOF Characterization

Digestion and Analysis by ^{1}H NMR of UiO-66-NHMe and -$NMe_3^+OTf^-$: approximately 10 mg of UiO-66 material was dried under vacuum and digested with sonication in 580 μL of DMSO-d_6 and 20 μL of HF (48% aqueous solution).

Digestion and Analysis by ^{1}H NMR of DMOF-1-NH_2, -NMe_2 and -$NMe_3^+OTf^-$: approximately 10 mg of DMOF-1 material was dried under vacuum and digested with sonication in 590 μL of DMSO-d_6 and 10 μL of DCl.

Thermal Analysis: Approximately 10 mg of DMOF was used for TGA measurements, after BET analysis (activated). Sample was analyzed under a stream of N_2 using a TGA/DSC 1 running from room temperature to 1000 ^{o}C with a scan rate of 10 ^{o}C/min.

Powder X-ray Diffraction: approximately 10 mg of DMOF-1 was air-dried for 1 min prior to PXRD analysis. PXRD data was collected at ambient temperature on a Bruker D8 Discover at 40 kV, 40 mA for CuKa (l = 1.5406 Å), with a scan speed of 1 sec/step, a step size of 0.02^{o} in 2θ, and a 2θ range of 5-55^{o}.

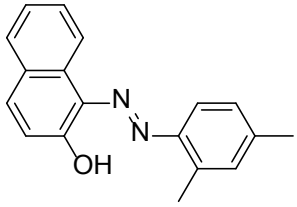
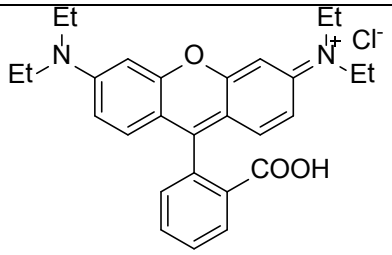
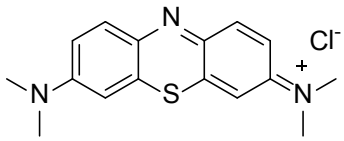
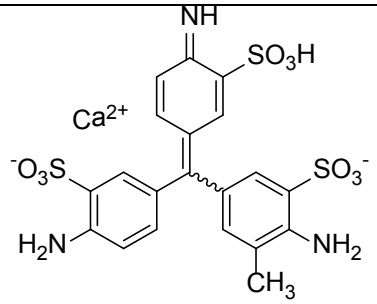
BET Surface Area Analysis: approximately 30-50 mg of DMOF-1 sample was evacuated under vacuum for a moment at room temperature. Samples were then transferred to a pre-weighed sample tube and degassed at 100 ^{o}C on a Micromeritics ASAP 2020 Adsorption Analyzer for a minimum of 12 h or until the outgas rate was <5 μmHg/min. The sample tube was re-weighted to obtain a consistent mass for the degassed MOF materials. High purity gases (N_2 and Ar: 99.999%) were used for the measurements. The linearized BET model was fit to the N_2 77 K adsorption data of MOFs within the relative pressure range $0.005 < P/P_0 < 0.1$, for calculation of surface area. Pore size

distribution was calculated using NLDFT model available from ASAP-2020 program package fitted to Ar 87 K adsorption data.[S5, S6]

V. Organic Dye Adsorption Experiment

Dye stock solution was prepared by dissolving a dye (Sudan II, Rhodamine B, Methylene Blue, or Acid Fuchsin calcium salt) in acetonitrile solvent with concentration of 20 ppm for Sudan II, Rhodamine B, Methylene Blue and 24 ppm for Acid Fuchsin calcium salt. The concentration of dye solution was determined by absorbance of the solution (Shimazu UV-Vis spectrometer, UV-2550). The calibration curve was drawn in a range of 1.25 – 20 ppm for Sudan II, Rhodamine B, Methylene Blue, and 2.5 – 40 ppm for Acid Fuchsin calcium salt. Adsorbent MOFs were dried overnight under dynamic vacuum at 100 °C to removal of residual solvent before dye adsorption experiments. The adsorbent (~2 mg) was soaked in the dye stock solutions (5 mL) followed by rigorous stirring with a magnetic bar during designated time (1 – 600 min) at room temperature. After adsorption for the designated time, the dye solution was separated from the adsorbents using a syringe filter (PTFE, 0.45 mm) and the dye concentration was determined by UV-Vis spectra.

Table S1 List and structural information of organic dye molecules.

Organic Dye Molecule	Structure	Molecular Formula
Sudan II (SII)		$C_{18}H_{16}N_2O$ Molecular Weight: 276.33
Rhodamine B (RB)		$C_{28}H_{31}ClN_2O_3$ Molecular Weight: 479.01
Methylene Blue (MB)		$C_{16}H_{18}ClN_3S$ Molecular Weight: 319.85
Acid Fuchsin calcium salt (AF)		$C_{20}H_{17}CaN_3O_9S_3$ Molecular Weight: 479.01

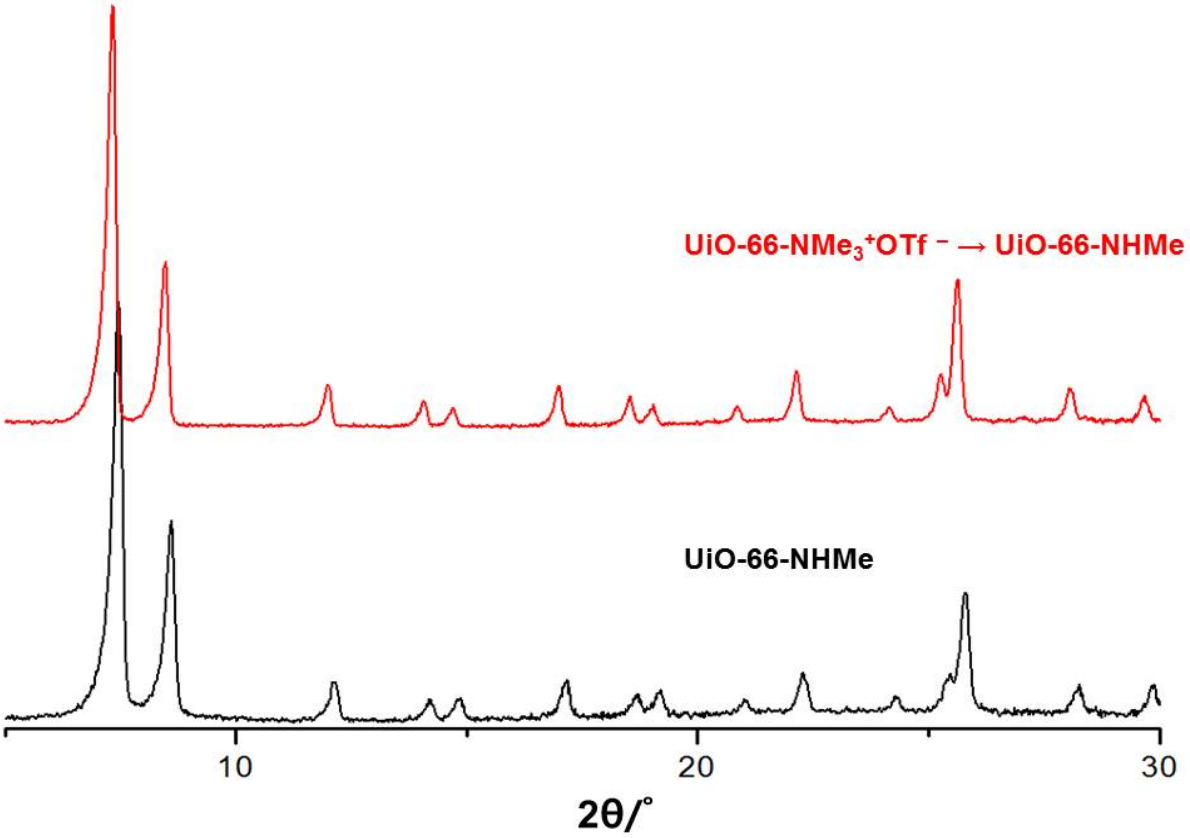


Fig. S1 PXRD patterns of UiO-66-NHMe and -$NMe_3^+OTf^-$.

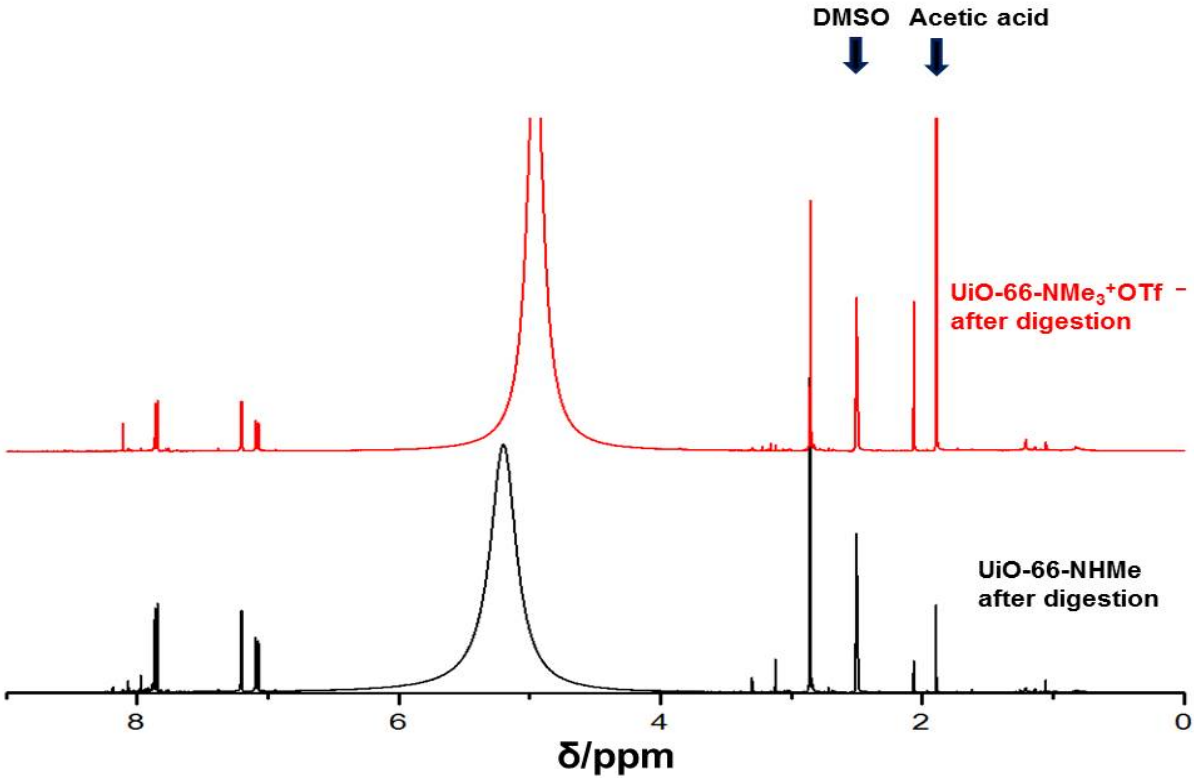
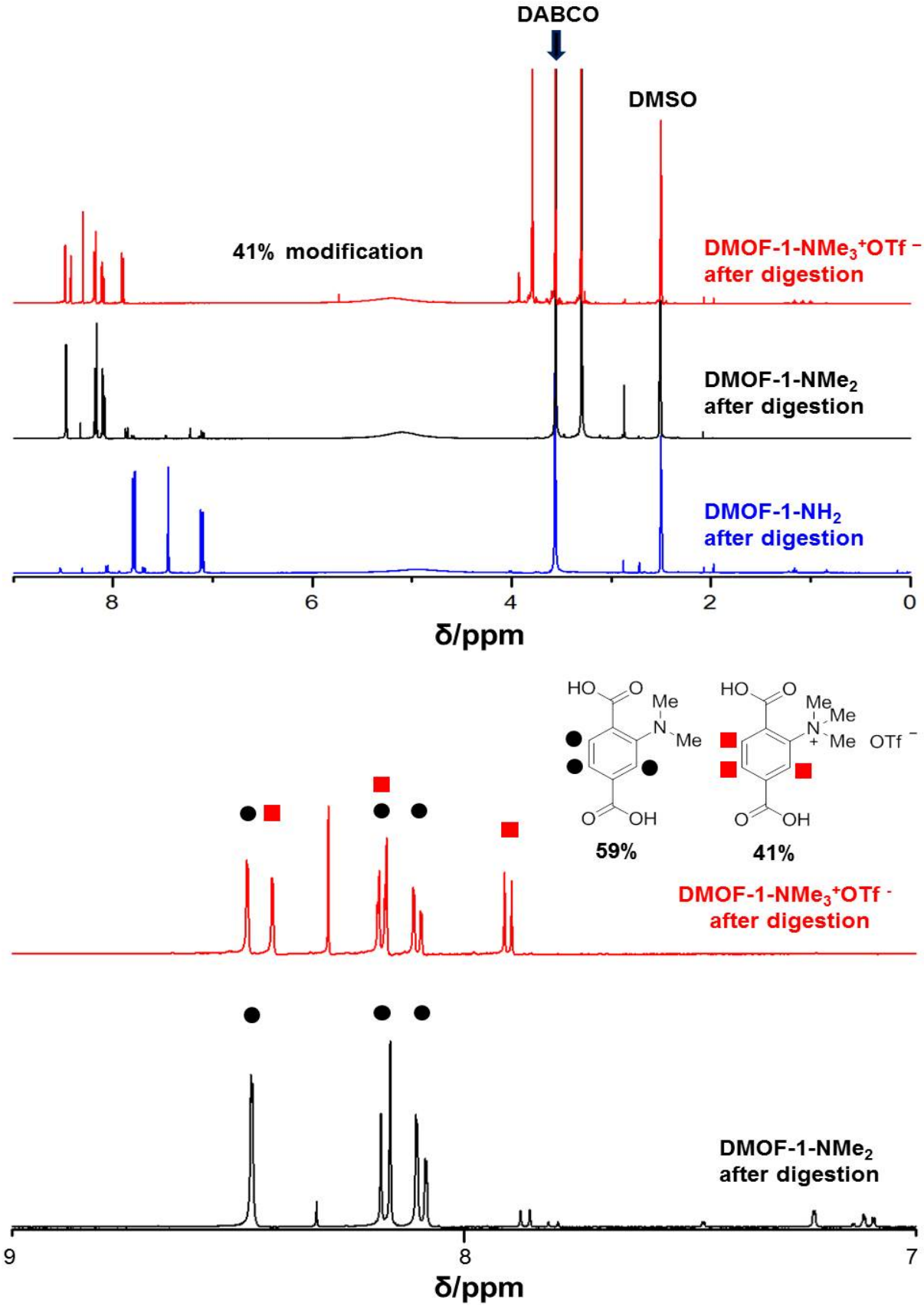


Fig. S2 ^{1}H NMR of UiO-66-NHMe and -$NMe_3^+OTf^-$ after acid digestion.


DABCO
DMSO
41% modification
DMOF-1-NMe3+OTf −
after digestion
DMOF-1-NMe2
after digestion
DMOF-1-NH2
after digestion
8
6
4
2
0
δ/ppm
HO
O
Me
N
Me
O
OH
59%
HO
O
Me
N+
Me
Me
OTf −
O
OH
41%
DMOF-1-NMe3+OTf -
after digestion
DMOF-1-NMe2
after digestion
9
8
7
δ/ppm

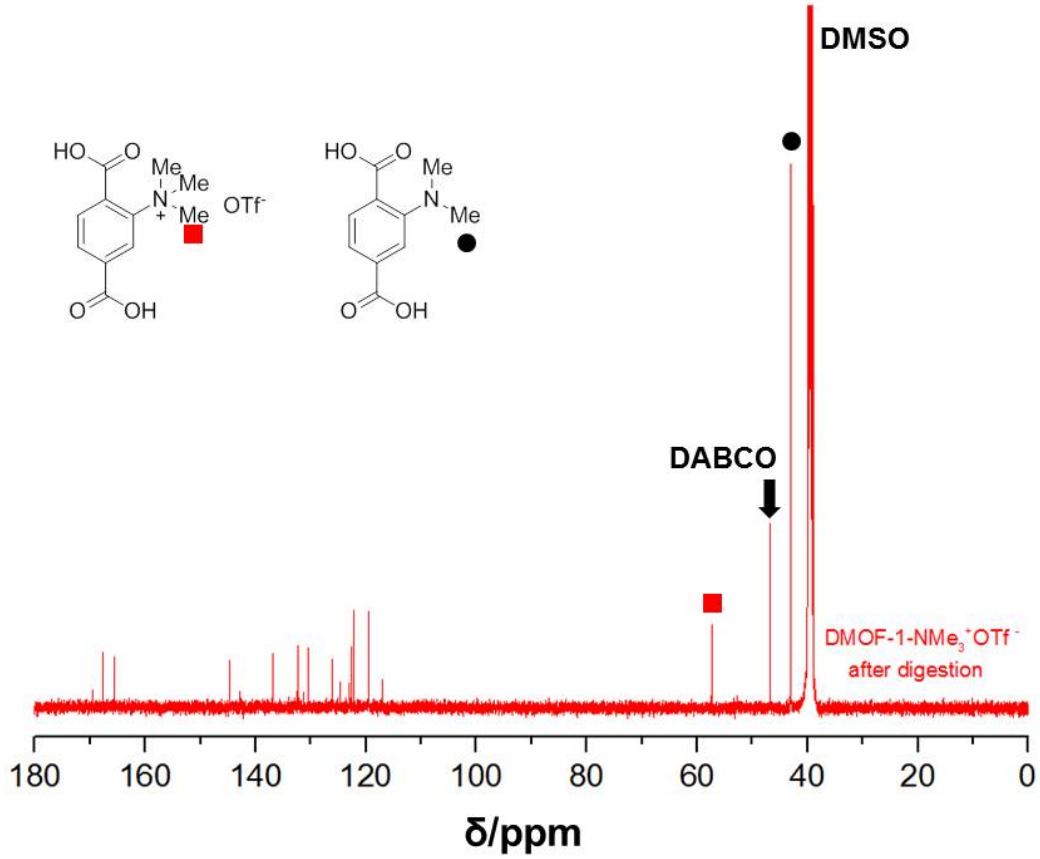


Fig. S3 ^{1}H NMR and ^{13}C NMR of DMOF-1-NH_2, -NMe_2 and -$NMe_3^+OTf^-$ after digestion (top: full-range, bottom: aromatic region).

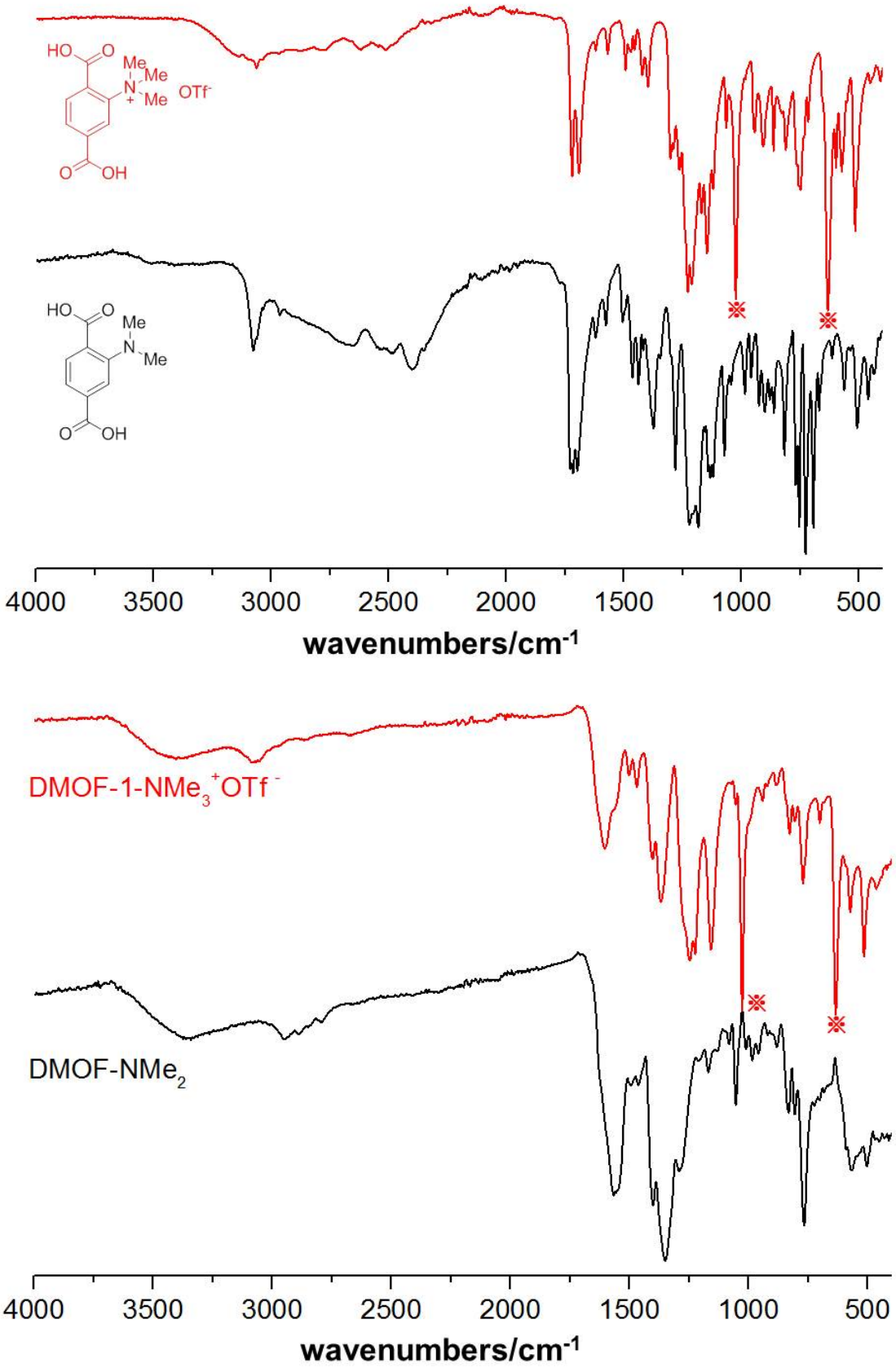


Fig. S4 IR spectrum changes of BDC ligands (top) and MOFs (bottom) after ammonium formations.

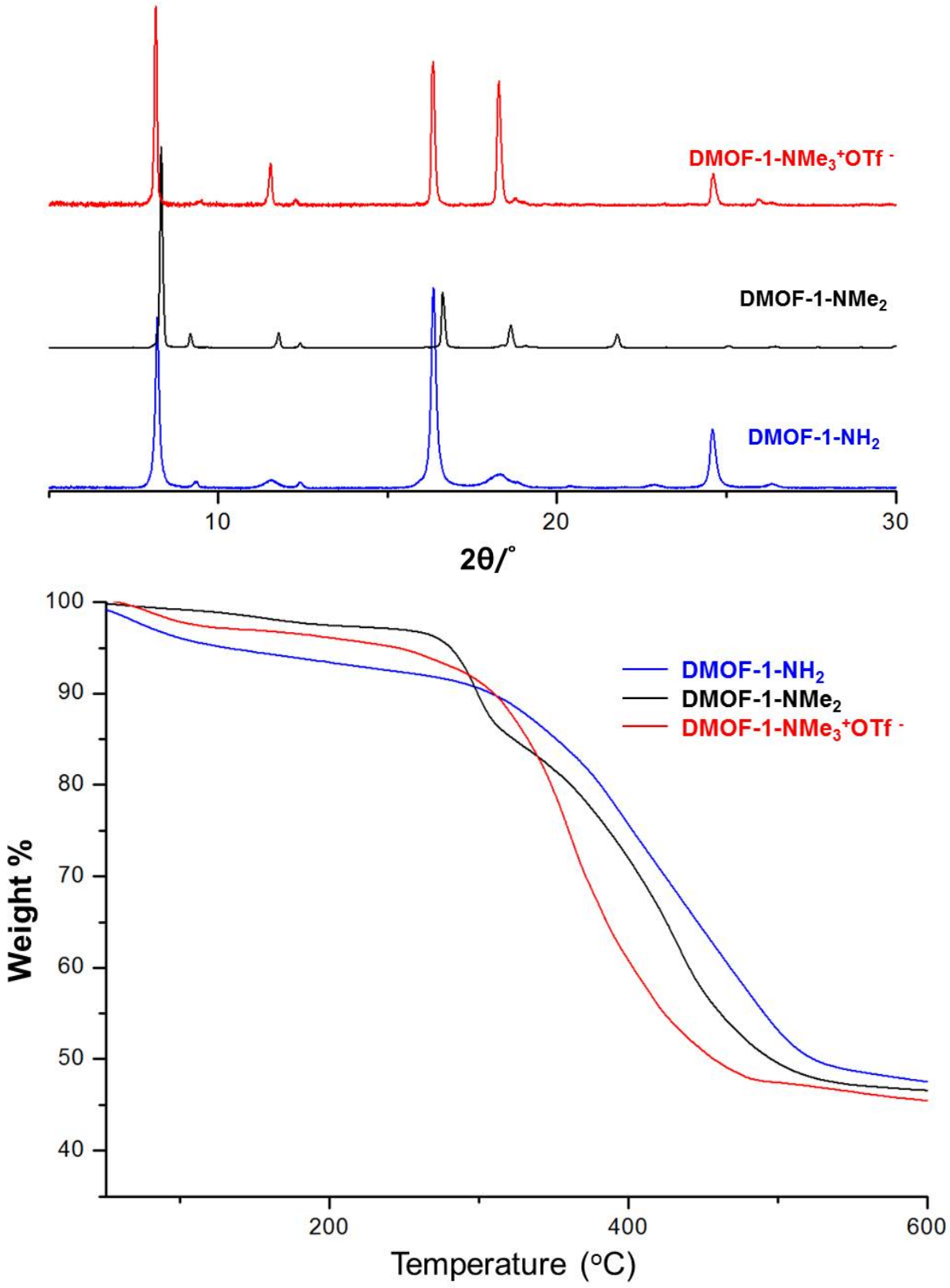


Fig. S5 PXRD (top) and TGA (bottome) of DMOF-NH_2, -NMe_2 and –$NMe_3^+OTf^-$.

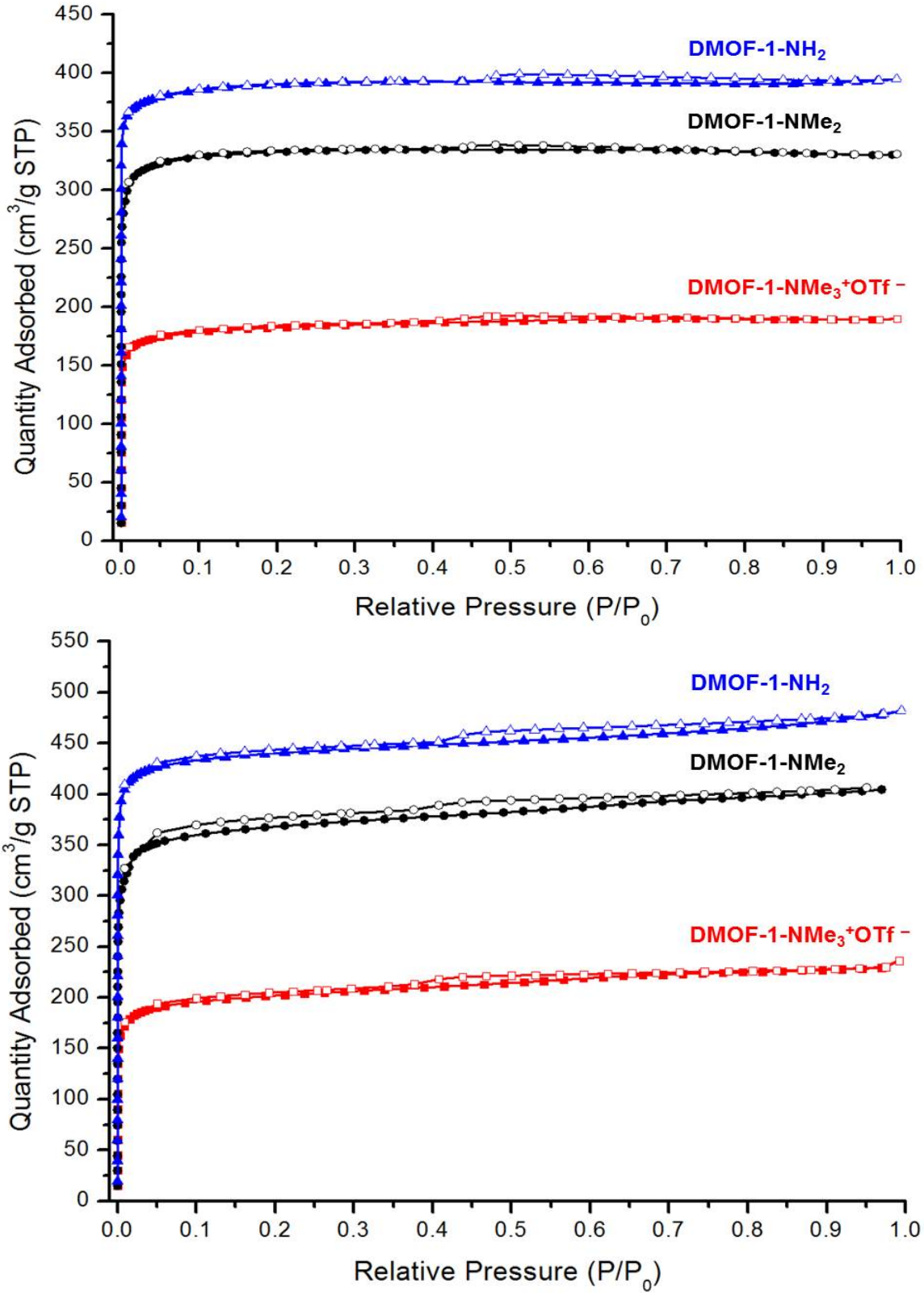


Fig. S6 N_2 (77K, top) and Ar (87 K, bottom) isotherms of DMOF-1-NH_2 (triangle, blue), -NMe_2 (circle, black) and -$NMe_3^+OTf^-$ (square, red). Adsorption and desorption traces are indicated by filled and open symbols, respectively.

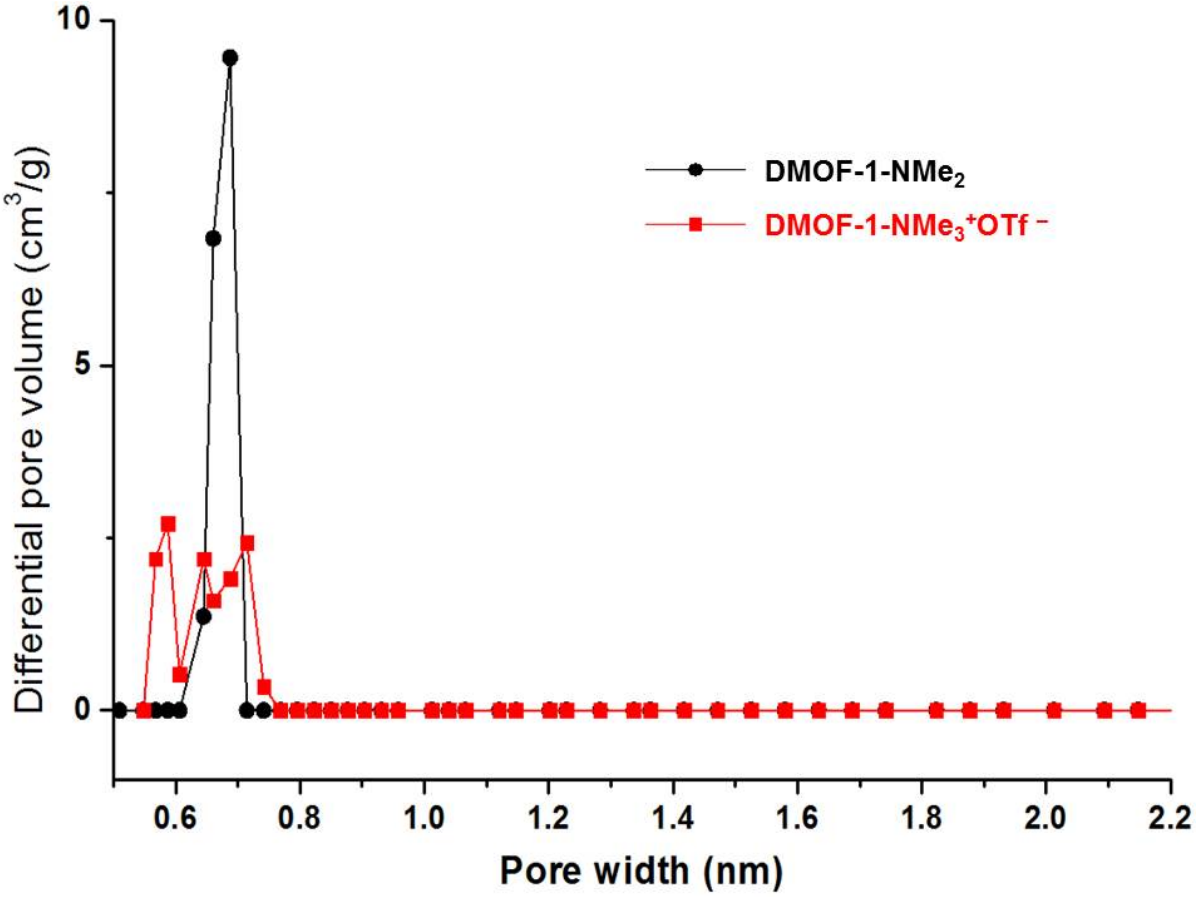
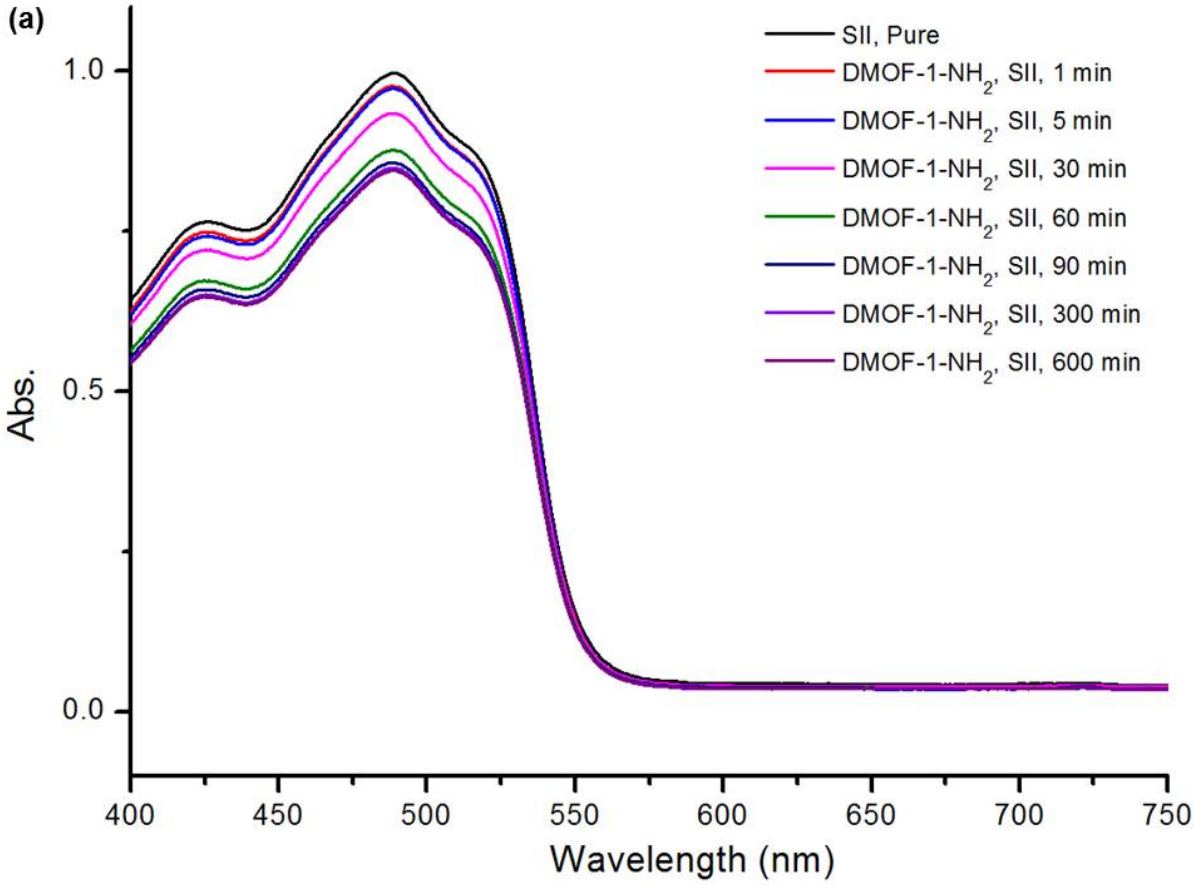
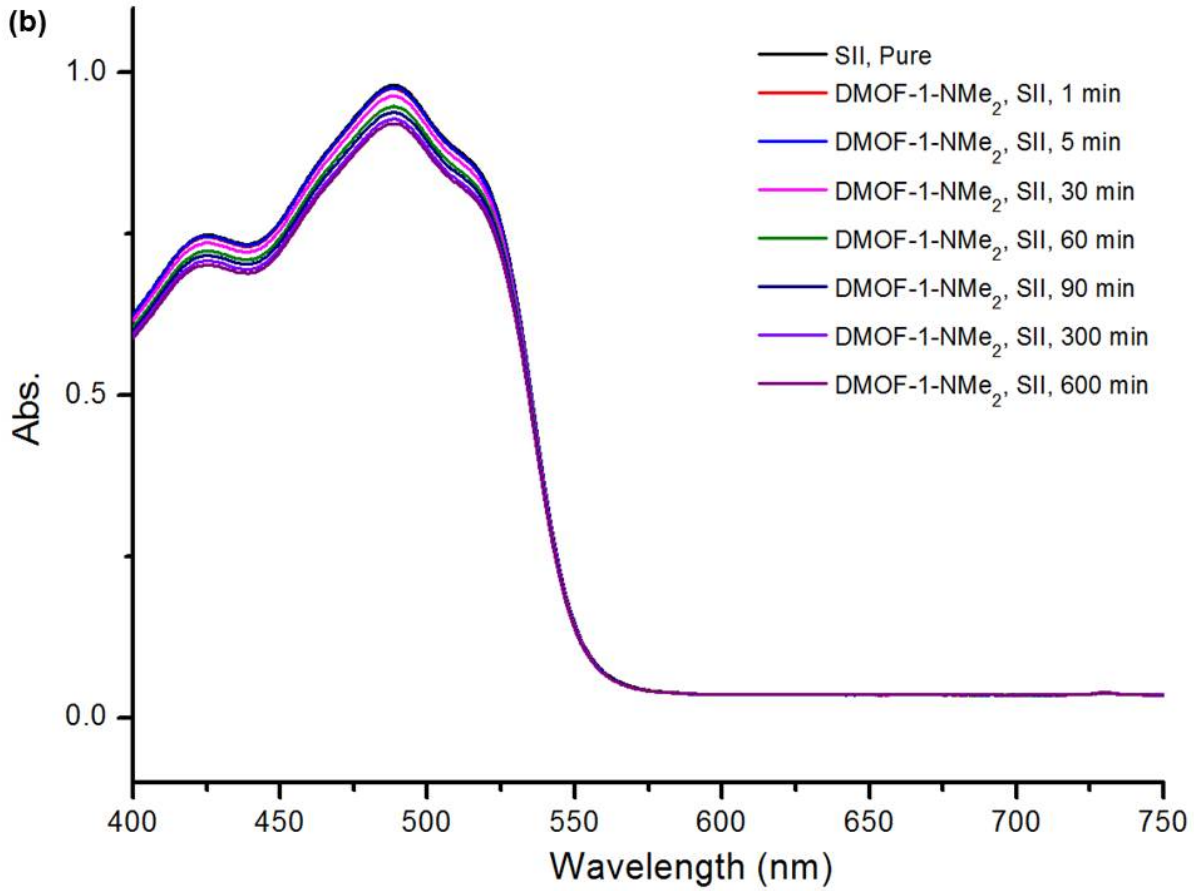


Fig. S7 Porosity distribution by NLDFT method analysis for DMOF-1-NMe_2 and DMOF-1-$NMe_3^+OTf^-$.


(a)
1.0
0.5
0.0
Abs.
400
450
500
550
600
650
700
750
Wavelength (nm)
SII, Pure
DMOF-1-NH2, SII, 1 min
DMOF-1-NH2, SII, 5 min
DMOF-1-NH2, SII, 30 min
DMOF-1-NH2, SII, 60 min
DMOF-1-NH2, SII, 90 min
DMOF-1-NH2, SII, 300 min
DMOF-1-NH2, SII, 600 min


(b)
1.0
0.5
0.0
Abs.
400
450
500
550
600
650
700
750
Wavelength (nm)
SII, Pure
DMOF-1-NMe2, SII, 1 min
DMOF-1-NMe2, SII, 5 min
DMOF-1-NMe2, SII, 30 min
DMOF-1-NMe2, SII, 60 min
DMOF-1-NMe2, SII, 90 min
DMOF-1-NMe2, SII, 300 min
DMOF-1-NMe2, SII, 600 min

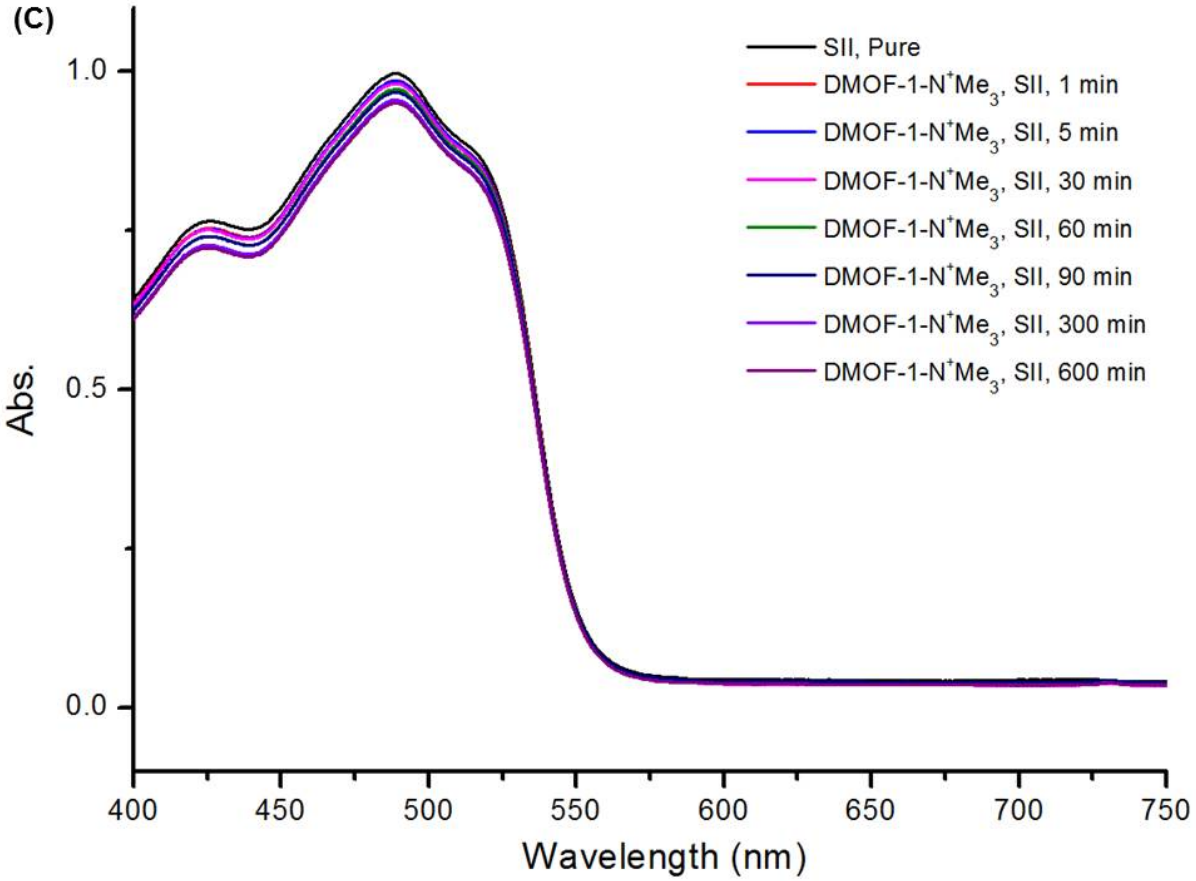


Fig. S8 UV-Vis spectra changes of 'Sudan II' in the presence of (a) DMOF-1-NH_2, (b) DMOF-1-NMe_2, and (c) DMOF-1-$NMe_3^+OTf^-$.

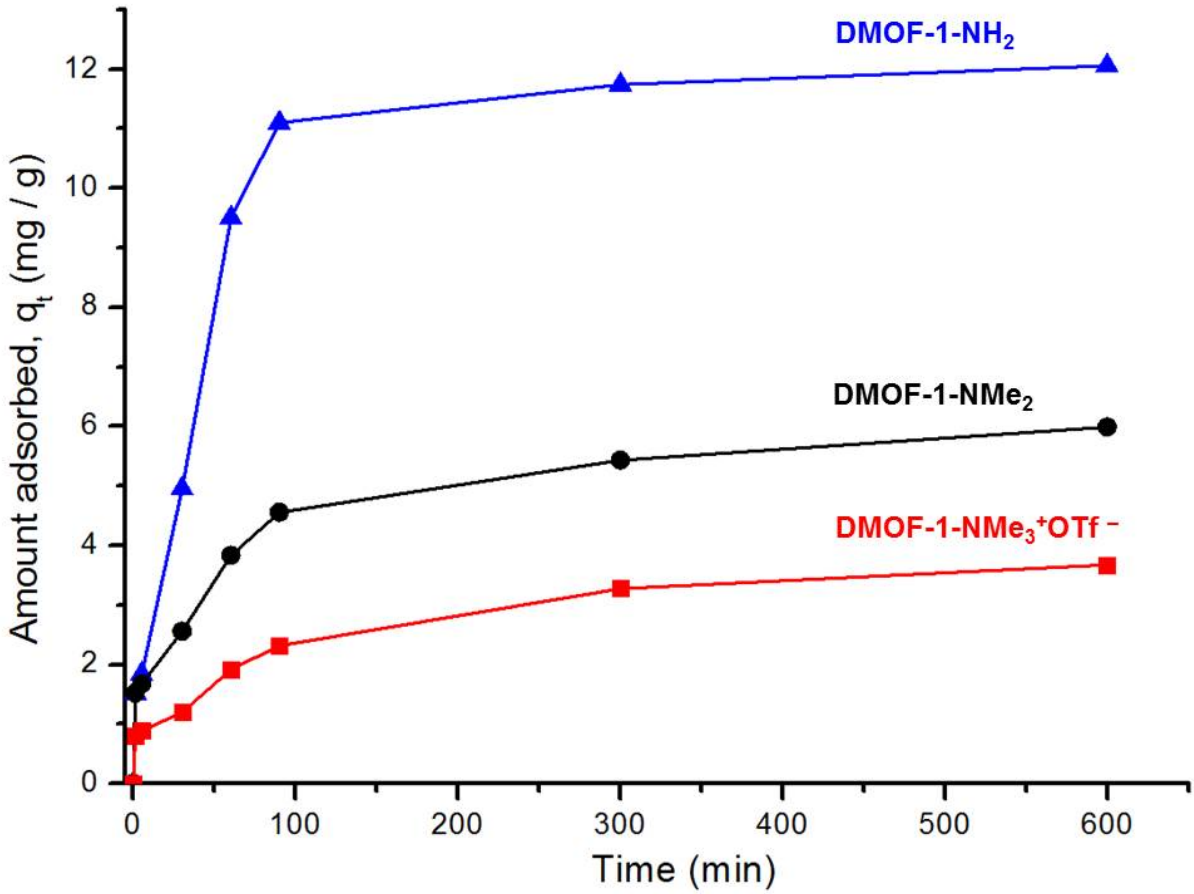
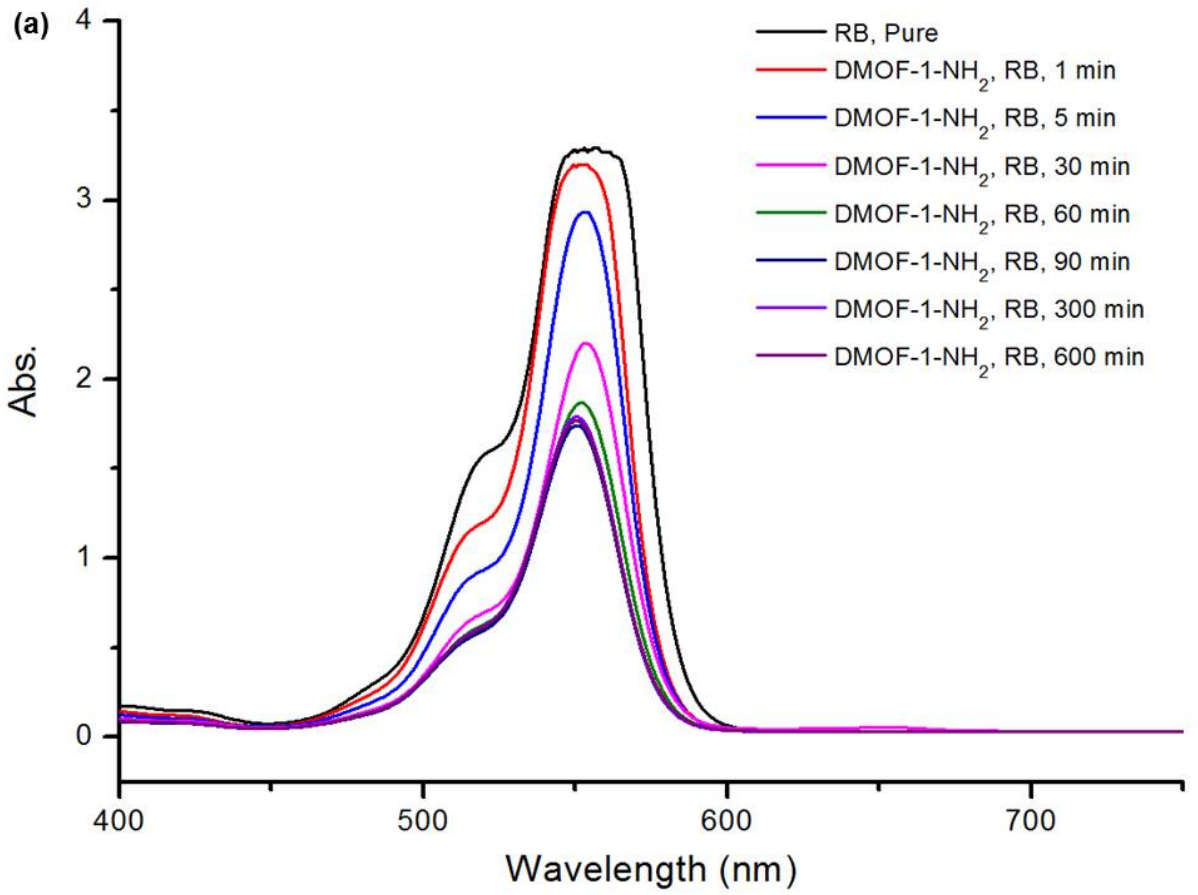
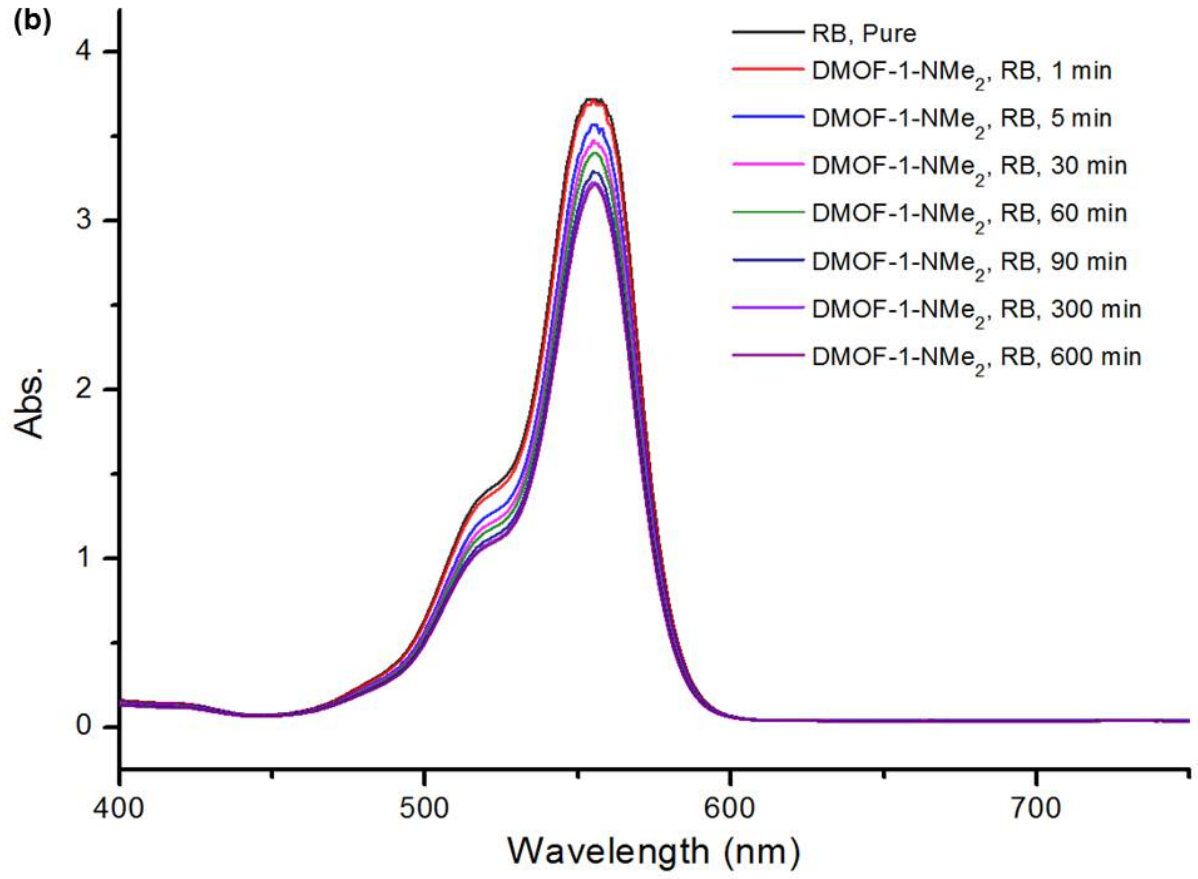


Fig. S9 Effect on the contact time and initial 'Sudan II' concentration on the adsorption of 'Sudan II' over DMOF-1-NH_2, DMOF-1-NMe_2, and DMOF-1-$NMe_3^+OTf^-$.


(a)
Abs.
Wavelength (nm)
RB, Pure
DMOF-1-NH2, RB, 1 min
DMOF-1-NH2, RB, 5 min
DMOF-1-NH2, RB, 30 min
DMOF-1-NH2, RB, 60 min
DMOF-1-NH2, RB, 90 min
DMOF-1-NH2, RB, 300 min
DMOF-1-NH2, RB, 600 min


(b)
Abs.
Wavelength (nm)
RB, Pure
DMOF-1-NMe2, RB, 1 min
DMOF-1-NMe2, RB, 5 min
DMOF-1-NMe2, RB, 30 min
DMOF-1-NMe2, RB, 60 min
DMOF-1-NMe2, RB, 90 min
DMOF-1-NMe2, RB, 300 min
DMOF-1-NMe2, RB, 600 min

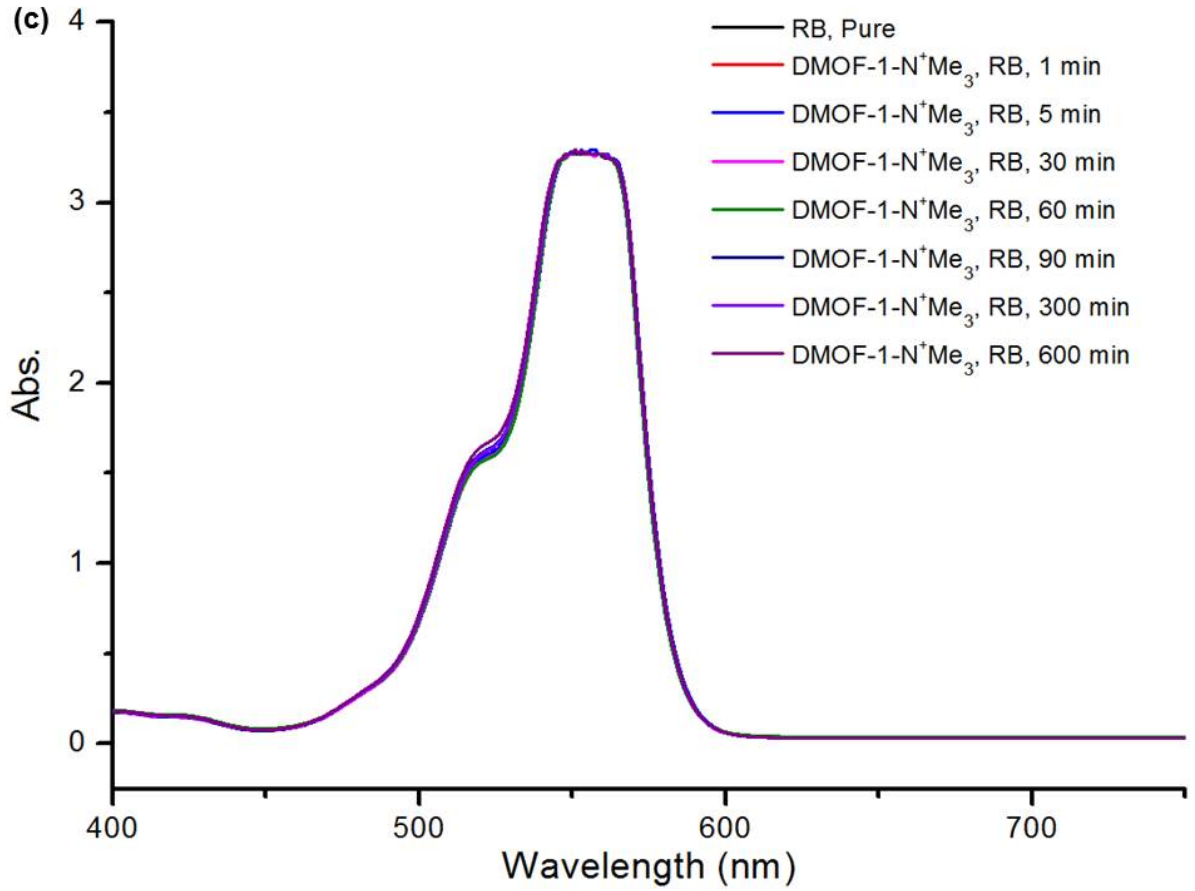


Fig. S10 UV-Vis spectra changes of 'Rhodamine B' in the presence of (a) DMOF-1-NH_2, (b) DMOF-1-NMe_2, and (c) DMOF-1-$NMe_3^+OTf^-$.

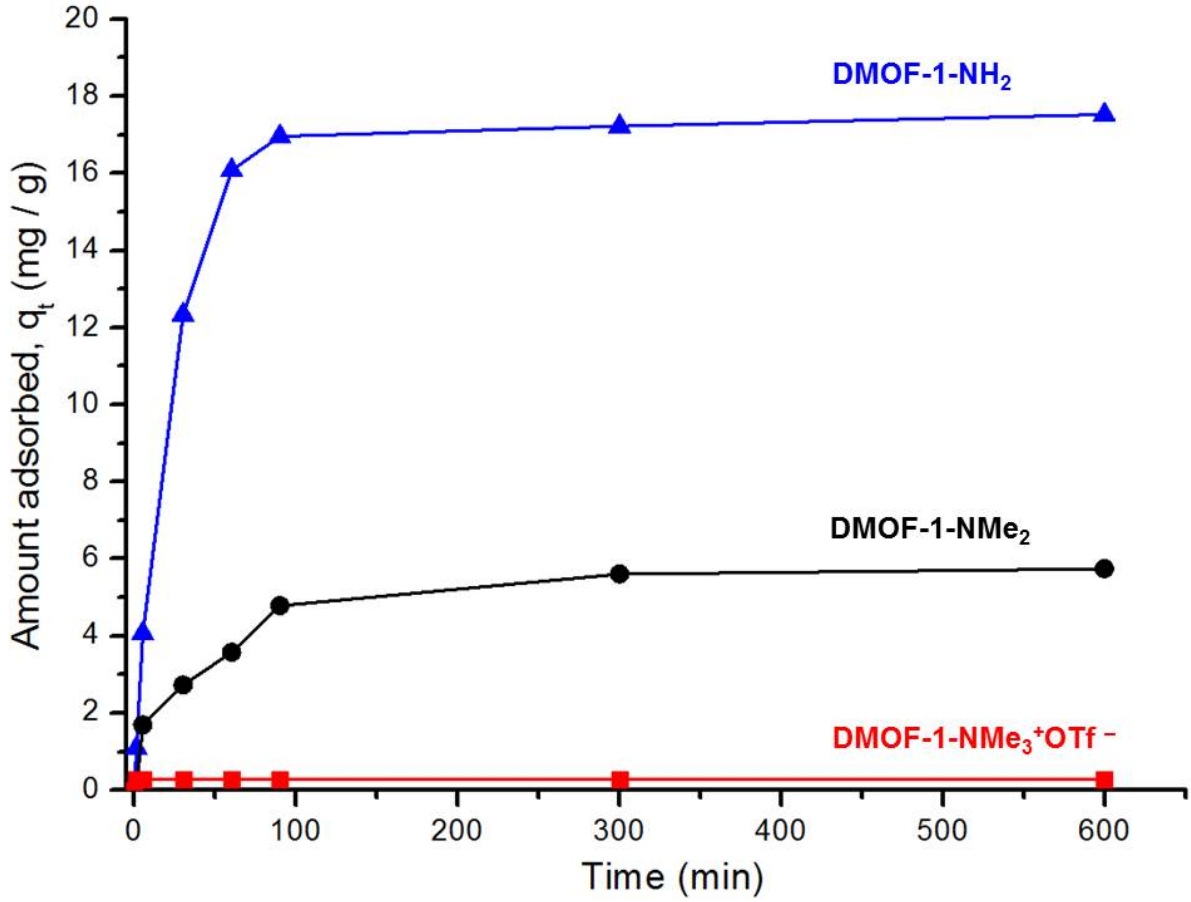
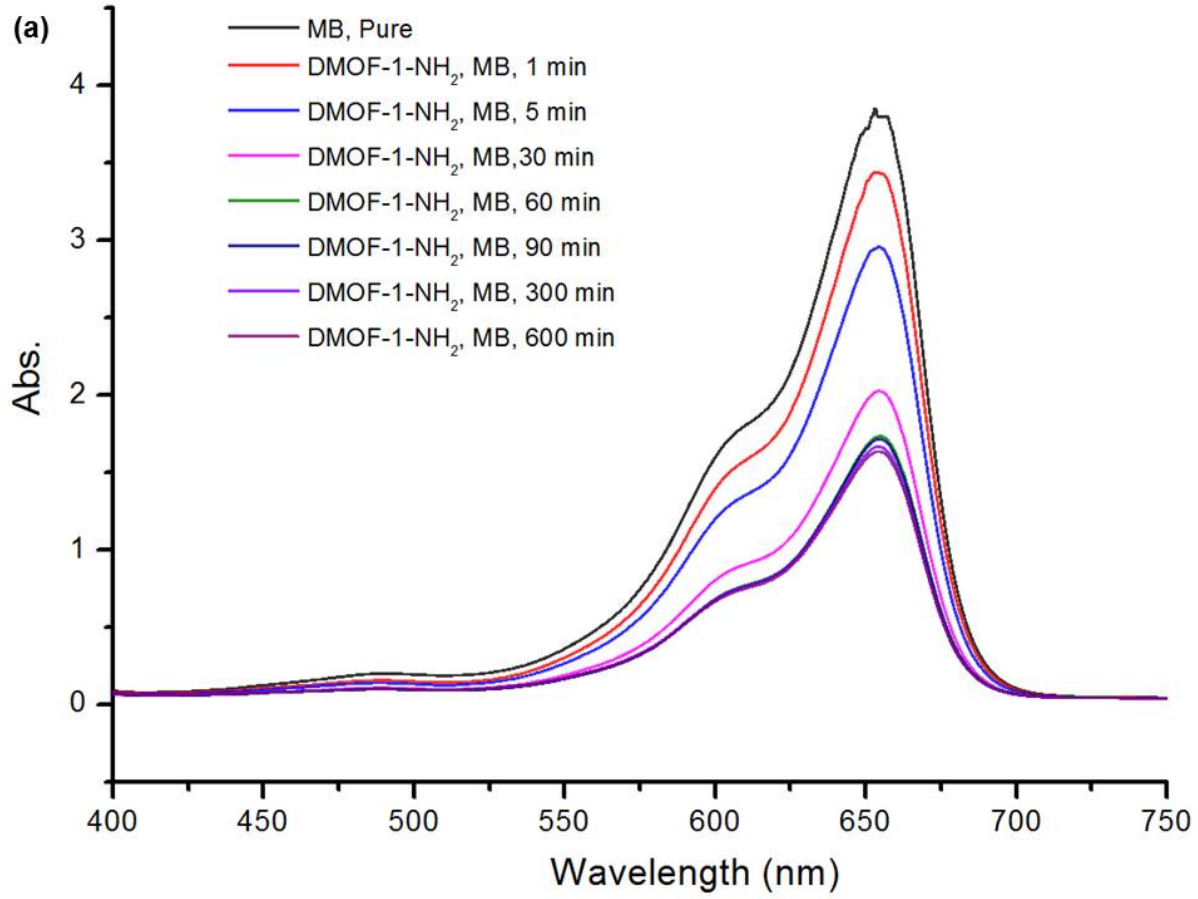
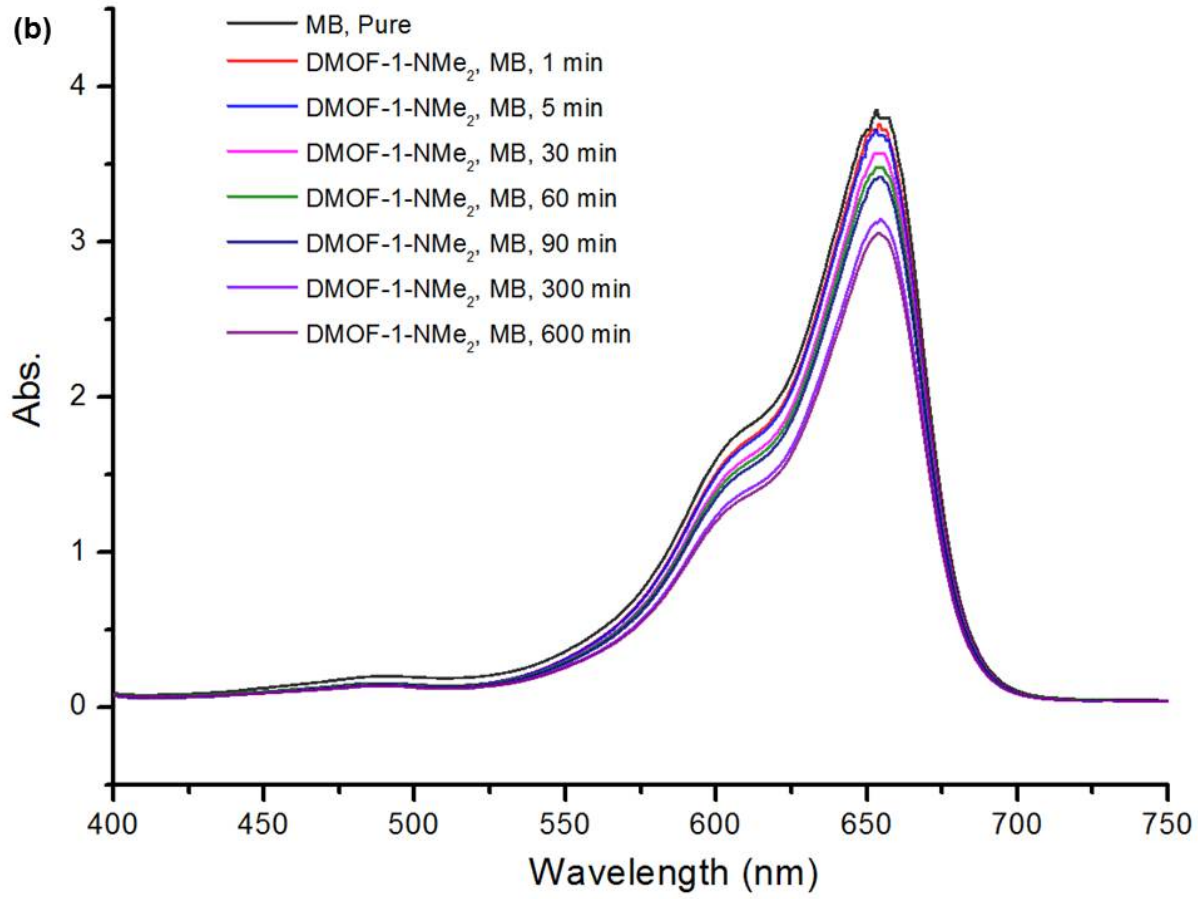


Fig. S11 Effect on the contact time and initial 'Rhodamine B' concentration on the adsorption of 'Rhodamine B' over DMOF-1-NH_2, DMOF-1-NMe_2, and DMOF-1-$NMe_3^+OTf^-$.


(a)
MB, Pure
DMOF-1-NH2, MB, 1 min
DMOF-1-NH2, MB, 5 min
DMOF-1-NH2, MB,30 min
DMOF-1-NH2, MB, 60 min
DMOF-1-NH2, MB, 90 min
DMOF-1-NH2, MB, 300 min
DMOF-1-NH2, MB, 600 min
Abs.
Wavelength (nm)


(b)
MB, Pure
DMOF-1-NMe2, MB, 1 min
DMOF-1-NMe2, MB, 5 min
DMOF-1-NMe2, MB, 30 min
DMOF-1-NMe2, MB, 60 min
DMOF-1-NMe2, MB, 90 min
DMOF-1-NMe2, MB, 300 min
DMOF-1-NMe2, MB, 600 min
Abs.
Wavelength (nm)

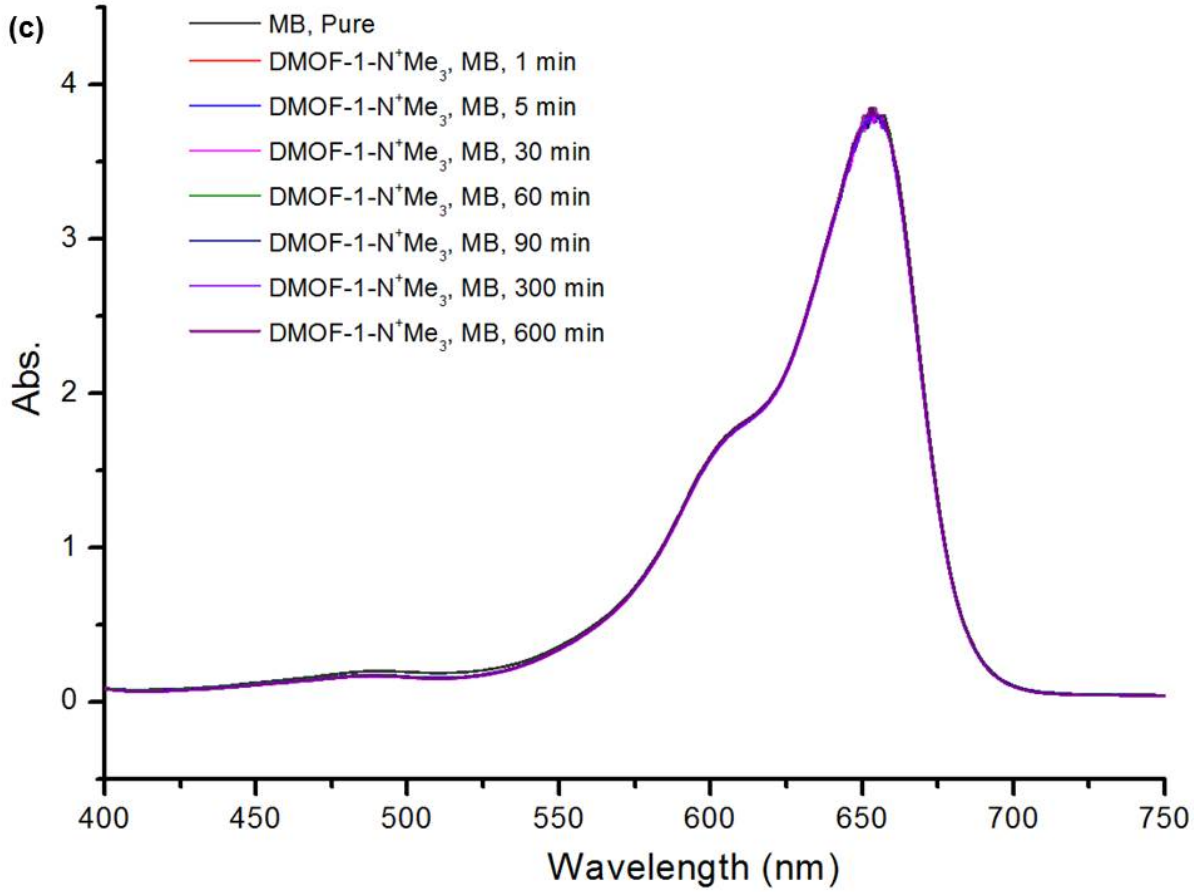


Fig. S12 UV-Vis spectra changes of 'Methylene Blue' in the presence of (a) DMOF-1-NH_2, (b) DMOF-1-NMe_2, and (c) DMOF-1-$NMe_3^+OTf^-$.

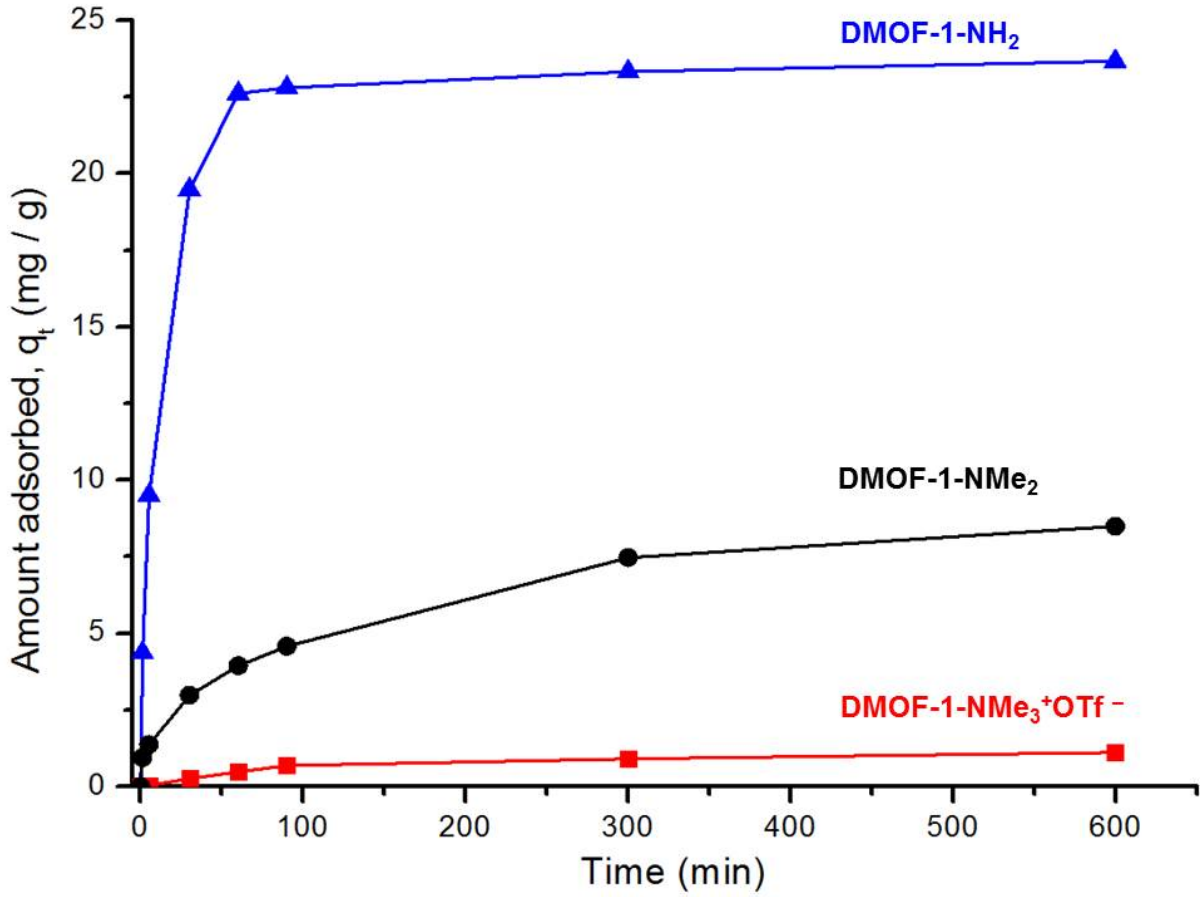
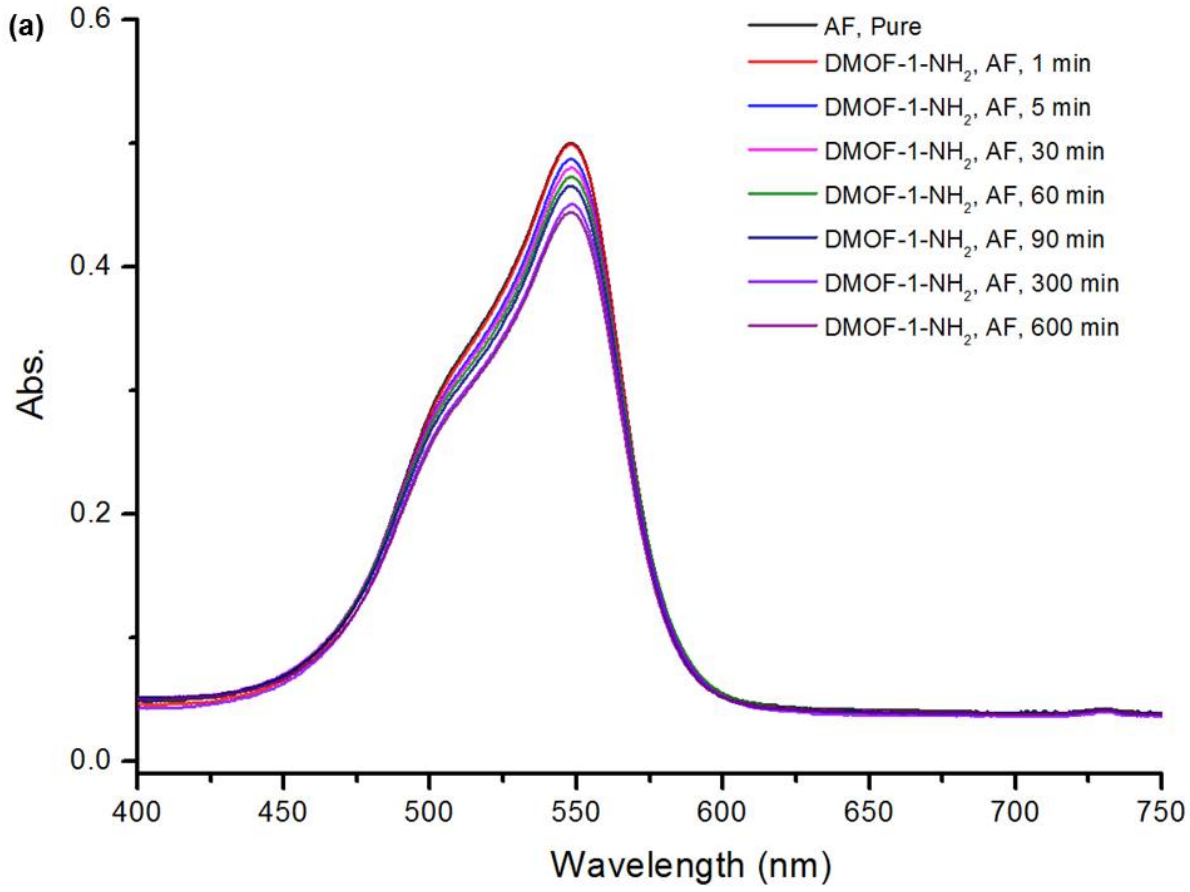
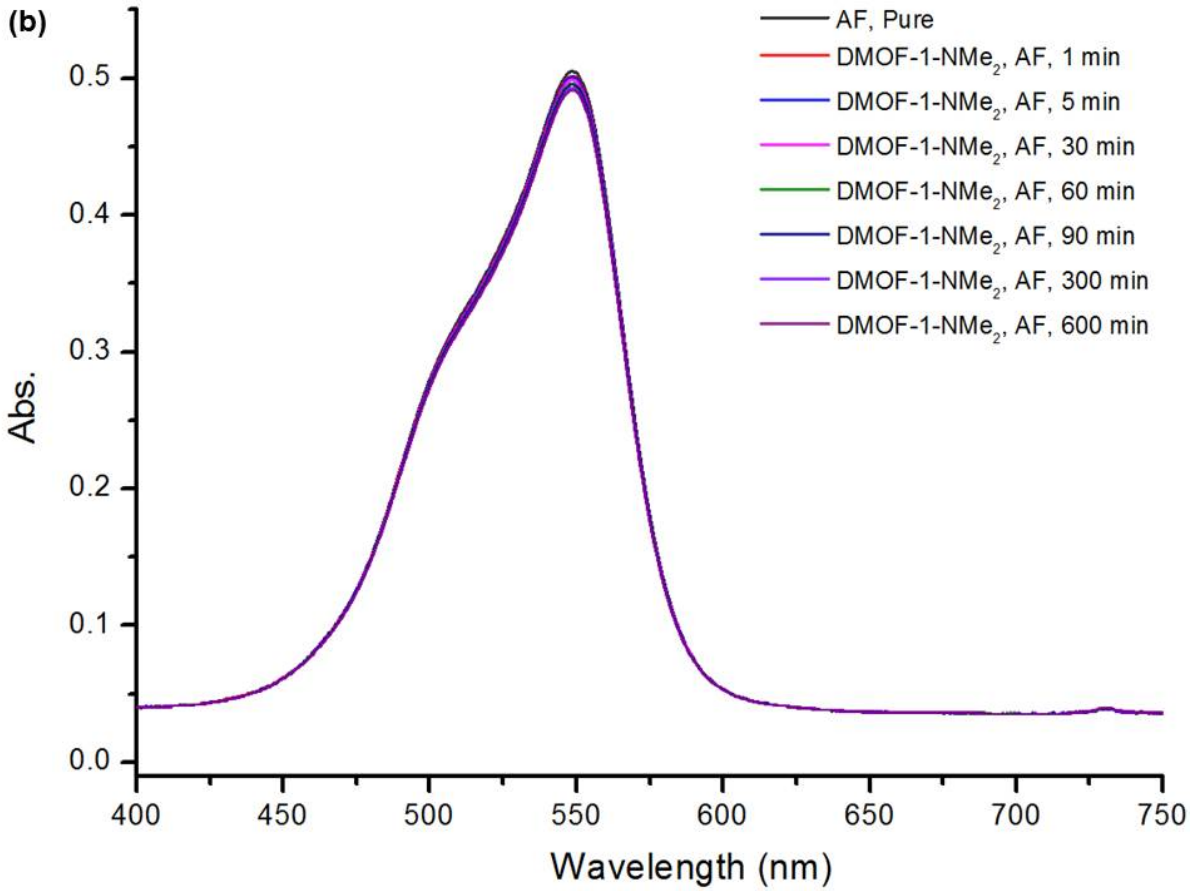


Fig. S13 Effect on the contact time and initial 'Methylene Blue' concentration on the adsorption of 'Methylene Blue' over DMOF-1-NH_2, DMOF-1-NMe_2, and DMOF-1-$NMe_3^+OTf^-$.


(a)
Abs.
Wavelength (nm)
AF, Pure
DMOF-1-NH2, AF, 1 min
DMOF-1-NH2, AF, 5 min
DMOF-1-NH2, AF, 30 min
DMOF-1-NH2, AF, 60 min
DMOF-1-NH2, AF, 90 min
DMOF-1-NH2, AF, 300 min
DMOF-1-NH2, AF, 600 min


(b)
Abs.
Wavelength (nm)
AF, Pure
DMOF-1-NMe2, AF, 1 min
DMOF-1-NMe2, AF, 5 min
DMOF-1-NMe2, AF, 30 min
DMOF-1-NMe2, AF, 60 min
DMOF-1-NMe2, AF, 90 min
DMOF-1-NMe2, AF, 300 min
DMOF-1-NMe2, AF, 600 min

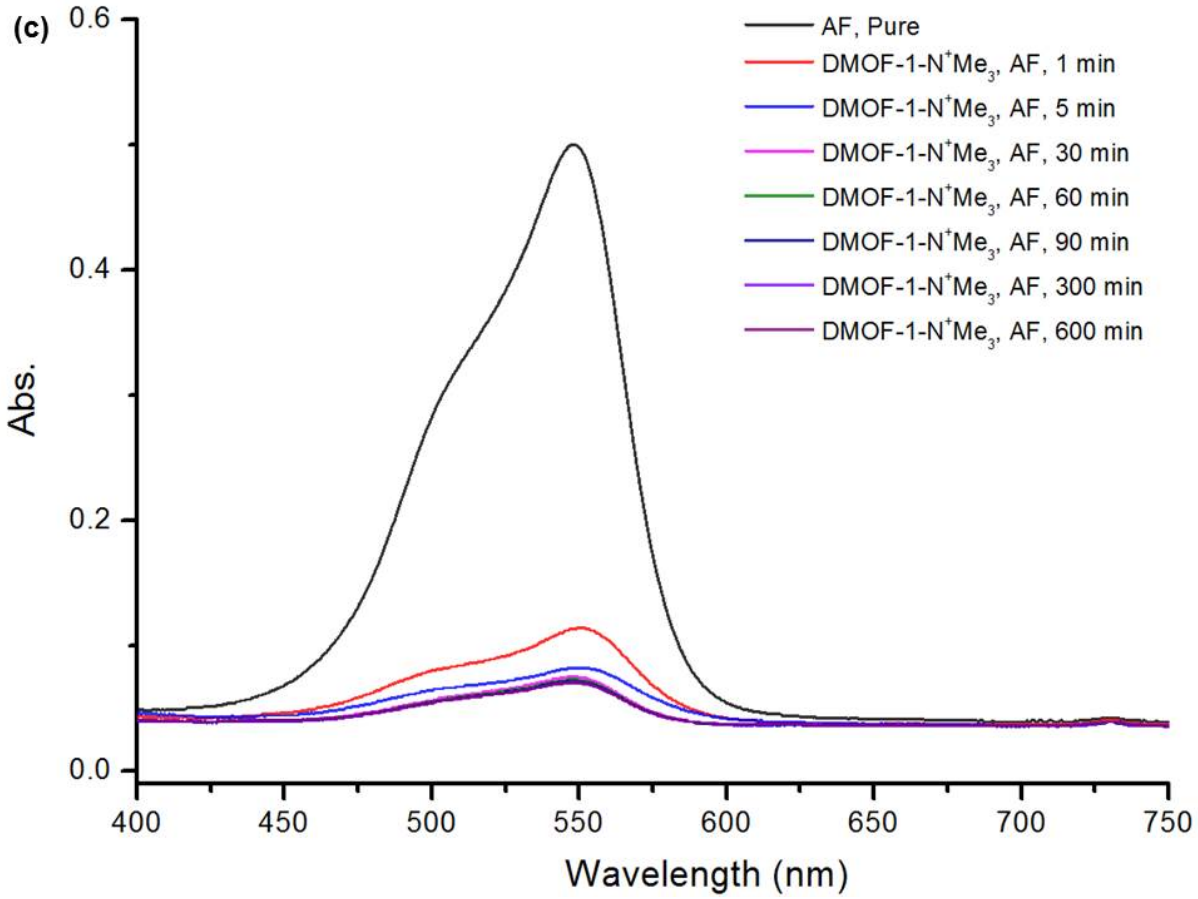


Fig. S14 UV-Vis spectra changes of 'Acid Fuchsin calcium salt' in the presence of (a) DMOF-1-NH_2, (b) DMOF-1-NMe_2, and (c) DMOF-1-$NMe_3^+OTf^-$.

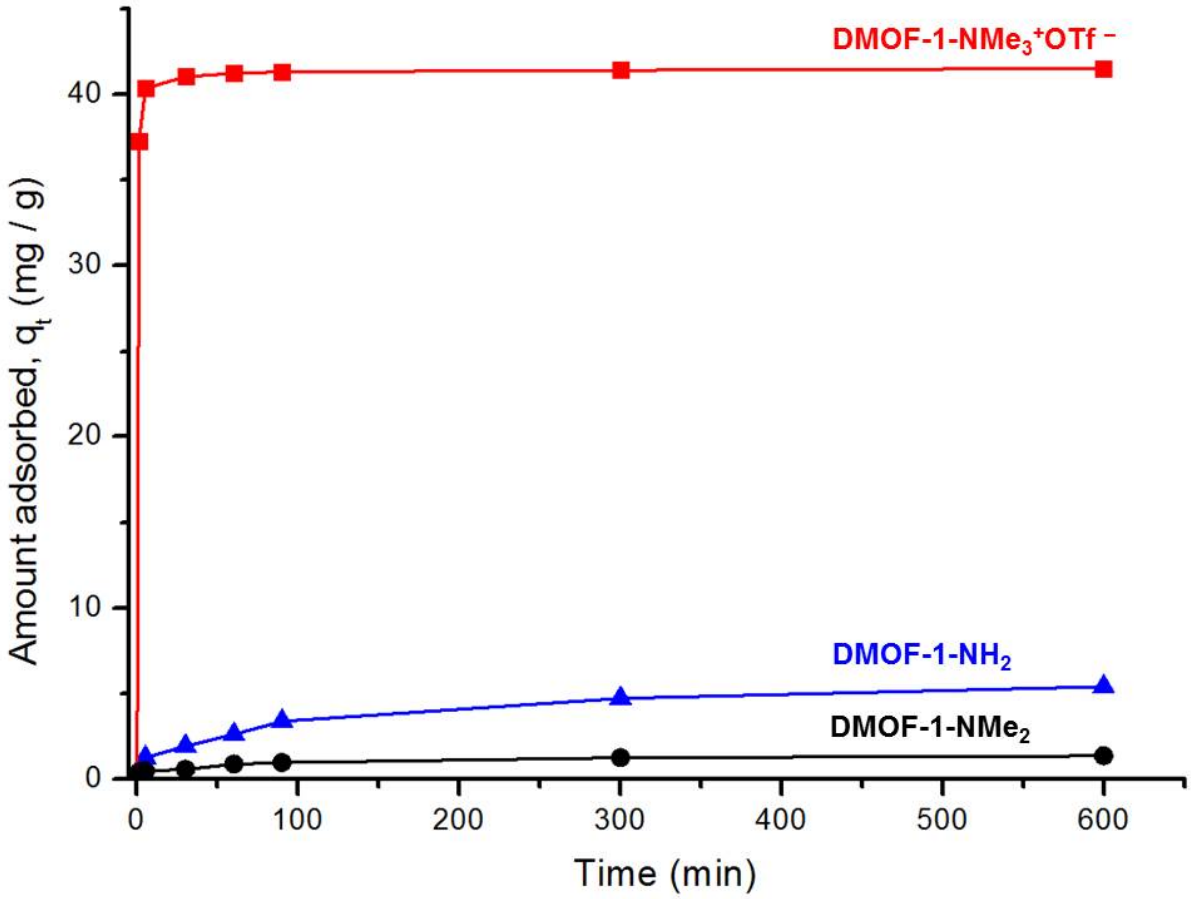
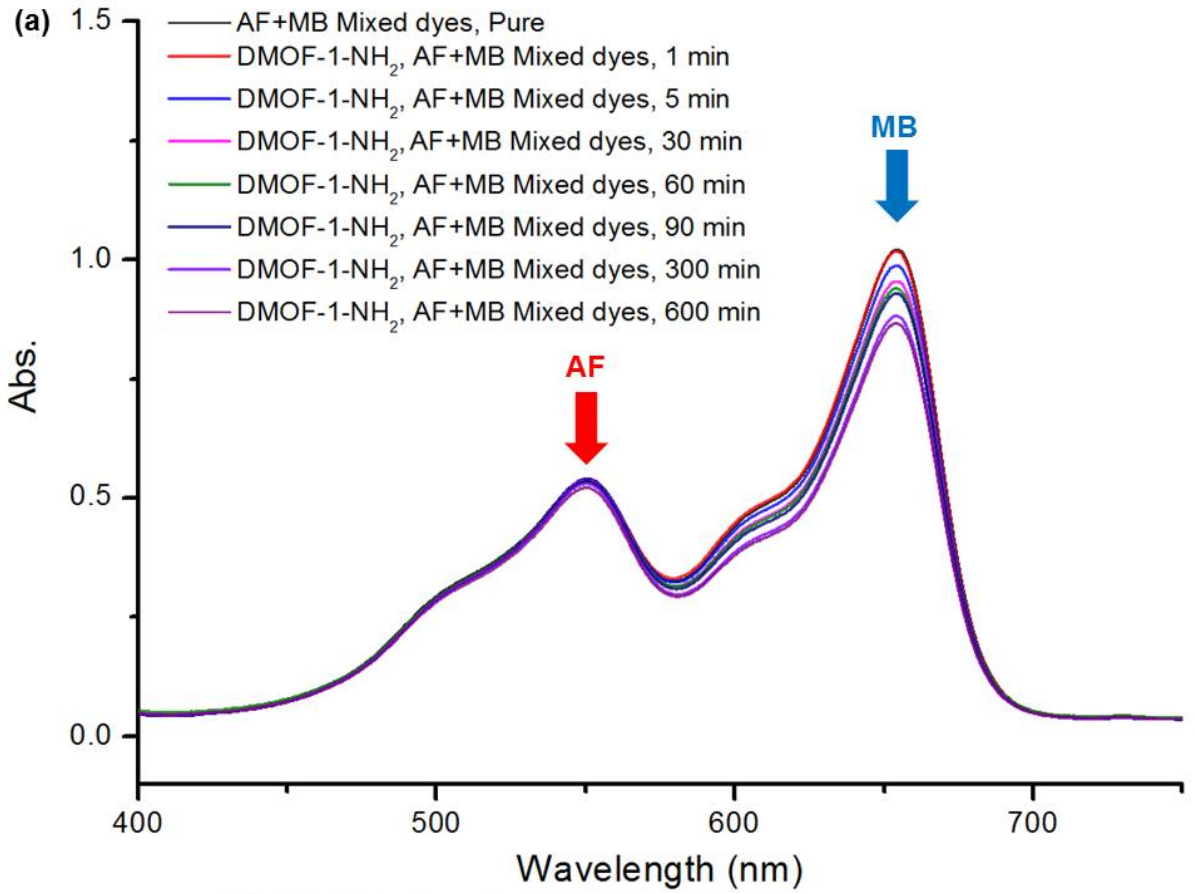
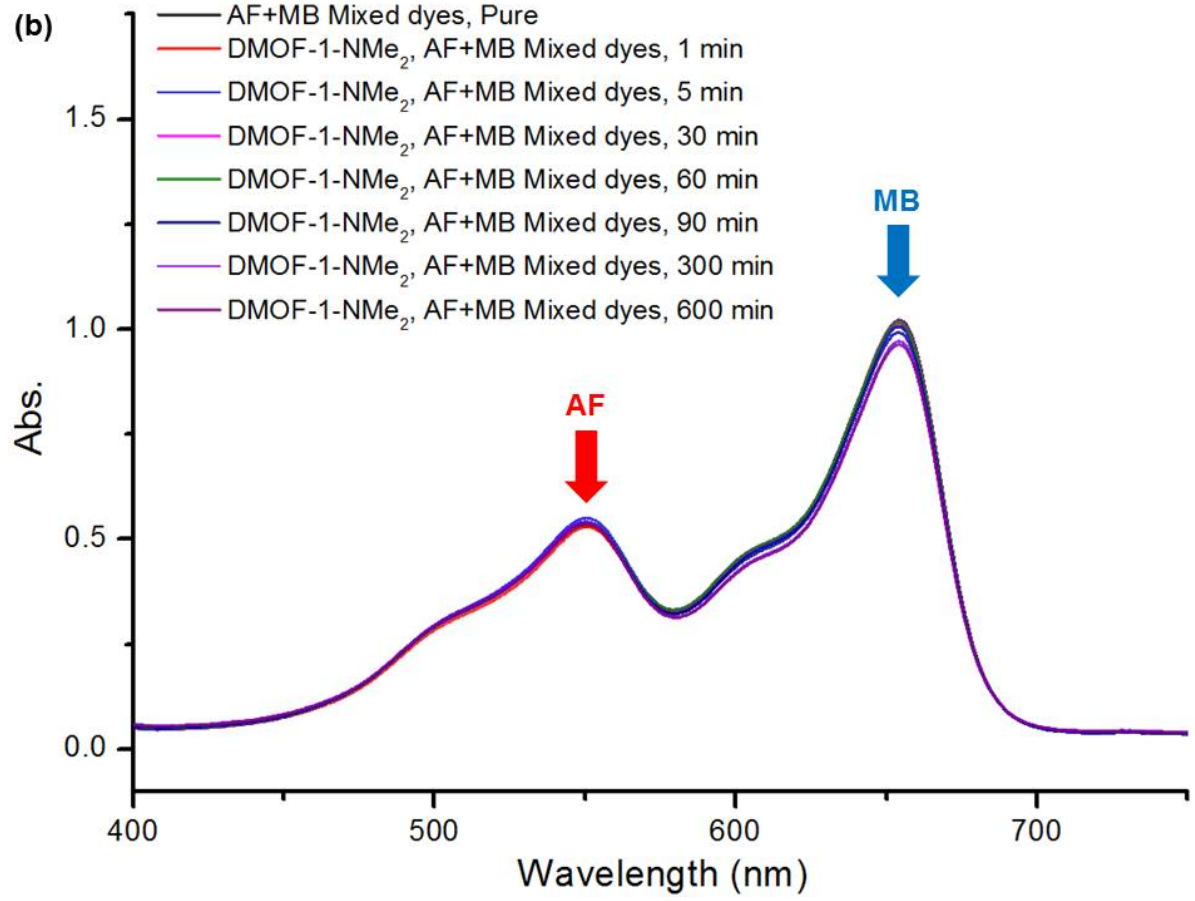


Fig. S15 Effect on the contact time and initial 'Acid Fuchsin calcium salt' concentration on the adsorption of 'Acid Fuchsin calcium salt' over DMOF-1-NH_2, DMOF-1-NMe_2, and DMOF-1-$NMe_3^+OTf^-$.


(a)
AF+MB Mixed dyes, Pure
DMOF-1-NH2, AF+MB Mixed dyes, 1 min
DMOF-1-NH2, AF+MB Mixed dyes, 5 min
DMOF-1-NH2, AF+MB Mixed dyes, 30 min
DMOF-1-NH2, AF+MB Mixed dyes, 60 min
DMOF-1-NH2, AF+MB Mixed dyes, 90 min
DMOF-1-NH2, AF+MB Mixed dyes, 300 min
DMOF-1-NH2, AF+MB Mixed dyes, 600 min
MB
AF
Abs.
Wavelength (nm)


(b)
AF+MB Mixed dyes, Pure
DMOF-1-NMe2, AF+MB Mixed dyes, 1 min
DMOF-1-NMe2, AF+MB Mixed dyes, 5 min
DMOF-1-NMe2, AF+MB Mixed dyes, 30 min
DMOF-1-NMe2, AF+MB Mixed dyes, 60 min
DMOF-1-NMe2, AF+MB Mixed dyes, 90 min
DMOF-1-NMe2, AF+MB Mixed dyes, 300 min
DMOF-1-NMe2, AF+MB Mixed dyes, 600 min
MB
AF
Abs.
Wavelength (nm)

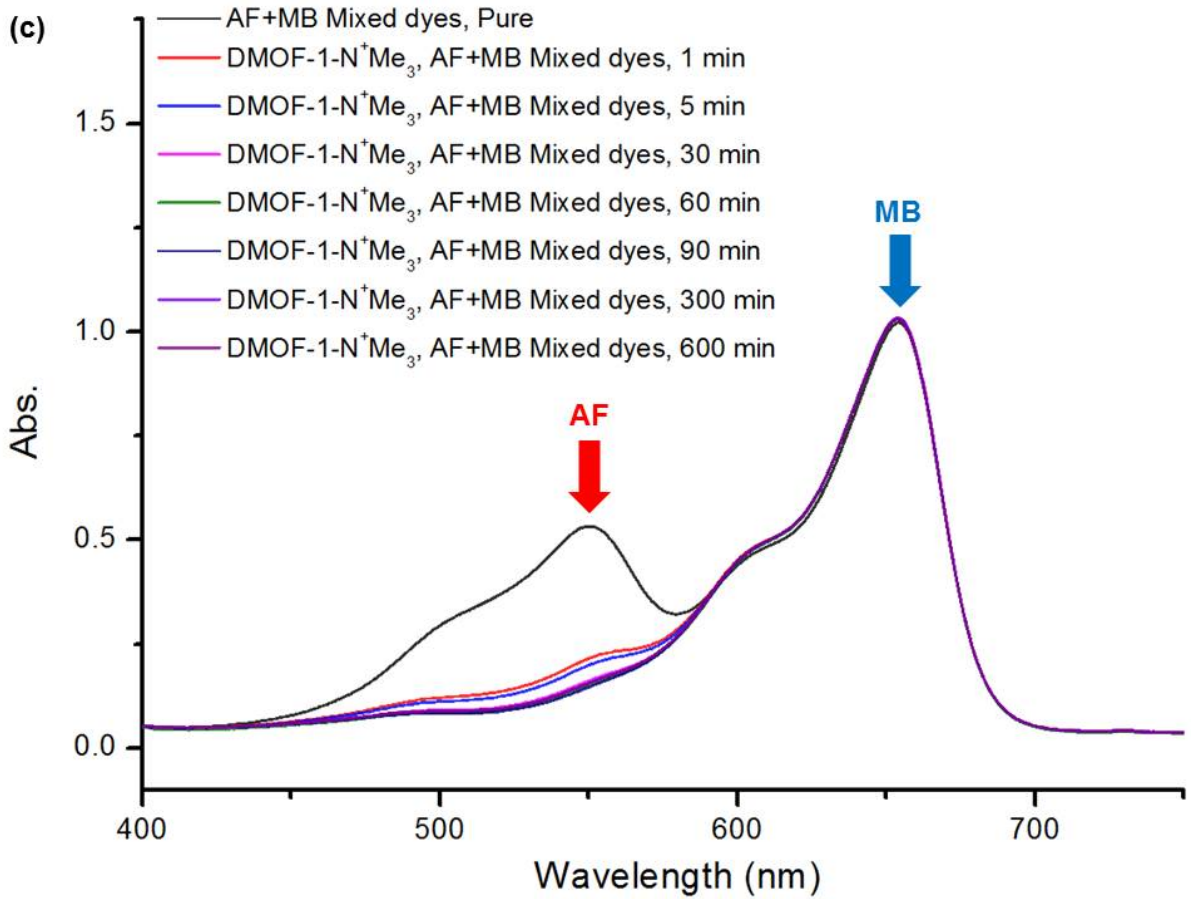


Fig. S16 Organic dye mixture (Methylene Blue and Acid Fuchsin calcium salt) separation experiment using (a) DMOF-1-NH_2, (b) DMOF-1-NMe_2, and (c) DMOF-1-$NMe_3^+OTf^-$.

References for ESI

S1 H. Hahm, H. Ha, S. Kim, B. Jung, M. Park, Y. Kim, J. Heo and M. Kim, *CrystEngComm*, **2015**, Advanced Article, DOI: 10.1039/c5ce00674k.

S2 J. T. Reeves, D. R. Fandrick, Z. Tan, J. J. Song, H. Lee, N. K. Yee and C. H. Senanayake, *Org. Lett*., **2010**, *12,* 4388.

S3 S. J. Garibay and S. M. Cohen, *Chem.Commun.,* **2010**, *46*, 7700.

S4 Z. Wang, K. K. Tanabe and S. M. Cohen, *Inorg. Chem*. **2009**, *48*, 296.

S5 C. Lastoskie, K. E. Gubbins and N. Quirke, *J. Phys. Chem.* **1993**, *97*, 4786.

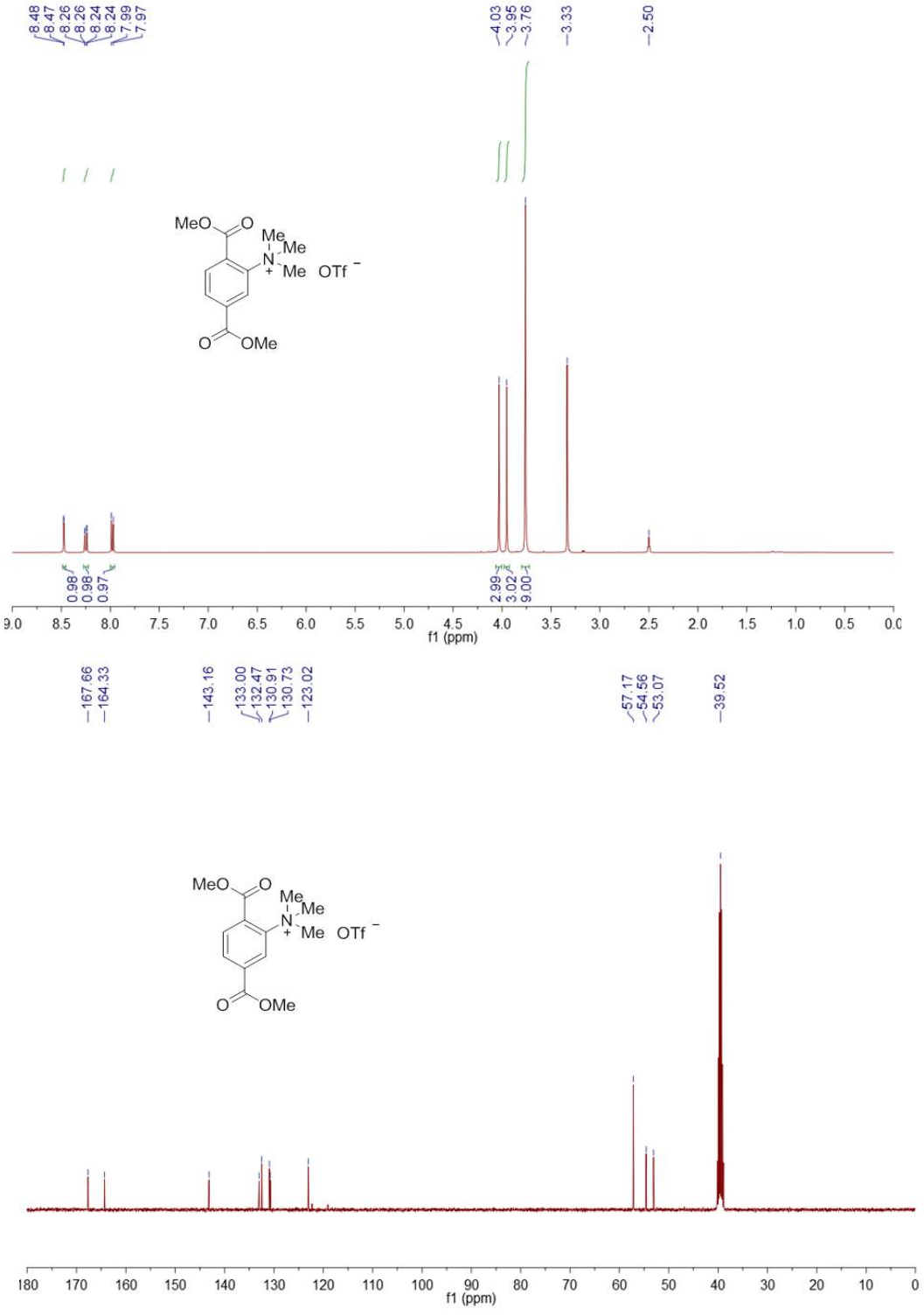
S6 P. Tarazona, U. Marini Bettolo Marconi and R. Evans, *Mol. Phys.* **1987**, *60*, 573.

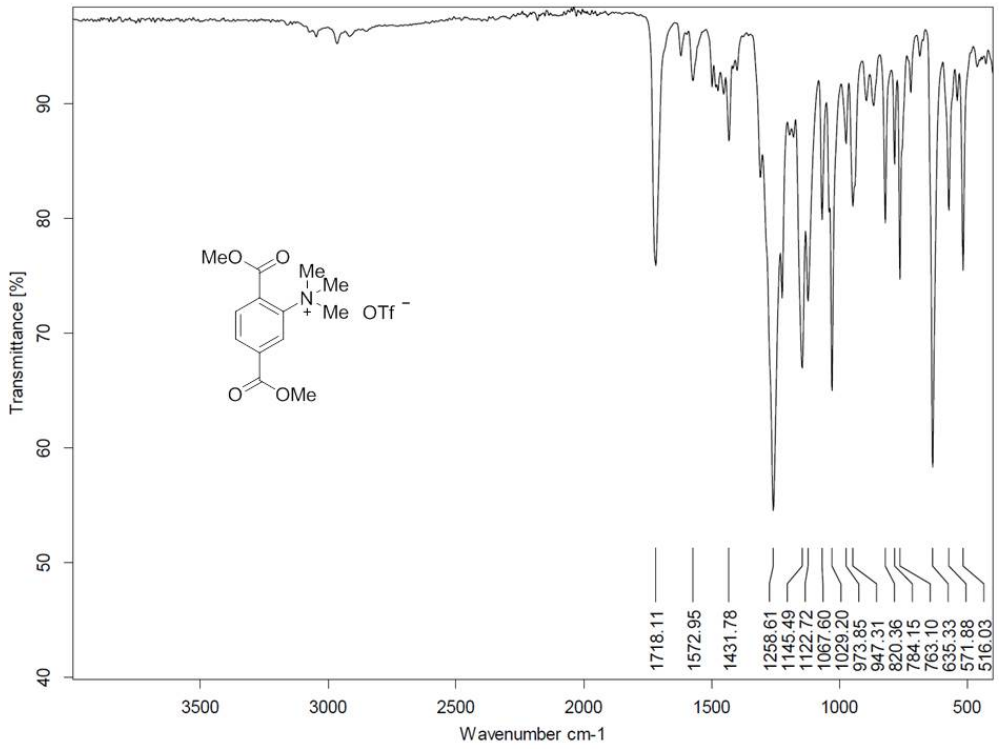
Appendix I.

^{1}H NMR, ^{13}C NMR and IR spectra of new ligands

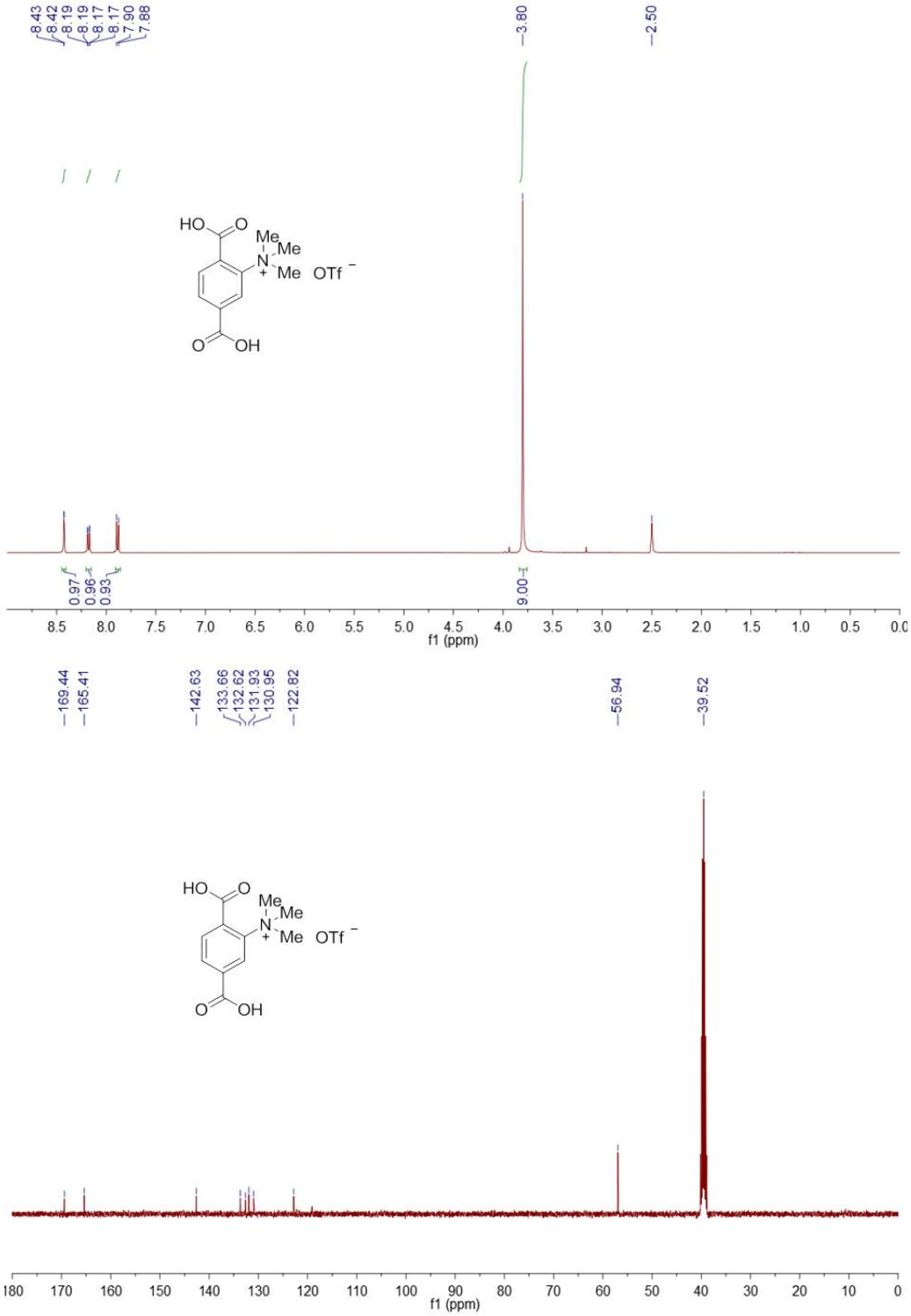
FAB-HR-MS spectra of MOF after digestion

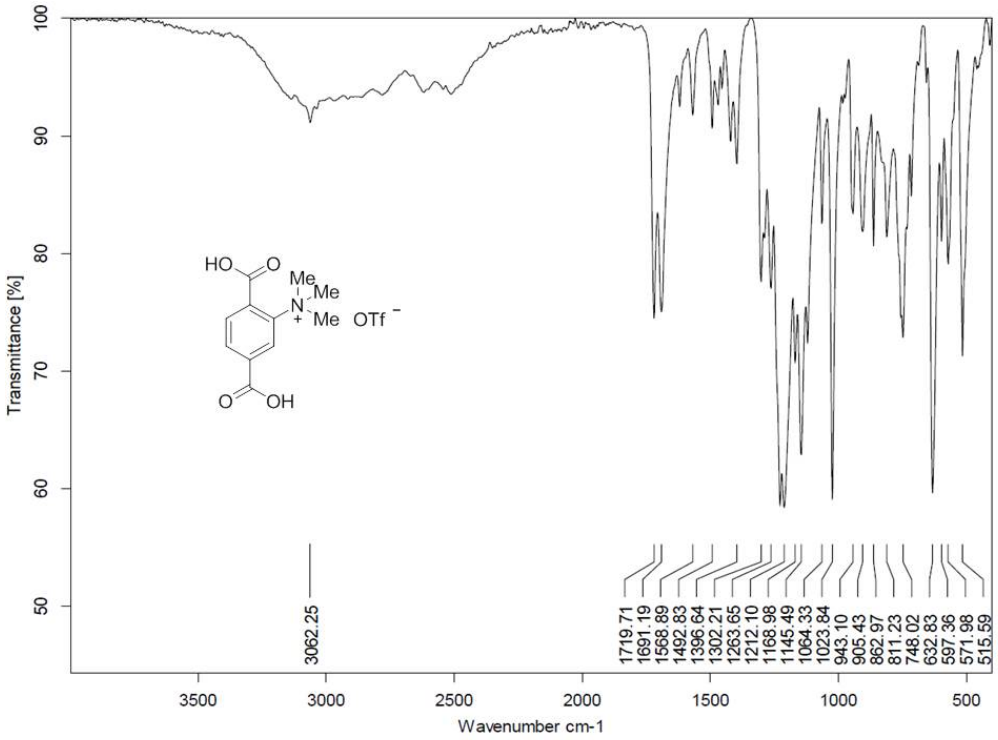
2,5-Bis(methoxycarbonyl)-*N*,*N*,N-trimethylbenzenaminum trifluoromethanesulfonate (**3**)

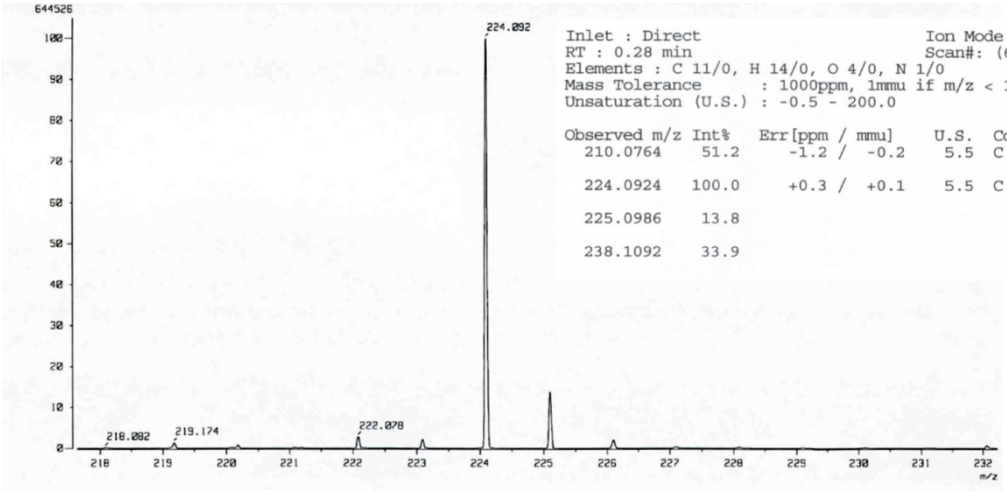



Transmittance [%]
90
80
70
60
50
40
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1
MeO
O
Me
Me
N
+
Me
OTf
−
O
OMe
1718.11
1572.95
1431.78
1258.61
1145.49
1122.72
1067.60
1029.20
973.85
947.31
820.36
784.15
763.10
635.33
571.88
516.03

2,5-Dicarboxy-*N*,*N*,*N*-trimethylbenzenaminium trifluoromethanesulfonate (**4**)




Transmittance [%]
100
90
80
70
60
50
HO
O
Me
Me
N
+
Me
OTf
−
O
OH
3062.25
1719.71
1691.19
1568.89
1492.83
1396.64
1302.21
1263.65
1212.10
1168.98
1145.49
1064.33
1023.84
943.10
905.43
862.97
811.23
748.02
632.83
597.36
571.98
515.59
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



Inlet : Direct
RT : 0.28 min
Elements : C 11/0, H 14/0, O 4/0, N 1/0
Mass Tolerance : 1000ppm, 1mmu if m/z < 1, 3mmu if m/z > 3
Unsaturation (U.S.) : -0.5 - 200.0

Ion Mode : FAB+
Scan#: (6,7)

Observed m/z	Int%	Err[ppm / mmu]	U.S.	Composition
210.0764	51.2	-1.2 / -0.2	5.5	C 10 H 12 O 4 N
224.0924	100.0	+0.3 / +0.1	5.5	C 11 H 14 O 4 N
225.0986	13.8			
238.1092	33.9			