

Supplementary Information for:

Redox-site accessibility of composites containing a 2D redox-active covalent organic framework: from optimization to application.

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1 General information - equipment and procedural details

1.1 Specific Brunauer-Emmet-Teller (BET) area and pore size distribution

All gas sorption analysis was performed using N₂ at 77 K on an ASAP 2020 unit (Micromeritics) in 1.27 cm (outer diameter) tubes. Filler rods were used during surface area measurements in order to use the instrument error prediction tables published by Micromeritics¹ (as error prediction formulae were based on filler rods being present). As the relative pressure ranges used for the BET plots were between 0.003 – 0.12 P/P₀, any thermal transpiration errors (typically only significant below 0.001 P/P₀)² were deemed minimal. Error ranges for both instrument uncertainty (based on formulae recommended by Micromeritics) and mass uncertainty were calculated and the larger of the two uncertainties was that which was reported. For pore size distribution plots, the data used was obtained by measurements without using a filler rod to avoid thermal transpiration errors and increase the accuracy at low relative pressures.² Free space measurements were performed by Helium dosing (with sample present) and the post-measurement evacuation time was 6 min for standard surface-area measurements. The free space post-measurement evacuation time was increased to 2 hrs, before pore-size distribution measurements were started, in order to reduce isotherm distortions at low partial pressures.^{2,3} The pore-size distribution plots were generated using the Micromeritics software (MicroActive Version 5.01) according to the DFT method, where a N₂ cylindrical-pore oxide-surface kernel was used. Isotherm fittings were made between the pressure range 0.000001 and 0.9 P/P₀ and the regularization was selected between 0.03160. All samples were degassed under vacuum for 6 hours at 90°C prior to analysis.

1.2 Powder X-ray diffraction (PXRD)

All powder X-ray diffractograms were acquired on a Bruker D8 Powder diffractometer using Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$), Bragg-Brentano geometry and a Lynxeye XE-T PSD detector. The samples were either deposited directly or wet ground in EtOH (96%) and then deposited as a slurry onto flat silicon crystal sample holders. Data collection time was 0.5 seconds per step and recorded in 0.02° increments. All diffractograms were processed to remove the background.

1.3 Thermogravimetric analysis (TGA)

All TGA measurements were made on either a TGA/DSC 3+ STARE or TGA 2 thermal analysis system (METTLER TOLEDO). Samples were packed into 70 μL aluminium oxide crucibles at two thirds of their depth. Air or N₂ flow rates were set to 60 mL/min and a heating rate of 10°C/min was applied once the sample reached 25°C and stopped at 800°C.

1.4 Elemental analysis (EA)

Samples were prepared by keeping them under vacuum for 24 hrs followed by backfilling with Ar. Each sample was analysed in duplicate by MEDAC LTD (United Kingdom) and treated as air sensitive samples (where pre-analysis sample preparation occurred in an argon glove box to avoid atmospheric nitrogen from entering into the pore space).

1.5 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5000 Versa Probe III supplied by ULVAC-PHI Inc., Japan equipped with a monochromatic Al K α radiation source. The electron binding energy of XPS was referenced to the C 1s peak at 284.6 eV.

1.6 Nuclear magnetic resonance spectroscopy (NMR)

For solution state ¹H-NMRs, spectra were referenced to the residual solvent peaks (δ : 7.26 for CDCl₃, 2.50 for (CD₃)₂SO). For solution state ¹³C-NMRs, spectra were referenced to the residual solvent peaks (δ : 77.16 for CDCl₃, 39.52 for (CD₃)₂SO).

1.7 Scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDX)

All samples were prepared by wet grinding the materials (using an agate pestle and mortar) in acetone until it evaporated. The residue was scooped up onto a spatula tip, dropped onto adhesive carbon disk stubs and then smeared over the stub's surface with the spatula. Both images and EDS maps were acquired on a Merlin Zeiss platform which used a Schottky FEG as the electron source and a silicon drift detector for X-ray detection. X-ray mapping and qualitative elemental analysis were processed using Aztec (INCA energy) software.

1.8 Fourier transform Infra-red adsorption spectroscopy (FT-IR)

All IR spectra depicted herein were obtained on a Perkin Elmer Spectrum Two FT-IR spectrometer which used a LiTaO₃ detector. When possible, samples were dissolved in a volatile solvent (either diethyl ether or acetone) and deposited over the aperture after making a background scan. Once the solvent had evaporated the spectrum was recorded and the compression screw was not used. For non-soluble solid samples, a small amount of the solid was placed over the aperture and the compression screw was used. All spectra were baseline corrected using the interactive baseline correction option which was part of the machine-specific software.

1.9 Particle-size distribution measurements

Particle size distributions were measured on the Mastersizer 3000 platform by wet dispersion (in either water or 95% ethanol) using the Hydro EV accessory. The particles sizes were measured via Mie scattering analysis from diffracting laser light at 632.8 nm generated by a He-Ne laser. The material's refractive index was chosen to be 1.700, its absorption index was selected at 0.090 and its density selected to be 0.65 g/mL.

1.10 Electrochemical measurements

All electrochemical measurements were performed either on a CHI 660D electrochemical workstation or on an Autolab PGSTAT302N potentiostat or bipotentiostat. Once prepared, the electrodes were analysed in a three-electrode setup by cyclic voltammetry (CV) using Ag/AgCl (3M NaCl) as the reference electrode, a coiled Pt wire as the counter electrode and a 0.5M pTSA solution as the electrolyte.

The average of the integrals (above the capacitive baseline) for the oxidative and reductive sweep on the second or third scan (at 0.005 V/s or 0.0005 V/s) was used to calculate the total charge

When performed, all peak fitting procedures were done in Origin 2019. All cyclic voltammograms were smoothed using the Savitsky—Golay algorithm (using 100 points of window and a 5th order polynomial). Baselines were established by manually anchoring points and using the bspline method. Once satisfactorily adjusted, the baseline was subtracted from the voltammogram and the residual plot was subjected to peak fitting using the gauss function wherein the areas of the fitted peaks were constrained to be equal.

In situ conductance measurements were obtained on G-IDECONAU10 DropSens (Metrohm) gold interdigitated array (IDA) electrodes where all CVs were acquired on an Autolab PGSTAT302N bipotentiostat at a 0.01 V potential bias. For measurements performed in organic solvents, 0.1M of an appropriate and soluble salt was used as the electrolyte. A silver wire in a solution of 0.01M AgNO₃ in the electrolyte was used as the reference electrode. The reference electrode was placed in a separate compartment to minimise Ag⁺ ion escape. A coiled platinum wire was used as the counter electrode and the potential scale was adjusted based on a Fc/Fc⁺ calibration run.

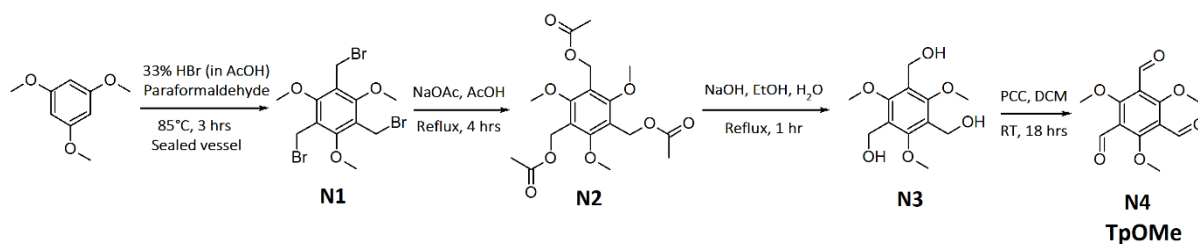
All performance measurements made on the air battery device were done so on a HZ-7000 potentiostat system (HOKUTO DENKO CORPORATION).

2 Synthesis details

2.1 Monomers

2,6-diaminoanthraquinone was purchased from Sigma Aldrich. 2,4,6-Trimethoxy-benzene-1,3,5-tricarbaldehyde (TpOMe) was synthesized as described below.

2.1.1 2,4,6-Trimethoxy-benzene-1,3,5-tricarbaldehyde (TpOMe)⁴



Scheme S 1. The reaction scheme used for the synthesis of the TpOMe monomer.

2.1.2 1,3,5-Tris(bromomethyl)-2,4,6-trimethoxybenzene (N1)

Compound **N1** was synthesized using a process based on previously published procedures by Castellano et al⁵ and Pittelkow et al.⁶ Prilled paraformaldehyde (11.000 g, 366.35 mmol, FW=30.026 g/mole) was added to a 250 mL pressure flask, followed by 10.0437 g (59.7164 mmol, FW=168.19 g/mole). After adding a magnetic stirring bead, 20 mL of glacial acetic acid was added and the mixture gently stirred at room temperature. Using a syringe connected to a long and wide diameter needle, 70 mL of 33% HBr in acetic acid was promptly added to the stirred mixture and the pressure vessel was quickly sealed. Addition of the 33% HBr solution caused the reaction flask to warm up and the mixture formed a dark clumpy mass. The sealed vessel and its contents were heated to 85°C for 3 hours while stirring continuously. After the allotted heating time, the vessel was cooled to room temperature, opened and poured into a separatory funnel containing 100 mL DCM. Any remaining contents in the reaction vessel was rinsed out with a little DCM directly into the separatory funnel. The DCM phase was rinsed with dH₂O until the aqueous layers were clear and no longer yellow (ca. 5 x 100 mL dH₂O). After the final rinse, the DCM phase was released into a round bottomed flask and the DCM was evaporated. The amount of residual acetic acid was reduced by adding 100 mL toluene and evaporating the lower boiling azeotrope and excess toluene under vacuum. The remaining residue was dissolved in 50 mL DCM and ca 30 g silica was added to the flask and the mixture evaporated in order to prepare it for dry loading onto a silica column (8-10 cm high, 8-9 cm diameter). Compound **N1** (*R_f* = 0.5) eluted first from the column using the mobile phase hexane:EtOAc (20:1). It was collected after initially passing ca 500 mL eluent and came out over ca 1 L of mobile phase. 10.205 g (22.832 mmol, FW=446.958 g/mol) of **N1**, at a yield of 38%, was recovered as a clean white powder. ¹H-NMR (400 MHz, CDCl₃) δ: 4.60 (s, 6H), 4.14 (s, 9H). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: 160.2, 123.4, 62.8, 22.6.

Note: we attempted to perform the multistep synthesis of TpOMe starting from crude N1, which had been obtained from only the aqueous work up described by Castellano et al,⁵ and this produced unreliable yields and emulsions during work-up in subsequent reaction steps (likely due to orange polymer side-products). Consequently, we recommend that compound N1 be rigorously purified using column chromatography to avoid such downstream problems.

Note: we found the base-washing step used in the work-up procedure described by Castellano et al⁵ produced a challenging emulsion which we sought to avoid. The ¹H-NMR and ¹³C-NMR were in excellent agreement with those from Castellano et al.⁵

2.1.3 1,3,5-Tris(acetoxymethyl)-2,4,6-trimethoxybenzene (**N2**)⁴

1,3,5-tris(bromomethyl)-2,4,6-trimethoxybenzene (5.0054 g, 11.199 mmol, FW=446.958 g/mol) was added into a stirred mixture of 100 mL glacial acetic containing 11.366 g (138.55 mmol, FW=82.034 g/mol) anhydrous sodium acetate. The round-bottomed flask was connected to a reflux condenser and briefly after applying heat, a fine white precipitate (presumably NaBr) was observed. The mixture was heated under reflux for 4 hours and after cooling to room temperature, 160 mL DCM was added to the flask. The contents were then vacuum filtered through a glass-frit filter funnel directly into a round-bottomed flask in order to remove the white precipitate. The bulk of the residual solvents were evaporated under vacuum until a wetted residue remained and ca 150 mL EtOAc was added to the flask along with the minimal amount of dH₂O needed to dissolve all the residues. Saturated NaHCO₃ solution (ca 60 mL) was added and the flask swirled and briefly sonicated to facilitate the neutralisation. The aqueous phase was checked on litmus paper until it turned green, any additional NaHCO₃ was spooned into the flask if was needed (followed by swirling and brief bouts of sonication). Once neutralised, the biphasic mixture was transferred to a separatory funnel and the phases separated. The aqueous phase was returned to the funnel and washed once with a 100 mL portion of EtOAc. The organic phases were combined and rinsed once with a 100 mL of a 70% saturated NaHCO₃ solution, once with 100 mL dH₂O and finally 20 mL of brine was carefully poured through the organic phase. After draining off the brine layer, the organic phase was dried with MgSO₄ and filtered by gravity into a pre-weighed round-bottomed flask. After removing the solvent in the rotary evaporator, 4.191 g (10.90 mmol, FW=384.378 g/mol) of crude white 1,3,5-tris(acetoxymethyl)-2,4,6-trimethoxybenzene (**N2**) was obtained at a yield of 97%. ¹H-NMR (400 MHz, CDCl₃) δ: 5.16 (s, 6H), 3.84 (s, 9H) 2.08 (s, 9H). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: 170.9, 162.1, 120.0, 64.0, 56.9, 21.2.

2.1.4 1,3,5-Tris(hydroxymethyl)-2,4,6-trimethoxybenzene (**N3**)

The crude 1,3,5-tris(acetoxymethyl)-2,4,6-trimethoxybenzene (4.103 g, 10.67 mmol, FW=384.378 g/mol) was suspended in 40 mL of ethanol (96%) followed by adding a solution of NaOH (1.5293 g, 38.235 mmol, FW=39.997 g/mol) dissolved in 25 mL dH₂O, after which the mixture soon turned clear and yellowish. The mixture was refluxed 1 hour and left stirring overnight at room temperature. The ethanol was removed by evaporating under vacuum where after 0.52 mL of concentrated HCl (37%) was slowly added to the remaining aqueous phase while swirling in order to neutralise the slight excess of NaOH that was added. The solution was then returned to the rotor evaporator and the bulk of the residual water was removed until a wetted residue remained. The remaining water in the residue was reduced by adding 100 mL of ethanol (100%) to the flask, sonicating the suspension, and co-evaporating it using the rotary evaporator. Acetone (ca 100 mL) was added to the dried residue and the suspension was thoroughly sonicated (5-10 min in an ultra sound cleaning bath) until a fine-particle cloudy suspension was formed. The suspension was vacuum filtered through a glass-frit funnel into a pre-weighed round bottomed flask. After removing the acetone by vacuum evaporation, 2.662 g (10.31 mmol, FW=258.268 g/mol) of an off-white and slightly waxy solid was recovered at 97% yield. ¹H-NMR (400 MHz, DMSO-d₆) δ: 4.78 (broad m, 3H), 4.46 (m, 6H), 3.87 (s, 9H). ¹³C {¹H} NMR (101 MHz, DMSO-d₆) δ: 159.2, 124.4, 63.7, 52.9.

Note: in our hands, several attempts to obtain compound **N3**, via the original extraction procedure of Banerjee et al,⁴ resulted in yields of 42% (for extraction with EtOAc) and 31% (for extraction with DCM). After realising that the transesterification reaction occurs rapidly and didn't require large excesses of NaOH or long reaction times to run to completion, we suspected that compound **N3** was quite water-soluble and getting discarded in the aqueous phase. Consequently, we modified the extraction process to that described above to first remove as much water as possible and then extract the organic product from the salts as well as to avoid using any typical drying salts to which the compound might stick to. The solubility of NaCl and sodium acetate were shown to be low in acetone, a strongly polar solvent that could easily dissolve compound **N3**.

Note: the addition of HCl was intended to only neutralise the excess NaOH used and not to convert the sodium acetate into acetic acid (which would all be extracted with the acetone) and would have been removed by evaporation under vacuum.

2,4,6-Trimethoxy-benzene-1,3,5-tricarbaldehyde (N4)

Three spatulas of activated 3Å molecular sieves were added to an oven-dried 50 mL round-bottomed flask followed by 0.4829 g of 1,3,5-Tris(hydroxymethyl)-2,4,6-trimethoxybenzene (1.870 mmol, FW=258.268 g/mol) and 2.0152 g (9.3487 mmol, FW=215.56 g/mol) pyridinium chlorochromate (PCC). The flask was closed with a rubber septum, evacuated and backfilled with N₂ three times before adding 15 mL of dry DCM under N₂. After stirring the mixture for 18 hrs under a N₂ atmosphere, the mixture was pipetted directly onto a silica plug (3 cm wide and 4.5 cm high) in DCM. The reaction flask was washed with 3 x 15 mL portions of DCM (the flask was sonicated briefly after each portion of DCM was added) which were also loaded onto the silica plug. The plug was washed with ca. 300 mL of a EtOAc:DCM (1:4) mixture or until a green band was eluted. After evaporating the solvent, the residue was dissolved in a minimal amount of the hexane:EtOAc (3:1) mobile phase mixture and wet-loaded onto a silica column (5 cm wide and 8 cm high) for purification. The product (R_f=0.43) appeared as a yellow band on the column and eluted after a trailing impurity after ca. 300 mL of mobile phase had passed. After evaporating the mobile phase, 0.3201 g (1.269 mmol, FW=252.220g/mol) of compound **N4** was isolated as an off-white solid at a yield of 68%. ¹H-NMR (400 MHz, CDCl₃) δ: 10.35 (s, 3H), 4.03 (s, 9H). ¹³C {¹H} NMR (101 MHz, CDCl₃) δ: 187.2, 169.8, 120.3, 65.7.

Note: molecular sieves (3Å) were prepared/activated by heating them at 180°C under vacuum overnight.

Note: DCM was dried by filtering it through an aluminium oxide column and storing it over activated molecular sieves for at least 48 hours.

Note: while the oxidation reported here was performed at a mole ratio of 1:5 (triol:PCC), an attempt to perform the reaction at the reduced ratio of 1:3.3 (triol:PCC), inferred by Brown et al's findings,⁷ did not show an appreciable reduction in yield. In order to reduce chemical waste and reduce the chances of over-oxidation, it is suspected that only 1.378 g of PCC is actually needed to oxidize 0.500 g of **N3**.

2.2 Covalent Organic Framework (COF) synthesis

2.2.1 TpOMe-DAQ⁴

The dark red monomer 2,6-diaminoanthraquinone (2.2143 g, 9.294 mmol, FW=238.241 g/mole) was placed into a smooth agate mortar containing 9.0601 g (47.63 mmol, FW=190.22 g/mole) para-toluenesulfonic acid monohydrate. The powdered ingredients were blended using the pestle until evenly mixed (the pTSA is hygroscopic and the mixture may form a dough-like consistency if it is humid) and deionised water(dH₂O) was added drop wise until the mixture formed a thick sticky paste. The second monomer 2,4,6-trimethoxy-benzene-1,3,5-tricarbaldehyde (1.4400 g, 5.709 mmol, FW=252.220 g/mole) was added to the paste and thoroughly mixed into the sticky mass using the pestle. A flat metal spatula was intermittently used to scrape down the sticky contents that accumulated on the pestle. More deionised water was added dropwise until the mixture formed a light brown paste, with the consistency of melted chocolate, which could be poured into small glass bowls forming 5 evenly sized blobs that could hold their shape. Each glass bowl was placed into a larger sealable container (with a few millilitres of dH₂O below the glass bowls to maintain a moist atmosphere) which was closed up and placed in an oven at 90°C for 18 hours. After opening the warm containers and letting them cool to room temperature, the solidified blobs (which kept their shape) were lightly crushed in a pestle and mortar containing dH₂O. The crushed slurry was transferred to a pre-weighed Erlenmeyer flask (E-flask), a large excess of water was added and the flask was heated to 85°C for 15 minutes. The warm water was discarded after decanting it from the E-flask and letting it filter through a piece of filter paper to catch any unsettled material. Any solid material captured in the filter paper could be returned to the E-flask for further washing steps. The solid product was washed as described twice more with room temperature dH₂O, followed thrice with MeOH, thrice with DCM and thrice with pentane. After the final pentane decantation and returning any solid material from the filter paper by rinsing it off with pentane, the E-flask was capped with a septum, punctured with a venting needle and the remaining pentane evaporated under a steady N₂ while heating the flask to just below the boiling point (BP) of pentane. After all the visible liquid pentane was removed, the temperature was increased to 140°C for 15 hours. The E-flask was cooled to room temperature where after the N₂ flow was replaced with air for a few seconds to flush the E-flask. The vent needle, gas flow and septum were removed and the flask was quickly weighed yielding 2.8151 g (yield 88.8%) of the orange solid.

After the synthesis procedure, the roughly sized material was constituted into a homogenous master batch by manually wet grinding (in 96% ethanol) it using an agate pestle and mortar until it formed a suspension that looked homogeneous (ca 20-50 min). The suspension was vacuum filtered and rinsed with 96% ethanol over a Buchner funnel and then transferred to an E-flask for drying by heating under N₂ flow.

Note: the successive solvent washing protocol could also be carried out in centrifuge tubes (provided tubes are compatible with the solvents used) for convenience. Centrifugation speeds up sedimentation and removes the need for catching stray particles on filter paper.

Note: the successive solvent washing and N₂ drying procedure was first proposed by Dichtel et al⁸ as means to preserve pore structure, especially in COFs possessing larger more delicate pores. The rationale behind the method was to reduce the forces that the pores might be exposed to during solvent evaporation by successively replacing each solvent with one that has a lower surface tension. Finally, the solvent with the lowest surface tension (pentane) could be gently removed by N₂ flow and heating. We applied this method to our COF synthesis to err on the side of caution, however, BET areas and PXRD patterns were not significantly affected when ether- or ethanol-soaked material was dried by vacuum for 24 hours followed by heating at 90°C under vacuum for 6 hours. Although not thoroughly tested, we suspect that the pore structure of this material is robust enough to negate concerns related to which drying procedure should be used.

Note: we were also interested in the mould forming potential of the mechano-chemical method first reported by Banerjee et al.⁹ However, we found that using the above-mentioned procedures, uncrushed larger moulded chunks of material possessed much reduced BET areas (ca 300 m²/g vs the expected 1530 m²/g)¹⁰ after being washed and dried. Even when these chunks

were crushed down into small pieces, their BET areas did not change significantly. It was only after lightly grinding and subjecting the crushed chunks to another washing cycle could the BET areas of ca. 1530 m²/g be obtained. These observations suggest that the pores of the moulded material (after oven backing) are likely filled with excess pTSA. It also highlights the importance of initially grinding the material down to small enough aggregates before the washing procedure such to enable solvent access throughout the aggregate's structure.

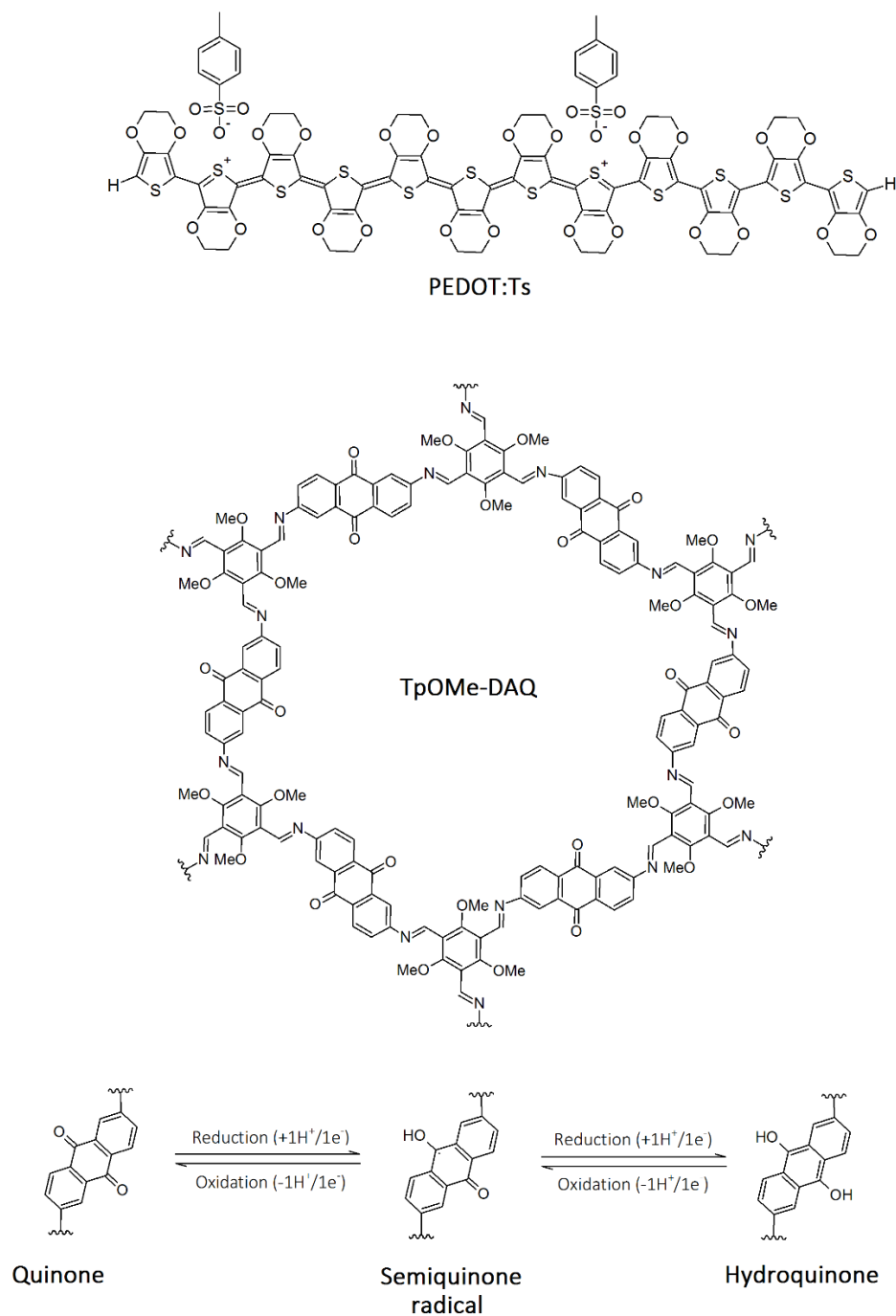


Figure S 1. The structure of the TpOMe-DAQ COF (middle) and the chemically reversible redox reactions that the anthraquinone units are likely undergoing (below). The ability of these anthraquinone units to reversibly store and release electrons imparts charge-storage potential into the material. The chemical structure of a PEDOT:Ts oligomer (top) which becomes electrically conducting after a certain applied potential.

2.3 PEDOT:Ts

The synthesis of PEDOT was carried out in the same way as the infusion procedure for a scaled-up batch (described below) but without the COF material. A stock solution of EDOT in MeCN was prepared at a concentration of 0.05057 mg/ μ L (0.3557 M). FeTs₃.6H₂O (2.8115 g, 4.1497 mmol, FW = 677.52 g/mol) was weighed off in a sample vial and ca. 3 mL MeCN was added and the mixture heated to 70°C in the closed vial. The solubilized portion was pipetted into a 50 mL centrifuge tube and the residue similarly dissolved in additional 1 mL portions of MeCN and then added to the 50 mL centrifuge tube. The volumes of the portions pipetted into the 50 mL tube were recorded to ensure all the FeTs₃.6H₂O could be delivered into the centrifuge tube in under 6080 μ L and any shortfall was made up by adding the necessary amount of MeCN to the centrifuge tube. Soon after transferring the warm FeTs₃.6H₂O in MeCN solution, 5000 μ L (0.2529 g, 1.779 mmol, FW = 142.17 g/mol) of the EDOT solution was pipetted into the centrifuge tube which was then capped, sealed with parafilm and placed in an oven at 37°C after a brief sonication (in a ultrasound cleaning bath) to help mix the suspension. After heating for 72 hrs, the tube was cooled to rt, centrifuged (2 min at 3300 RCF) to pool any condensate and the MeCN removed overnight under a gentle N₂ stream. 25 mL of dH₂O was added and the tube was sonicated briefly where after it was centrifuged at 3300 RCF for 15 min. The supernatant was removed carefully and the material was rinsed again with one portion of 25 mL 0.5M pTSA solution and one more portion of 25 mL dH₂O, each time sonicating and centrifuging in between. After removing the aqueous supernatant, the material was washed similarly three more times with 95% Ethanol.

Following the final wash and careful supernatant removal, a sparing as possible amount of ethanol was added to the material to aid in transferring it from the plastic centrifuge tube into a pre-weighed round bottom flask. Several rinses with small portions of ethanol were necessary to transfer all the material. The round-bottomed flask was capped with a septum and pierced with a needle and the ethanol was evaporated under gentle N₂ flow while heating the flask at 50°C for 12 hrs. The flask was then placed under vacuum overnight, back filled with nitrogen and flushed with air before weighing. 0.3192 g of the dark blue solid PEDOT:Ts was obtained.

Note: the EDOT:FeTs₃.6H₂O stoichiometry of 1:2.33 used herein was based on the 1:2 described by Elschner et al,¹¹ but excess was added based on assuming all EDOT units added will be adjacently connected i.e. a ratio of 6:14 EDOT:FeTs₃.6H₂O

2.4 Composites

2.4.1 Eppendorf screening method (1-2 mg scale)

The general method described below was used to generate the redox site accessibility plots as a function of EDOT:COF mass loading ratios. The general procedure will be described for a control and two samples loaded with EDOT at mass ratios of 0.3 and 0.5 EDOT:TpOMe-DAQ. However, the procedure can be easily adapted to study more loading ratios. We used to the procedure up to a loading ratio of 1:1 EDOT:COF.

FW $\text{FeTs}_3 \cdot 6\text{H}_2\text{O}$ = 677.52 g/mol

FW EDOT = 142.17 g/mol

FW pTSA = 190.22 g/mol

Loading ratio = EDOT mass used : COF mass used

pTSA = para-toluene sulfonic acid

PVDF = Polyvinylidene fluoride

Stock solutions:

A solution of EDOT in MeCN was made up in a 10 mL volumetric flask at 0.0500 mg/ μL (0.3517 M)

A solution of $\text{FeTs}_3 \cdot 6\text{H}_2\text{O}$ in MeCN was made up in a 10 mL volumetric flask at 0.1000 mg/ μL (0.1476 M).

A solution of PVDF in DMF was made up in a 5 mL volumetric flask at 0.00500 mg/ μL .

Procedure:

The COF material was weighed out in a small agate mortar on a 0.00 mg resolution balance. The amount of sample was aimed at 1.00 mg per sample and after a stable mass reading, 100 μL MeCN was added to the mortar, the material finely wet ground and pipetted into a 2 mL Eppendorf tube and marked. This transfer was made as quantitatively as possible by rinsing and transferring any residues on the pestle and mortar with more 100 μL portions of MeCN and adding them to the sample tube. After repeating this process for three Eppendorf tubes marked “control”, “0.3”, “0.5” and recording the respective masses, the tubes were centrifuged at ca. 15000 RCF for 10 min and the excess MeCN carefully removed without disturbing the pellet. The 0.100 mg/ μL solution of $\text{FeTs}_3 \cdot 6\text{H}_2\text{O}$ solubilized in MeCN was pipetted into the tubes “control”, “0.3” and “0.5” at 55.5 μL , 33.3 μL and 55.5 μL respectively. The tubes were capped and sonicated (avoiding sputtering) briefly in an ultrasound cleaning bath to ensure proper mixing and infusion of the FeTs_3 solution with the COF. After opening, the MeCN was evaporated under a gently N_2 stream until no visible liquid could be seen and a damp pellet remained. A controlled amount of excess MeCN was added to each tube (23.7 μL for the “control”, 9.7 μL for sample “0.3” and 13.7 μL for sample “0.5”) in order to keep the total liquid:solid ratio of the different suspensions as similar as possible. After briefly sonicated the tubes again, the 0.0500 mg/ μL EDOT in MeCN solution was added at 0 μL , 6.0 μL and 10.0 μL to the tubes marked “control”, “0.3” and “0.5” respectively. The tubes were capped, sonicated again and placed in sealed sample vials and incubated in the oven at 37°C for 72 hrs. After heating for 72 hrs, the tubes were cooled to rt, briefly centrifuged to pool any condensate and the MeCN removed under a N_2 (g) stream. 500 μL of dH_2O was added to each tube, followed by briefly sonicating and then centrifuging at 15000 RCF for 15 minutes and carefully removing the supernatant without disturbing the pellet. This washing process was repeated with a 500 μL portion of 0.5M pTSA solution, another 500 μL water, two times with 500 μL portions of 96% ethanol and finally with 500 μL DMF. After

removing the DMF supernatant, the 0.00500 mg/ μL PVDF in DMF solution was pipetted into the tubes at 22.2 μL , 28.9 μL and 33.3 μL for “control”, “0.3” and “0.5” respectively. The tubes were carefully sonicated to avoid sputtering and their entire content was pipetted onto pre-cut, washed, dried and weighed (described in the electrode preparation section) graphite foil electrodes. The DMF was evaporated by heating and the electrodes on a hotplate. The electrodes were washed, dried and weighed according to the electrode preparation procedure described later.

Once prepared, the faradaic capacity of the material on the electrodes was evaluated by cyclic voltammetry (CV) in a 0.5M pTSA solution according to the procedure described under the electrochemical analysis section. The theoretically expected capacity for the material could be calculated from the known amount of material that was weighed in the mortar. The procedure described here assumes no COF material originally weighed in the mortar gets lost during the procedure. Consequently, the procedure relies on high relative centrifugal forces (RCFs), carefully removing the supernatant and ensuring transfers are performed leaving behind minimal residues. Losses due to COF solubilization during the washing steps is also assumed to be negligible

Note: The $\text{FeTs}_3.6\text{H}_2\text{O}$ is not totally soluble in MeCN at room temperature at this concentration so heating to help dissolve it in as much MeCN as possible, then cooling and then adding the last bit of MeCN to the mark seemed to work. Once the rt solution was made to the mark in the volumetric flask, it was transferred to a sample vial, sealed and warmed up to 70°C to ensure the $\text{FeTs}_3.6\text{H}_2\text{O}$ was solubilized before pipetting it. Pipetting warm solutions would be expected to compromise accuracy, but seemed necessary to ensure a fully solubilised solution.

Note: The ultrasound was just used to help agitate the suspension and was performed by briefly sonicating for a second or two and then removing and repeating if necessary. Splashing and spattering of the suspension on the inside of the tub should be avoided.

Note: The loading ratio of EDOT can be varied by adding more of the EDOT solution but the amount of $\text{FeTs}_3.6\text{H}_2\text{O}$ oxidant needs to be changed accordingly using the EDOT: $\text{FeTs}_3.6\text{H}_2\text{O}$ mole ratio of 1:2.33. Also noteworthy, is the total volume:mass ratio during the EDOT infusion process which should be kept at 3.62 (in μL of EDOT solution plus excess MeCN to mg of COF plus $\text{FeTs}_3.6\text{H}_2\text{O}$ used) e.g 6 μL + 9.7 μL = 15.7 μL per solid material mass of 1.00 mg COF + 3.33 mg $\text{FeTs}_3.6\text{H}_2\text{O}$ = 4.33 mg gives 3.62 $\mu\text{L}/\text{mg}$. When infusing at higher EDOT loading ratios, more excess MeCN might be needed after the evaporation step to compensate for the extra $\text{FeTs}_3.6\text{H}_2\text{O}$ that will also be needed. This infusion volume:mass ($\mu\text{L}:\text{mg}$) ratio of 3.62 worked well for TpOMe-DAQ but needed to be adjusted to 2.74 for PQ-COF and might need to be modified for other materials.

Note: Infusion procedures using ethanol as the solvent did not yield good results. The use of MeCN seemed to be a key factor. However, it might be possible to dissolve and load the $\text{FeTs}_3.6\text{H}_2\text{O}$ via an ethanol solution as it has a much higher solubility in EtOH. In this case a more thorough drying would be need to remove residual EtOH before EDOT infusion/polymerization in MeCN.

Note: All the polymerisations performed were called situ polymerisation whereby EDOT was added to a tube containing both TpOMe-DAQ and $\text{FeTs}_3.6\text{H}_2\text{O}$ and incubated according to the procedure described above. An ex-situ-polymerisation-control measurement was also performed by adding the EDOT to a separate tube containing only $\text{FeTs}_3.6\text{H}_2\text{O}$ and no TpOMe-DAQ. Both tubes (one containing TpOMe-DAQ in MeCN and the other containing EDOT, $\text{FeTs}_3.6\text{H}_2\text{O}$ and MeCN) were incubated at the same temperature for the same time according to the procedure above. After incubation, the PEDOT in the separate tube was added to the tube containing TpOMe-DAQ, sonicated and then treated according to the procedure described above.

2.4.2 Scaled-up batch method (100-200 mg scale)

In order to produce larger amounts of the PEDOT infused material needed for characterisation and applications, the screening process described above was scaled up using the procedure below, exemplified by a 0.4 EDOT:TpOMe-DAQ infusion

Stock solutions:

A solution of EDOT in MeCN was made up in a 10 mL volumetric flask at 0.0500 mg/uL (0.3517 M)

Procedure:

COF material (100 mg) was heated in a sample vials on a hotplate at 100°C for an hour to dry it. The hot vial was capped and the material was then cooled to rt in a closed vial which was then weighed. The vial was opened, its contents quickly tipped into a 50 mL plastic centrifuge tube, closed and weighed again. The difference gave the precise amount of COF used. The sides of the 50 mL centrifuge tube were rinsed down with ca. 1.5 mL of MeCN so all the static particles settled to the bottom of the tube.

444.15 mg of the $\text{FeTs}_3 \cdot 6\text{H}_2\text{O}$ was weighed into a sample vial and heated with 2 mL of MeCN at 70°C while capped. The solubilised portion was transferred to the 50 mL centrifuge tube. Consecutive 500 μL mL portions of MeCN were added to the remaining FeTs_3 residue in the sample vial, heated and transferred to the centrifuge tube until all the FeTs_3 was quantitatively transferred. The 50 mL centrifuge tube was capped and the bottom of the tube was very briefly placed into an ultrasound bath to help evenly mix and distribute the material. The MeCN was carefully evaporated under a $\text{N}_2(\text{g})$ stream until no liquid was visible in the material and a damp pellet remained.

Once most of the solvent was removed, 1170 μL of excess MeCN was added to the tube and it was briefly mixed by sonication as described previously. After the brief sonication, 800 μL of the 0.0500 mg/ μL EDOT solution in MeCN was added and the tube capped and mixed again by brief sonication. The capped tube was sealed with parafilm and placed in an incubator oven set at 37°C. After 72 hrs, the tube was cooled to rt centrifuged (2 min at 3300 RCF) to pool any condensate and the MeCN removed under a gentle $\text{N}_2(\text{g})$ stream. 25 mL of dH_2O was added and the tube was sonicated briefly where after it was centrifuged at 3300 RCF for 15 min. The supernatant was removed carefully and the material was rinsed again with one portion of 25 mL 0.5M pTSA solution and one more portion of 25 mL dH_2O , each time sonicating and centrifuging in between. After removing the aqueous supernatant, the material was washed similarly three more times with 95% Ethanol.

Following the final wash and careful supernatant removal, a sparing as possible amount of ethanol was added to the material to aid in transferring it from the plastic centrifuge tube into a pre-weighed round bottom flask. Several rinses with small portions of ethanol were necessary to transfer all the material. The round-bottomed flask was capped with a septum and pierced with a needle and the ethanol was evaporated under gentle $\text{N}_2(\text{g})$ flow while heating the flask at 65°C. The flask was then placed under vacuum overnight, back filled with nitrogen and flushed with air before weighing.

If the amount of COF initially used is known and one assumes none of it was lost during the procedure, the percent COF in the final composite could be calculated from the final mass value.

Table S 1.: The percent TpOMe-DAQ in the composites using the initial-mass method compared to evaluation by EA-XPS.

Composite	Percent TpOMe-DAQ by initial-mass method	Percent TpOMe-DAQ evaluated by EA-XPS
0.2EDOT@TpOMe-DAQ	82.4%	80.3%
0.4EDOT@TpOMe-DAQ (Batch 1)	70.6%	-
0.4EDOT@TpOMe-DAQ (Batch 2)	65.3%	68.5%
0.8EDOT@TpOMe-DAQ	47.0%	52.7%

Note: The COF material is stable to heating in air up to 140°C (checked by TGA). Alternative drying methods might be needed for other materials.

Note: The plastic centrifuge tube could be pre-wetted with a few drops of MeCN to reduce the static when transferring the pre-weighed material.

Note: The ultrasound was just used help agitate the suspension and was performed by briefly sonicating for a second or two and then removing and repeating if necessary. Splashing and spattering of the suspension on the inside of the tub should be avoided.

Note: Long term storage of the material under a N₂ atmosphere is recommended just a precaution. The material has not been observed nor is suspected to degrade in air. However, no long-term stability tests have been performed to confirm this yet.

Note: The loading ratio of EDOT can be varied by adding more of the EDOT solution but the amount of FeTs₃.6H₂O oxidant needs to be changed accordingly using the EDOT:FeTs₃.6H₂O mole ratio of 1:2.33. Also noteworthy, is the total volume:mass ratio during the EDOT infusion process which should be kept at 3.62 (in μL of EDOT solution plus excess MeCN to mg of COF plus FeTs₃.6H₂O) e.g. 800 μL + 1170 μL = 1970 uL per solid material mass of 100 mg COF + 444.15 mg FeTs₃.6H₂O = 544.15 mg gives 3.62 μL/mg. When infusing at higher EDOT loading ratios, more excess MeCN might need to be added after the evaporation step to compensate for the extra FeTs₃.6H₂O needed. This infusion volume:mass (μL:mg) ratio of 3.62 worked well for TpOMe-DAQ but needed to be adjusted to 2.74 for PQ-COF and might need to be modified for other materials.

Note: Two batches of 0.4EDOT@TpOMe-DAQ were made which differed in their total volume:mass (volume of EDOT solution plus excess MeCN used in μL:mass of COF plus the FeTs₃.6H₂O used in mg) ratios. Batch 1 was made at a volume:mass ratio of 3.62 μL/mg and formed a composite with 29.4% PEDOT while Batch 2 was made at a volume:mass ratio of 1.80 μL/mg and produced a composite containing 34.7% PEDOT. This result highlights that the volume:mass ratio could have an effect on the final PEDOT loaded into the COF and that more concentrated infusion mixtures lead to larger amounts of PEDOT being infused.

3 Electrode preparation and exemplary redox-site accessibility (RSA) calculation

A solution of PVDF in DMF was prepared in a 5 or 10 mL volumetric flask at a concentration of 0.00500 mg/ μ L.

The graphite foil was pre-cut according to the shape of a master electrode template. The electrode surface was wiped with 95% ethanol using a tissue paper and heated to 100°C on a clean hotplate for 10-20 min to ensure the electrode surface was dry. The electrode was cooled in a sealed dry sample vial and weighed on a 0.00 mg sensitive balance.

Ca 1.75 mg of composite material was weighed off (and recorded) into a small mortar. If the mass of composite is known and the concentration of PVDF is known then the amount of PVDF-in-DMF solution can be calculated (using $V = (M-0.9M)/0.9C$) to give a 10% PVDF in composite mixture (normally between 30 and 50 μ L).

$$V = (M-0.9M)/0.9C$$

V = volume of PVDF in DMF solution in μ L.

M = mass of composite material weighed off in mg

C = concentration of PVDF in DMF (mg/ μ L)

The slurry of composite, PVDF and DMF is carefully ground with the pestle until a homogenous (1-2 minutes) suspension is formed. The slurry is pipetted up and deposited onto the clean electrode surface (leaving a small distance to the edge of the electrode). A few microliters of additional DMF can be added if necessary (but too much will cause running during the heating). There will be a residue left on the pestle and mortar. The electrode surface looks like the image below after depositing the slurry.

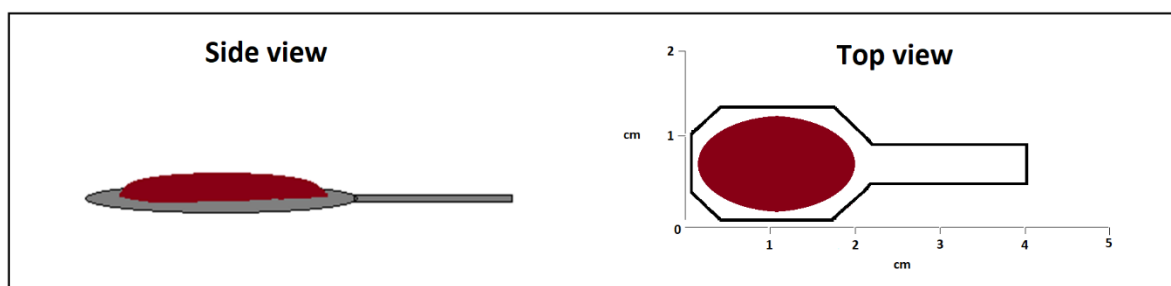


Figure S 2. An image depicting the approximate size and shape of the graphite-foil based electrodes used during the RSA studies

The electrode is then placed onto a clean hotplate at 100°C to evaporate the DMF. After most of the DMF appears to have dried off (1-2 min), the electrode is cooled and carefully placed into a vial of dH₂O and removed to rinse it (this is repeated 3 times). A final rinsing with 95% ethanol is performed similarly (3 times). The electrodes are very sensitive to shaking a bumping so rinsing is done by gently submerging the electrode in the liquid. The electrode is then placed on a clean hotplate again at 100°C to evaporate all the ethanol (10-20 minutes). The electrode is cooled in a closed dry vial and removed from the vial before weighing it at room temperature. By knowing the mass of the empty electrode and the electrode with material on it, the difference gives the amount of composite and binder. If the binder is 10% then 90% of the mass difference is the composite loaded on the electrode.

If the amount of COF in the composite is known then the theoretically expected capacity can be calculated.

Similar electrode preparations could also be easily be applied to glassy carbon electrodes.

The preparation of electrodes containing carbon additives were prepared by weighing off ca. 80 mg of the conductive carbon powder (e.g. BP2000, PBX51 and SuperP) into a clean dry 10 mL pre-weighed volumetric flask. The accurate mass was obtained by weighing the flask with its contents and subtracting the mass of the empty flask. The flask was then half filled with DMF, sonicated (30 min in an ultrasonic cleaning bath) and then made to the mark. A small magnetic stirring bead was inserted in to the flask. Before electrode preparation, the volumetric flasks were sonicated for 30 min and then kept stirred during the pipetting procedure. A know amount of COF material was weighed off in a small agate mortar, a calculated volume (based on the desired carbon:COF mass ratio) of the 0.00800 mg/ μ L carbon suspension in DMF was pipetted from the stirred volumetric flask into the mortar. Also, a calculated volume of the PVDF-in-DMF solution was pipetted into the mortar again using the formula $V = (M - 0.9M) / 0.9C$. The mixture was ground and homogenized using the pestle (and DMF left to evaporate if necessary) until it formed a suspension of desirable consistency to be pipetted onto the prepared graphite foil electrodes. After evaporating the DMF, the electrodes were prepared as described above. If one assumes that the composition of the carbon:COF:binder remains constant throughout the procedure, and by knowing the mass of composite on the electrode surface (by weighing the electrode before and after deposition), the theoretically expected capacity can be calculated.

A sample calculation for evaluating the redox site accessibility of TpOMe-DAQ in a PBX51 carbon and TpOMe-DAQ mixture is provided below.

A final electrode composition of C:COF:PVDF (mass ratio) of **25:65:10** was desired so a C:COF ratio of **0.3846** was selected.

1.05 mg of TpOMe-DAQ was weighed into the mortar which then required 0.4038 mg of PBX51.

If the PBX51 stock solution was 0.008006 mg/mL, **50.4** μ L was pipetted into the mortar.

With a net composite mass of 1.45 mg, the amount of PVDF needed (calculated from $V = (M - 0.9M) / 0.9C$) was **32.4** μ L if the stock solution of PVDF in DMF was 0.004982 mg/ μ L.

After preparing and weighing the electrode as described previously, the final amount of material (composite and binder) on the electrode was **1.50** mg. A quantitative transfer would have resulted in 1.62 mg of material on the electrode and so only 92.6% was transferred from the mortar. If one assumes the composition remaining in the mortar is the same as on the electrode surface, then **92.6%** of the original 1.05 mg TpOMe-DAQ was on the electrode (**0.9722** mg).

To obtain the theoretical capacity, we assumed a perfect and infinitely connected polymer with its smallest repeating monomer unit (depicted below) having a molecular mass of 555.546 g/mol. Each one of these repeating units would be expected to possess a redox capacity of 3 electrons.

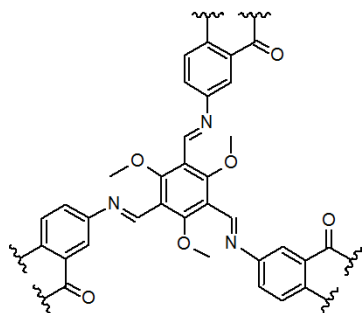


Figure S 3. A repeating formula fragment for TpOMe-DAQ COF with a molecular mass of 555.546 g/mol which was used to calculate the theoretical capacity.

The number of moles of repeating units in 0.975 mg TpOMe-DAQ is

$$n = \frac{m}{M} = \frac{0.0009722 \text{ g}}{555.546 \text{ g/mol}} = 1.750 \times 10^{-6} \text{ mol}$$

As each unit is expected to take up or release 3 electrons and the Faraday constant is 98485.3321 C/mol, the expected capacity is

$$\text{capacity} = 3 \times 1.750 \times 10^{-6} \text{ mol} \times 98485.3321 \text{ C/mol} = 0.5171 \text{ C}$$

By using cyclic voltammetry (at a scan rate of 0.005 V/s), the total amount of faradaic charge could be evaluated as depicted below. We chose to integrate the current time plots from using the time values recorded by the instruments during the CV measurements. Alternatively, the CV can be integrated and the I.V area divided by the scan rate (V/s) to obtain the charge in coulombs.

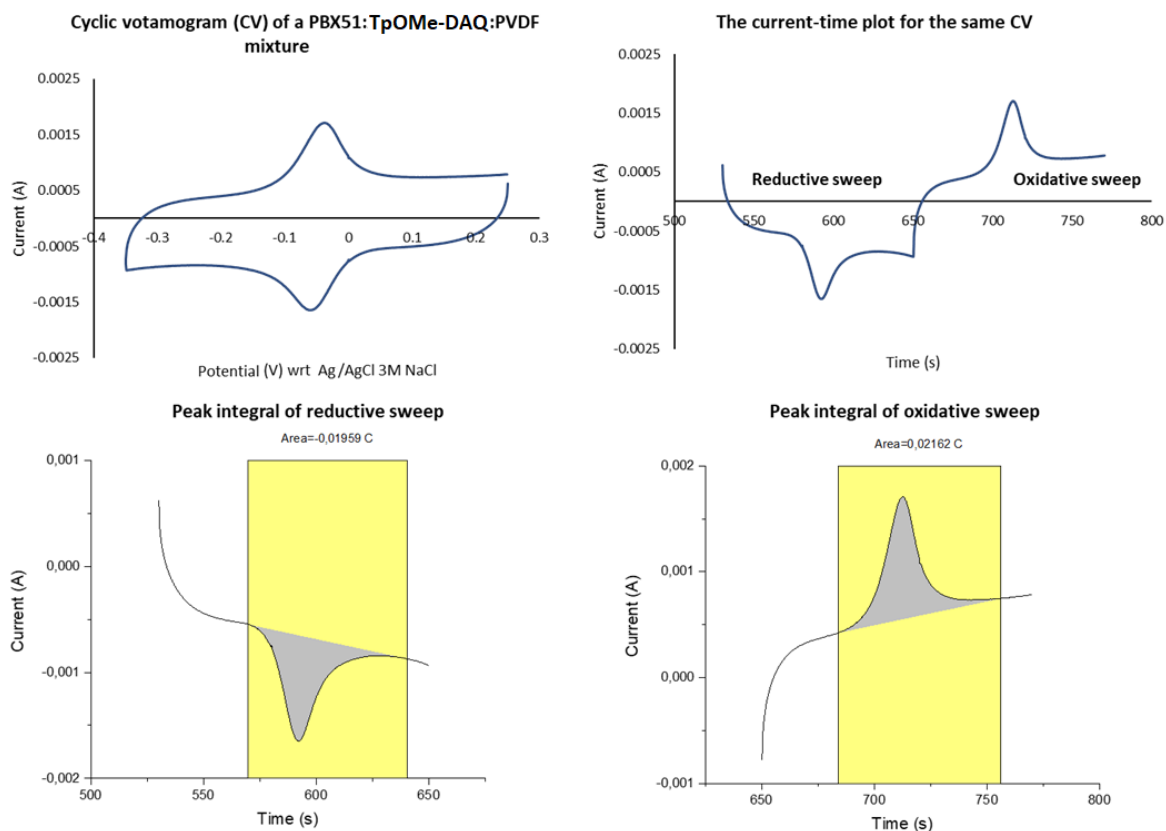


Figure S 4. Experimental data plots depicting how the faradaic charge was extracted from the electrode. We assumed all faradaic charge obtained under the peaks was due to the RACOF present in the composite mixtures. Non-faradaic charge was excluded by only integrating above the background currents. Top left: CV of the electrode taken at 0.005 V/s. Top right: the current-time plot for the CV taken in the top left. Bottom left: the integral of the peak from the reductive sweep in the current-time plot on the top right. Bottom right: the integral of the peak from the oxidative sweep in the current-time plot on the top right.

From the above values, the average charge was taken as:

$$\text{Average charge} = \frac{0.01959 \text{ C} + 0.02162 \text{ C}}{2} = 0.020605 \text{ C}$$

The redox-site accessibility (RSA) was calculated as:

$$\text{RSA} = \frac{\text{experimental capacity}}{\text{theoretical capacity}} \times 100 = \frac{0.020605 \text{ C}}{0.5171 \text{ C}} \times 100 = 3.99 \%$$

4 RSA Studies

All RSA studies were performed on material that was drop cast onto graphite foil electrodes over an approximate area of 2.25 cm^2 as described above and all CVs were acquired in 0.5 M aqueous solution of *para*-toluensulfonic acid (HpTSA) as the electrolyte. The TpOMe-DAQ COF used in all composite blends was used from the same large-scale synthesis batch of TpOMe-DAQ which was ground by pestle and mortar, well mixed and thoroughly characterised. A CV of the blank electrode material over the potential region of interest is depicted below. The blank current collecting material was shown to possess a surface area of $22.9 \pm 0.3 \text{ m}^2/\text{g}$ (BET plot depicted below) which is likely the reason for the electrode's high capacitive currents. The subtle bumps located around 0.4 V (vs Ag/AgCl) were suspected to arise from a small amount of surface functionalisation giving rise to various redox reactions which became clearer at lower scan rates.

Note: The effect of the washing procedure (washing with 3 X H₂O rinses plus 3 X 95% ethanol rinses and heating on a hotplate to dry) on the graphite foil electrodes mass was investigated by washing them and weighing them followed by washing again and weighing again. The differences in their masses before and after washing were not more than the observed variance from repeat measurements of the same object on the balance. We concluded that the washing procedure did not influence the electrode mass to any level outside of typical experimental error. However, after 25 cycles at 0.01 V/s in 0.5 M pTSA (between -0.35 and 0.95 V vs Ag/AgCl 3M NaCl), and then applying the washing procedure, their masses were significantly different (they increased 4.6% of their original mass). Consequently, no mass measurements used for RSA studies could be done on electrodes after cycling. This mass gain after cycling was further investigated by SEM-EDX in figure S7 below.

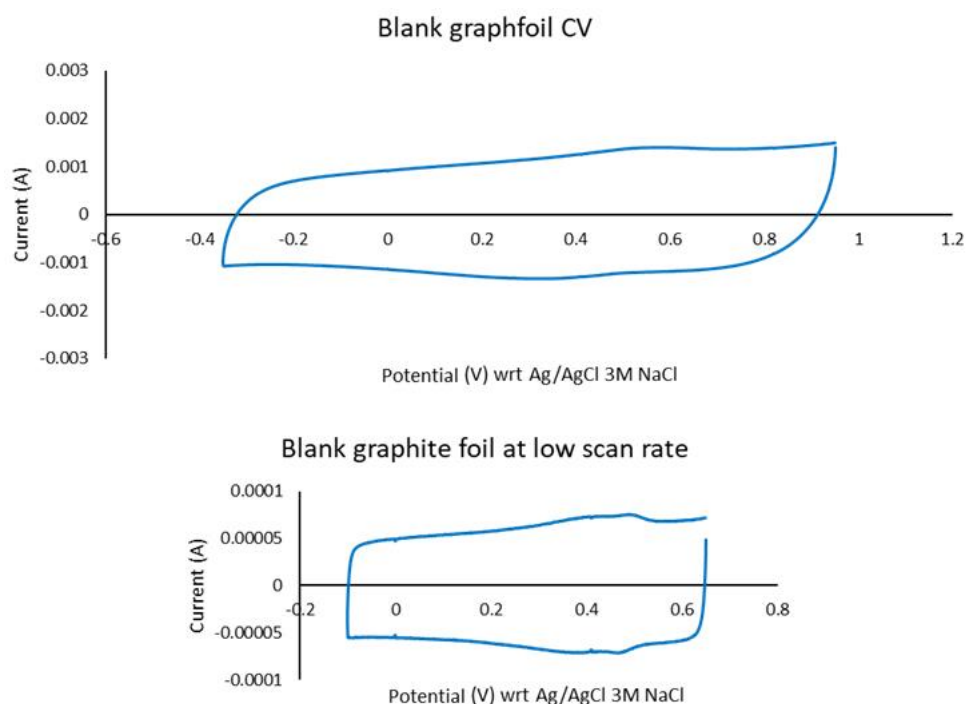


Figure S 5. Cyclic voltammograms of the blank graphite foil electrodes taken in an aqueous solution of 0.5 M pTSA. The upper CV was taken at a scan rate of 0.01 V/s to show the general features of the current collect over the voltage window of interest. The lower CV was taken at a scan rate of 0.0005 V/s to clarify the bumpy features from the upper scan. The peaks shifting to alignment at lower scan rates supports the idea that their origin might be due to various edge-functionalised redox active species.

BET plot for the blank graphite foil electrodes

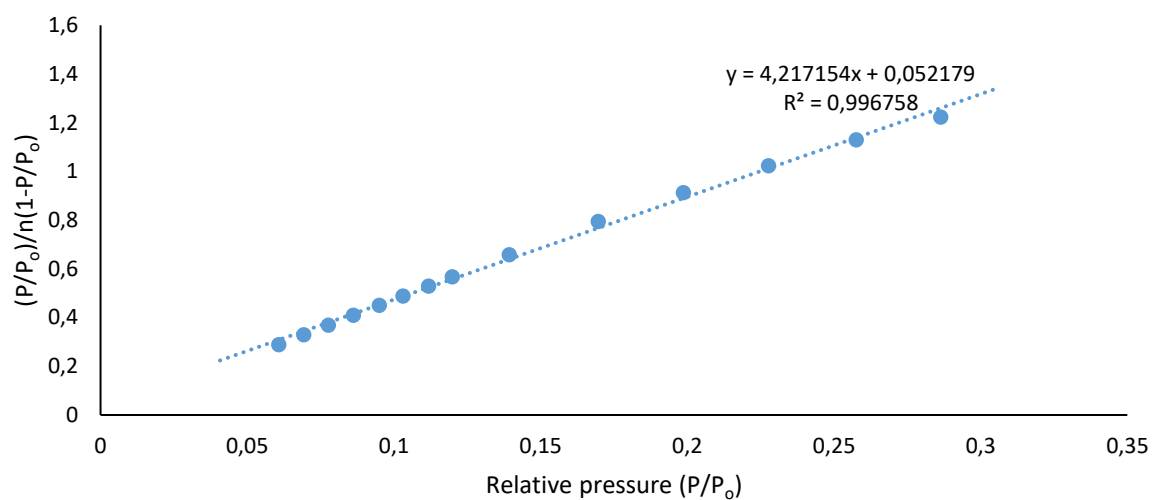


Figure S 6. The BET-plot of cut up graphite foil using data (relative pressures between 0.05 and 0.3 P/P₀) from its adsorption isotherm according to the Rouquerol criteria.¹² The intercept and gradient values were used to calculate the C value (82), monolayer quantity (0.234 mmol/g) and surface area (22.9 ± 0.3 m²/g). The calculated relative pressure (0.0995 P/P₀) was within 10% of the experimental P/P₀ value for the calculated monolayer quantity.

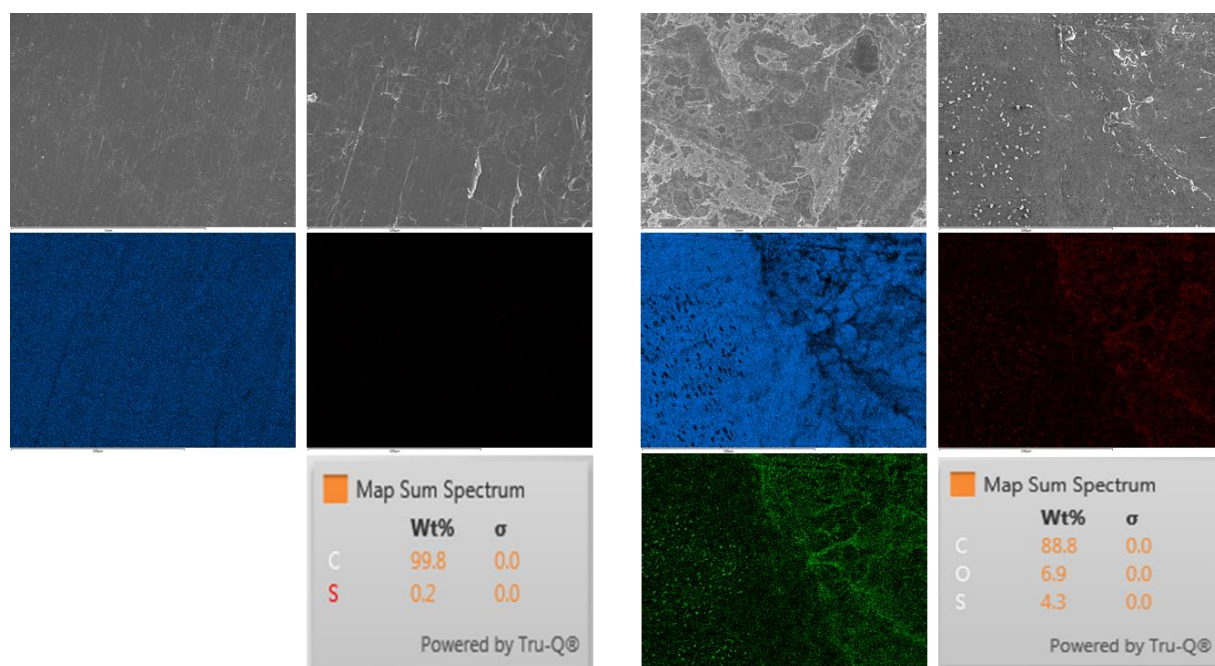


Figure S 7, SEM images (top) and EDS maps (bottom) of the graphite foil current collector before (left) and after (right) cycling in 0.5 M pTSA aqueous electrolyte. The mass of the foils increased after cycling and the EDS maps showed they had a significantly higher S and O content presumably from incorporating tosylate anions or pTSA from the electrolyte into its structure.

4.1 Electrode loading

Mixtures of TpOMe-DAQ and PVDF (10-12 % of the combined mass) could adhere to the graphite foil current collector to form a mechanically stable enough electrode to work with. However, these electrodes were not robust and required gentle submersion into any washing solvents used, as well as care taken to avoid bumping them. We investigated if the amount of material loaded onto a fixed amount of surface area (areal loading in mg/cm^2) had an effect on the RSA parameter. The mass component of the areal loading value includes the redox active material, conductive additives and binder used.

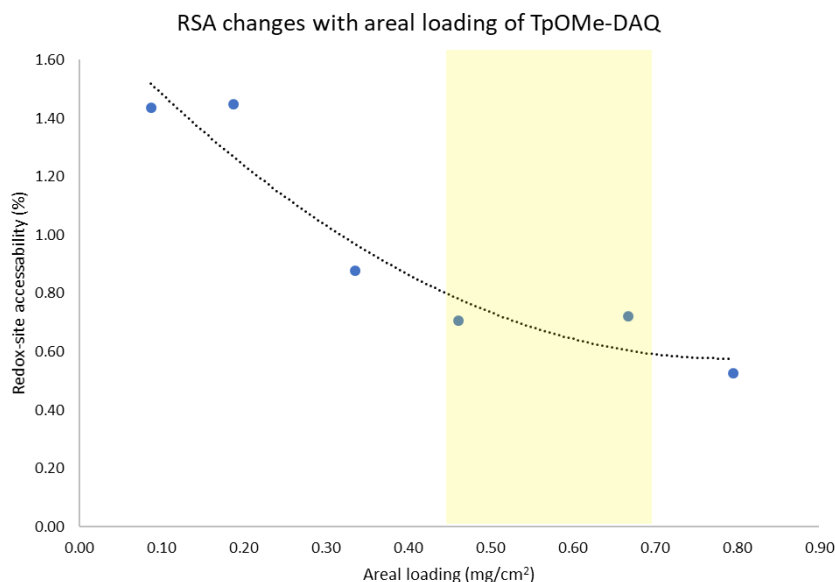


Figure S 8. A plot depicting how the RSA of the TpOMe-DAQ changed at different areal loadings. RSA measurements were made from CVs obtained at a scan rate of 0.005 V/s. The electrodes were prepared by weighing a known amount of TpOMe-DAQ and adding a corresponding amount of PVDF (using a PVDF in DMF mixture) to obtain mixture that would contain 5-11% of PVDF. The DMF suspension was drop cast over a known surface area of the graphite foil electrode. The areal loading values were calculated for only TpOMe-DAQ and the mass contribution from the PVDF binder was excluded.

The reliability of the above plot could be improved by making duplicate or triplicate measurements for each point instead of only a single measurement, as was done here. However, using its information anyway, the plot suggests that confining areal loadings to the yellow linear region (i.e., between 0.45 and 0.70 mg/cm^2) would be good for comparative RSA studies of TpOMe-DAQ when it is not blended with a conductivity enhancer. Apart from material adherence and film cracking problems at higher areal loadings, RSA values would be expected to fall to lower values for materials/composites suffering from poor conductivity throughout their bulk. This was observed for one electrode that was loaded at 0.80 mg/cm^2 (but with 5% PVDF) which produced a RSA of 0.53%.

The average RSA for 4 electrodes prepared with TpOMe-DAQ COF and PVDF (where PVDF made up 10-12% of the mixtures mass) and deposited at areal loadings between 0.45 and 0.70 mg/cm^2 was 0.76% with a standard deviation (sample) of $\pm 0.06\%$.

4.2 Carbon loading

Redox active electrode materials are often blended with conductive carbon to improve the bulk conductivity of the composite. This would be expected to enable higher areal loadings without reducing the RSA. However, the addition of excess carbon will ultimately reduce the gravimetric capacity of the composite and so finding the smallest amount needed could be beneficial when blending composites. We investigated the effect of increasing the amount of conductive carbon on the RSA of TpOMe-DAQ.

Despite the unexpectedly low RSAs for the carbon:COF blends investigated, we did observe that more than doubling the areal loading from 0.70 mg/cm² to 1.67 mg/cm² in a 25% BP2000 blend with TpOMe-DAQ did not affect its RSA to any degree outside of experimental error.

An interesting, but not unexpected, observation during these studies highlighted the effect of sonication time on RSA for the blends. Increasing the amount of sonication time of the conductive carbon in DMF solutions before blending from 10 minutes to 30 min increased the RSA of TpOMe-DAQ by 0.98%. Further sonication (8 min) of the carbon TpOMe-DAQ mixture after blending (performed according to the eppendorf tube method described above) increased RSA values by 1.3%.

Also noteworthy, was that sonicating a mixture of TpOMe-DAQ and PBX51 at a mass/mass ratio of 0.48 PBX51:TpOMe-DAQ for 40 minutes in EtOH (96%) using a high powered probe sonicator (VCX 500) did not improve TpOMe-DAQ's RSA beyond 4%. It resulted in a RSA value of 3.99% which was close to the value obtained for the triplicate study (3.95% ± 0.10%). The figure below highlights that factors such as the carbon-dispersion solvent, sonication time and sonication strength do influence RSA measurements, however, their overall impact is fairly minor (±1.2%) when compared to the low RSA values of pristine TpOMe-DAQ (0.76% ± 0.06%) and the much higher RSA values obtained for 0.4EDOT@TpOMe-DAQ (90.3% ± 1.7%).

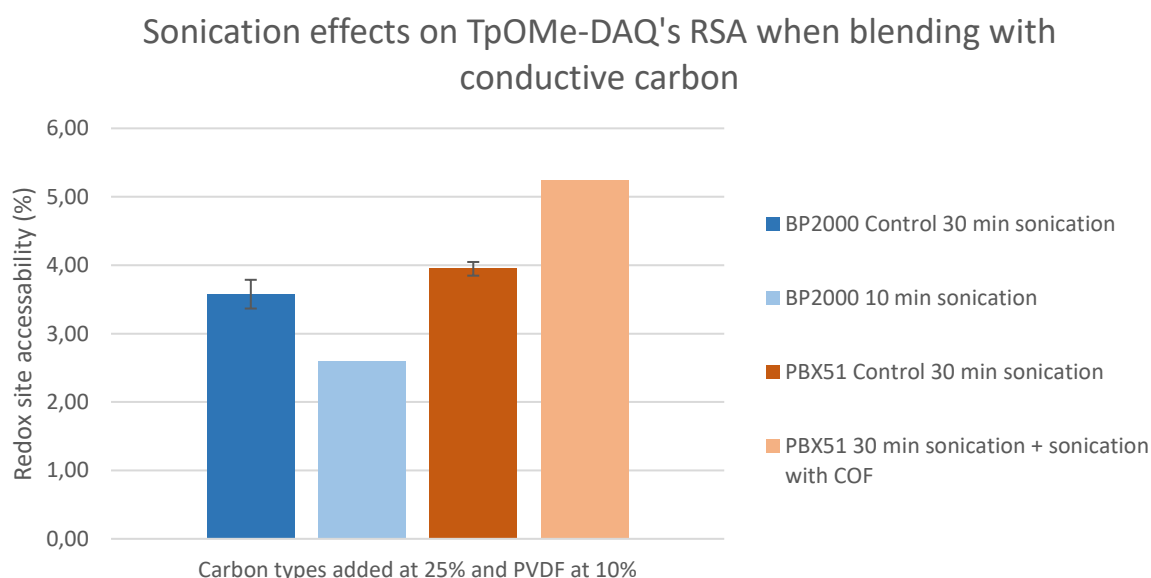


Figure S 9. A bar graph showing how the length of sonication (in a cleaning bath sonicator) of the conductive carbon stock solutions affected the RSA of TpOMe-DAQ when blended at a 0.38 mass/mass ratio Carbon:TpOMe-DAQ. The sample with the highest RSA (tan coloured bar) was achieved by sonicating TpOMe-DAQ together with PBX51 in DMF.

5 Material characterisation

2,6-diaminoanthraquinone (DAAQ)

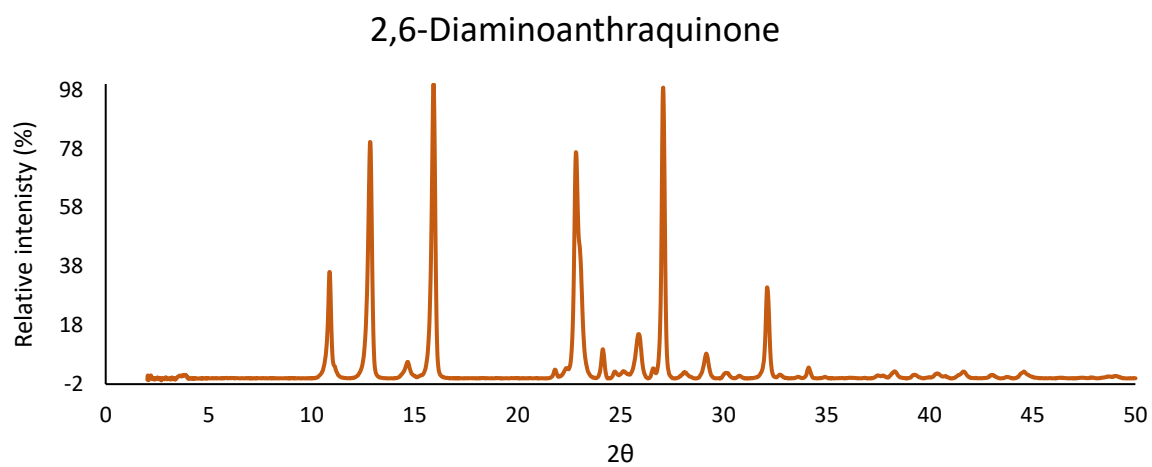


Figure S 10. PXRD diffractogram of DAAQ used as a powder pattern control.

2,4,6-Trimethoxy-benzene-1,3,5-tricarbaldehyde (TpOMe)

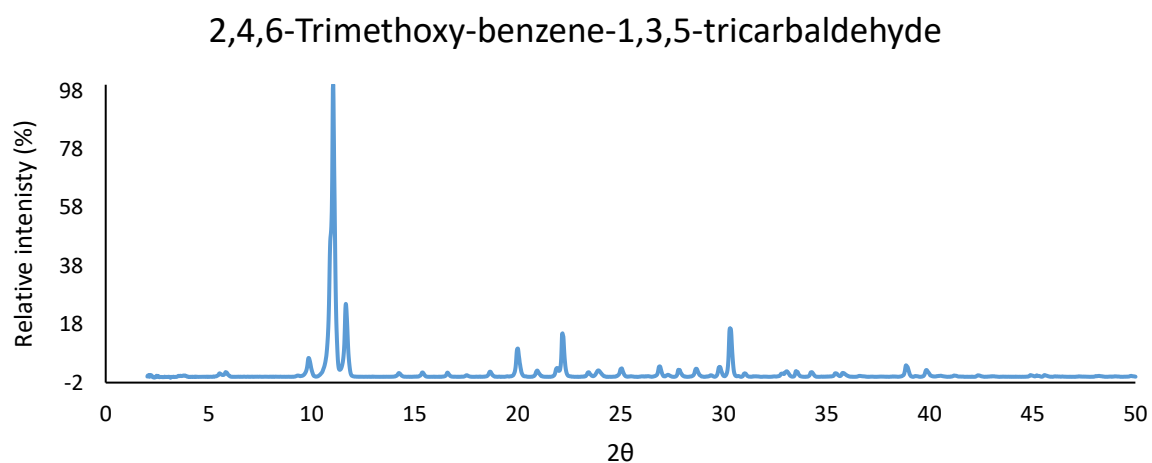


Figure S 11. PXRD diffractogram of TpOMe used as a powder pattern control.

5.1 TpOMe-DAQ

The material has previously been characterized by Halder et al¹⁰. The degassing protocol (holding the sample at 90°C for 6 hours under vacuum) was investigated by successive degas-measurement cycles on the same sample. It was shown that degassing at higher temperatures (150°C and 170°C) for shorter times (3 hours) successively decreased the surface area of the material.

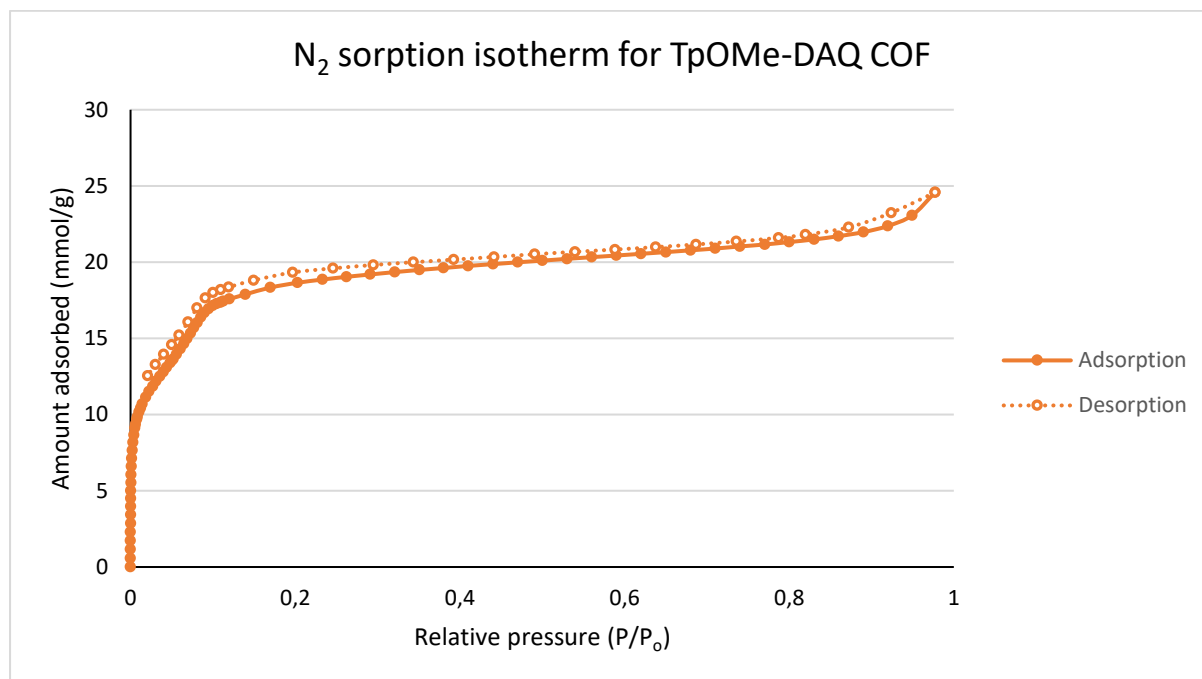


Figure S 12. The N₂ adsorption isotherm for TpOMe-DAQ COF.

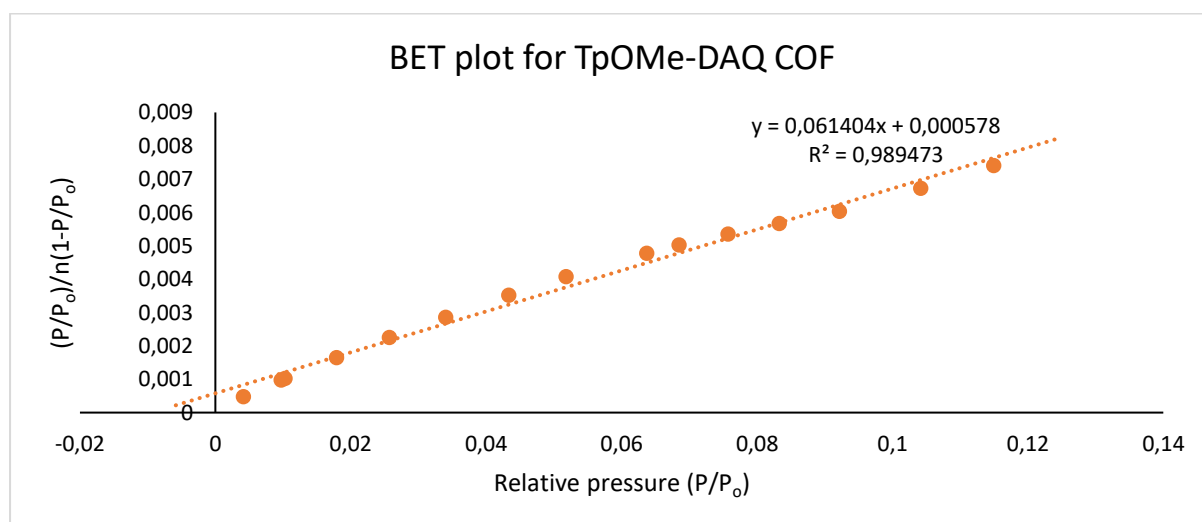


Figure S 13. The BET-plot of TpOMe-DAQ using data (relative pressures between 0.003 and 0.12 P/P₀) from its adsorption isotherm according to the Rouquerol criteria¹². The intercept and gradient values were used to calculate the C value (107), monolayer quantity (16.13 mmol/g) and surface area (1574 ± 14 m²/g). The calculated relative pressure (0.088 P/P₀) was within 10% of the experimental P/P₀ value for the calculated monolayer quantity.

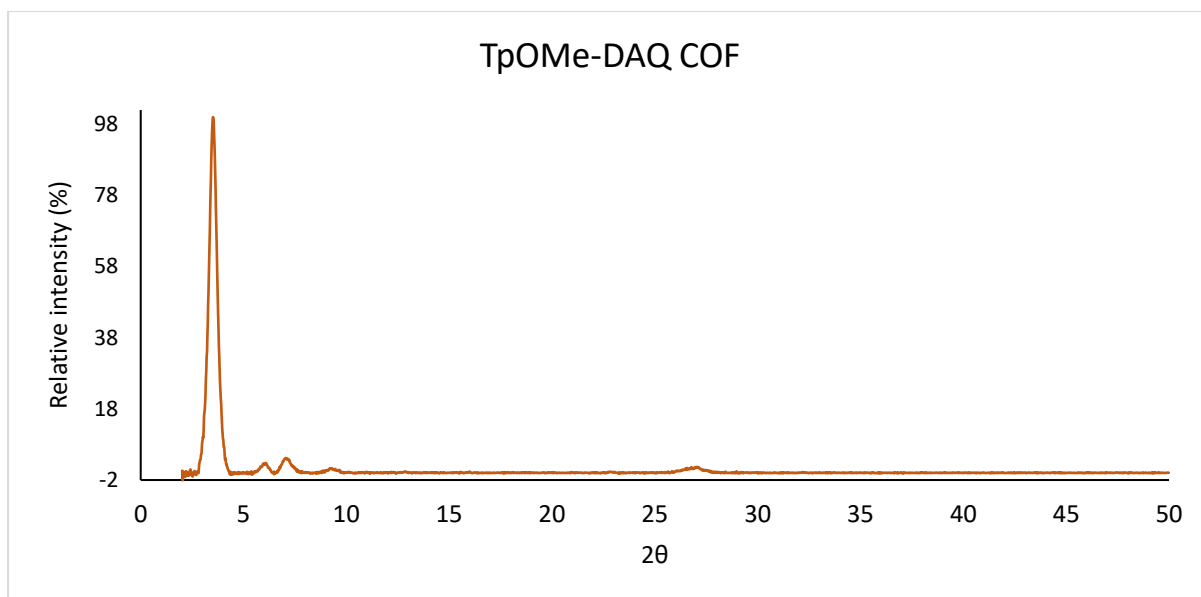


Figure S 14. PXRD diffractogram of TpOMe-DAQ COF confirming the presence of microcrystalline domains and matching well with the diffractograms previously published by Halder et al¹⁰ with peaks at 3.5, 6.1, 7.1, 9.4 and 27.1 2θ.

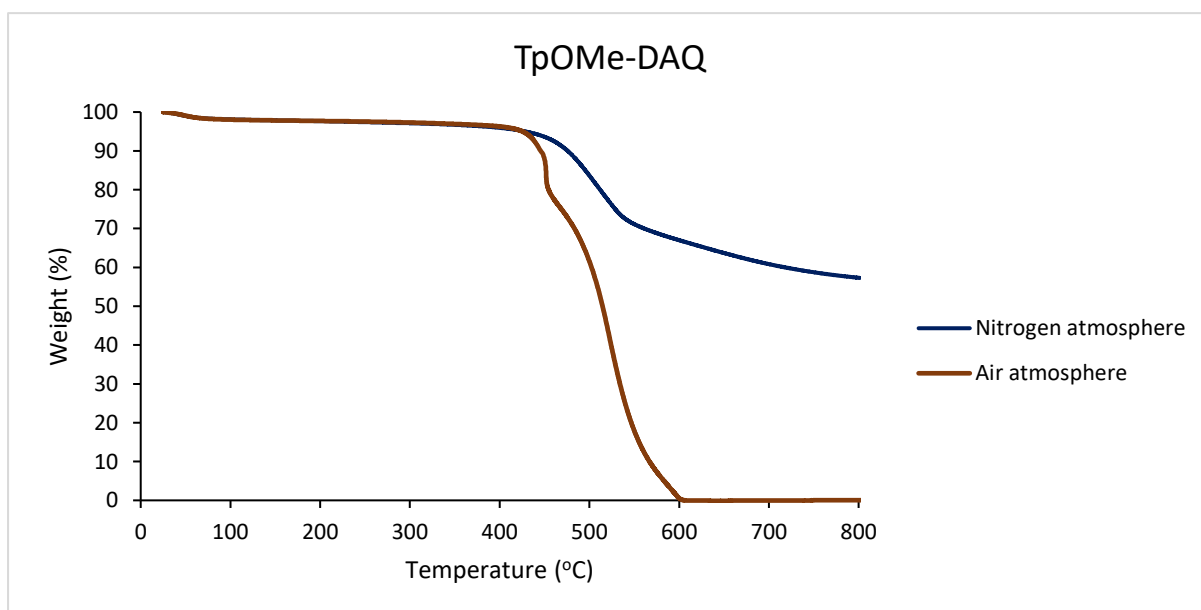


Figure S 15. The thermo-gravimetric profile of TpOMe-DAQ combustion under a nitrogen atmosphere and an air atmosphere.

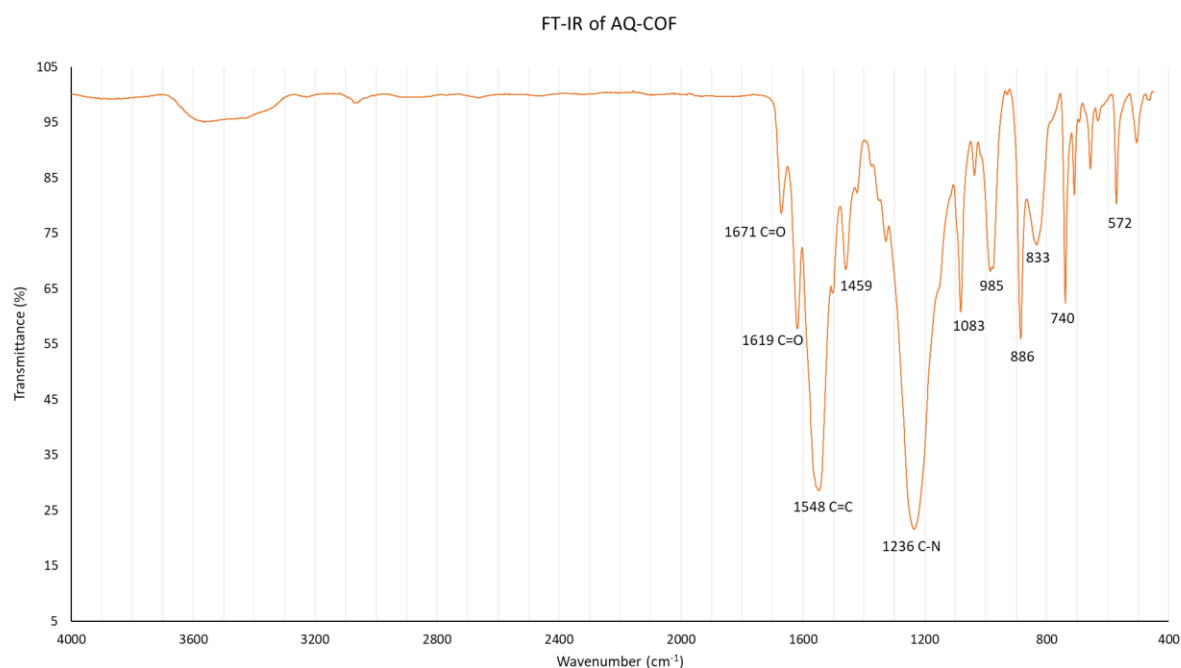


Figure S 16. An FT-IR spectrum of TpOMe-DAQ COF. The overall pattern and key absorption features match well with that previously reported by Banerjee et al.¹⁰

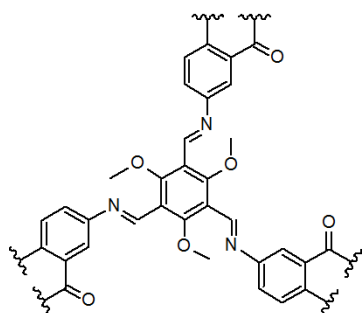


Figure S 17. Repeating formula fragment for TpOMe-DAQ containing 33 C, 6 O, 3 N and 21 H. The fragments molecular mass is 555.546 g/mole and each fragment contains 1.5 anthraquinone units for every 1 trimethoxytricarbaldehyde unit.

Table S 2. Elemental analysis results for TpOMe-DAQ

Element:	C (%)	H (%)	N (%)	S (%)
Expected:	71.35	3.81	7.56	0.00
Found 1:	67.57	3.34	7.93	0.71
Found 2:	67.94	3.42	7.98	0.76
Found Average:	67.76	3.38	7.96	0.74

The higher than expected amounts of sulphur was likely due to trapped ptsa molecules within the material's aggregates. Further washing cycles (adding solvent, briefly sonicating in a sonication bath and precipitating by centrifugation) in dH₂O (3 times) and 96% EtOH (3 times) reduced the sulphur content to below the detection limit.

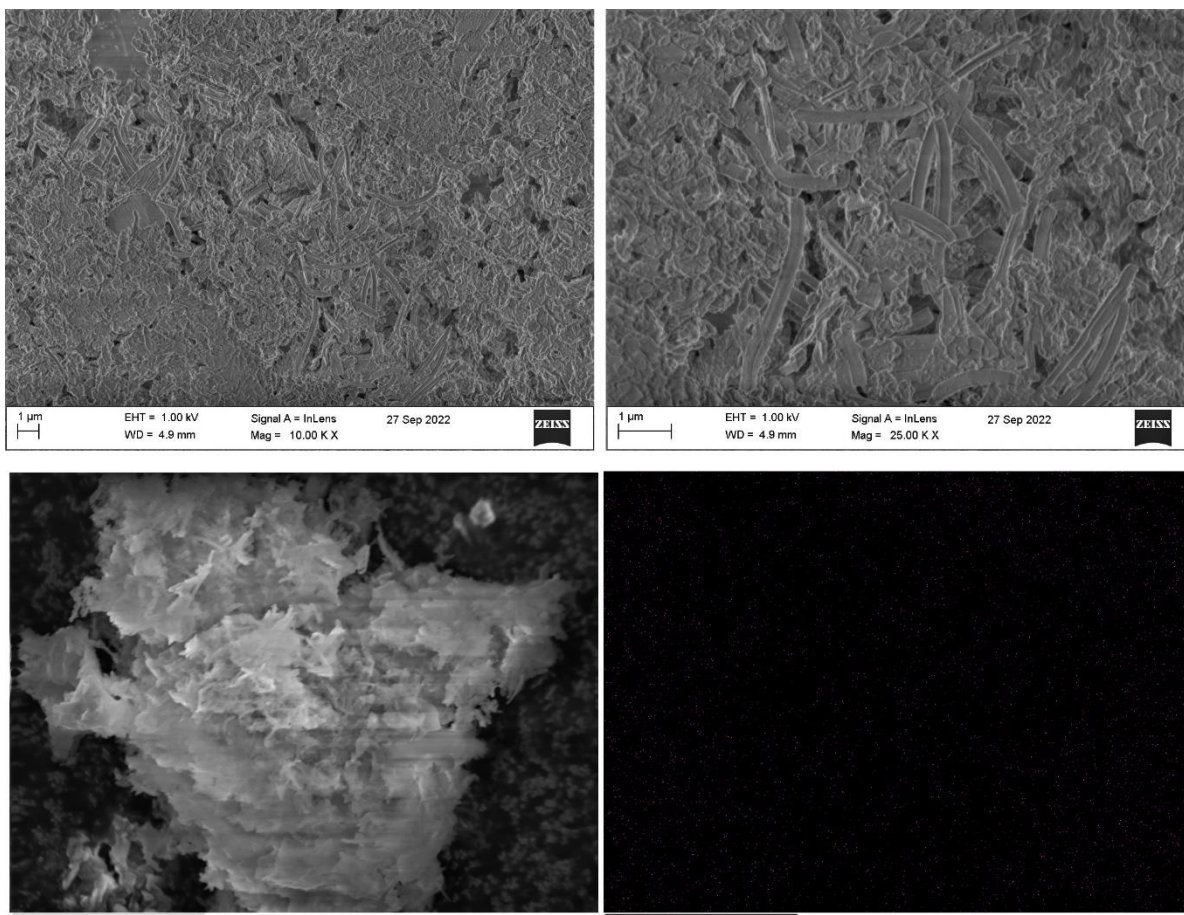


Figure S 18. SEM images of TpOMe-DAQ COF particles and their aggregates deposited on adhesive carbon (top). An SEM image of a piece of TpOMe-DAQ COF and its corresponding EDX sulphur map (bottom) showing the presence of sulphur in the material.

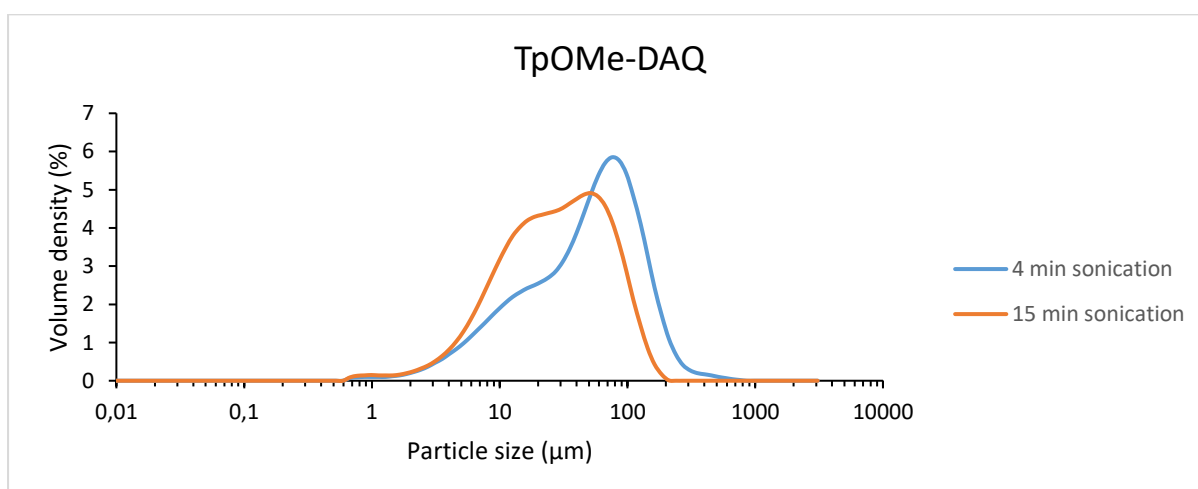


Figure S 19. The particle size distribution of the TpOMe-DAQ master batch showing peak distributions at 20 and 80 µm after 4 min of sonication which was applied to facilitate dispersion. Prolonged sonication further reduced the size of the aggregates.

5.2 PEDOT (pTs doped)

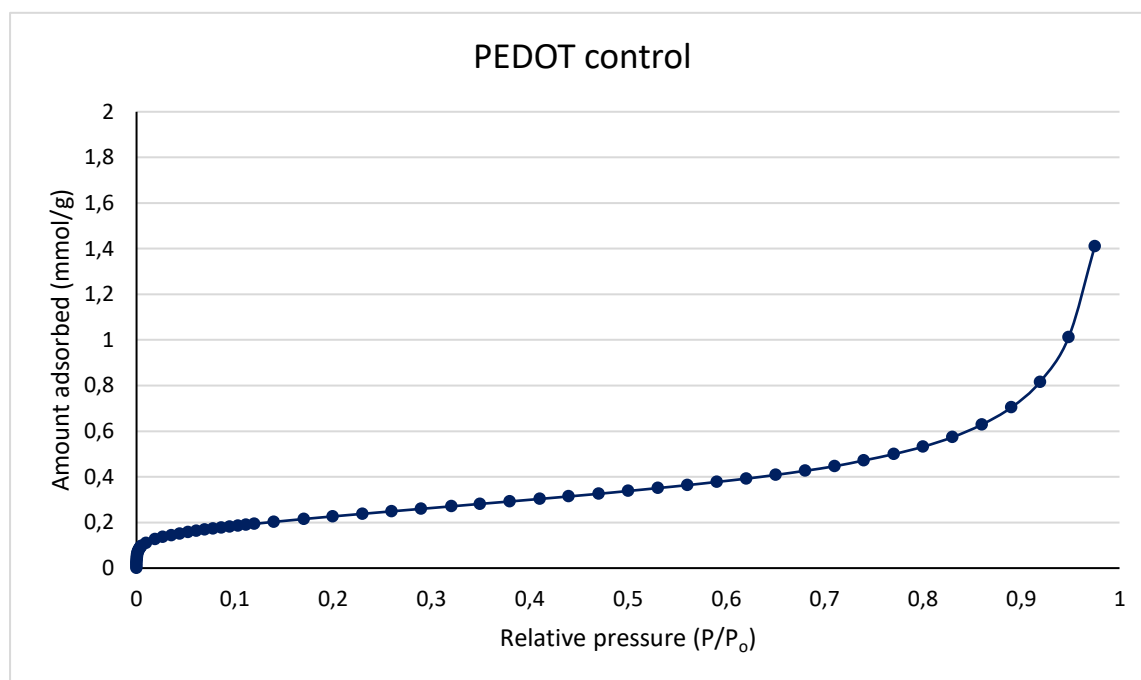


Figure S 20. The N₂ adsorption isotherm for PEDOT:Ts.

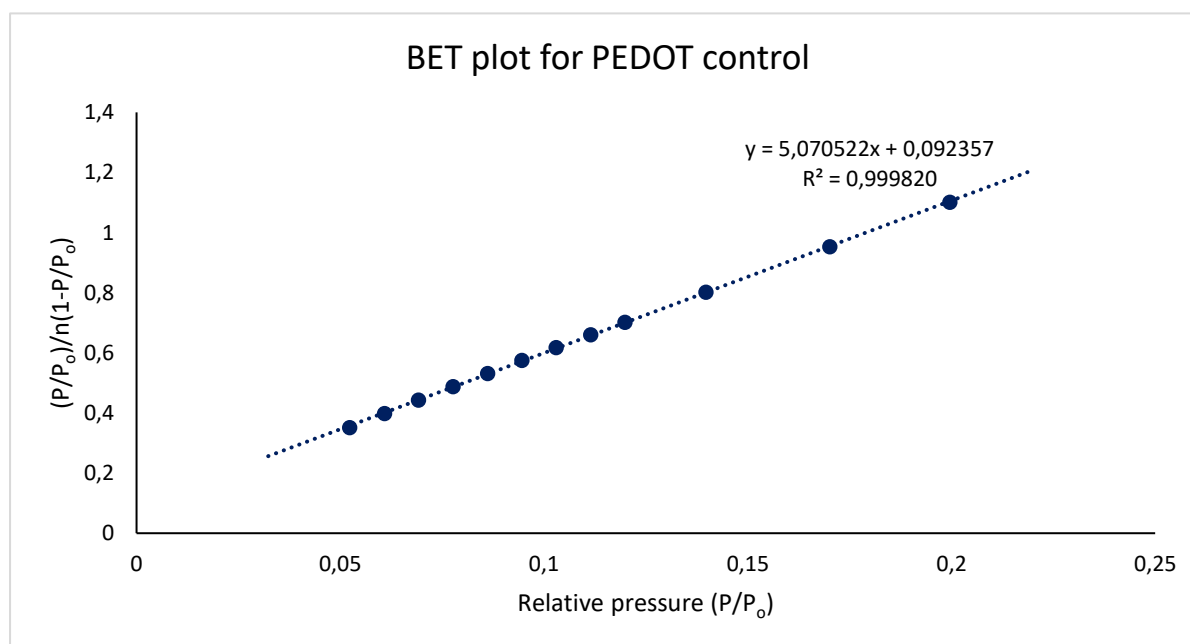


Figure S 21. The BET-plot of PEDOT:Ts using data (relative pressures between 0.05 and 0.3 P/P₀) from its adsorption isotherm according to the Rouquerol criteria.¹² The intercept and gradient values were used to calculate the C value (56), monolayer quantity (0.194 mmol/g) and surface area (18.9 ± 1.3 m²/g). The calculated relative pressure (0.118 P/P₀) was within 10% of the experimental P/P₀ value for the calculated monolayer quantity.

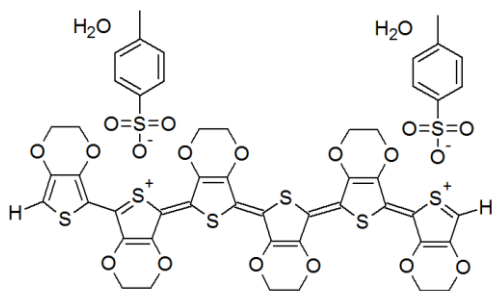


Figure S 22. Repeating formula fragment for PEDOT containing 50 C, 20 O, 0 N and 44 H. The fragment's molecular mass is 1221.362 g/mol and each fragment was thought to contain 2 tosylate doping anions for every 3 polymerised EDOT units. Experimental values agree better when each tosylate anion is associated with a water molecule.

Table S 3. Elemental analysis results for PEDOT (pTs doped)

Element:	C (%)	H (%)	N (%)	S (%)
Expected:	49.17	3.63	0.00	21.00
Found 1:	48.94	3.51	<0.10	20.87
Found 2:	48.95	3.51	<0.10	20.52
Found Average:	48.95	3.51	<0.10	20.70

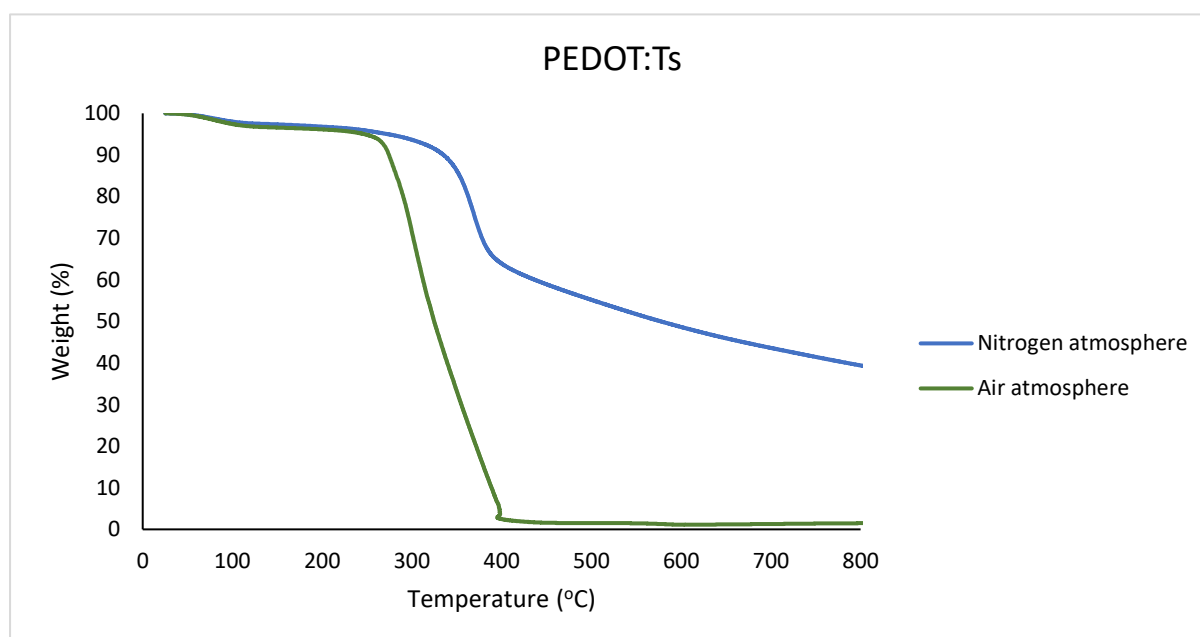


Figure S 23. The thermo-gravimetric profile of PEDOT:Ts combustion under a nitrogen atmosphere and an air atmosphere. A small reddish-brown combustion residue was found after analysis and thought to be Fe_2O_3 suggesting a small amount of the oxidizing agent (FeTs_3) is trapped within the polymer and unable to be removed by the procedure that was used.

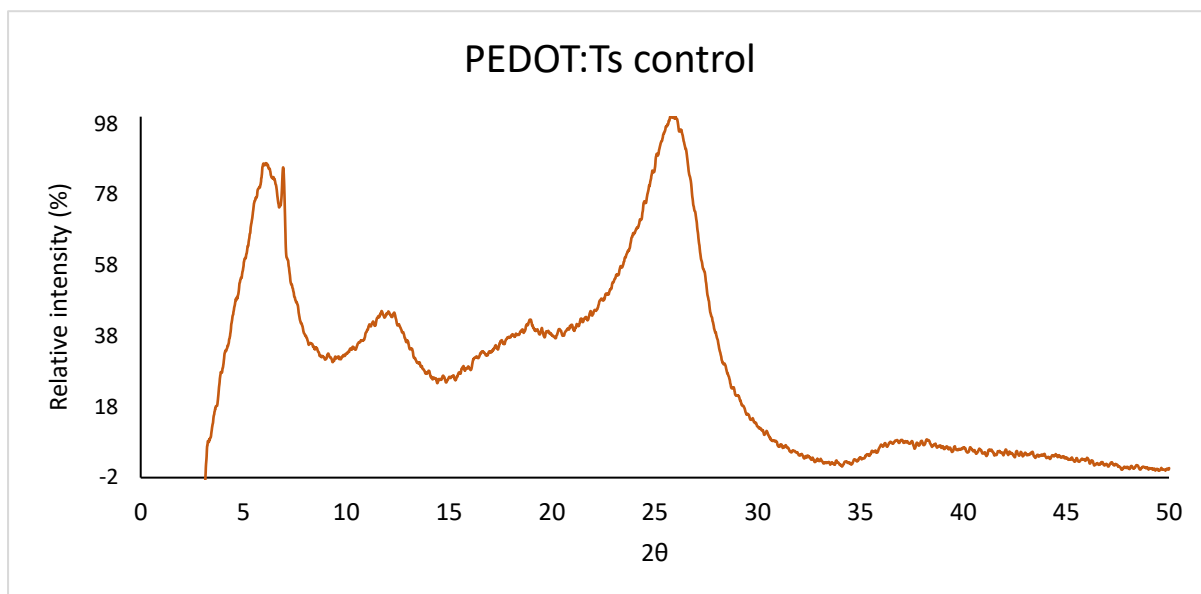


Figure S 24. PXRD diffractogram of PEDOT:Ts used as a powder pattern control.

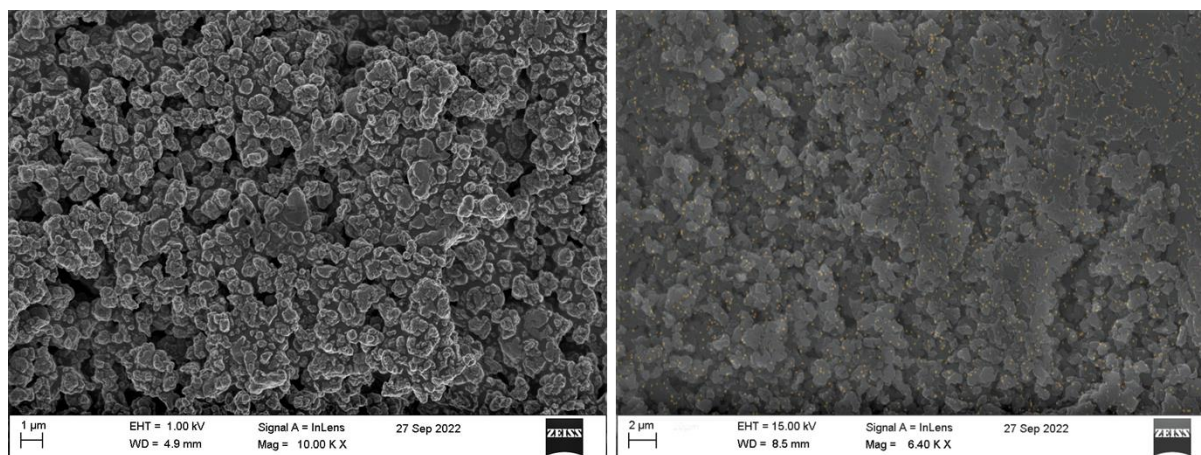


Figure S 25. SEM Images of the PEDOT:Ts control. The image on the right is an overlay with an EDS map for Fe. The orange spots confirmed the presence of Fe and showed that its was evenly distributed throughout the material.

5.3 0.4EDOT@TpOMe-DAQ

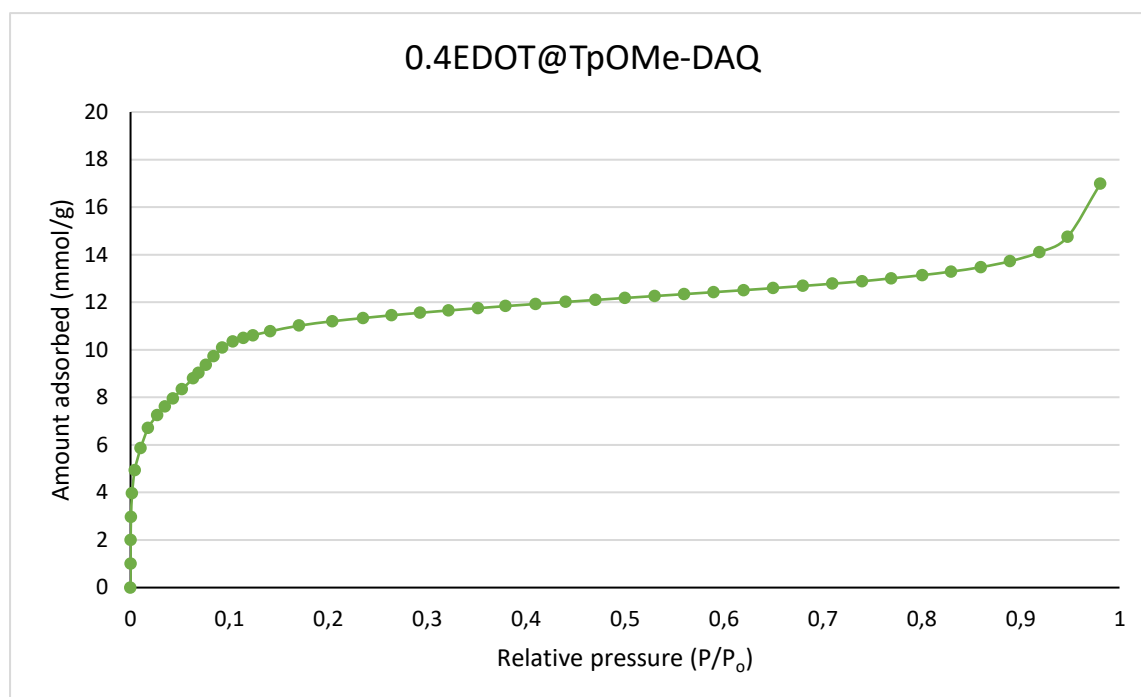


Figure S 26. The N₂ adsorption isotherm for 0.4EDOT@TpOMe-DAQ.

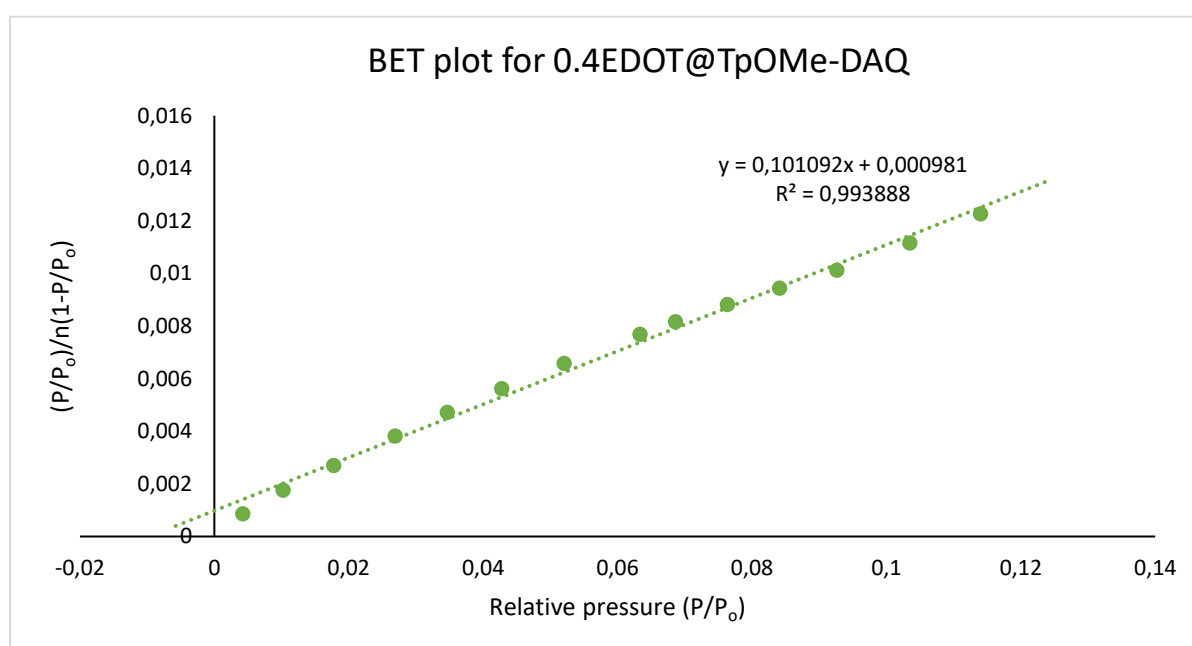
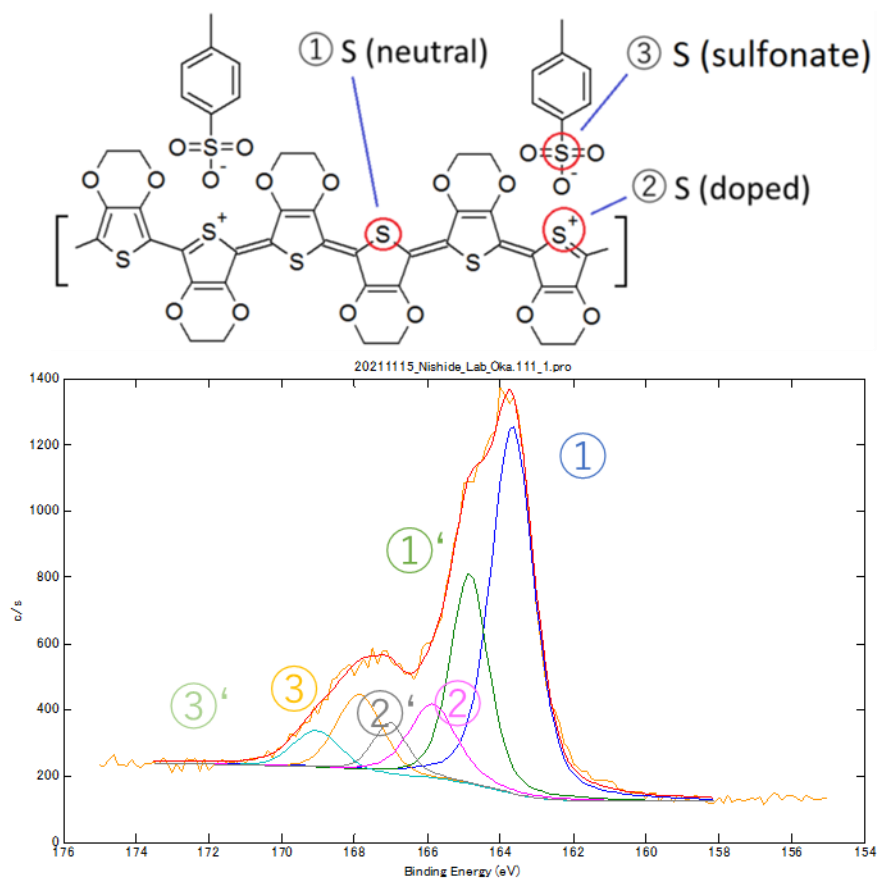


Figure S 27. The BET-plot of 0.4EDOT@TpOMe-DAQ using data (relative pressures between 0.003 and 0.12 P/P₀) from its adsorption isotherm according to the Rouquerol criteria.¹² The intercept and gradient values were used to calculate the C value (104), monolayer quantity (9.80 mmol/g) and surface area (956 ± 5 m²/g). The calculated relative pressure (0.089 P/P₀) was within 10% of the experimental P/P₀ value for the calculated monolayer quantity.



Cycle	Band	Pos	PosSep	B_FWHM	FWHM	Height	%Gauss	Area	%Area	ChiSquared
1	1	163.67	0.00	1.40	1.40	1111	60	1974	46.25	1.83
2	2	164.85	1.18	1.23	1.23	635	60	987	23.13	
3	3	165.85	2.19	1.57	1.57	225	50	465	10.89	
4	4	167.03	3.37	1.13	1.13	156	50	232	5.44	
5	5	167.87	4.20	1.49	1.49	234	80	407	9.53	
6	6	169.05	5.38	1.52	1.52	115	80	203	4.76	

Figure S 28. The S2p XPS spectrum for 0.4EDOT@TpOMe-DAQ with the S2p_(3/2) and S2p_(1/2) peaks fitted for the different sulphur environments (depicted in the image above the spectrum and circled in red). As each oxidised (doped) sulphur in the PEDOT chain would be expected to be charge neutralised by a tosylate anion, the combined areas of sulphurs 2 and 3 were averaged in order to estimate the relative amount of tosylate anions present in the polymer chain. According to the data above and after averaging, 15.31 % of the sulphur present was expected to be in the tosylate form (Mw = 171.192 g/mole) and the remaining 84.69 % in the doped or neutral form making up the PEDOT chain (where each sulphur atom represents an averaged molecular weight of 140.322 g/mole).

Table S 4. Elemental analysis results for 0.4EDOT@TpOMe-DAQ. Predicting the expected percent C, H, N, S was not possible due to unknown polymerisation yields and tosylate doping ratios. However, once the doping ratio was estimated using XPS, the sulphur value content determined by elemental analysis could be used to estimate the percent PEDOT:Ts making up the composite.

Element:	C (%)	H (%)	N (%)	S (%)
Expected:				
Found 1:	61.49	3.94	4.9	6.97
Found 2:	60.91	4.07	4.96	6.99
Found Average:	61.20	4.01	4.93	6.98

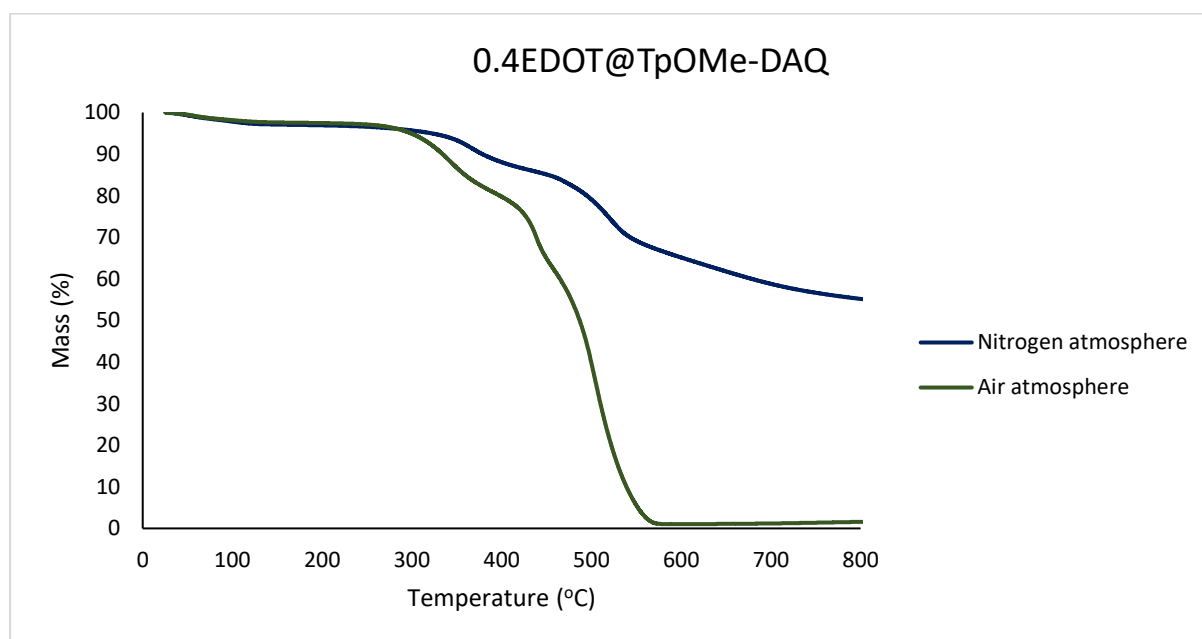


Figure S 29. The thermo-gravimetric profile of 0.4EDOT@TpOMe-DAQ combustion under a nitrogen atmosphere and an air atmosphere.

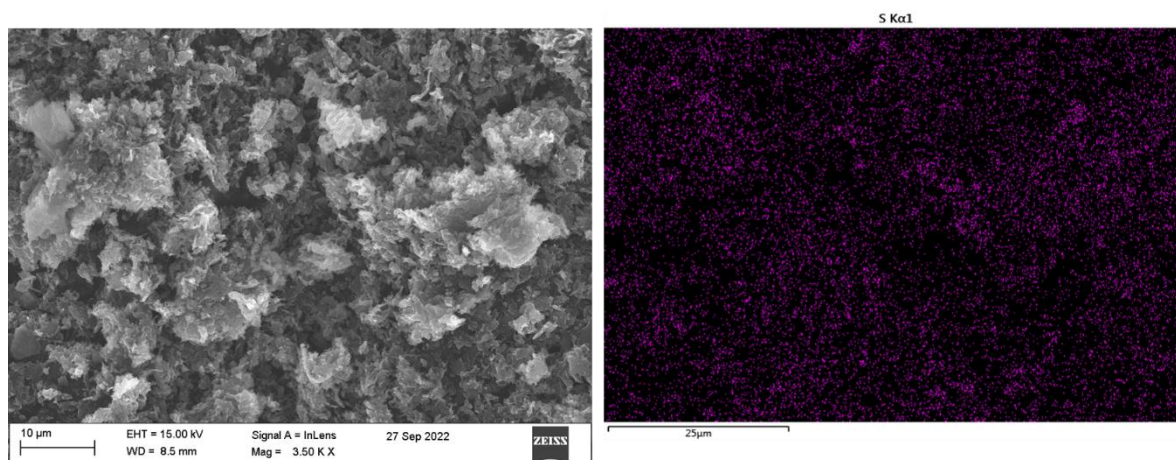
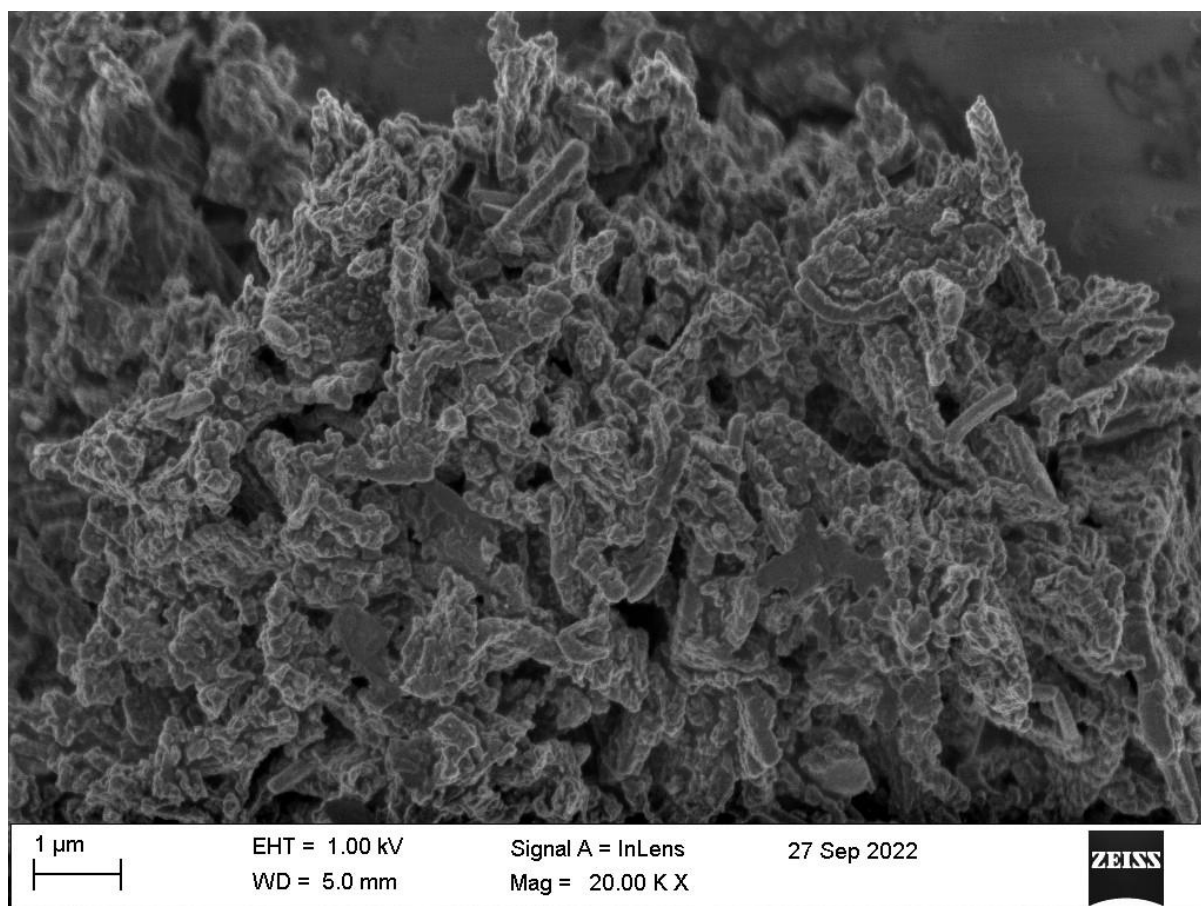


Figure S 30. An SEM image of the 0.4EDOT@TpOMe-DAQ composite showing the cauliflower-like PEDOT:Ts coating over the TpOMe-DAQ structures (top). A sulphur EDS map (bottom right) and the corresponding SEM image (bottom left) showing a relatively even surface distribution of the PEDOT:Ts coating.

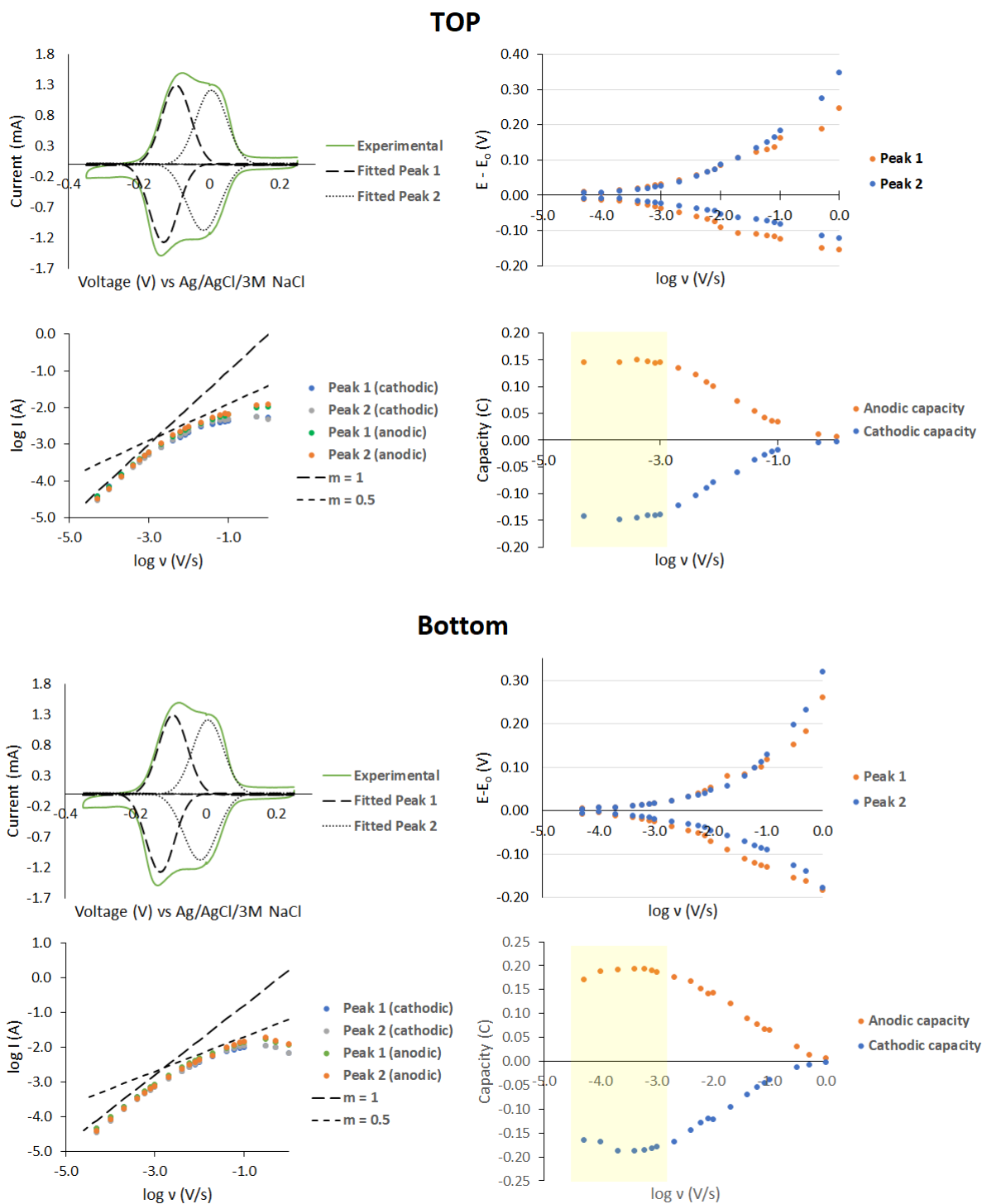


Figure S 31. Electrochemical characterisation data based on scan rate studies for 0.4EDOT@TpOMe-DAQ (top) and the same composite mixed with PBX51 at mass/mass ratio of 0.38 composite:PBX51 (bottom). The similar shapes of the plots suggest very little improvement is achieved by adding conductive carbon to the composite.

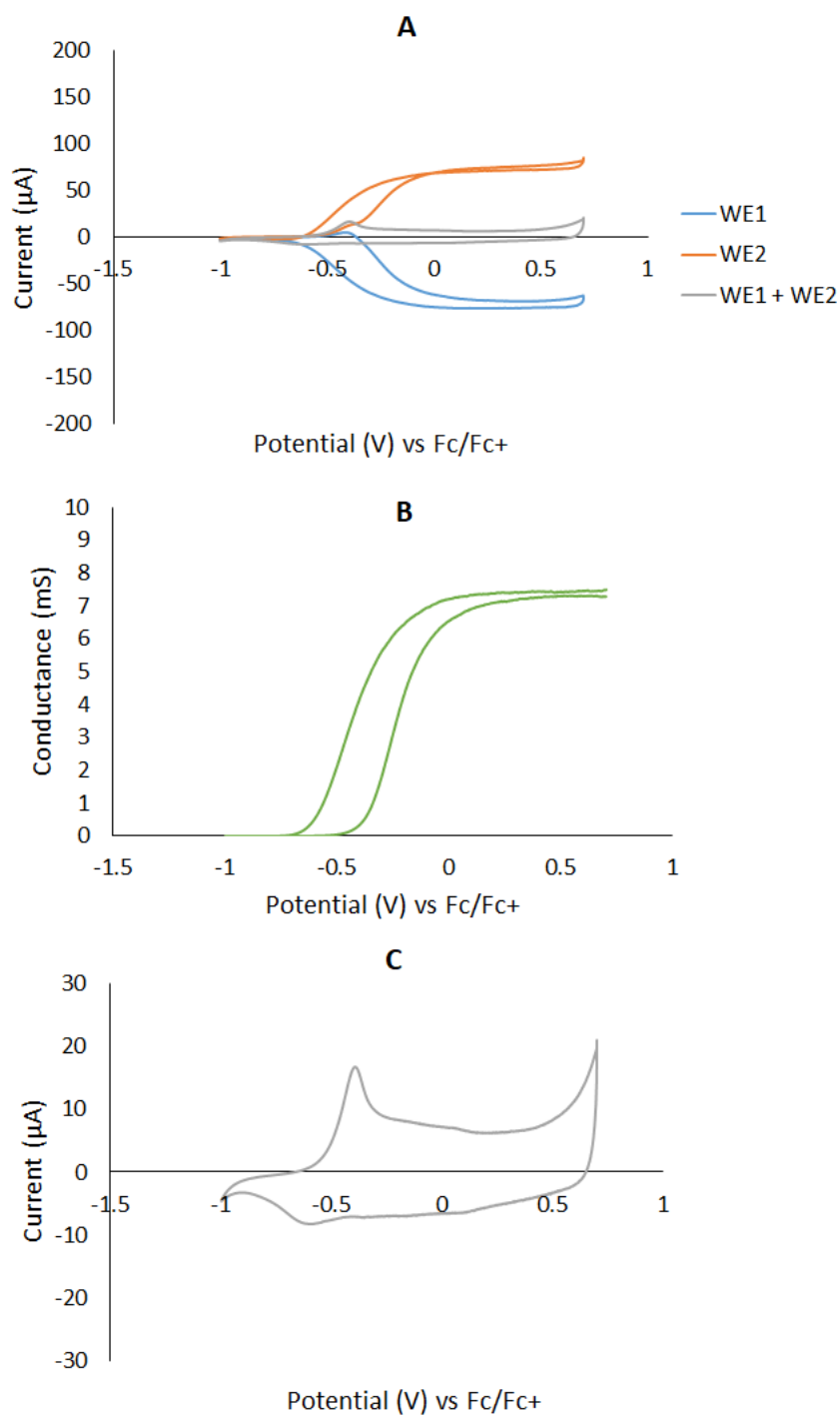


Figure S 32. IDA studies of 0.4EDOT@TpOMe-DAQ performed in MeCN using 0.1M TBAPF₆ as the electrolyte. The scan rate was 0.001 V/s. A) Depicts the current split due to the applied voltage bias between the working electrodes (WE1 and WE2) when the conductive polymer becomes conductive. B) A plot of the film's conductance at different applied potentials. C) Is a CV of the composite obtained by summing the currents from the working electrodes and resembles a typical CV for PEDOT.

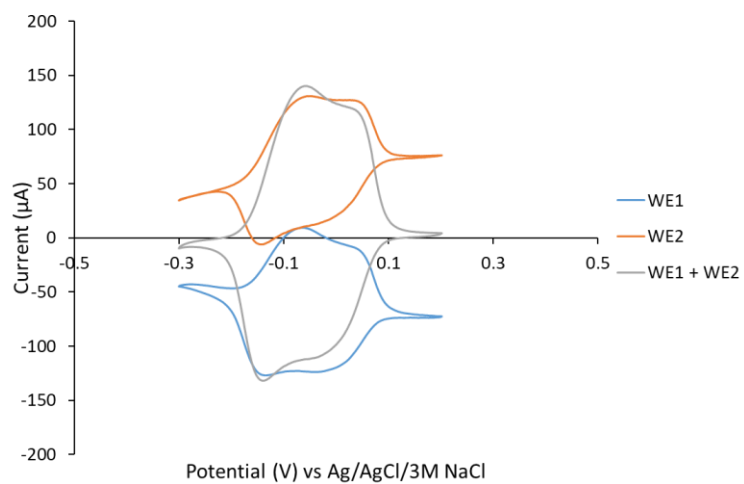


Figure S 33. IDA studies of 0.4EDOT@TpOMe-DAQ performed in water using 0.5M pTSA as the electrolyte. The scan rate was 0.0005 V/s. A) Depicts the current split due to the applied voltage bias between the working electrodes (WE1 and WE2) when the conductive polymer becomes conductive.

5.4 0.2EDOT@TpOMe-DAQ

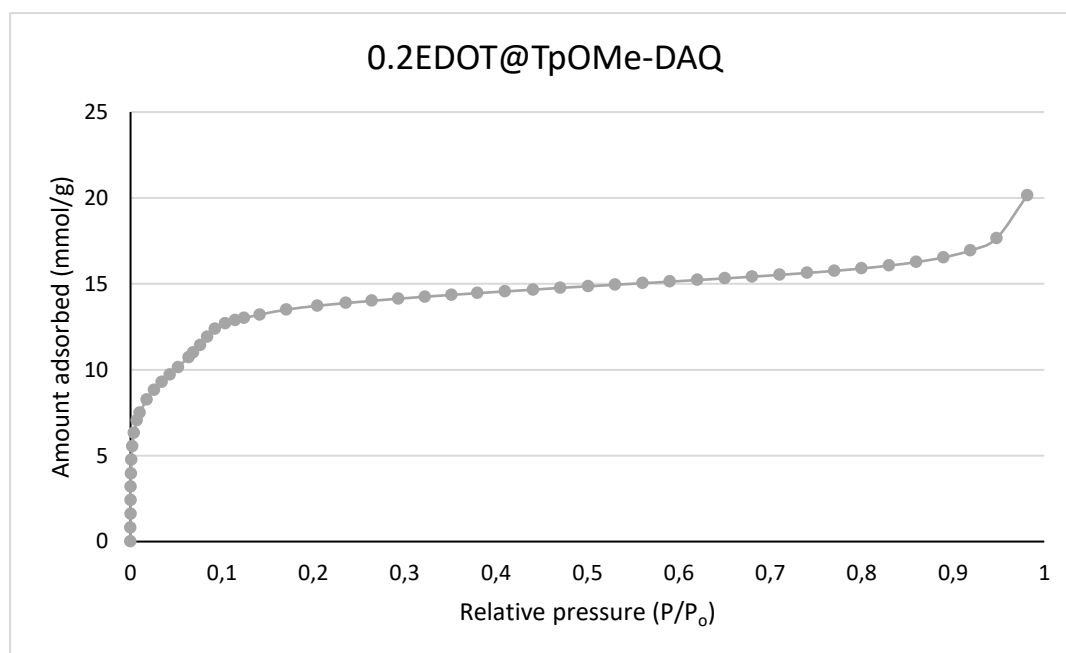


Figure S 34. The N₂ adsorption isotherm for 0.2EDOT@TpOMe-DAQ.

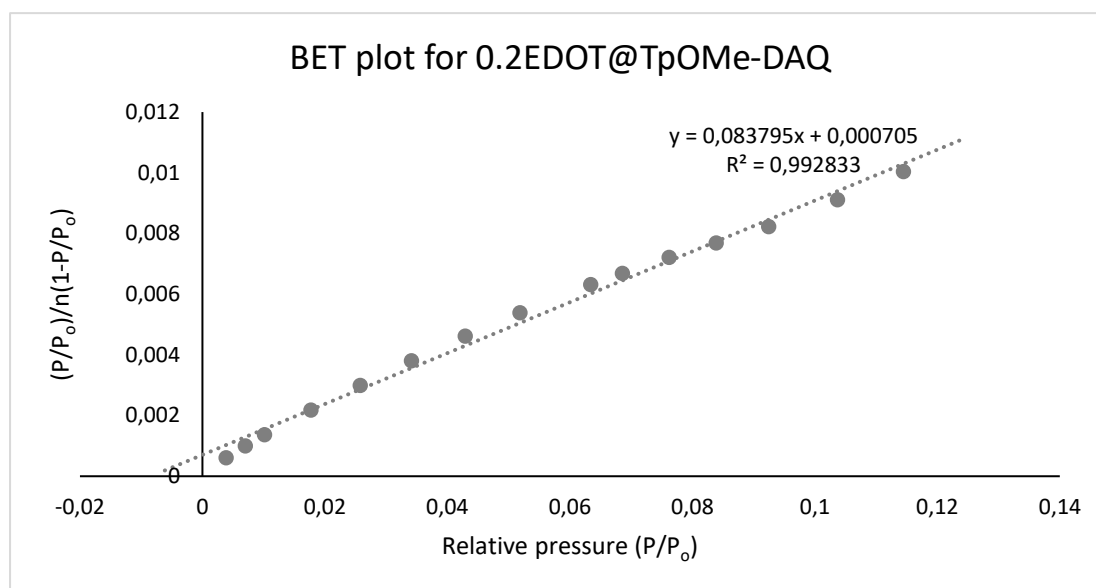
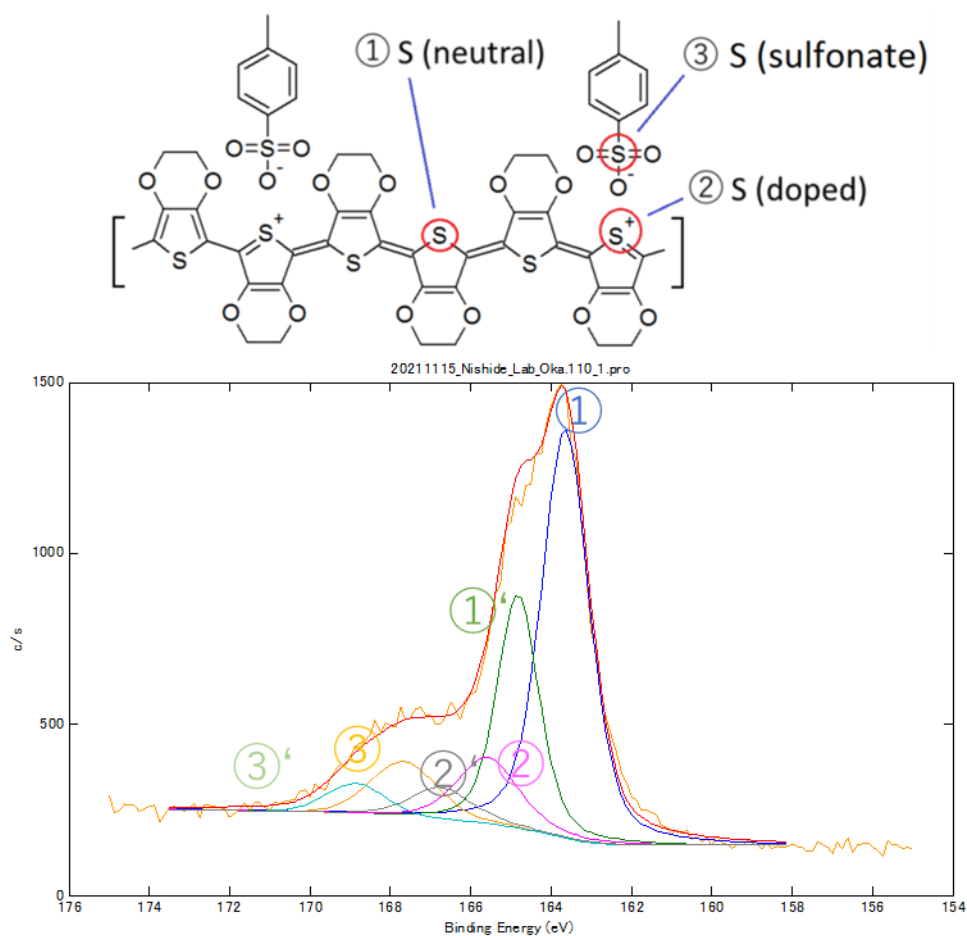


Figure S 35. The BET-plot of 0.2EDOT@TpOMe-DAQ using data (relative pressures between 0.003 and 0.12 P/P₀) from its adsorption isotherm according to the Rouquerol criteria.¹² The intercept and gradient values were used to calculate the C value (120), monolayer quantity (11.83 mmol/g) and surface area (1155 ± 7 m²/g). The calculated relative pressure (0.084 P/P₀) was within 10% of the experimental P/P₀ value for the calculated monolayer quantity.



Cycle	Band	Pos	PosSep	B_FWHM	FWHM	Height	%Gauss	Area	%Area	ChiSquared
①	①	163.65	0.00	1.40	1.40	1197	60	2127	47.85	3.11
①'	①'	164.83	1.18	1.23	1.23	684	60	1063	23.92	
②	②	165.58	1.94	1.80	1.80	196	50	463	10.42	
②'	②'	166.76	3.12	1.84	1.84	95	50	232	5.21	
③	③	167.67	4.03	1.95	1.95	164	80	373	8.40	
③'	③'	168.85	5.21	1.75	1.75	91	80	187	4.20	

Figure S 36. The S2p XPS spectrum for 0.2EDOT@TpOMe-DAQ with the S2p_(3/2) and S2p_(1/2) peaks fitted for the different sulphur environments (depicted in the image above the spectrum and circled in red). As each oxidised (doped) sulphur in the PEDOT chain would be expected to be charge neutralised by a tosylate anion, the combined areas of sulphurs 2 and 3 were averaged in order to estimate the relative amount of tosylate anions present in the polymer chain. According to the data above and after averaging, 14.12 % of the sulphur present was expected to be in the tosylate form (Mw = 171.192 g/mole) and the remaining 85.88 % in the doped or neutral form making up the PEDOT chain (where each sulphur atom represents an averaged molecular weight of 140.322 g/mole).

Table S 5. Elemental analysis results for 0.2EDOT@TpOMe-DAQ. Predicting the expected percent C, H, N, S was not possible due to unknown polymerisation yields and tosylate doping ratios. However, once the doping ratio was estimated using XPS, the sulphur value content determined by elemental analysis could be used to estimate the percent PEDOT:Ts making up the composite.

Element:	C (%)	H (%)	N (%)	S (%)
Expected:				
Found 1:	64.26	3.65	6.37	4.42
Found 2:	64.38	3.72	6.46	4.34
Found Average:	64.32	3.69	6.415	4.38

5.5 0.8EDOT@TpOMe-DAQ

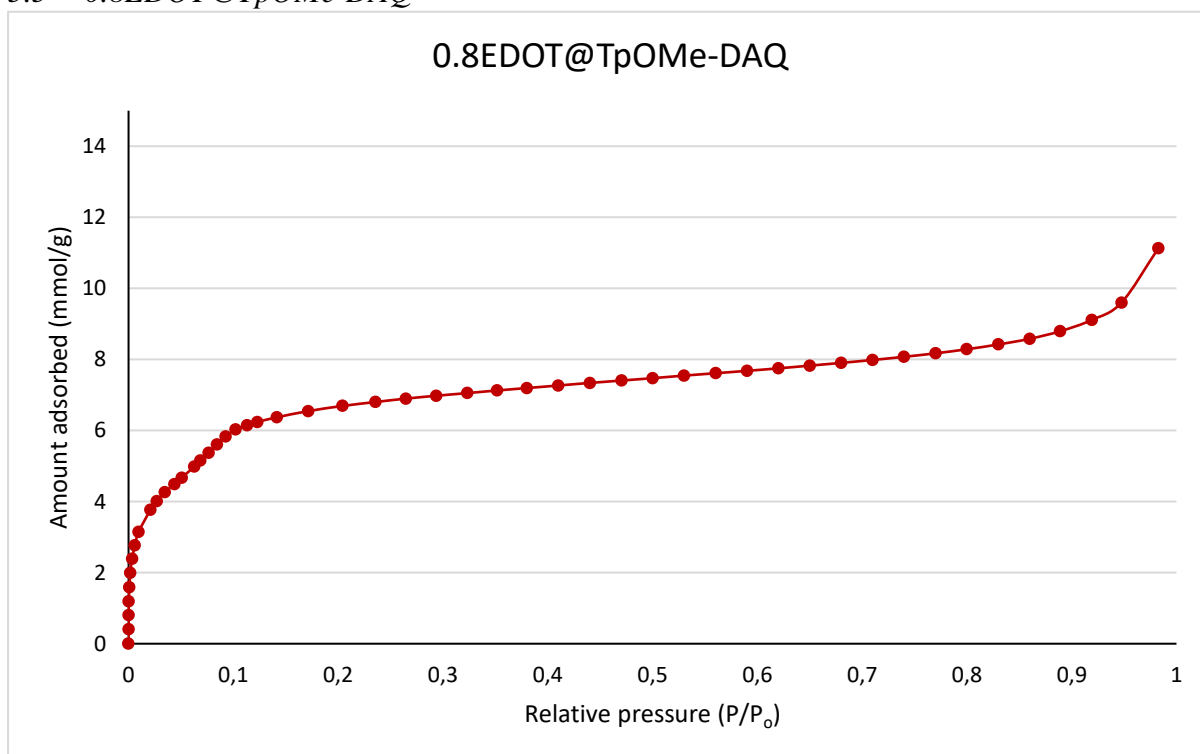


Figure S 37. The N₂ adsorption isotherm for 0.8EDOT@TpOMe-DAQ.

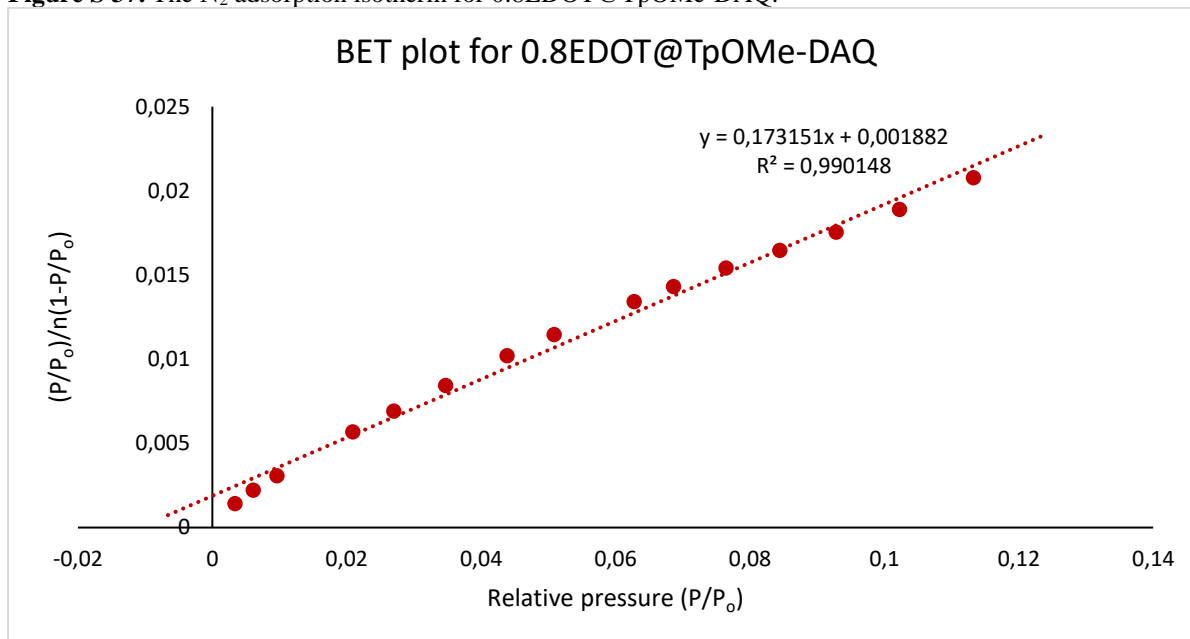
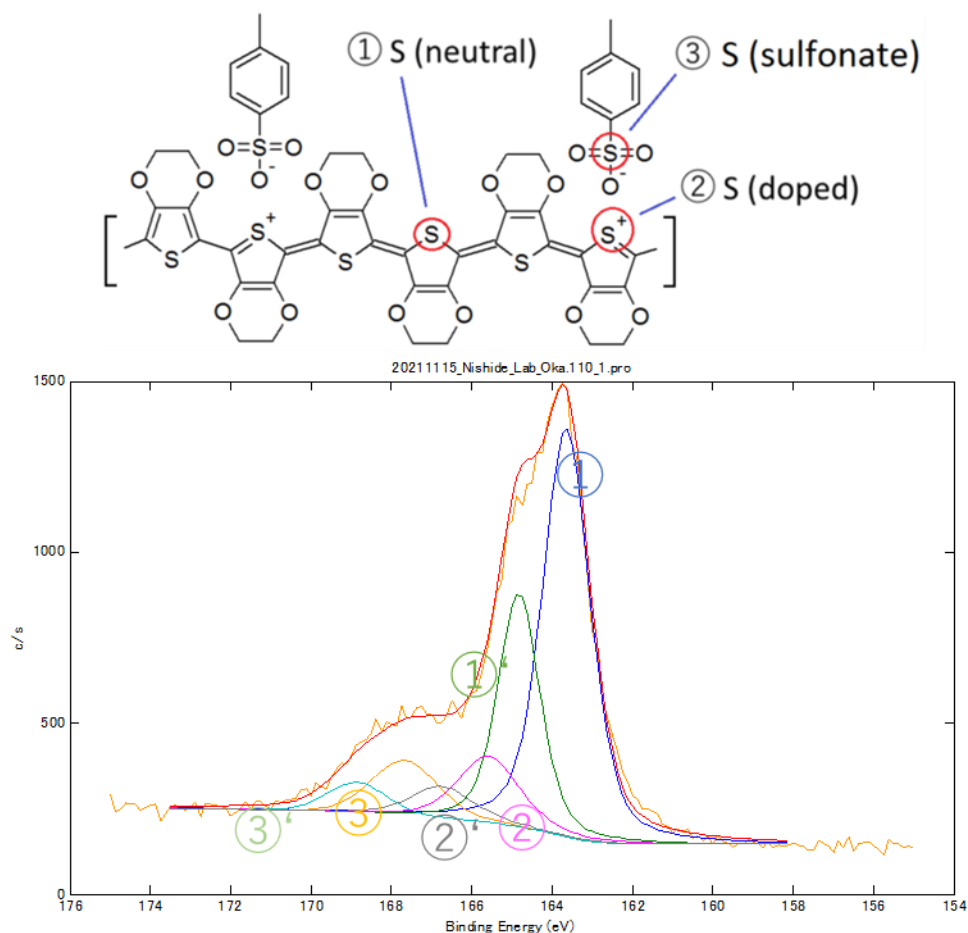


Figure S 38. The BET-plot of 0.8EDOT@TpOMe-DAQ using data (relative pressures between 0.003 and 0.12 P/P₀) from its adsorption isotherm according to the Rouquerol criteria.¹² The intercept and gradient values were used to calculate the C value (93), monolayer quantity (5.71 mmol/g) and surface area (557 ± 2 m²/g). The calculated relative pressure (0.094 P/P₀) was within 10% of the experimental P/P₀ value for the calculated monolayer quantity.



Cycle	Band	Pos	PosSep	B_FWHM	FWHM	Height	%Gauss	Area	%Area	ChiSquared
1	1	163.71	0.00	1.40	1.40	1063	60	1888	48.56	2.33
2	2	164.89	1.18	1.23	1.23	607	60	944	24.28	
3	3	165.80	2.08	1.55	1.55	200	50	409	10.51	
4	4	166.98	3.26	1.29	1.29	120	50	204	5.25	
5	5	167.99	4.27	1.71	1.71	148	80	296	7.60	
6	6	169.17	5.45	1.78	1.78	66	60	148	3.80	

Figure S 39. The S2p XPS spectrum for 0.8EDOT@TpOMe-DAQ with the S2p_(3/2) and S2p_(1/2) peaks fitted for the different sulphur environments (depicted in the image above the spectrum and circled in red). As each oxidised (doped) sulphur in the PEDOT chain would be expected to be charge neutralised by a tosylate anion, the combined areas of sulphurs 2 and 3 were averaged in order to estimate the relative amount of tosylate anions present in the polymer chain. According to the data above and after averaging, 13.58 % of the sulphur present was expected to be in the tosylate form (Mw = 171.192 g/mole) and the remaining 86.42 % in the doped or neutral form making up the PEDOT chain (where each sulphur atom represents an averaged molecular weight of 140.322 g/mole).

Table S 6. Elemental analysis results for 0.8EDOT@TpOMe-DAQ. Predicting the expected percent C, H, N, S was not possible due to unknown polymerisation yields and tosylate doping ratios. However, once the doping ratio was estimated using XPS, the sulphur value content determined by elemental analysis could be used to estimate the percent PEDOT:Ts making up the composite.

Element:	C (%)	H (%)	N (%)	S (%)
Expected:				
Found 1:	58.07	3.76	3.84	10.52
Found 2:	57.84	3.89	3.75	10.55
Found Average:	57.96	3.83	3.80	10.54

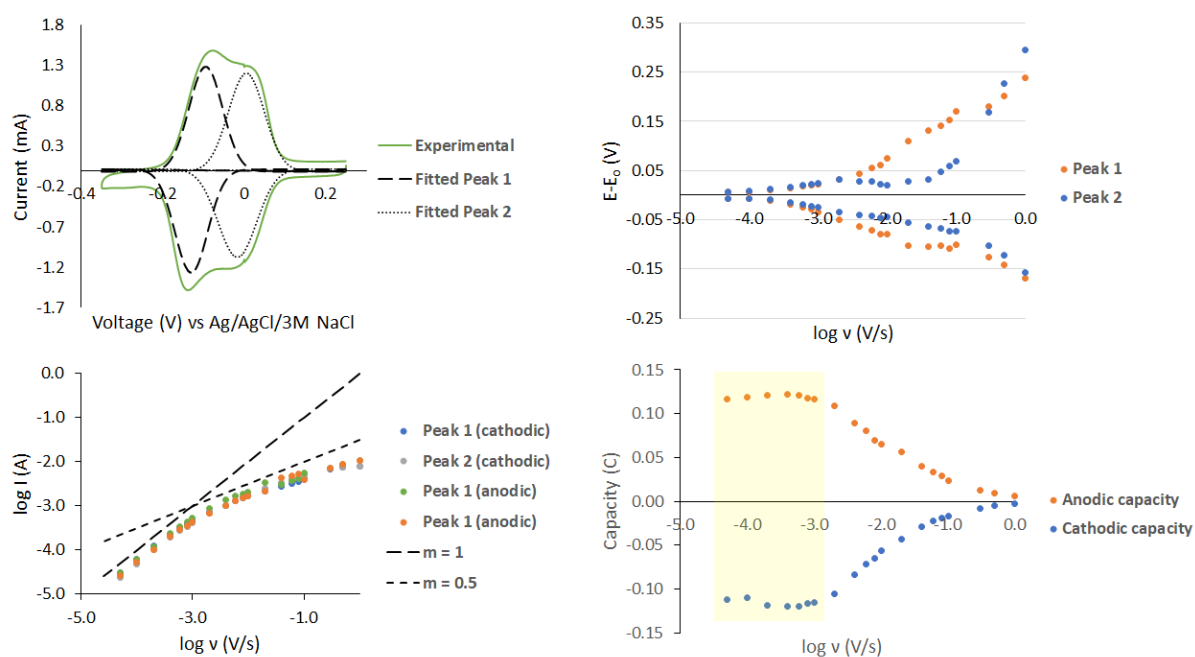


Figure S 40. Electrochemical characterisation data based on scan rate studies for 0.8EDOT@TpOMe-DAQ. The similar shapes of the plots compared to those from 0.4EDOT@TpOMe-DAQ suggest very little improvement is achieved by doubling the amount of conductive polymer in the composite.

5.6 Overlays and Summaries.

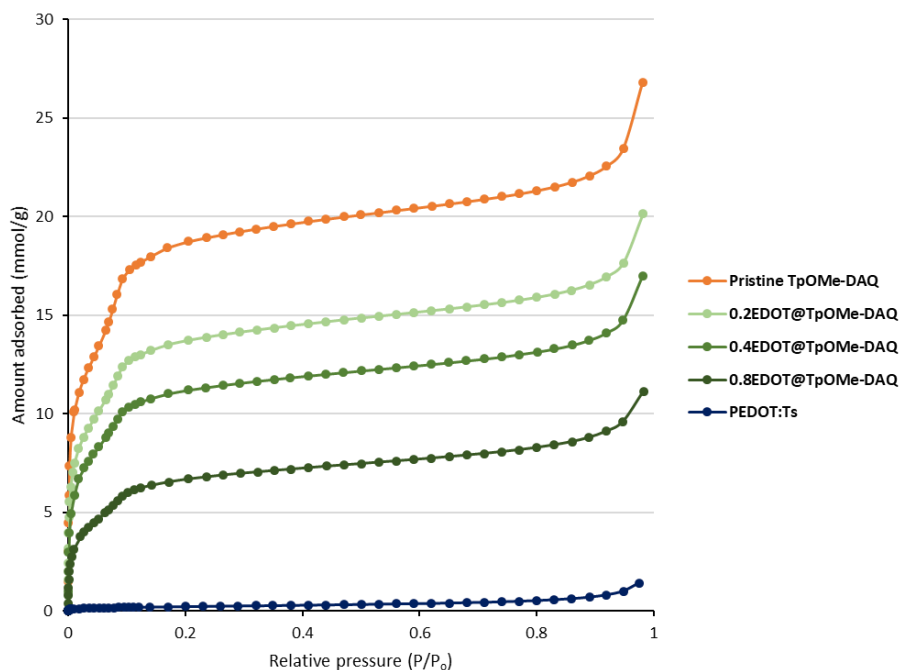


Figure S 41. Overlay plots of the N₂ adsorption profiles for the in situ EDOT polymerized series as well as the pristine TpOMe-DAQ and ex situ polymerized EDOT (PEDOT:T_s control).

Table S 7. A summary of the BET area calculated from the N₂ sorption plots (Figure 42 above) used to calculate the expected BET areas in the composites based on the values obtained for pristine TpOMe-DAQ and the PEDOT:T_s control.

% TpOMe-DAQ in composite	Measured BET area (m ² /g)	BET area predicted assuming only mixing of TpOMe-DAQ and PEDOT (m ² /g)	Difference
100 (0.0EDOT)	1574	1574	0
82.4 (0.2EDOT)	1155	1300	145
70.6 (0.4EDOT)	956	1117	161
47.0 (0.8EDOT)	557	750	193
0 (100EDOT)	19	19	0

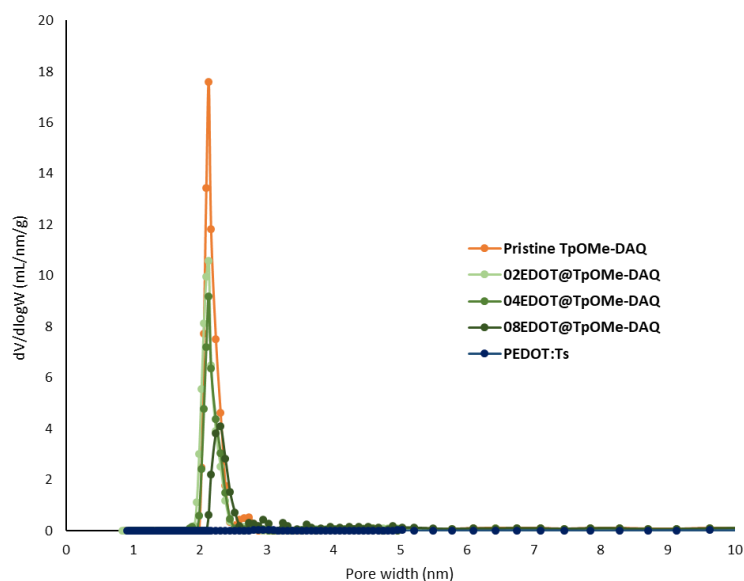


Figure S 42. Overlay plots of the pore-size distributions for the in situ EDOT polymerized series as well as the pristine TpOMe-DAQ and ex situ polymerized EDOT (PEDOT:Ts control).

Table S 8. A summary of the pore-size distribution plots (Figure 43 above) used to calculate the expected cumulative pore volumes in the composites based on the values obtained for pristine TpOMe-DAQ and the PEDOT:Ts control.

% TpOMe-DAQ in composite	Measured cumulative pore volume (mL/g) up to 14 nm pore width	Cumulative pore volume predicted assuming only mixing of TpOMe-DAQ and PEDOT (mL/g)	Percent pores blocked (%)
100 (0.0EDOT)	0.71	0.71	0
82.4 (0.2EDOT)	0.53	0.59	10
70.6 (0.4EDOT)	0.44	0.51	14
47.0 (0.8EDOT)	0.27	0.34	20
0 (100EDOT)	0.016	0.016	0

6 Electrode preparation and air battery fabrication

The anode was prepared by dispersing 0.4EDOT@TpOMe-DAQ in *N*-methylpyrrolidone, and the solution was coated on a glassy carbon plate or a graphite plate. The mass loading of 0.4EDOT@TpOMe-DAQ was adjusted to ca. 1.0 mg .

The battery fabrication and evaluation were conducted following a procedure previously reported.¹³ A tailor-made beaker cell (20 cm² electrolyte) was employed as the electrochemical cell. Separation of the compartments was achieved using a fine glass filter, allowing only the electrolyte to pass during the measurement. Both anode and cathode sections were filled with 0.5 M H₂SO₄ aqueous solution. The battery evaluation tests using similarly fabricated batteries were performed at least three times.

7 SI References

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3. *Application Note Helium Effects on ASAP Series Micropore Analyses.* www.micromeritics.com.
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