

Supplementary Materials for

Polyimide-linked Covalent Organic Frameworks: Pitfalls (and Successes) for the Synthesis of Ordered Materials

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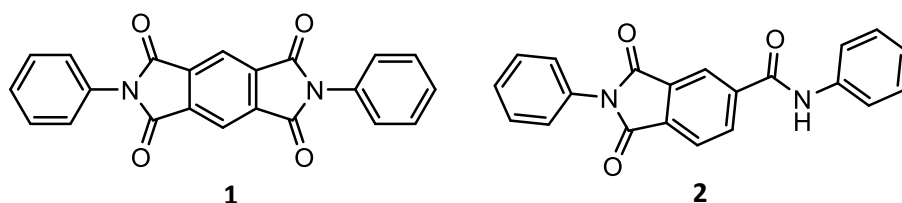
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Unless otherwise noted, all reagents were purchased from commercial sources and used as received.

Microwave syntheses were performed using an Anton Parr Multiwave Pro microwave reactor. Oven reactions were performed using a Thermo scientific Lindberg Blue M box furnace set at 200 °C, 250 °C, and 300 °C. Calibration of the oven temperature was performed using a DiGi-Sense Dual JTEK thermocouple thermometer, which determined operational temperatures of 167 °C, 256 °C, and 310 °C, respectively. Due to the use of N,N-dimethylpyrrolidione (NMP), pressure reactors were used for reactions taking place at 256 °C and 310 °C, well above the solvent boiling point at 202 °C. NMR data were collected on a Bruker Advance III 400 MHz NMR spectrometer at room temperature. Spectra were referenced to residual DMSO (2.50 ppm, ¹H) or CDCl₃ (7.26 ppm, ¹H) with chemical shifts reported in δ values (ppm) and J values in hertz (Hz). The following abbreviations are used to describe peaks: brs (broad singlet), m (multiplet). Due to carboxylic anions, integrations of carboxylic acids of the organic salt materials are excluded. Infrared spectra were collected on a Perkin Elmer Spectrum Two FT-IR spectrometer with an ATR attachment and TEM images were taken on a FEI Tecnai G2 F20 S-Twin operating at 200 keV. HRMS experiments were performed using a Voyager-DE PRO MALDI-TOF mass spectrometer. Powder x-ray diffraction (PXRD) were collected using a Rigaku Smart Lab X-ray diffractometer, with real spacings (nm) calculated using Bragg's law ($n = 1, \lambda = 1.54 \text{ \AA}$). Thermogravimetric Analysis (TGA) with simultaneous differential scanning calorimetry (DSC) were collected using a TA instrument Q200. BET analyses were collected using a Micromeritics ASAP 2020 run under nitrogen gas.

Model reaction studies



Compounds **1** and **2** were synthesized using the following two methods.

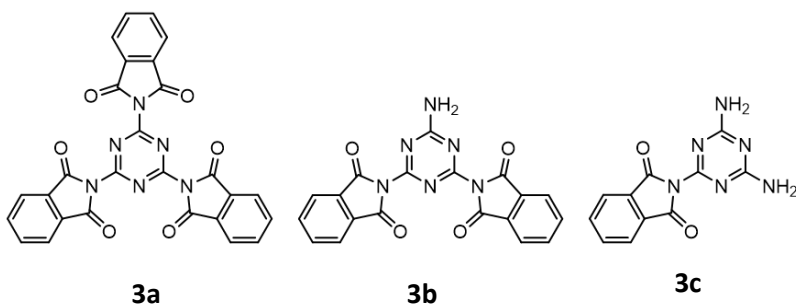
Condition A: Pyromelic dianhydride (1 equiv, 0.122 g, 0.559 mmol) was added to a 5 mL glass ampule followed by aniline (2.3 equiv, 0.12 mL, 1.314 mmol) and NMP (4 mL). The vessel containing all reagents and solvent was sealed and heated via box furnace at 167 °C for 3 days. The solution was observed to become dark brown with insoluble crystal formation as the reaction progressed. After three days of reacting, the vessel was taken out of the furnace, opened, and diluted with DI water (20 mL). The flaky crystals were collected through vacuum filtration washing with water (3X 20 mL) to yield compound **1** (0.161 g, 0.437 mmol, 78% yield). IR: 1702, 1118 cm⁻¹. ¹H NMR DMSO-d₆: δ 8.39(5) (s, 2H), 7.55(1) (m, 10H).

Condition B: Pyromelic dianhydride (1 equiv, 0.122 g, 0.559 mmol) was added to a teflon MW reaction vessel followed by aniline (2.3 equiv, 0.12 mL, 1.314 mmol) and NMP (6 mL). The vessel containing all reagents and solvent was capped and heated with stirring via microwave irradiation at 200 °C for 2 hours (15 minute ramp time). After two hours of reacting and cooling for 30 minutes post reaction completion, the vessel was taken out of the MW, opened, and diluted with DI water (20 mL). The grey powder was collected through vacuum filtration washing with DI water (3X 20 mL) to yield a mixture of

compounds **1** and **2** (0.169 g, 82% combined yield). Compound **1** was separated and purified through recrystallization from minimal amounts of DMSO to yield the off-white powder (0.086 g, 0.233 mmol, 51% yield).

The remaining oil containing compound **2** was subjected to an aqueous work up using a mixture of DI water (50 mL) and dichloromethane (50 mL). The organic layer was extracted from the aqueous layer (3X 50mL), followed by drying with magnesium sulfate, filtering, and rotary evaporation.

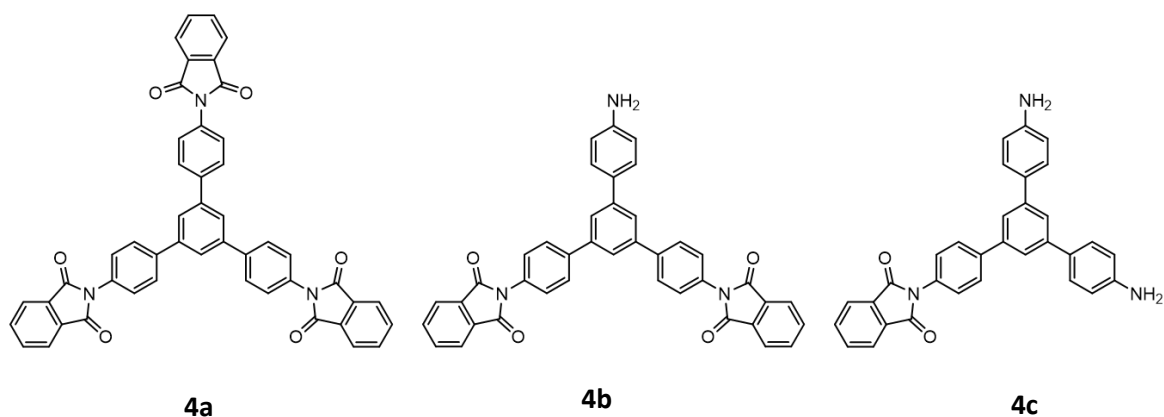
Compound **2** was vacuum pumped for 2 hours to yield a translucent, dark orange oil (0.083 mg, 0.242 mmol, 49% yield). IR: 3408, 1662, 1018 cm^{-1} . $^1\text{H NMR}$ CDCl_3 : δ 9.91(7) (s, NH), 8.09(5) (s, 1H), 7.95 (d, 1H, $J = 7.8$ Hz), 7.50(6) (d, 1H, $J = 5.0$ Hz), 7.25(6) (d, 2H, $J = 8.1$ Hz), 6.98(3) (t, 2H, $J = 6.6$ Hz), 6.90(0) (d, 3H, $J = 7.4$ Hz), 6.80(5) (t, 2H, $J = 8.5$ Hz), 6.58(5) (t, 1H, $J = 7.4$ Hz). LRMS m/z : calc for $\text{C}_{21}\text{H}_{14}\text{N}_2\text{O}_3$ $[(M + 1\text{H})^{+1}]$ 343, found 343.



Compounds **3b-3c** were synthesized using the following two methods.

Condition A: Phthalic anhydride (3.2 equiv, 0.408 g, 2.755 mmol) was added to a 5 mL glass ampule followed by melamine (1 equiv, 0.108 g, 0.856 mmol) and NMP (4 mL). The vessel containing all reagents and solvent was sealed and heated via box furnace at 167 °C for 3 days. The translucent yellow solution was observed to become dark brown as the reaction progressed. After three days of reacting, the vessel was taken out of the furnace and opened. Reaction directly plated for MS analysis. MADLI-TOF MS/MS: **3b** $\text{C}_{19}\text{H}_{10}\text{N}_6\text{O}_4$ $[M+1]$ calc: 387.32 m/z , found: 387.96 m/z . **3c** $\text{C}_{11}\text{H}_8\text{N}_6\text{O}_2$ $[M+1]$ calc: 256.22 m/z , found: 256.95 m/z .

Condition B: Phthalic anhydride (3.2 equiv, 0.409 g, 2.762 mmol) was added to a teflon MW reaction vessel followed by melamine (1 equiv, 0.108 g, 0.856 mmol) and NMP (6 mL). The vessel containing all reagents and solvent was capped and heated with stirring via microwave irradiation at 200 °C for 2 hours (15 minute ramp time). After two hours of reacting and cooling for 30 minutes post reaction completion, the vessel was taken out of the MW and opened. Reaction was diluted with water and vacuum filtered to obtain **3b – 3c** as a brown powder (0.076 g mixture). MADLI-TOF MS/MS: **3b** $\text{C}_{19}\text{H}_{10}\text{N}_6\text{O}_4$ $[M+1]$ calc: 387.32 m/z , found: 387.96 m/z . **3b** $\text{C}_{19}\text{H}_{10}\text{N}_6\text{O}_4$ $[M+\text{Na}]$ calc: 409.31 m/z , found: 409.00 m/z . **3c** $\text{C}_{11}\text{H}_8\text{N}_6\text{O}_2$ $[M+1]$ calc: 256.22 m/z , found: 256.95 m/z .



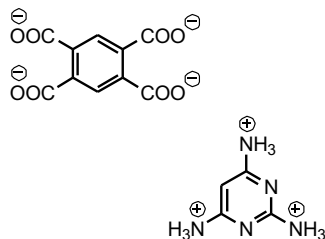
Compounds **4a-4c** were synthesized using the following two methods.

Condition A: Phthalic anhydride (3 equiv, 0.001(3) g, 0.009 mmol) was added to a 2 mL glass ampule followed by TAPB (1 equiv, 0.001 g, 0.003 mmol) and NMP (0.8 mL). The vessel containing all reagents and solvent was sealed and heated via box furnace at 167 °C for 3 days. The translucent yellow solution was observed to become dark brown as the reaction progressed. After three days of reacting, the vessel was taken out of the furnace and opened. Due to low quantities, reaction was directly plated for MS analysis without obtaining yield. MADLI-TOF MS/MS: uncyclized **4a** C₄₈H₃₀N₃NaO₈ [M + Na]: calc 800.19 m/z, found 800.61 m/z.

Condition B: Phthalic anhydride (3 equiv, 0.001(3) g, 0.009 mmol) was added to a teflon MW reaction vessel followed by TAPB (1 equiv, 0.001 g, 0.003 mmol) and NMP (6 mL). The vessel containing all reagents and solvent was capped and heated with stirring via microwave irradiation at 200 °C for 2 hours (15 minute ramp time). After two hours of reacting and cooling for 30 minutes post reaction completion, the vessel was taken out of the MW and opened. Due to low quantities, reaction was directly plated for MS analysis without obtaining yield. MADLI-TOF MS/MS: **4a** C₄₈H₂₇N₃O₆ [M+1] calc: 742.75 m/z, found: 742.49 m/z. **4b** C₄₀H₂₅N₃O₄ [M+1] calc: 612.25 m/z, found: 612.46 m/z. **4c** C₃₂H₂₃N₃O₂ [M+1] calc: 482.55 m/z, found: 482.35 m/z. Decarboxylation products: **4a-CO** C₄₇H₂₉N₃O₅ [M+1] calc: 716.21 m/z, found: 716.49 m/z. **4a-2CO** C₄₆H₃₁N₃O₄ [M+1] calc: 690.23 m/z, found: 690.46 m/z. **4a-3CO** C₄₅H₃₃N₃O₃ [M+1] calc: 664.25 m/z, found: 662.42 m/z. **4b-CO** C₃₉H₂₇N₃O₃ [M+1] calc: 586.20 m/z, found: 586.44 m/z.

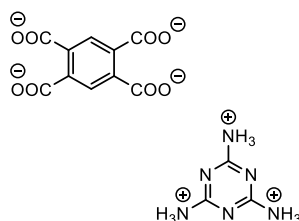
General Procedure for Organic Salt Formation (Adapted from: Taublaender, M. J.; Reiter, M.; Unterlass, M. M. Highly Crystalline, Nanostructured Polyimide Microparticles via Green and Tunable Solvothermal Polymerization. *Macromolecules* 2019, 52 (16), 6318–6329.)

The aryl anhydride (1 equiv) is placed in a two neck round bottom flask and suspended in DI water with stirring. The reaction is purged with argon and heated to reflux, until anhydride is dissolved and the solution becomes translucent. The amine source (1 equiv) is then added all at once and the reaction is refluxed for an additional hour, monitoring precipitation formation. After the hour of reflux, the solution is cooled to room temperature, diluted with DI water, and vacuum filtered washing with water followed by drying in atmosphere to give the ionic organic compounds. Charges on the organic composite mixtures were determined based on ratios illustrated in the titration of **PI** and **PMDA** starting material detailed in SI figures S31-S32.



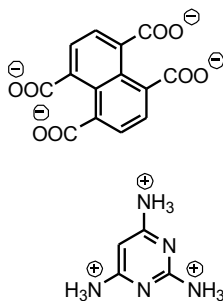
PI & PMDA

PI & PMDA: Added PMDA (0.575 g, 2.636 mmol) and 2,4,6-triaminopyrimidine (0.336 g, 2.685 mmol). Isolated white powder (0.943 g, 2.486 mmol, 94% yield). IR: 3342, 3156, 1659 cm^{-1} . ^1H NMR DMSO- d_6 : δ 8.56(8) (s, 2H), 7.13(0) (d, 9H), 5.05(4) (s, 1H).



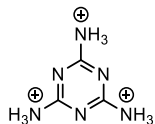
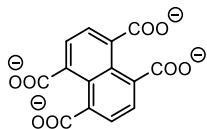
MA & PMDA

MA & PMDA: Added PMDA (1.053 g, 4.828 mmol) and Melamine (0.611 g, 4.845 mmol). Isolated white powder (1.116 g, 2.935 mmol, 61% yield). IR: 3396, 3095, 1671 cm^{-1} . ^1H NMR DMSO- d_6 : δ 8.69(5) (s, 2H), 7.31(5) (s, 9H).



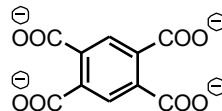
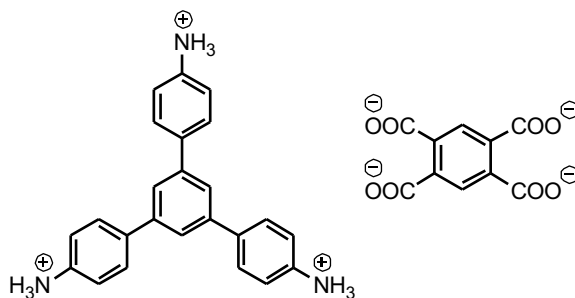
PI & NTDA

PI & NTDA: Added NTDA (0.501 g, 1.868 mmol) and 2,4,6-triaminopyrimidine (0.245 g, 1.958 mmol). Isolated off-white powder (0.569 g, 1.325 mmol, 71% yield). IR: 3333, 3090, 1701 cm^{-1} . ^1H NMR DMSO- d_6 : δ 8.47(0) (d, 2H, $J = 7.5$ Hz), 7.97(0) (d, 2H, $J = 7.5$ Hz), 7.27(4) (s, 3H), 6.98(5) (s, 6H), 4.95(2) (s, 1H).



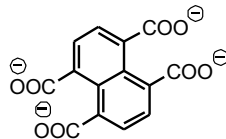
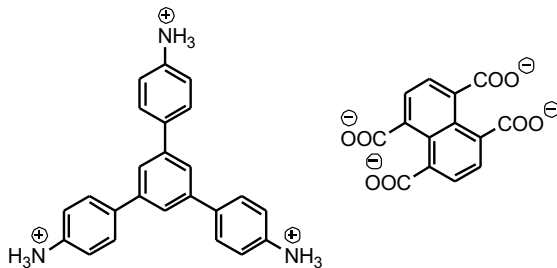
MA & NTDA

MA & NTDA: Added NTDA (0.641 g, 2.390 mmol) and Melamine (0.308 g, 2.442 mmol). Isolated light orange powder (0.766 g, 1.803 mmol, 75% yield). IR: 3382, 3080, 1796 cm^{-1} . ^1H NMR DMSO- d_6 : δ 8.52(4) (d, 2H, $J = 7.5$ Hz), 8.09(7) (d, 2H, $J = 7.5$ Hz), 6.42(7) (s, 9H).



TAPB & PMDA

TAPB & PMDA: Added PMDA (0.185 g, 0.848 mmol) and TAPB (0.293 g, 0.834 mmol). Isolated lime green powder (0.500 g, 0.826 mmol, 99% yield). IR: 2972, 2598, 1548, 1512 cm^{-1} . ^1H NMR DMSO- d_6 : δ 8.04(5) (s, 2H), 7.51(8) (d, 9H, $J = 8.0$ Hz), 6.73(2) (d, 6H, $J = 8.9$ Hz).



TAPB & NTDA

TAPB & NTDA: Added NTDA (0.049 g, 0.183 mmol) and TAPB (0.059 g, 0.168 mmol). Isolated tan powder (0.094 g, 0.155 mmol, 92% yield). IR: 3435, 3355, 1768 cm^{-1} . ^1H NMR DMSO- d_6 : δ 8.58(7) (d, 2H, $J = 7.9$ Hz), 8.21(9) (d, 2H, $J = 8.4$ Hz), 7.47(9) (d, 9H, $J = 8.0$ Hz), 6.67(1) (d, 6H, $J = 8.9$ Hz), 5.27(0) (s, 9H).

General Procedures for COF Polymerization

Amine to anhydride ratios were reacted in separate reactions containing both (1.2 : 1) and (1 : 1.5) mixtures. Both ratios produced matching FT-IR and PXRD data for multiple polymers. Characterization of the COFs both before and after oven drying was performed to ensure no structural changes as a result of the heating. (see Adv. Mater. 2020, doi.org/10.1002/adma.201905776).

Condition A: anhydride moiety was added to a 5 mL glass ampule followed by amine source and NMP (4 mL). The vessel containing all reagents and solvent was sealed and heated via box furnace at 167 °C for 3 days. After three days of reacting, the vessel was taken out of the furnace, opened, and diluted with DI water (20 mL). The flaky crystals were purified through Soxhlet extraction of water (24 hours) followed by ethanol (24 hours). The resulting precipitate was collected, and oven dried at 100 °C for 24 hours.

Condition A, using salt starting material: anhydride/amine organic salt was added to a 5 mL glass ampule followed by NMP (4 mL). The vessel containing all reagents and solvent was sealed and heated via box furnace at 167 °C for 3 days. After three days of reacting, the vessel was taken out of the furnace, opened, and diluted with DI water (20 mL). The flaky crystals were purified through Soxhlet extraction of water (24 hours) followed by ethanol (24 hours). The resulting precipitate was collected, and oven dried at 100 °C for 24 hours.

Condition B: anhydride moiety was added to a teflon MW reaction vessel followed by amine source and NMP (4 mL). The vessel containing all reagents and solvent was capped and heated with stirring via microwave irradiation at 200 °C for 2 hours (15 minute ramp time). After two hours of reacting and cooling for 30 minutes post reaction completion, the vessel was taken out of the MW, opened, and diluted with DI water. The flaky material was purified through Soxhlet extraction of water (24 hours) followed by ethanol (24 hours). The precipitate was collected, and oven dried at 100 °C for 24h.

Condition B, using salt starting material: anhydride/amine organic salt was added to a teflon MW reaction vessel followed by NMP (4 mL). The vessel containing all reagents and solvent was capped and heated with stirring via microwave irradiation at 200 °C for 2 hours (15 minute ramp time). After two hours of reacting and cooling for 30 minutes post reaction completion, the vessel was taken out of the MW, opened, and diluted with DI water. The flaky material was purified through Soxhlet extraction of water (24 hours) followed by ethanol (24 hours). The resulting precipitate was collected, and oven dried at 100 °C for 24 hours.

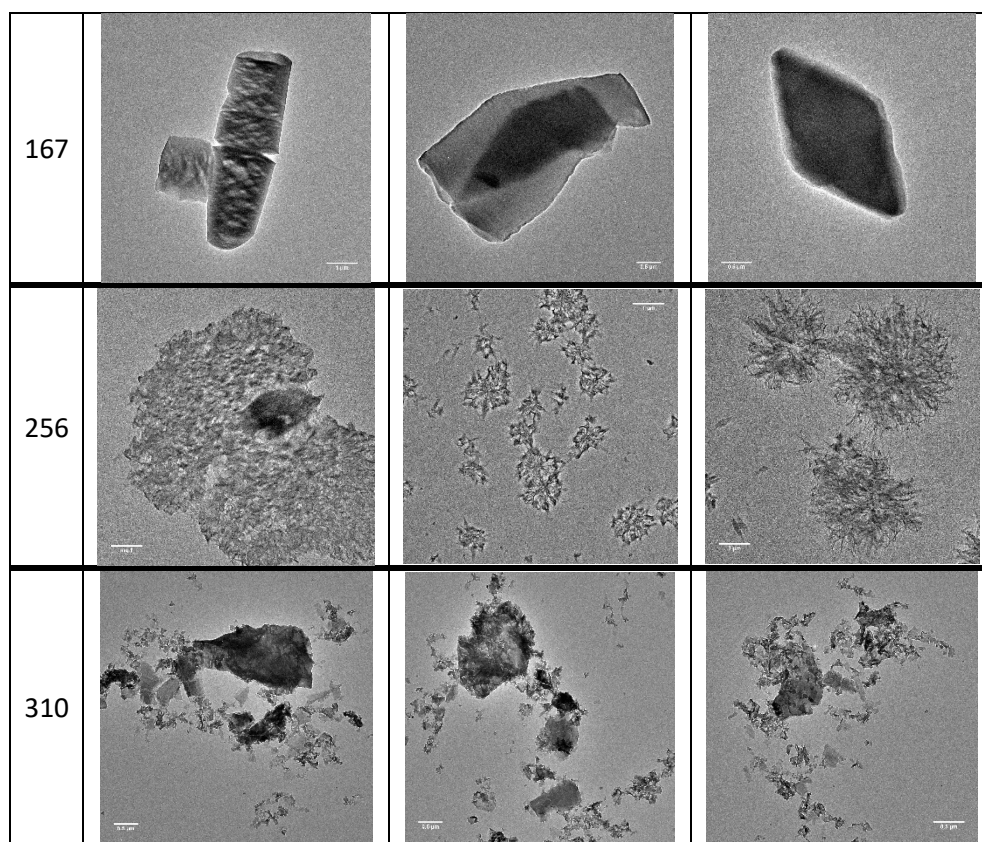
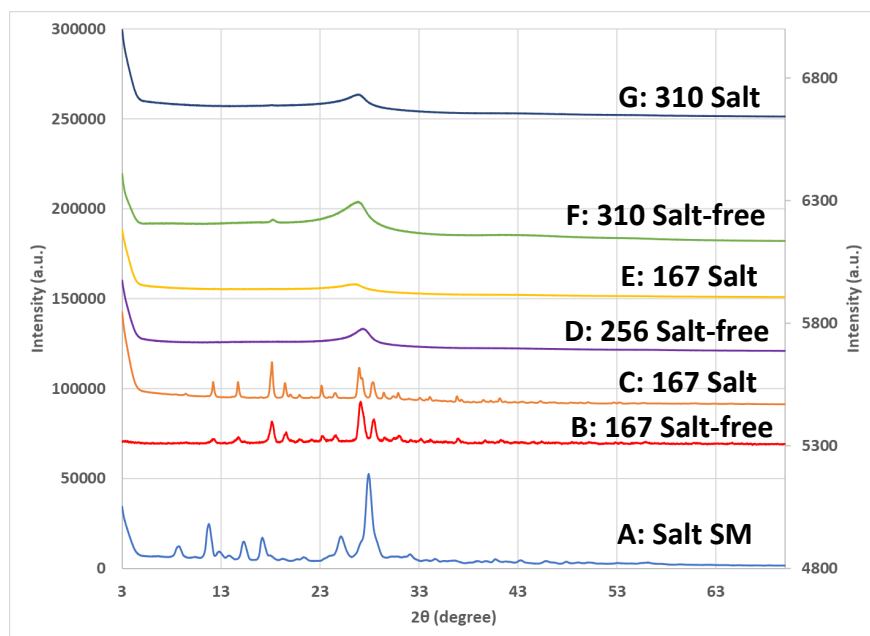


Figure S1. PXRD data of COF **MA/PMDA** (top) comparing over reaction temperatures. (A) Organic salt starting material, (B) salt free reaction at 167 °C, (C) salt reaction at 167 °C, (D) salt free reaction at 256 °C, (E) salt reaction at 256 °C, (F) salt free reaction at 310 °C, (G) salt reaction at 310 °C. TEM images **MA/PMDA** COF (bottom) (using organic salt SM) comparing over reaction temperatures at 167 °C, 256 °C, and 310 °C.

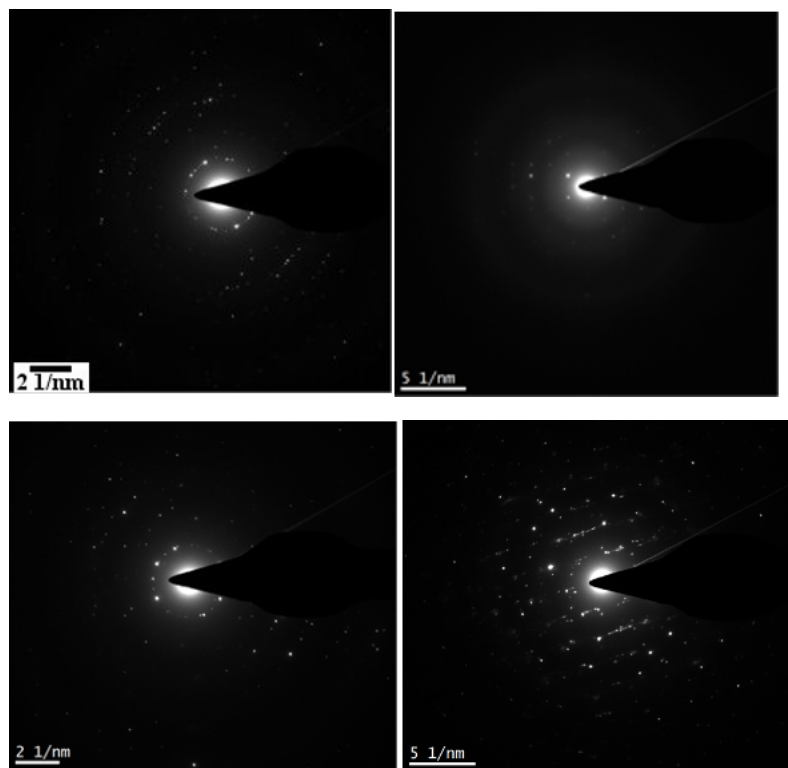


Figure S1b. Top: Electron diffraction of C and D in Figure 2 of manuscript. Bottom: Electron diffraction of B and D in Figure 4 of manuscript

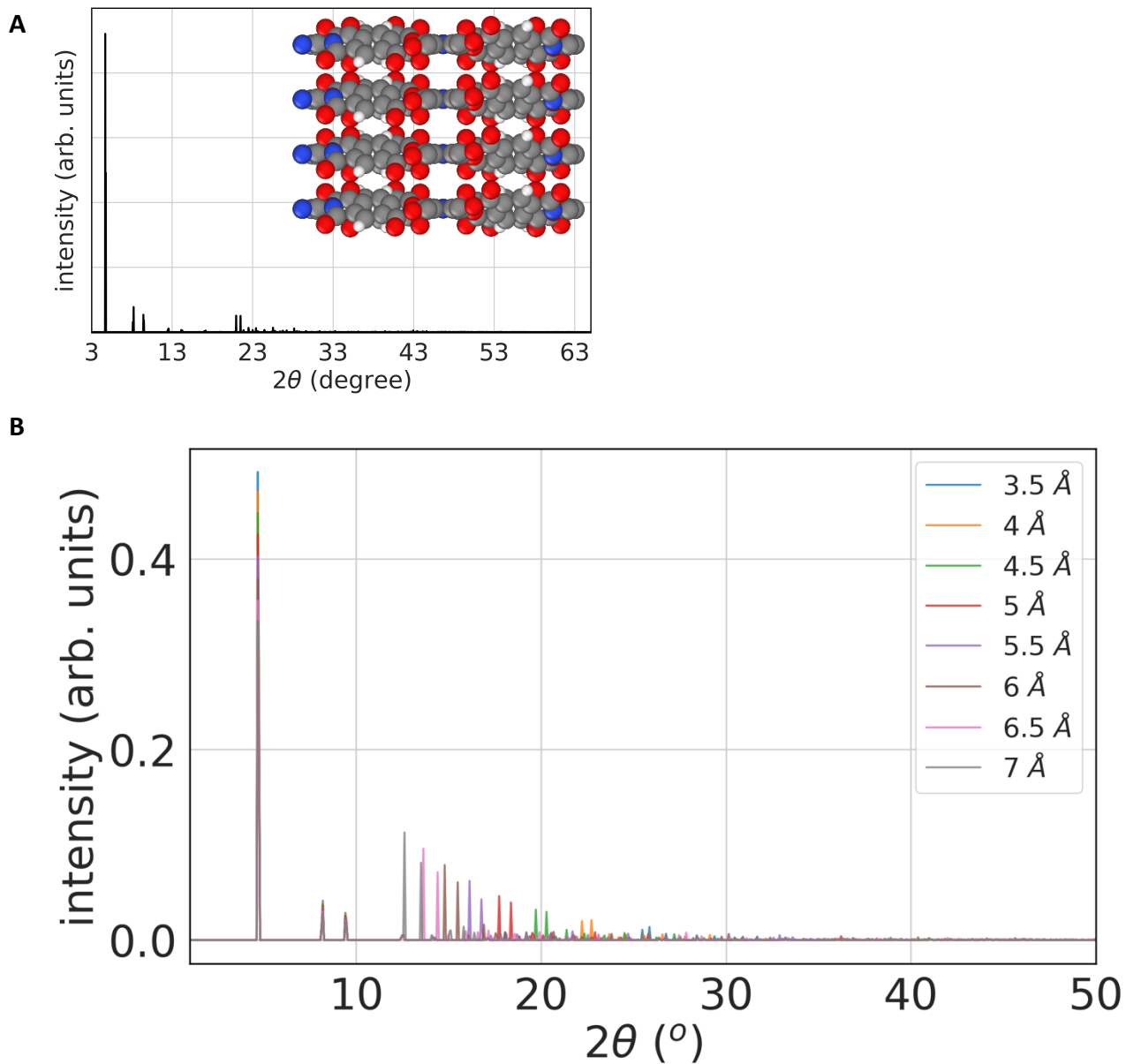


Figure S2. Simulated PXRD of COF **MA/PMDA** (A) with AA stacking and (B) with varying interlayer distances; illustrating that the first three (main) peaks remain in the same location, but the two larger right peaks ($> 10^\circ$) shift right and become comparatively (to the other peaks) less intense as the distance between the layers shrinks.

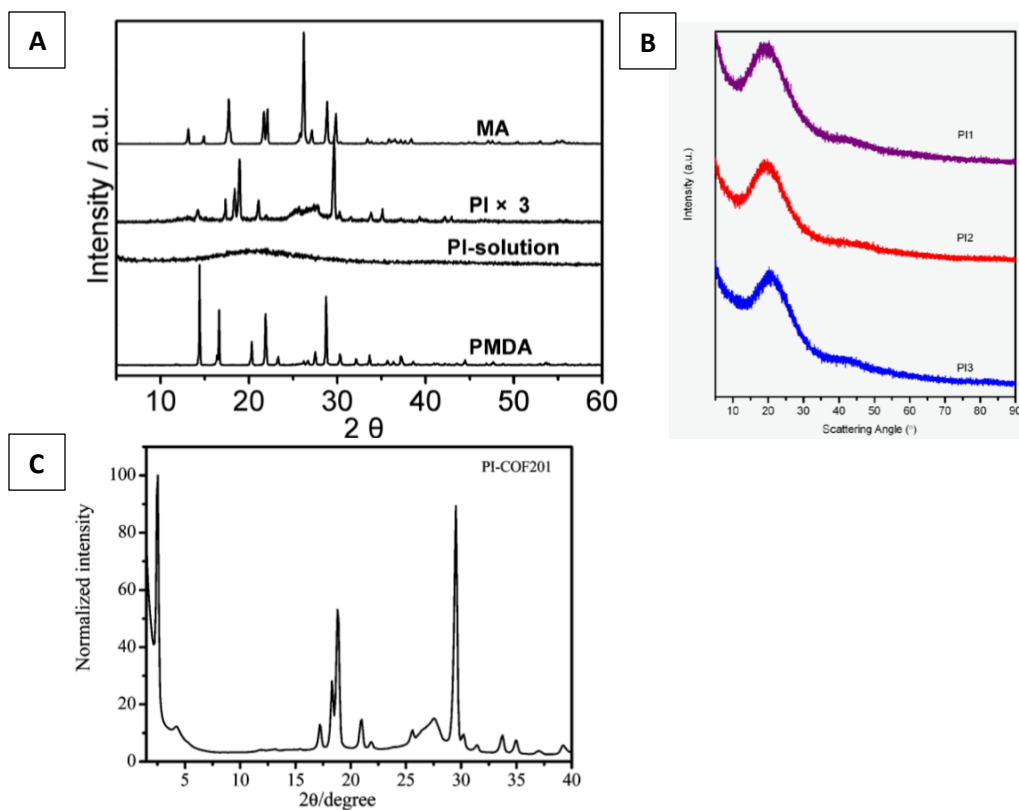


Figure S3. PXRD data of COF MA/PMDA from previous reports (A – C).

A: *J Mater Chem* **2012**, 22 (31), 15519. <https://doi.org/10.1039/c2jm32595k>.

B: *Chem Commun* **2011**, 47 (27), 7704. <https://doi.org/10.1039/c1cc11466b>.

C: *New J Chem* **2017**, 41 (23), 14272–14278. <https://doi.org/10.1039/C7NJ02134H>.

BET analysis: N₂ isotherms

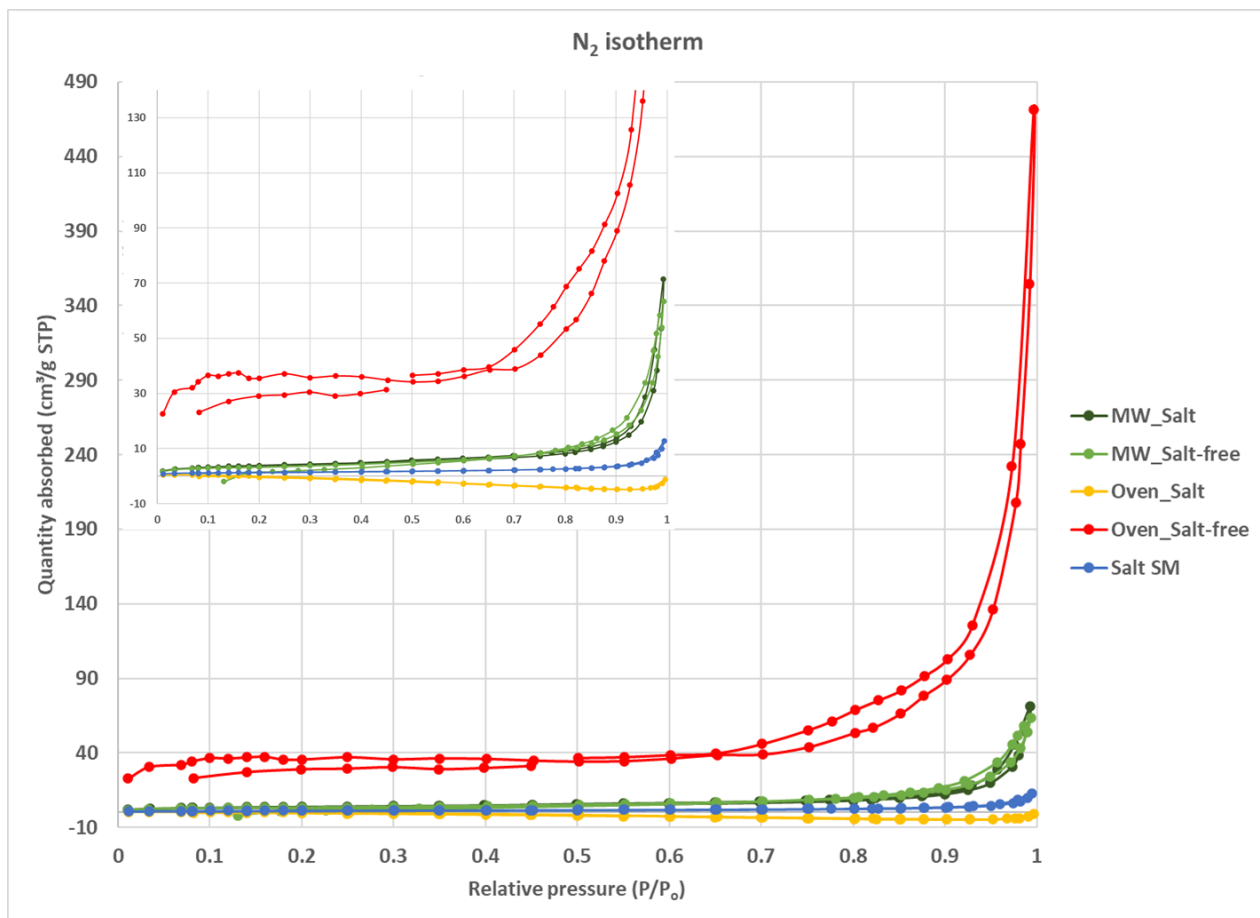


Figure S4. COF MA/PMDA isotherm plots. Inset graph of enhanced y-axis.

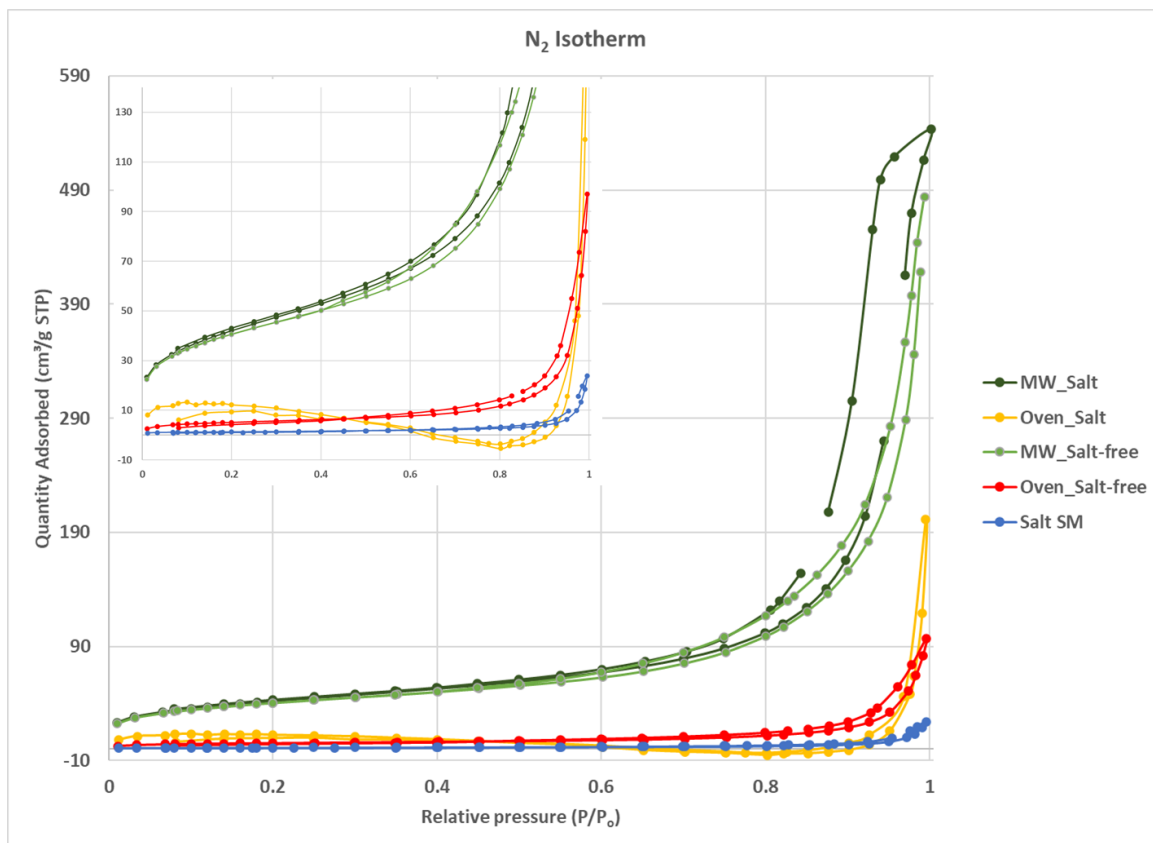


Figure S5. COF MA/NTDA isotherm plots. Inset graph of enhanced y-axis.

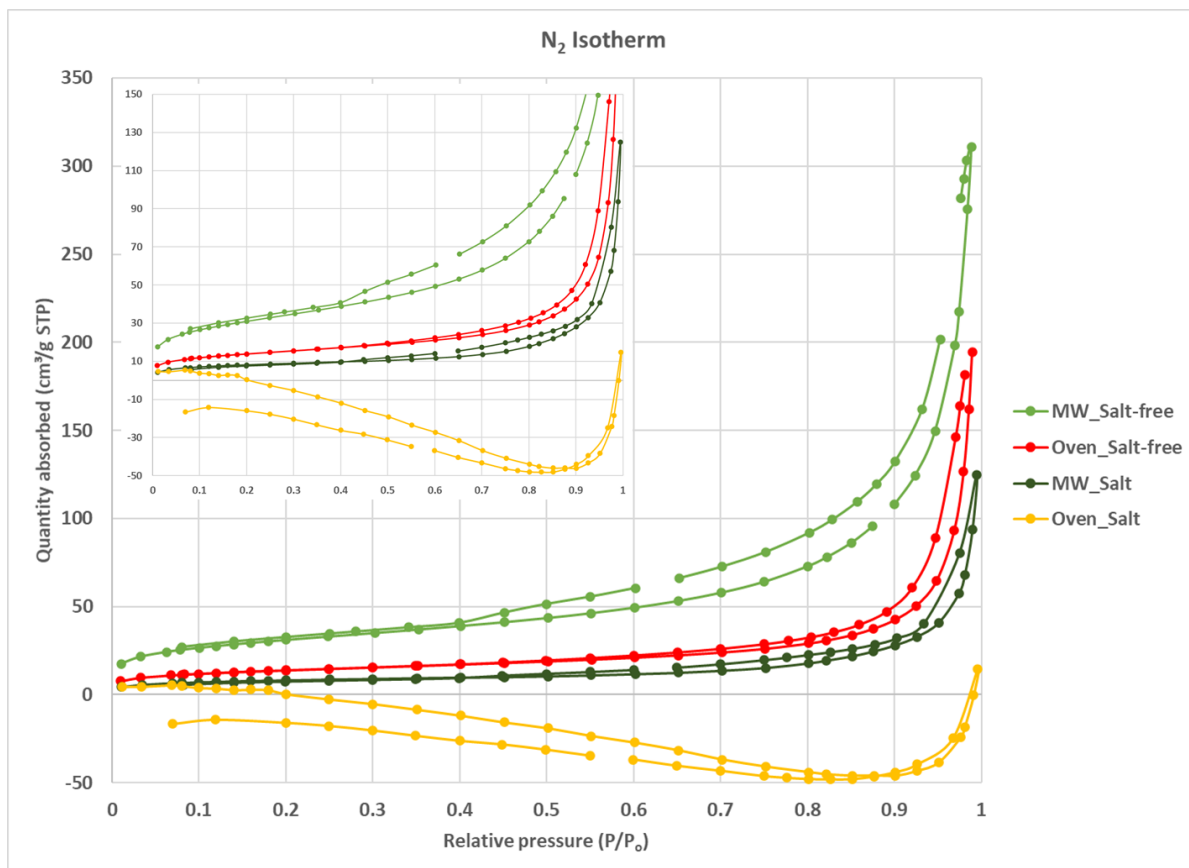
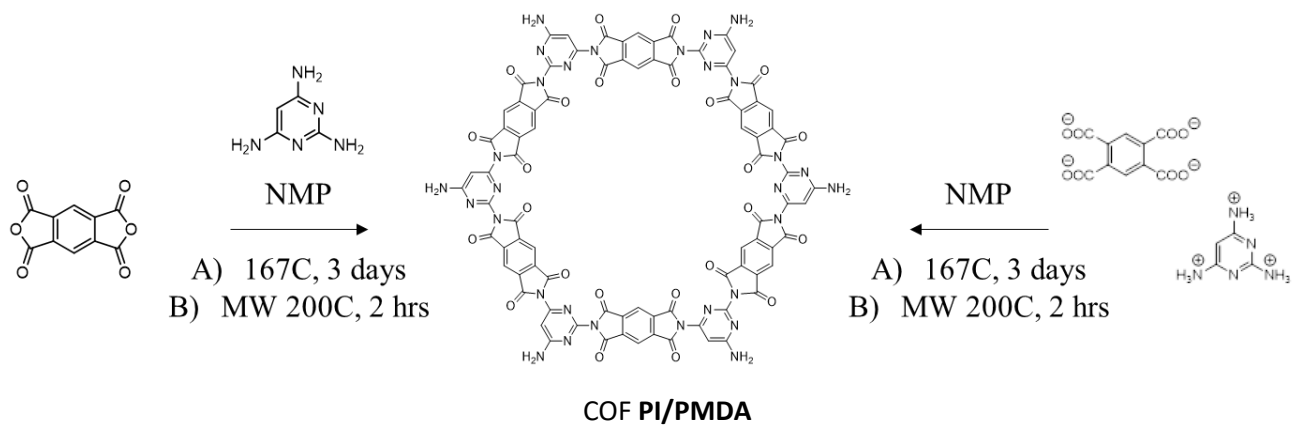


Figure S6. COF PT/NTDA isotherm plots. Inset graph of enhanced y-axis.



FT-IR

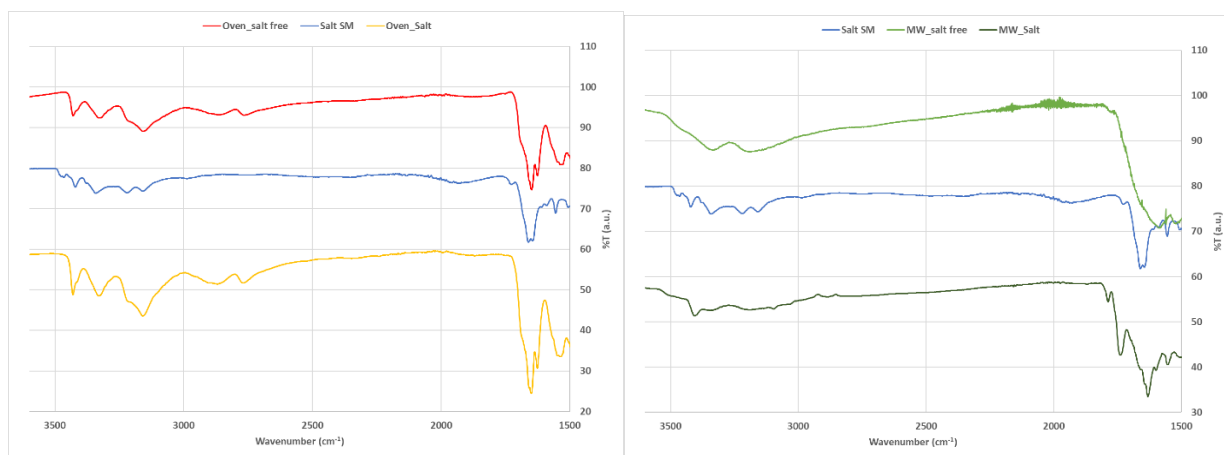


Figure S7. FT-IR of COF PI/PMDA reactions compared to organic salt precursor.

PXRD

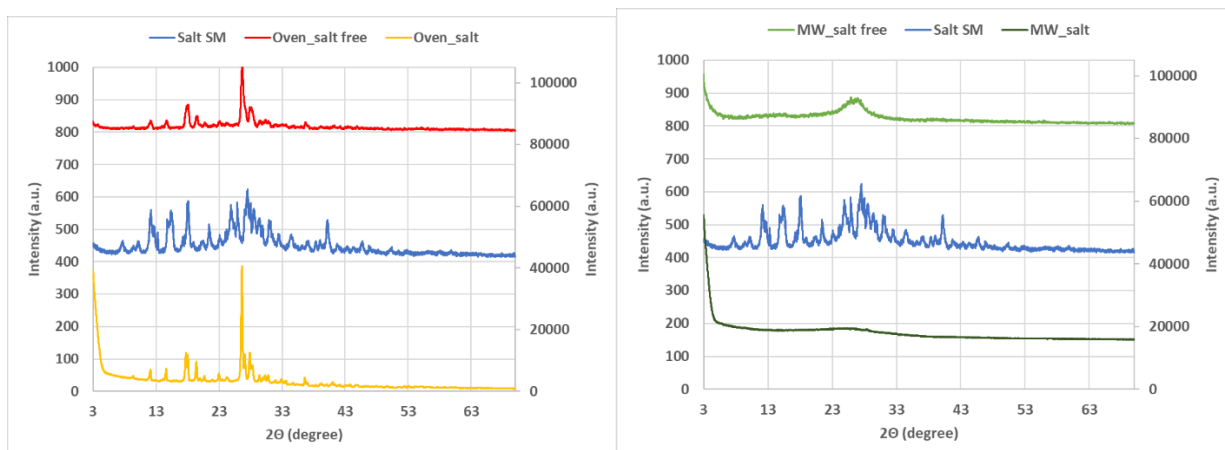


Figure S8. COF PI/PMDA reactions and starting material PXRD.

TEM

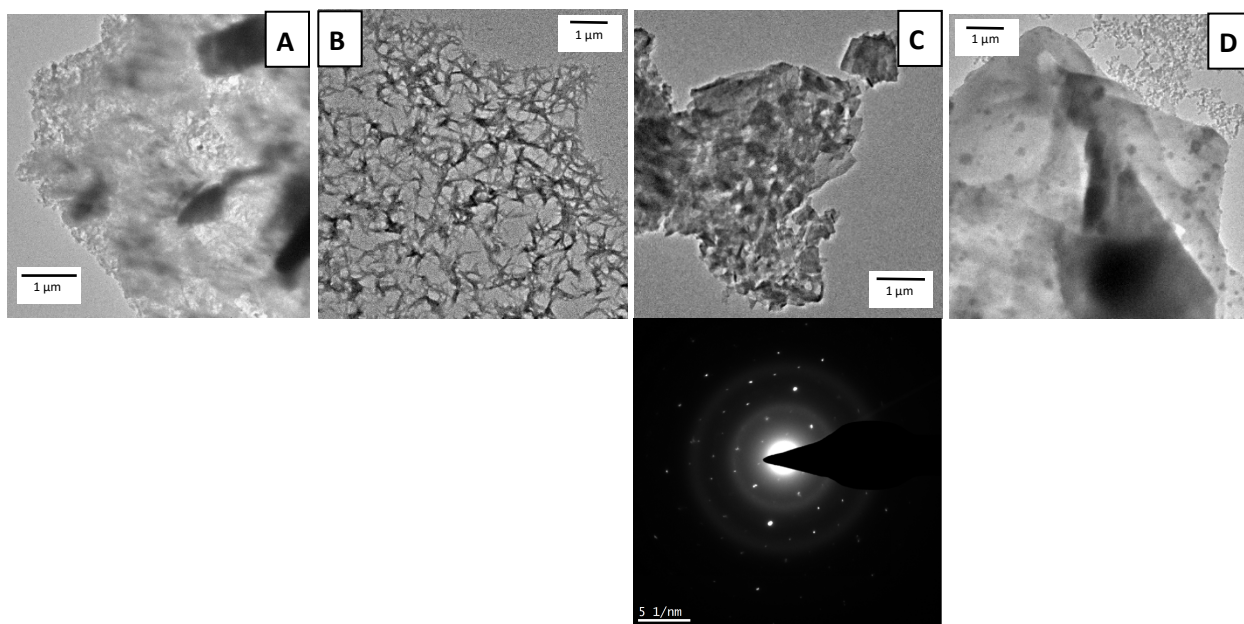
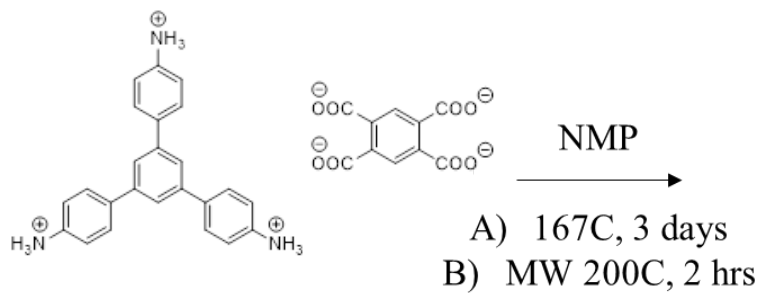


Figure S9. TEM images (top) and corresponding electron diffraction of COF PI/PMDA from reaction of PMDA and pyrimidine precursors as both neutral starting materials and salts. (A) furnace reaction of salt precursors, (B) furnace reaction of neutral precursors, (C) microwave reaction of salt precursors, (D) microwave reaction neutral precursors.



COF TAPB/PMDA

FT-IR

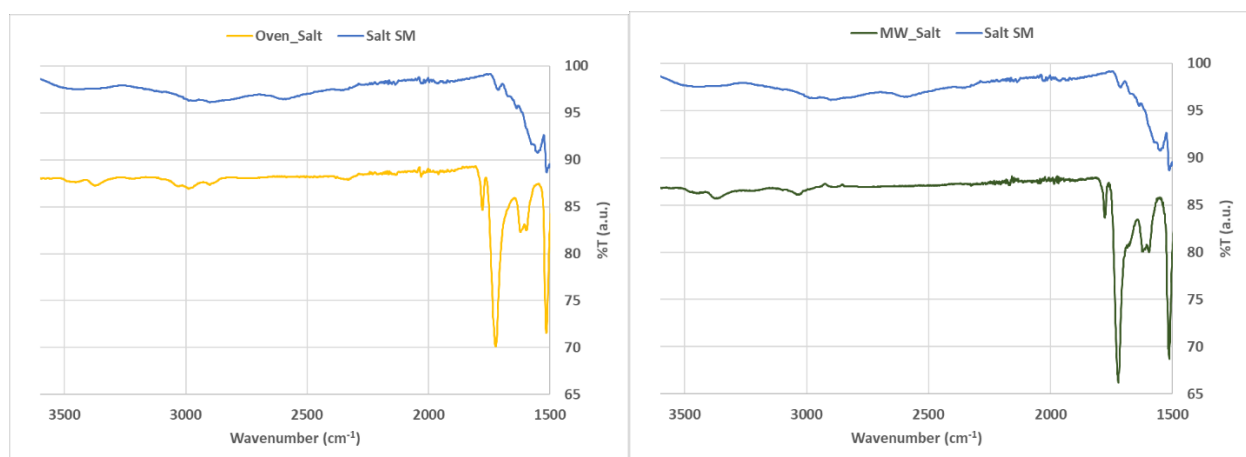


Figure S10. FT-IR of COF TAPB/PMDA reactions and organic salt precursor.

PXRD

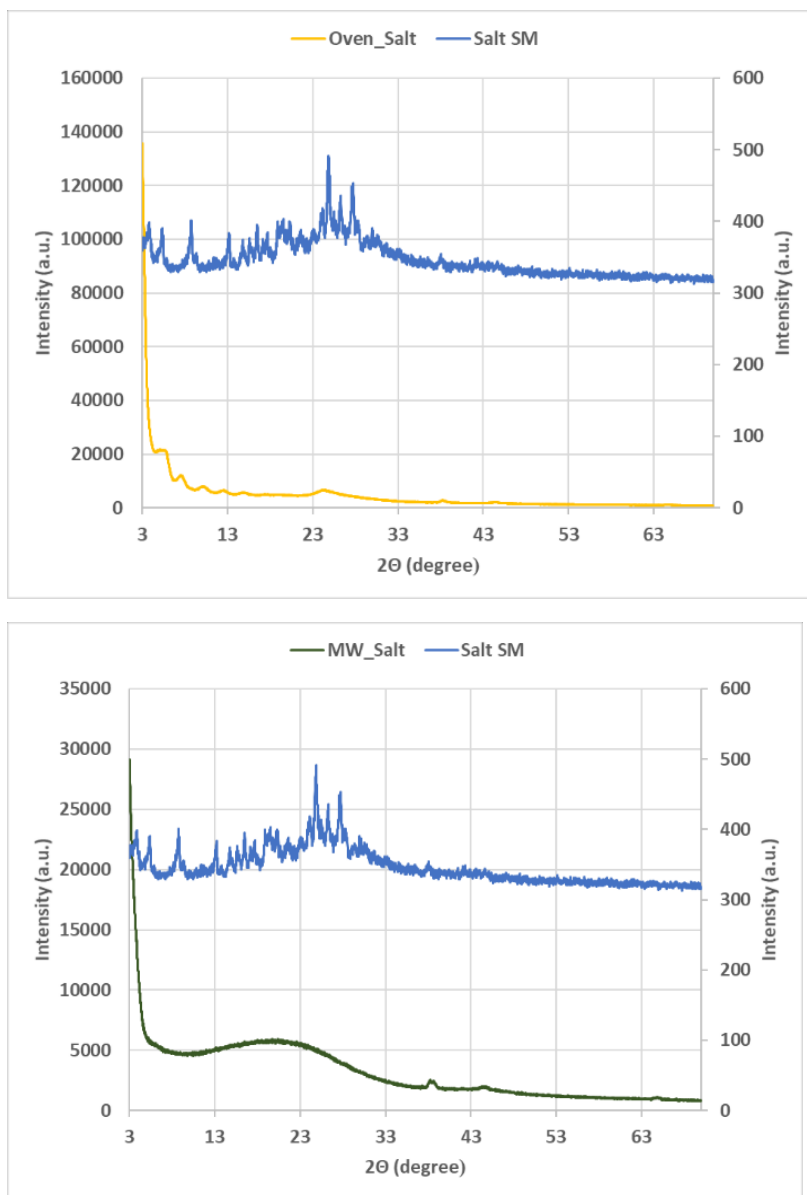


Figure S11. COF TAPB/PMDA reactions and starting material PXRD.

TEM

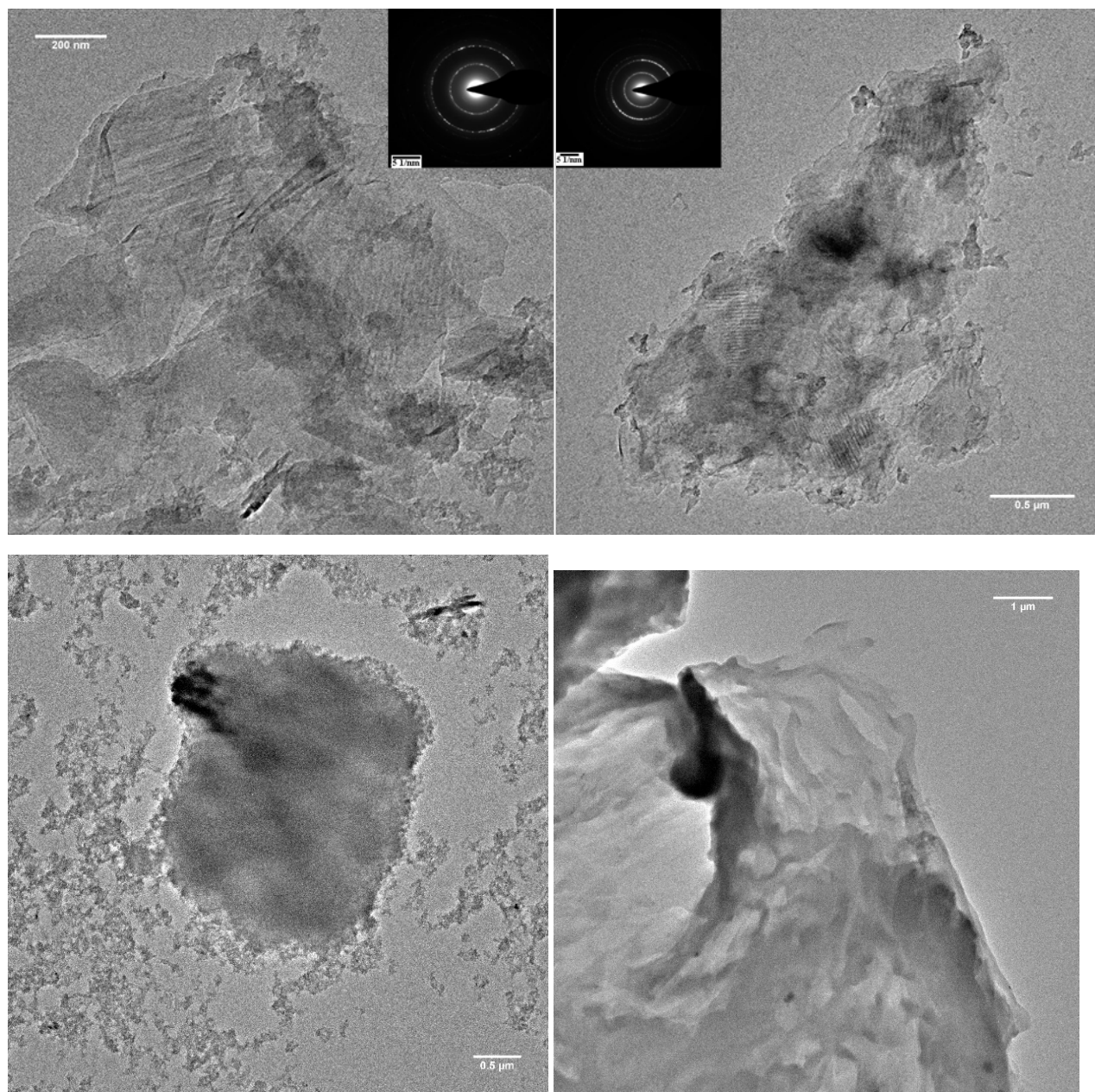
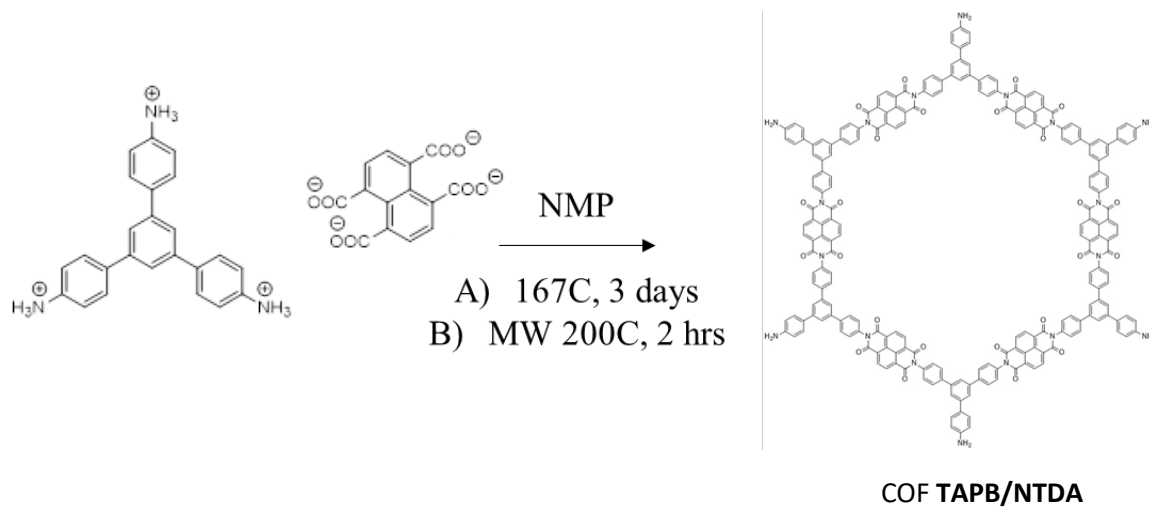


Figure S12. BF-TEM images of COF TAPB/PMDA (using organic salt SM) dispersed in DMF synthesized via box furnace (left) and MW (right) conditions.



FT-IR

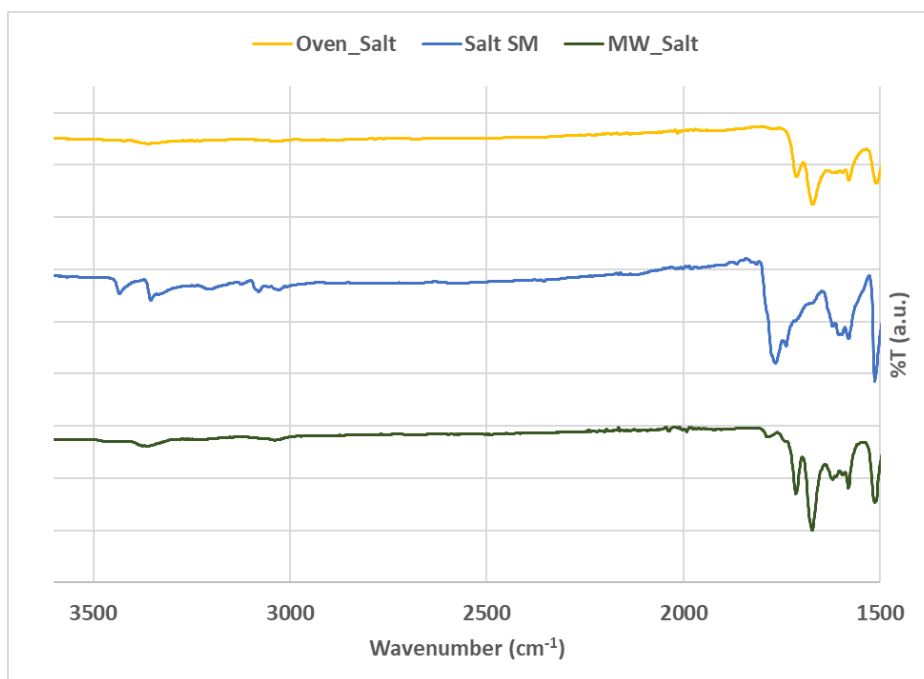


Figure S13. FT-IR of COF TAPB/NTDA reactions (using salt SM) and organic salt precursor.

PXRD

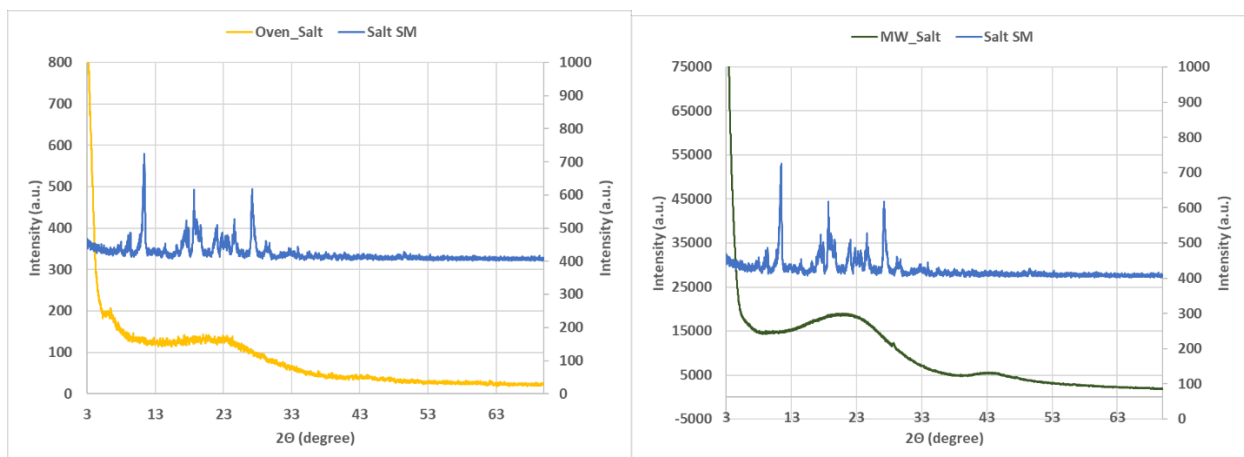


Figure S14. COF TAPB/NTDA synthesized via furnace and starting material PXRD.

TEM

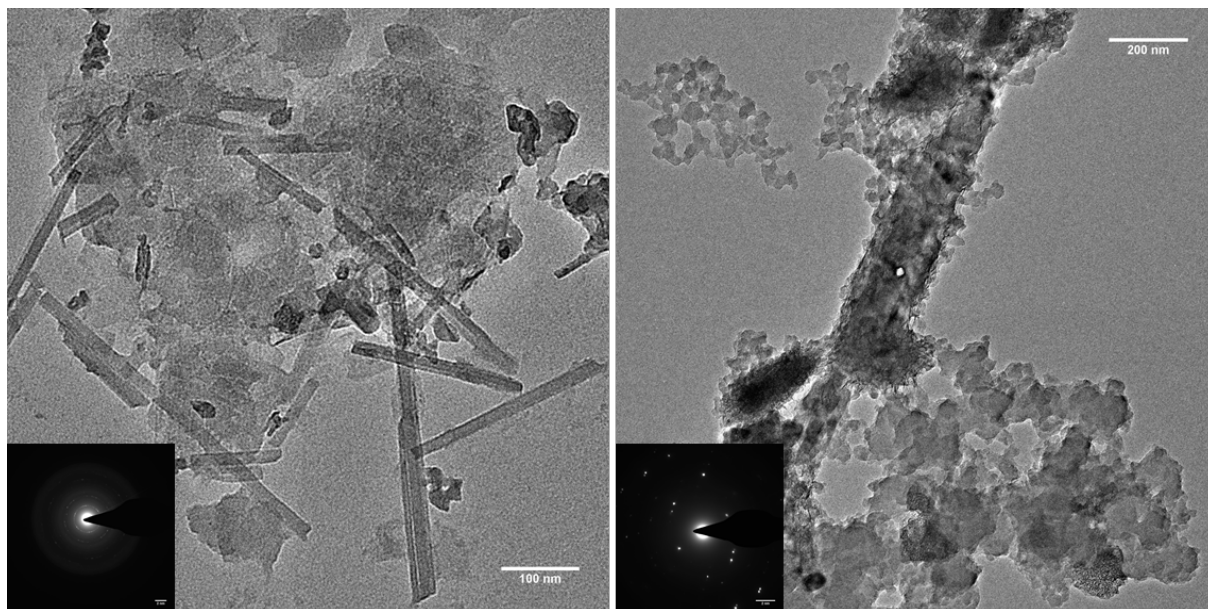


Figure S15. BF-TEM images of COF TAPB/NTDA (using organic salt SM) dispersed in DMF synthesized via box furnace (left) and MW (right) conditions

Starting Material TEM

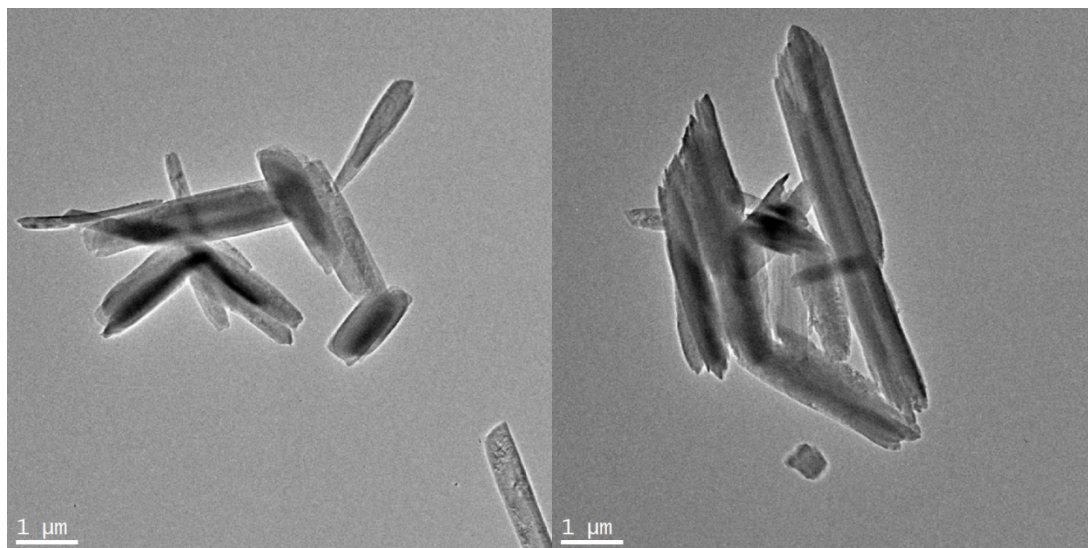


Figure S16. TEM COF **MA/PMDA** organic salt starting material.

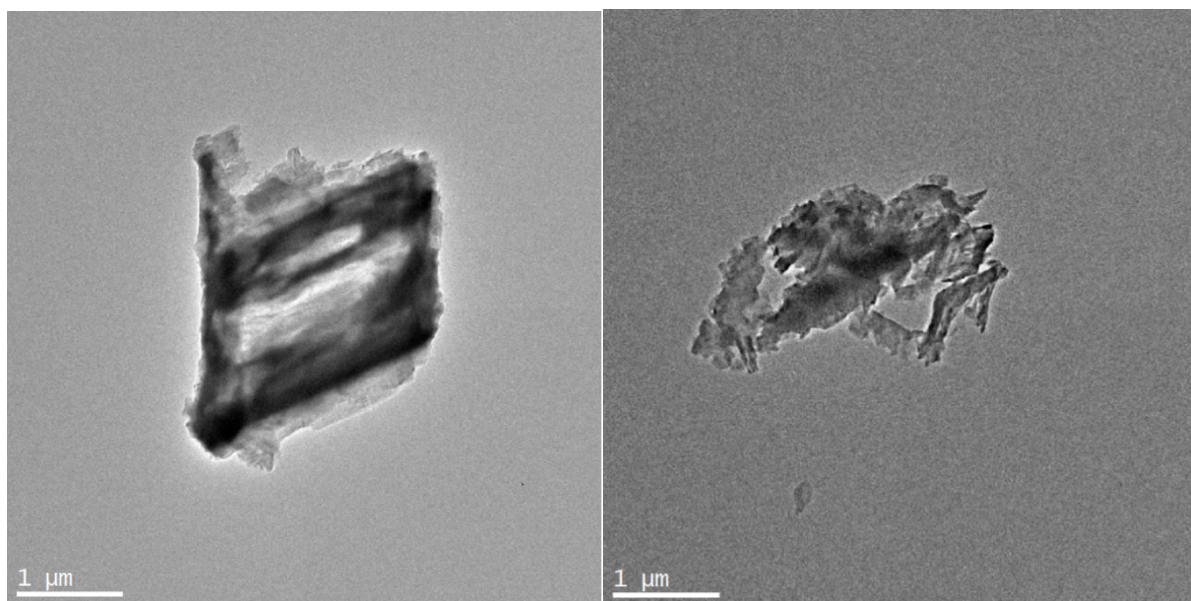


Figure S17. TEM COF **MA/NTDA** organic salt starting material.

Characterization Data Model Studies

NMR

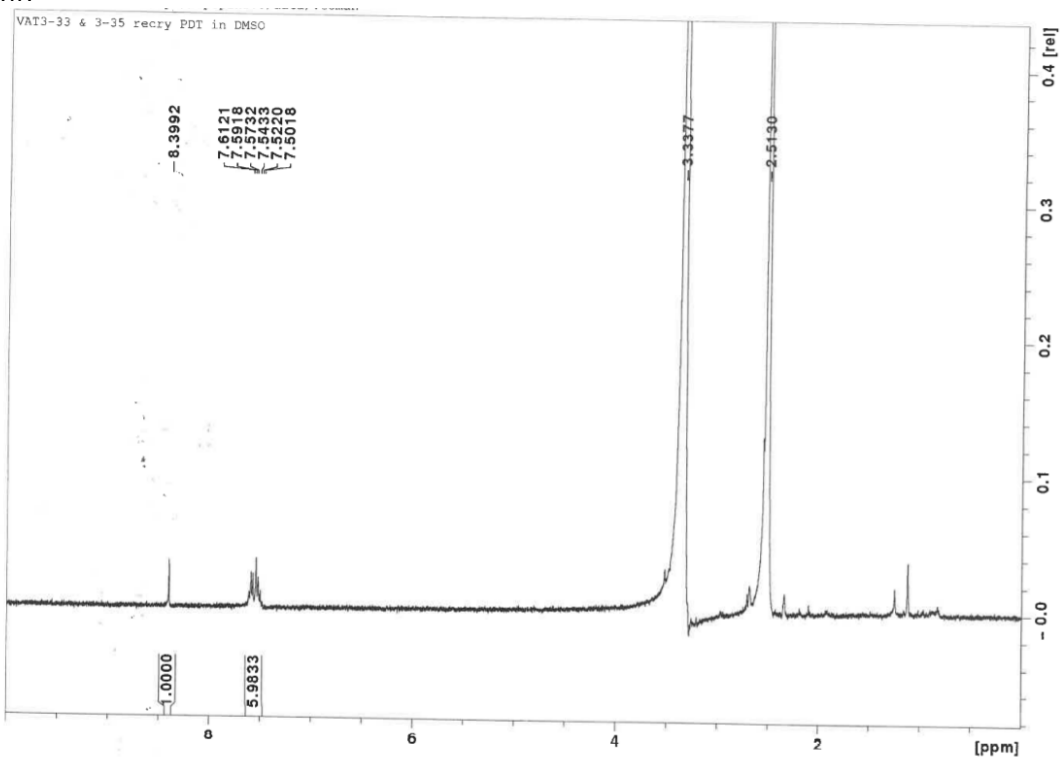


Figure S18. ^1H NMR of **1** in DMSO-d_6

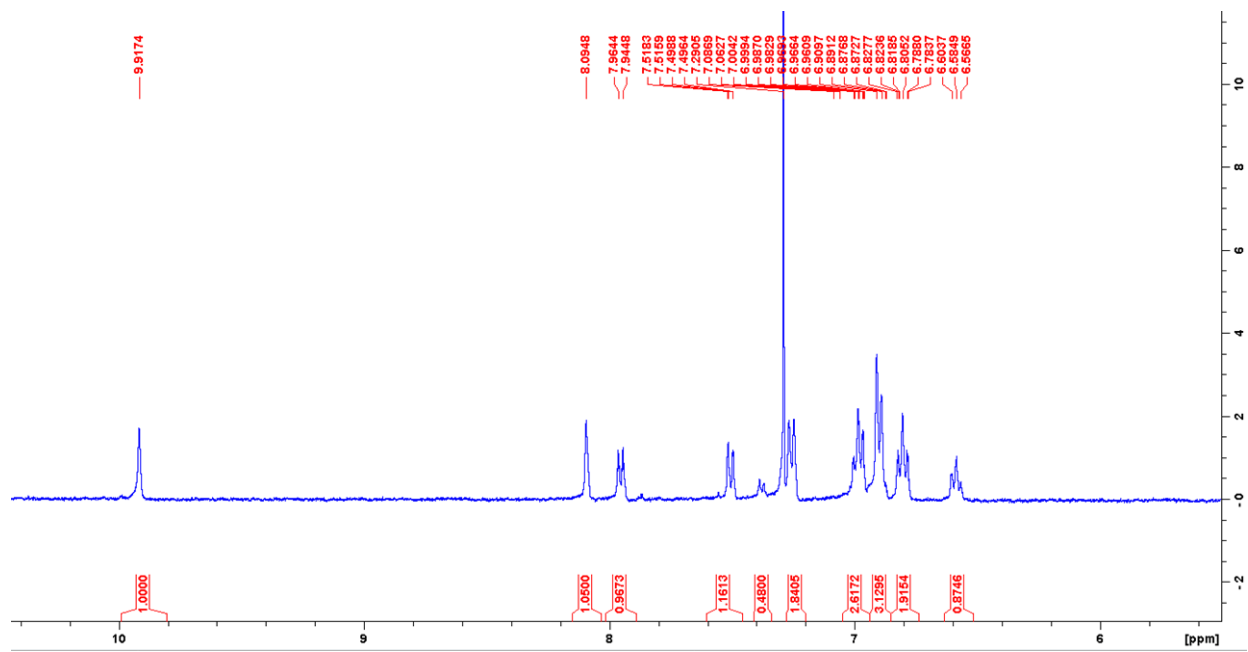


Figure S19. ^1H NMR of **2** in CDCl_3 . Range 0 – 5.5 ppm omitted for clarity.

FT-IR

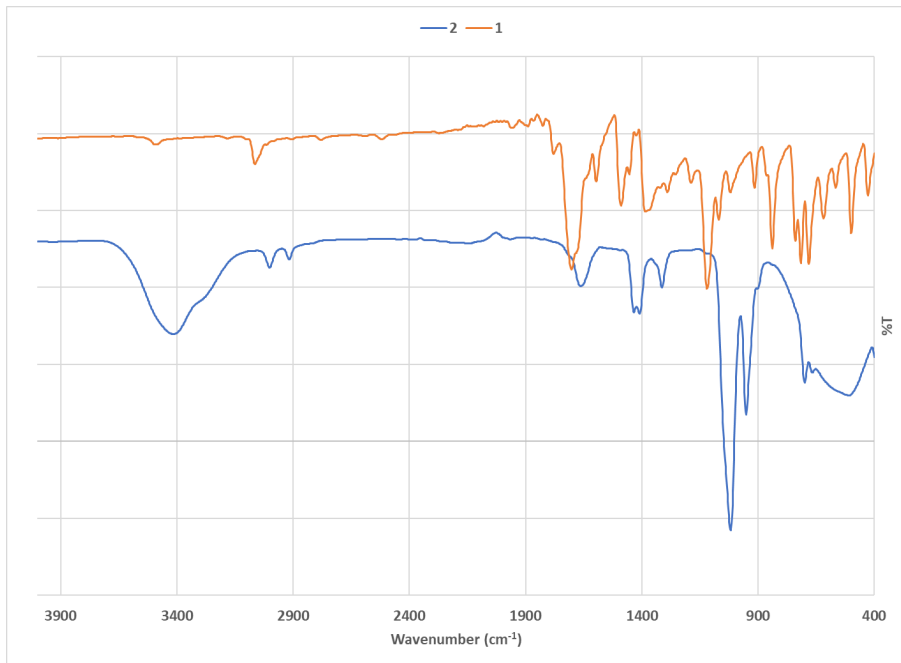


Figure S20. FT-IR of compounds **1** and **2**

LCMS Data

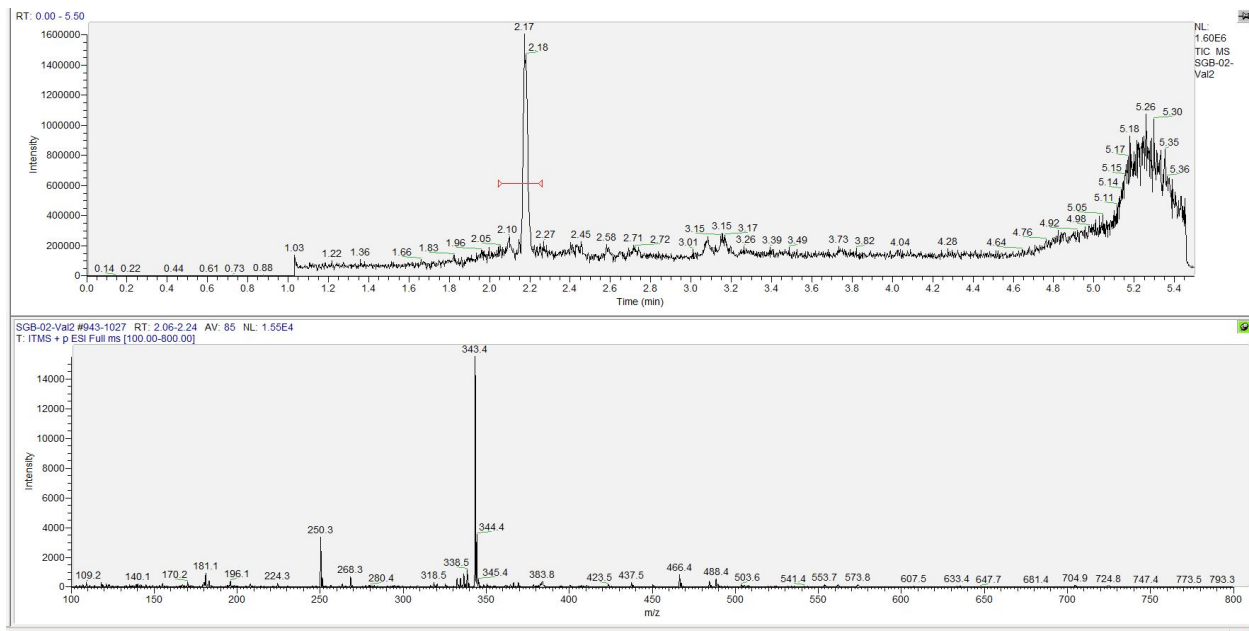


Figure S21. LCMS of compound **2**.

MALDI-TOF MS

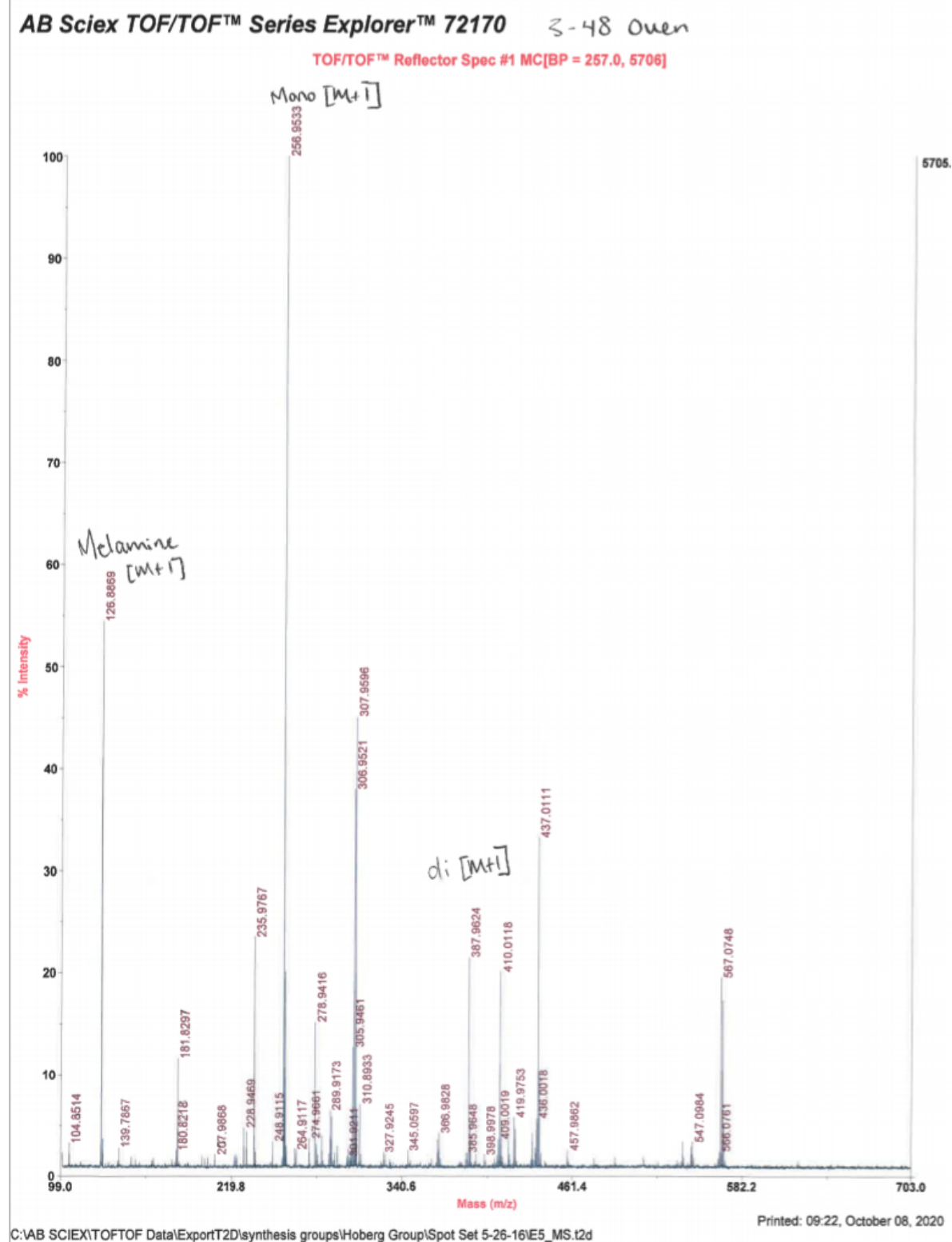
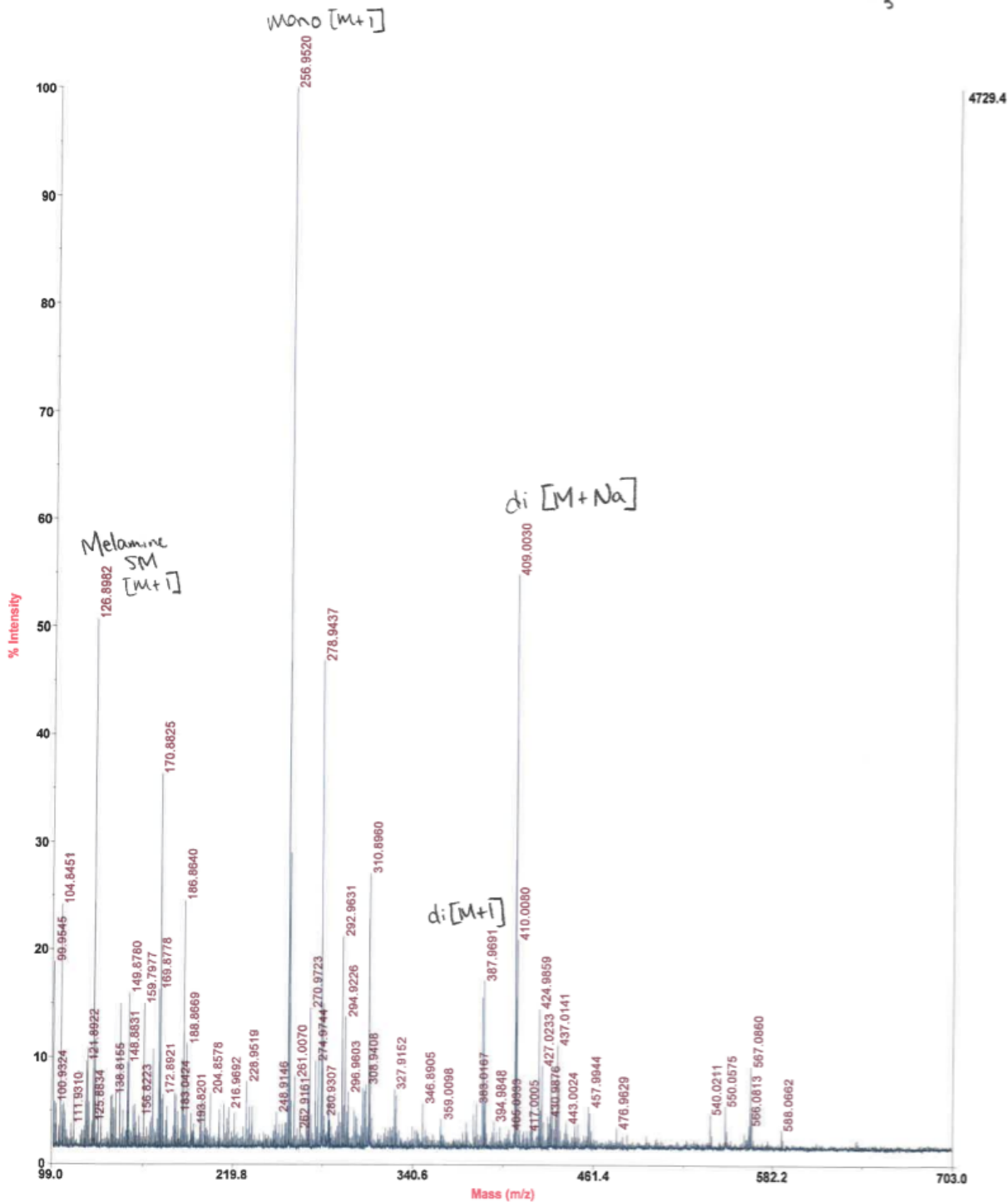


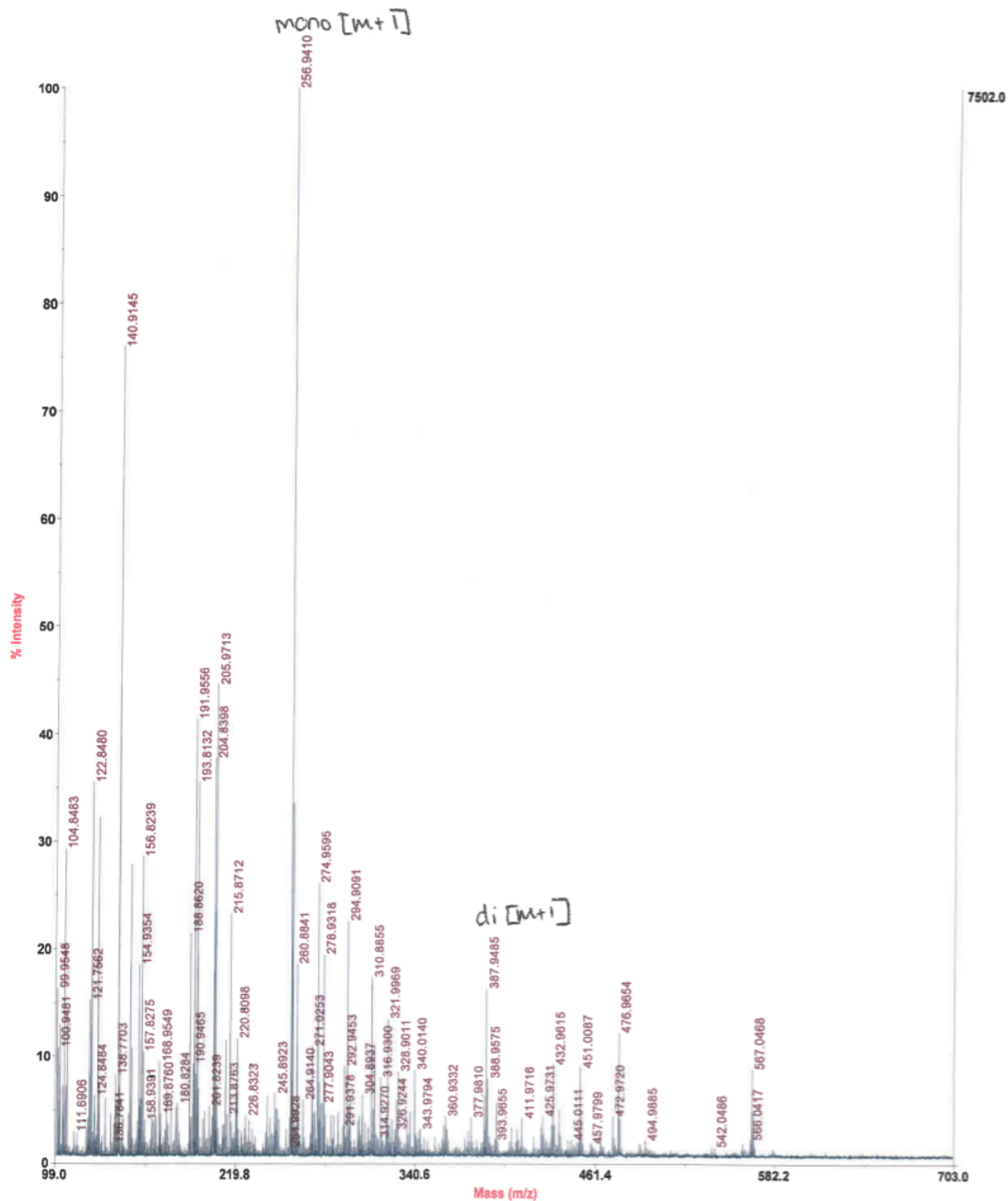
Figure S22. MALDI-TOF MS full spectrum of 3a-3c synthesized in the furnace.



C:\AB SCIEX\TOF\TOF Data\Export\2D\synthesis groups\Hoberg Group\Spot Set 5-26-16\IC7_MS.12d

Printed: 13:28, October 07, 2020

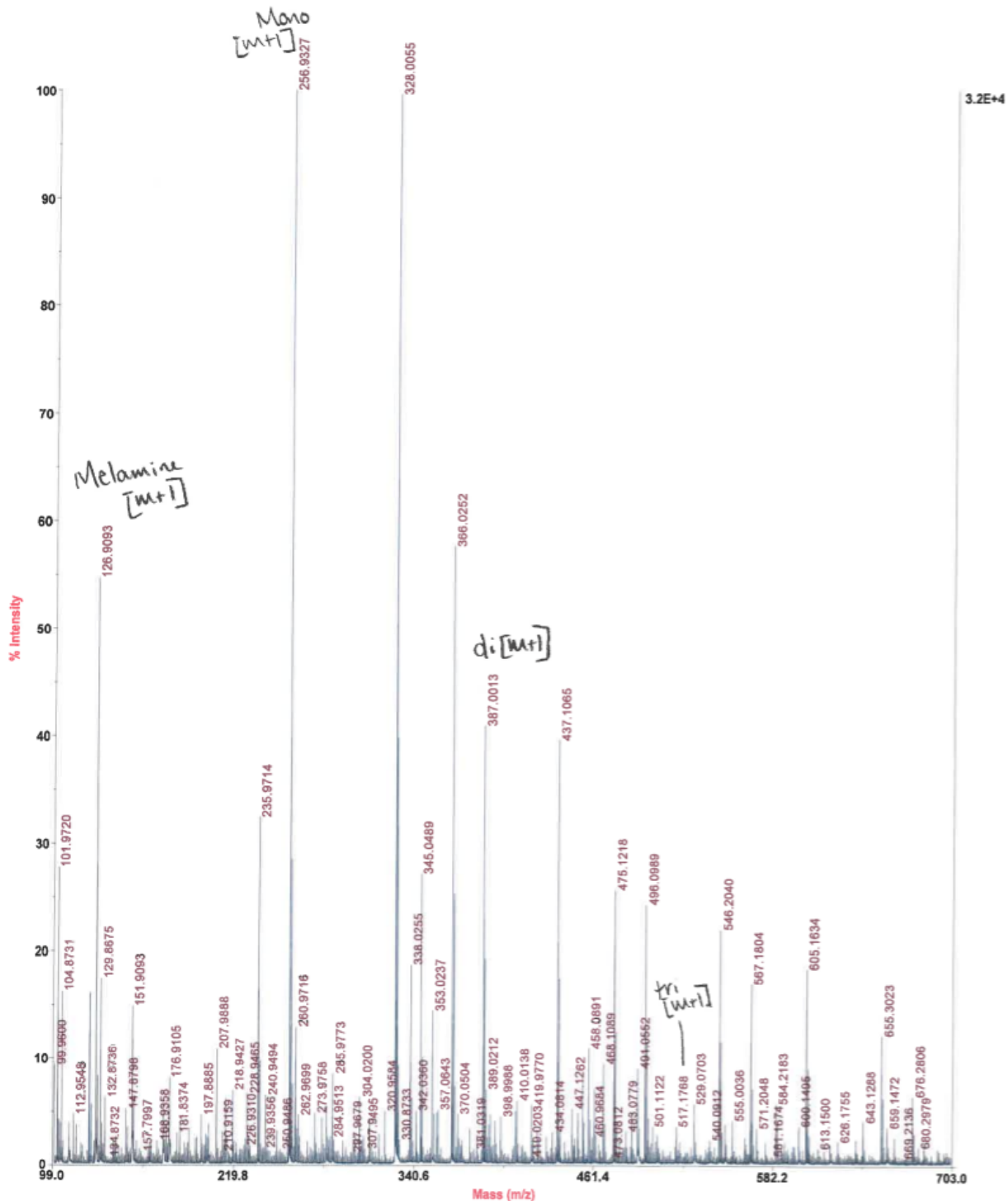
Figure S23. MALDI-TOF MS full spectrum of 3a-3c synthesized in the MW.



C:\AB SCIEX\TOF\TOF Data\Export\T2D\synthesis groups\Hoberg Group\Spot Set 5-26-16\B9_MS.t2d

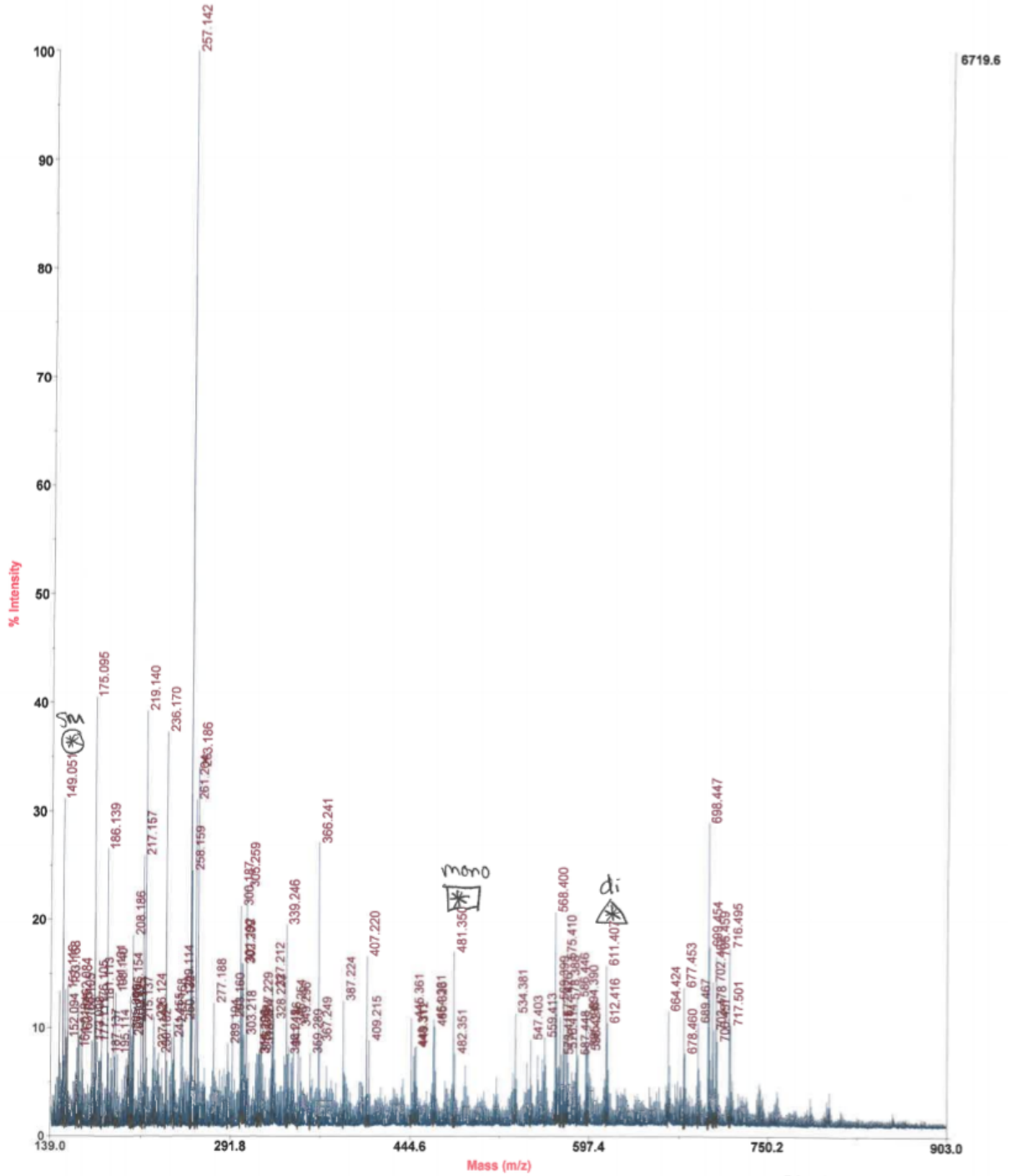
Printed: 13:30, October 07, 2020

Figure S24. MALDI-TOF MS full spectrum of 3a-3c synthesized in the MW.



C:\AB SCIEX\TOFTOF Data\ExportT2D\synthesis groups\Hoberg Group\Spot Set 5-26-16\E7_MS.t2d

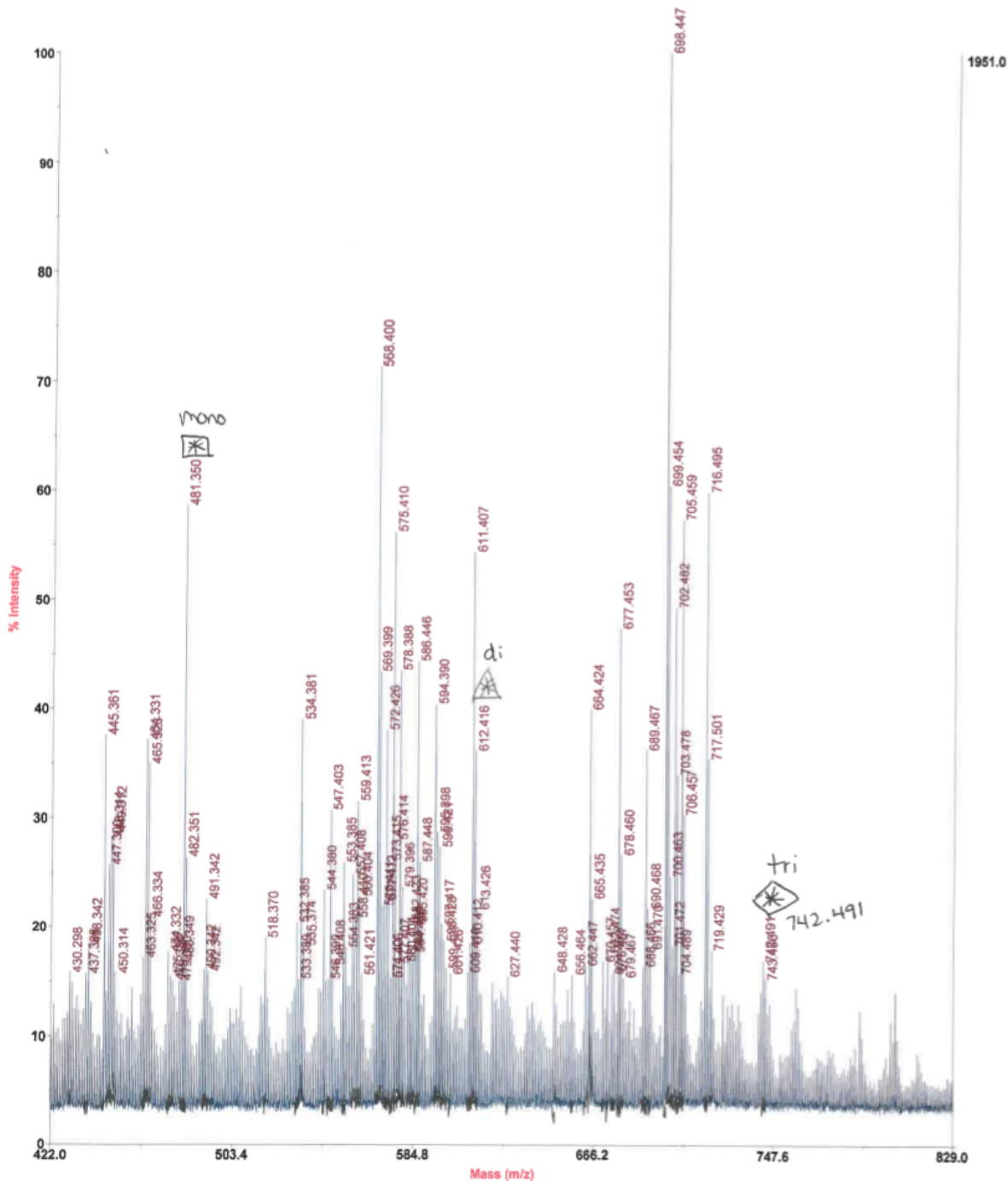
Figure S25. MALDI-TOF MS full spectrum of 3a-3c synthesized in the MW.



C:\AB SCIEX\TOF\TOF Data\Export\T2D\synthesis groups\Hoberg Group\Spot Set 5-26-16\F5_MS.T2d

Printed: 09:56, October 20, 2020

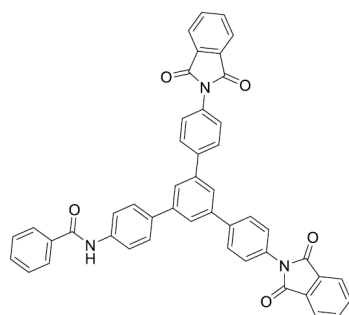
Figure S26. MALDI-TOF MS full spectrum of 4a-4c synthesized in the MW.



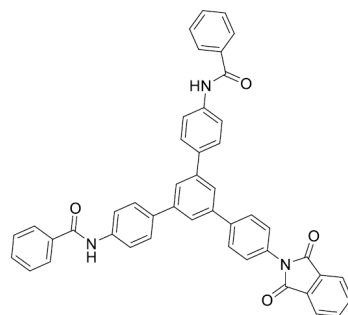
C:\AB SCIEX\TOF\TOF Data\ExportT2D\synthesis groups\Hoberg Group\Spot Set 5-26-16\F5_MS.t2d

Printed: 09:56, October 20, 2020

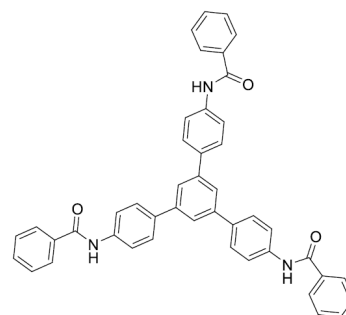
Figure S27. MALDI-TOF MS of 4a-4c synthesized in the MW (139 m/z – 420 m/z omitted for clarity).



Molecular Weight: 715.77

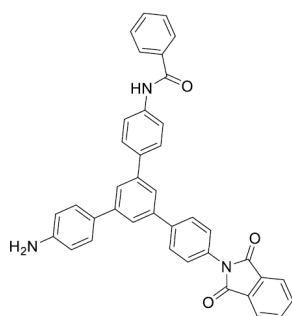


Molecular Weight: 689.77



Molecular Weight: 663.78

4a-CO [M+1]: calc 716.77 m/z, found 716.49 m/z. **4a-3CO** [M+1]: calc 664.78 m/z, found 664.42 m/z.

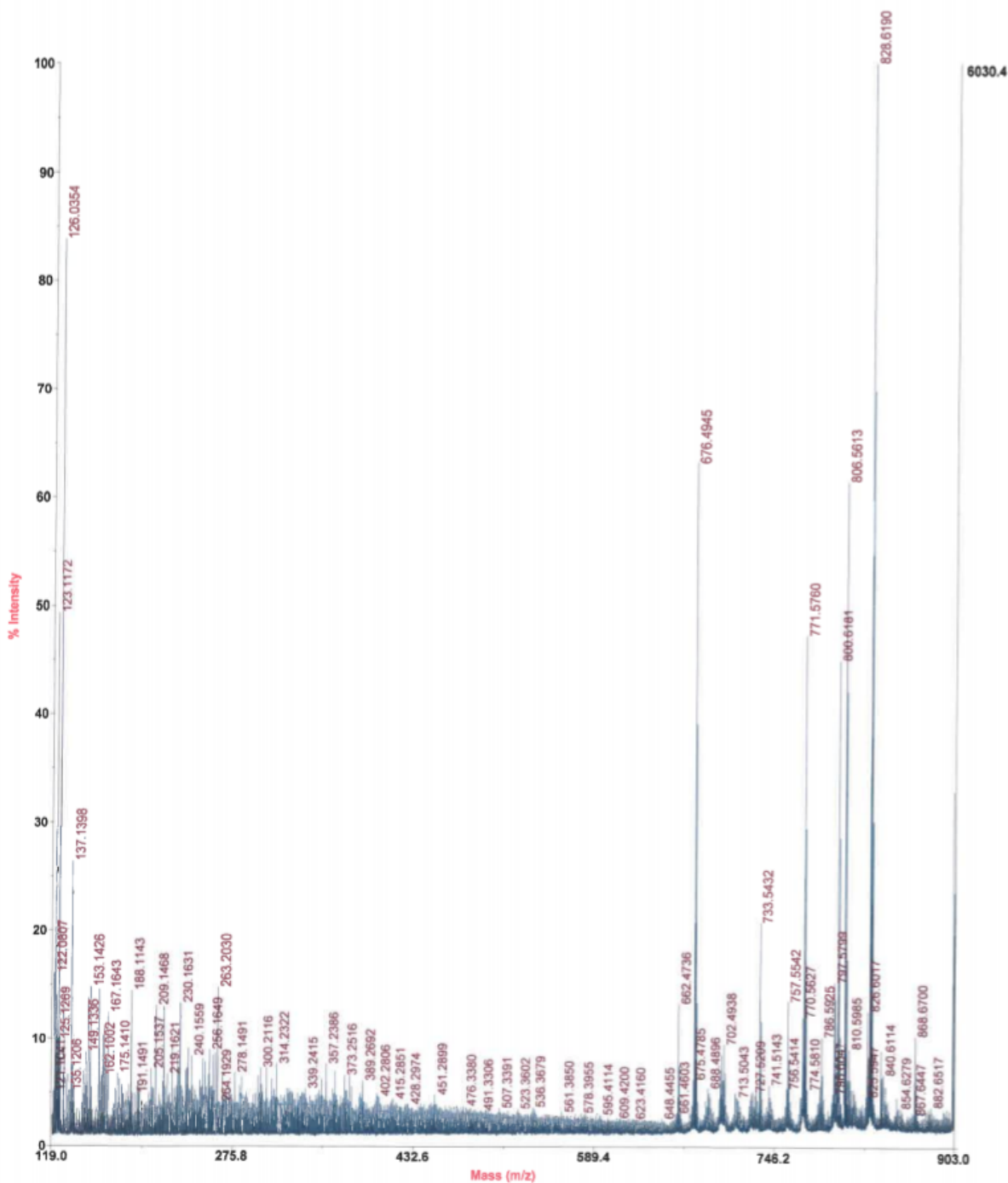


Molecular Weight: 585.66

4b-CO [M+1]: calc 586.66 m/z, found 586.44 m/z.

AB Sciex TOF/TOF™ Series Explorer™ 72170 3-50 oven

TOF/TOF™ Reflector Spec #1 MC[BP = 828.6, 6030]



C:\AB SCIEX\TOF\TOF Data\Export\T2D\synthesis groups\Hoberg Group\Spot Set 5-26-16\F7_MS.t2d

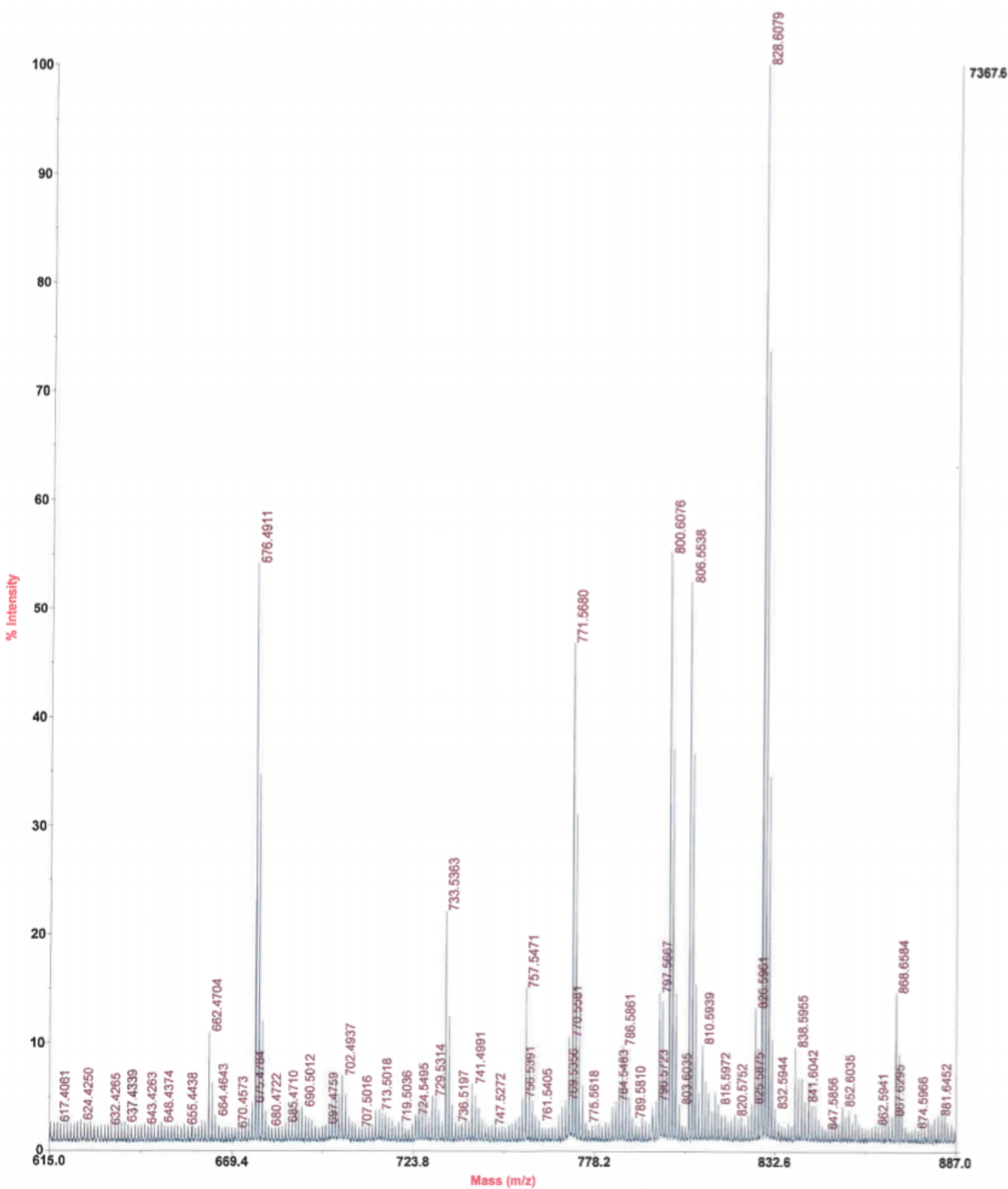
Printed: 09:21, October 22, 2020

Figure S28. MALDI-TOF MS full spectrum of 4a-4c synthesized in the furnace.

AB Sciex TOF/TOF™ Series Explorer™ 72170

3-50 oven w/ PEG

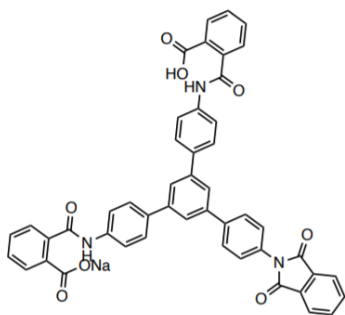
TOF/TOF™ Reflector Spec #1 MC[BP = 261.2, 17371]



C:\AB SCIEX\TOFTOF Data\Export\T2D\synthesis groups\Hoberg Group\Spot Set 5-26-16\F8_MS.t2d

Printed: 09:24, October 22, 2020

Figure S29. MALDI-TOF MS of **4a-4c** synthesized in the oven (119 m/z – 615 m/z omitted for clarity). Alkali metal salts have been observed for similar reported compounds.¹



$C_{48}H_{30}N_3NaO_8$ [M + 1]: calc 800.19 m/z, found 800.61 m/z

Computational approach

The X-ray diffraction patterns for the MA/PMDA COF were calculated using the diffraction algorithm² as implemented in LAMMPS³. The wavelength was chosen to match the experiments (1.541838 Å), and a value of 1 was used for the mesh spacing in reciprocal space along all three cartesian directions. The periodic unit cells used for these calculations are shown in the main text in Fig.1. The lattice parameters and atomic positions were optimized using the tight binding package dftb+⁴ using the ob2 Slater–Koster set⁵. The convergence criteria for the geometry optimization and the self-consistent energy calculation were set to 1×10^{-4} Ha/Bohr ($\sim 5.1 \times 10^{-3}$ eV/Å) and 1×10^{-5} Ha ($\sim 2.7 \times 10^{-4}$ eV), respectively. A cubic unit cell was enforced, as required by the diffraction algorithm. The computed lattice parameters are $a = 21.75$, $b = 37.22$ and $c = 4.24$ Å, where c corresponds to the interlayer spacing. Patterns were obtained for three stacking configuration (AA with aligned layers, AA with offset layers, and AB). The geometry was optimized using the conjugate gradient algorithm implemented in the dftb+ software and the Brillouin zone was sampled with a Monkhorst–Pack⁶ $3 \times 3 \times 3$ k-point grid. Figure S30 shows a section of the simulated PXRD spectrum for the AA and AB stacking configurations extending from 3 to 53 degrees with the y-axis scaled to show the smaller peaks beyond 3 degrees. The visualization software VESTA² was used to reproduce the COF images in Fig. 1.

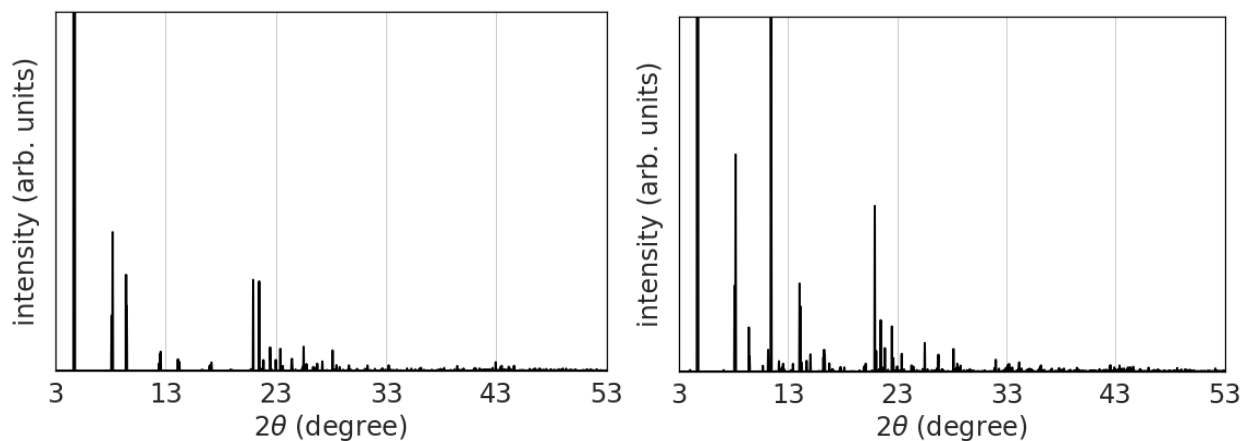


Figure S30. Section of the simulated PXRD for the MA/PMDA assuming AA stacking (left) and AB stacking (right) with a 4.2 Å distance between the layers.

The Quantum Espresso⁷ calculations were performed with the Perdew Zunger exchange correlation functional within the local density approximation (LDA) and non-relativistic ultrasoft pseudopotentials for all of the DFT calculations performed, which are readily available from the standard solid-state pseudopotentials library⁸. The plane wave energy cut off was set to 50 Ry for all calculations, along with a 1×10^{-7} Ry ($\sim 1.4 \times 10^{-6}$ eV) convergence threshold. The atomic positions were optimized until forces were smaller than 1×10^{-7} Ry/Bohr ($\sim 2.6 \times 10^{-6}$ eV/Å). A periodic cubic cell of 30 Bohr (~ 15.9 Å) was found to be suitably large (final energies did not change by increasing the box size further). The initial configurations used to perform the DFT calculations were obtained using the dftb+ package⁴ using the ob2 Slater–Koster set⁵, with the respective energy and force tolerances set to 1×10^{-5} Ha and 1×10^{-7} Ha/Bohr. The molecules shown in the main text were reproduced with the Open-Visualization Tool (OVITO)³.

Titration characterization

Amine and carboxylic acid groups were titrated using a HCl solution (0.0971 M, standardized by 0.0950 M NaOH solution, that was standardized by potassium acid phthalate (KHP) primary standard, Mallinckrodt Chemical Works). To prepare the solution, 0.020 g of salt starting material PI & PMDA was dispersed in 22 ml of 0.0950 M NaOH solution and stirred. After surpassing the solution equivalence point (Solution EP1), the amine equivalence point (Salt SM EP2) and carboxylic acid equivalence point (Salt SM EP3) were reached and calculated to have a ~1: 1.3 ratio (amine : COOH). The number of COOH and amine moles were calculated based on the consumption of the standardized HCl solution, which is equal to $V_{\text{HCl}} \times C_{\text{HCl}}$, with V_{HCl} being the titrant volume (L) and C_{HCl} the molar concentration of the titrant.

In separate beakers, preparation of polymer solutions were performed using the oven material (0.006 g in 25 mL of 0.0950 M NaOH) and microwave material (0.008 g in 25 mL of 0.0950 M NaOH). After surpassing the solution equivalence point (Solution EP2), both polymers exhibited a second equivalence point in the microwave material (MW EP1) and oven material (Oven EP1) at pH's of 5.6 and 4.9, respectively.

All equivalence points were observed in the $d(\text{pH})/d(\text{mL})$ versus mL graph as points.

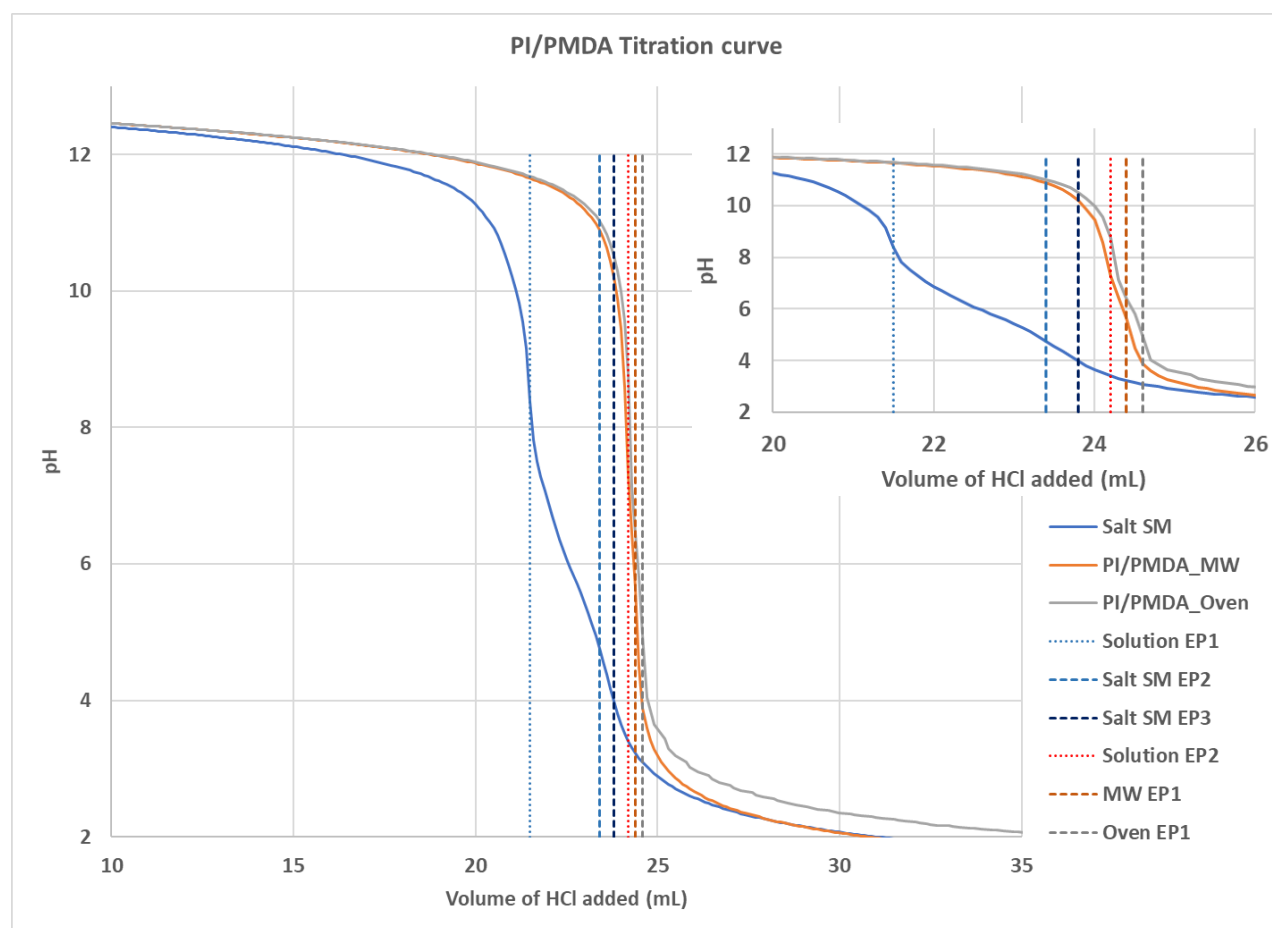


Figure S31. Titration curves for salt starting material PI and PMDA (blue), polymer synthesized (using this salt SM) in both the microwave (orange) and oven (grey). Inset graph highlights the regions of interest. Equivalence points for the acid-base solutions are indicated by small, dashed lines and functional group

equivalence points are indicated by long dashed lines. All equivalence points were determined from the derivative plot in figure S32.

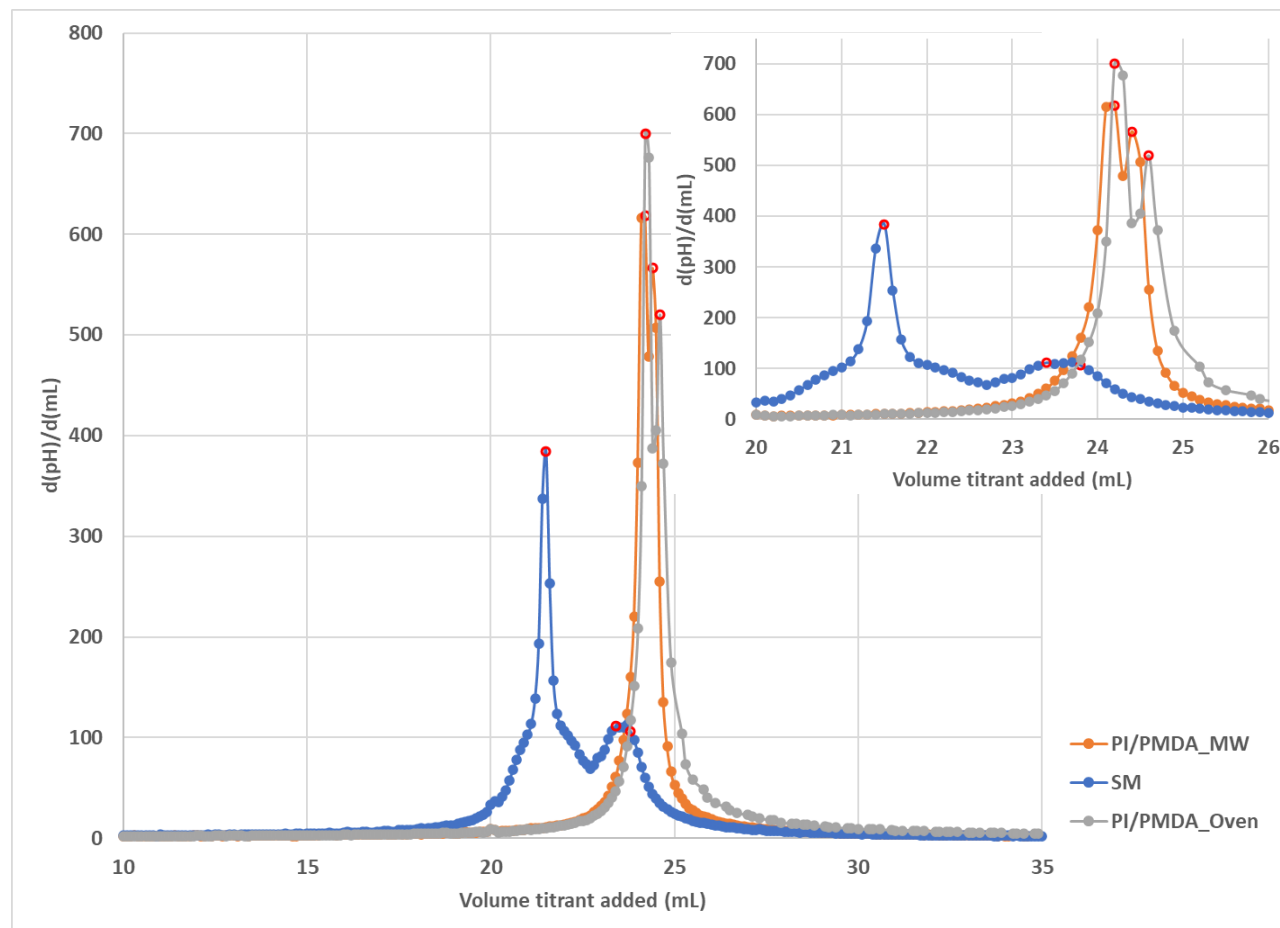


Figure S32. Titration derivative plot for salt starting material (blue) and polymer synthesized in the microwave (orange) or oven (grey). Intense peaks indicate the equivalence point reached with respect to the volume of HCl titrant added. Data points showing exact equivalence points are highlighted in red. Inset graph shows the regions of interest.

Table S1. Example titration calculation for salt starting material PI & PMDA

0.020 g Salt SM	HCl added between EPs	mol calculated
Amine titration results	SM EP3 – SM EP2 = 23.8 mL – 23.4 mL = 0.4 mL HCl	0.388×10^{-4} mol amine
COOH titration results	END – SM EP3 = 24.3 mL – 23.8 mL = 0.5 mL HCl	0.485×10^{-4} mol COOH
Theoretical ratio of amine to COOH = 1 : 1.3		0.485×10^{-4} mol COOH/ 0.388×10^{-4} mol amine = 1.25 (~1.3)

Table S2. Example titration calculation for MW polymer

0.008 g MW COF	HCl added between EPs	mol calculated
Titration results	END – MW EP1 = 25.0 mL – 24.5 mL = 0.5 mL HCl	4.855×10^{-5} mol COOH

Edge calculation: 1 micron particle

$$10^{-6} \text{ m} / (2.1 \times 10^{-9} \text{ m/unit cell}) = 4.7 \times 10^2 \text{ unit cells}$$

$$\text{Rhombus } 4.7 \times 10^2 \text{ unit cells} \times 4 \text{ edges} = 1.9 \times 10^4 \text{ edge cells}$$

$$4\text{-CO}_2^- \text{ per unit cell} = 7.6 \times 10^3 \text{ edge CO}_2^-$$

$$\text{Versus } (4.7 \times 10^2)^2 \text{ bulk unit cells} = 2.2 \times 10^5$$

3.4% of all possible carboxylates

$$\text{In } 8 \times 10^{-3} \text{ grams of COF at } 860 \text{ g/mol unit cell} = 9.3 \times 10^{-6} \text{ moles of unit cells}$$

$$\# \text{ of possible carboxylates} = (8) \times (9.3 \times 10^{-6})$$

Moles of 74×10^{-6} total possible carboxylates

$$4.8 \times 10^{-5} \text{ moles of H}^+ \text{ from titration (from table S2)}$$

$$(74 \times 10^{-6}) / (48 \times 10^{-6}) = 1.55 \text{ carboxylates titrated per unit cell}$$

TGA:DSC Data

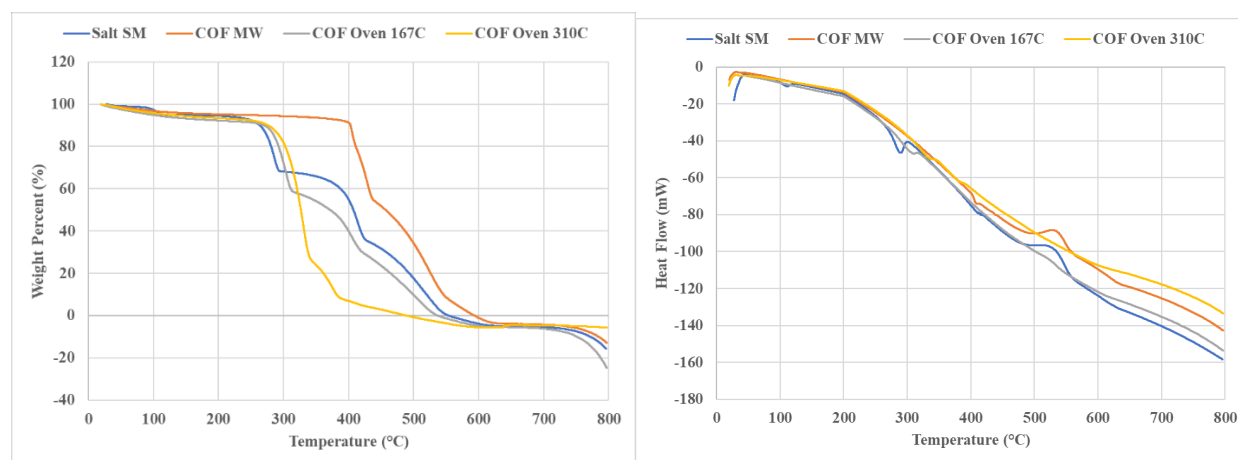


Figure S33. TGA:DSC Data of COF MA/PMDA (using organic salt SM) and starting material.

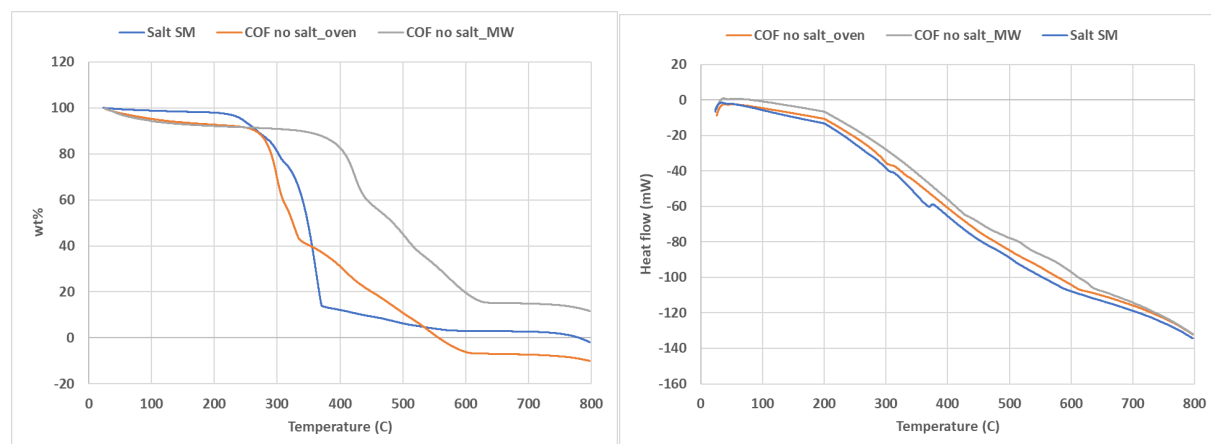


Figure S34. TGA: DSC Data of COF MA/NTDA and starting material.

References

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