Supporting information

Phosphoric acid-merged Squaraine conjugated mesoporous polymer with high proton conductivity

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Section S1 Experimental Section

1-1. Materials

3,4 dihydroxycyclobut-3-ene-1,2-diene (98%, AmBeed), 5,5',5" -(Benzene-1,3,5-triyl) tris(pyridine-2-amine) (97%, vwr), 2,5-diaminopyridine (DAPy, 97%, Sigma-aldrich), Scandium trifluoromethane sulfonate (97%, abcr), phosphoric acid (PA, 85% in H_2O, Wako chemical), tetrahydrofuran (THF, 99.5%, Wako chemical) and Acetone (Linegal Chemicals).

1-2. Synthesis

The Sq-DAPy-COF was synthesised under solvothermal conditions through the condensation of Squaric acid (2.25 mmol) and DAPy (2.25 mmol) in 8 ml each of dichlorobenzene/butanol (1:1 by vol.) in the presence of Scandium (III) Triflate catalyst (12.3 g). At the start of the reaction the reactants and catalyst were filled into the reaction tube and the N_2 gas was flushed into the tube via a ballon then solvents were filled in and the reaction tube was sealed and sonicated. After 20 minutes sonication, the reaction tube is heated to 150°C for 6 days without stirring. The resulting precipitate was collected by first filtering with THF, till supernatant is clear and then with acetone. After 2 hours of drying the precipitate is washed again by Soxhlet extraction with THF overnight to remove unreacted molecules and then dried at room temperature under vacuum to provide the Sq-DAPy-COF as a black powder in 63% yield.

Similarly the porous sample was synthesised with TAPyB (1.5 mmol) and Squaric acid (2.25 mmol) as reactants in 6 ml each of dichlorobenzene/butanol (1:1 by vol.) in the presence of Scandium(III) Triflate catalyst (12.3 g), creating an orange precipitate of Sq-TAPyB-COF with 93% yield.

The Sq-TAPyB-COF and Sq-DAPy-COF sample thus prepared were permeated with 85% phosphoric acid (PA), respectively by immersing the powder sample into PA (5 ml each) for 2 hours with stirring, to provide the proton conducting properties. Later on, the highly viscous powders were collected by centrifuge and washed by dissolving in THF (50 ml) and centrifuge with THF till the samples can be collected back, this removes the excess PA. At the end, place the samples in the desiccator to dry overnight.

For the synthesis conditions different catalysts and different mixed solvents were also examined and the best combination of solvent and catalyst was selected based on the yield of products (see table below).

Table 1. Product yield with different catalyst in different mixed solvents.

Catalyst	**Solvent 1**	**Solvent 2**	**% yield CMP**
Sc(OTf)3	BuOH	DCB	93.75
		Mesitylene	78.40
		Toluene	81.60
		M-Cresol	93.02
Water			91.04
Isoquinoline	BuOH	DCB	82.66
		Mesitylene	78.15
		Toluene	39.9
		M-Cresol	78.15
DMAP	BuOH	DCB	44.96
		Mesitylene	37.65
		Toluene	80.7

1-3. Characterizations

The SmartLab X-ray diffractometer (Rigaku) was used for measuring the Powder X-ray diffraction (PXRD) pattern. The thermal stability of the samples was evaluated by differential scanning calorimetry and thermal gravimetry (TG-DSC) using the NETZSCH STA 449 F1 Jupiter instrument between room temperature and 800°C, at a heating rate of 5 °C min^{-1} using a Pt

crucible under an argon atmosphere. FT-IR was measured using the Thermo Scientific Nicolet iS10 FT-IR spectrometer in the 4000–500 cm^{-1} range. The plane-wave method of density functional theory in the VASP package is used for the geometry optimization calculations, with PAW19 pseudopotentials expressed in the plane-wave basis set with a cutoff of 400eV. The BET surface analyzer (3P, Micro 200) was used to analysed the surface area using the Brunauer-Emmet-Teller (BET) method. The samples were degassed in the vacuum at 150 ◦C for 1 hour to remove moisture before all the measurements. Proton conductivities were determined in the frequency range of 7 MHz to 10 Hz using an electrochemical analyser with a frequency response analyzer (SP-300-2CH, Bio-logic) and AC impedance spectroscopy. Teflon-coated carbon paper (TGP-H-060H; Chemix) with ϕ=10 mm on both sides was used to compress and pelletize the powdered samples for ten minutes in a stainless cell. The pelletizing pressure was 250 MPa which is the lowest pressure at which a COF powder may be moulded without destroying the COF's framework structure.

Section S2 FT-IR of samples

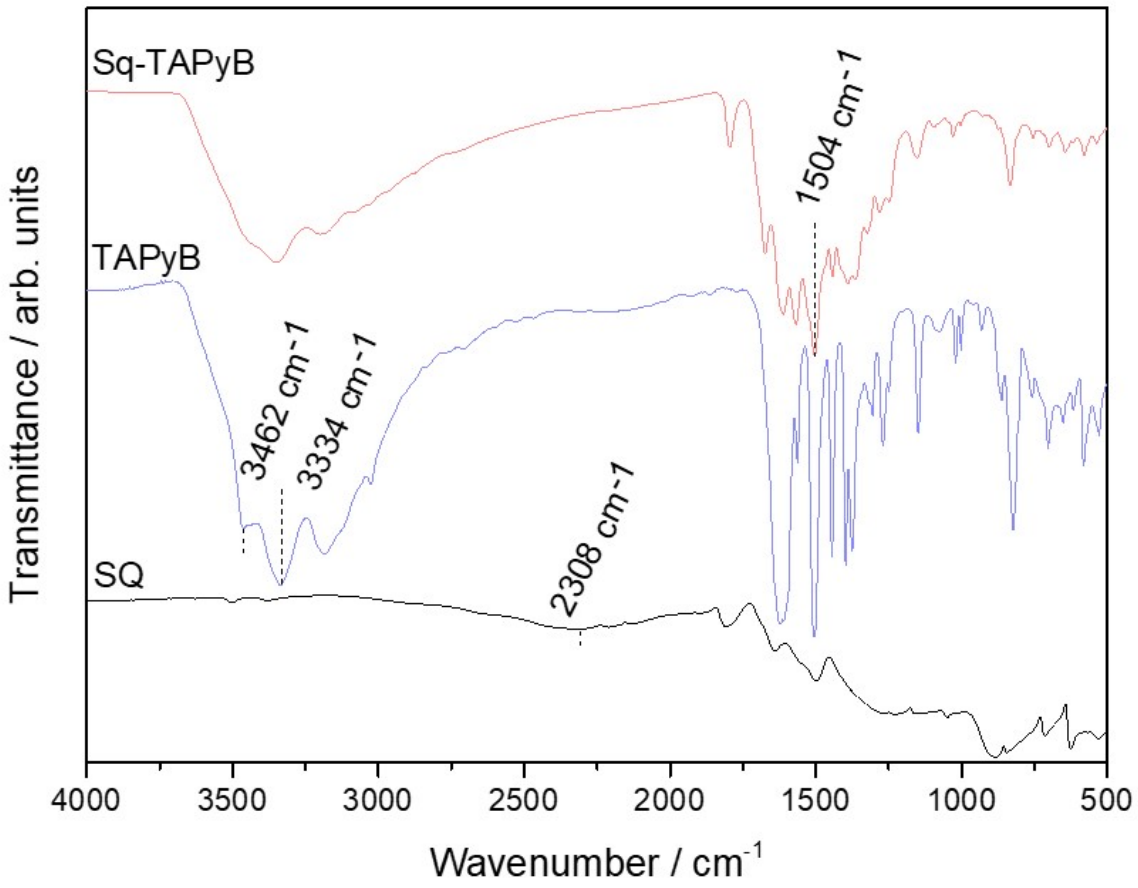

Fig. S1. Full FT-IR spectra of Sq, TAPyB and Sq-TAPyB (bottom to top respectively).

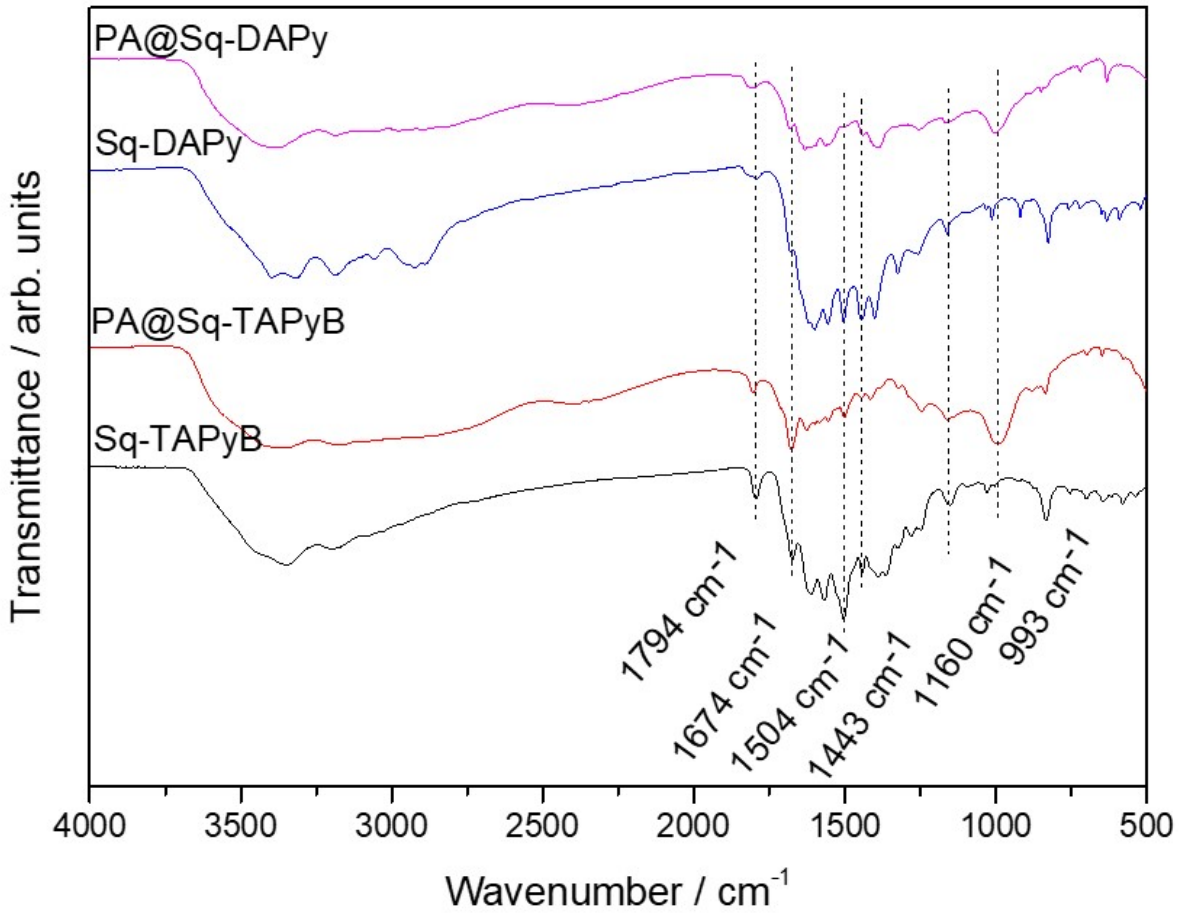

Fig. S2. Complete FT-IR spectra of samples Sq-TAPyB-COF, PA@ Sq-TAPyB-COF, Sq-DAP and PA@Sq-DAPy (bottom to top respectively).

Section S3 Thermal analysis

3-1. Differential scanning calorimetry (DSC)

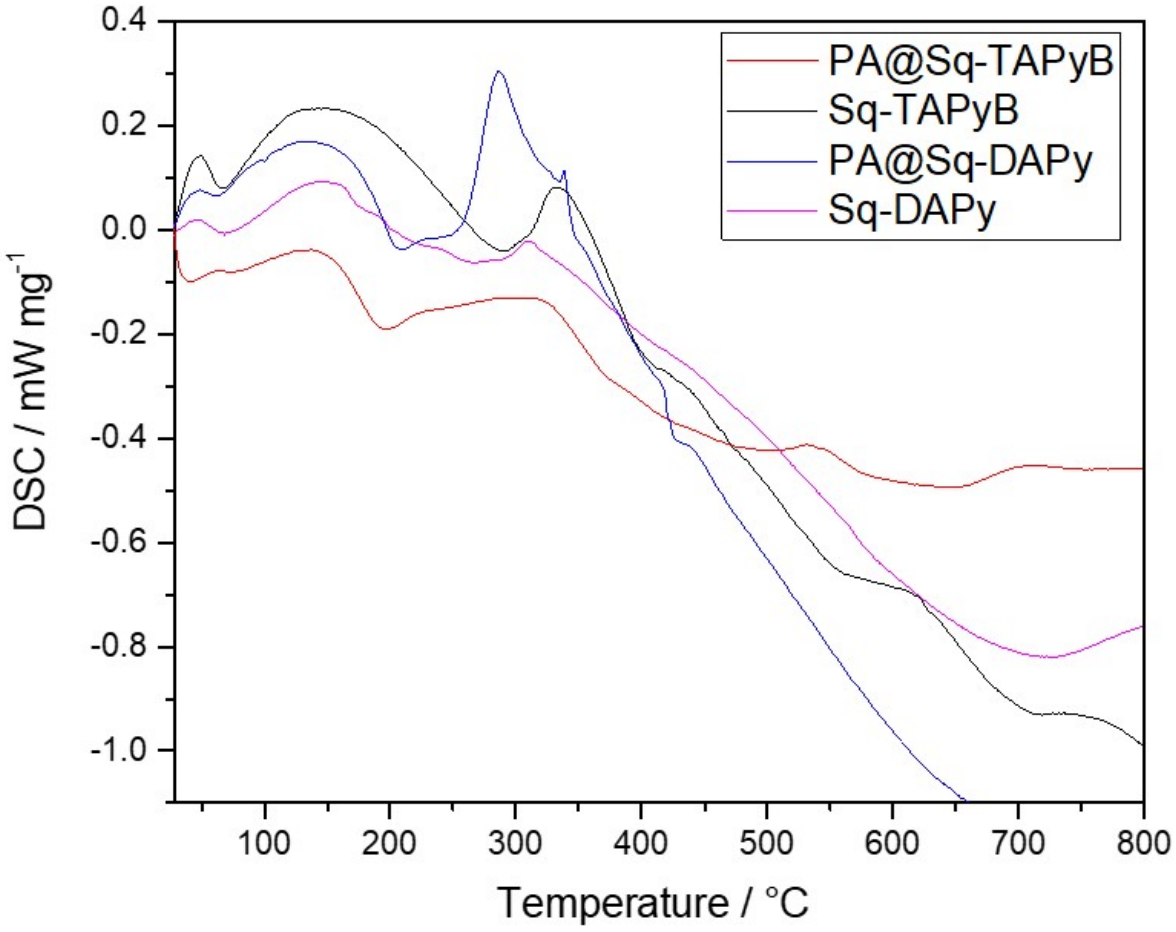

Fig. S3. Differential scanning calorimetry curves of samples before and after doping Sq-TAPyB (back), PA@Sq-TAPyB (red), Sq-DAPy (pink) and PA@Sq-DAPy (blue).

3-2. Thermogravimetric analysis (TGA)

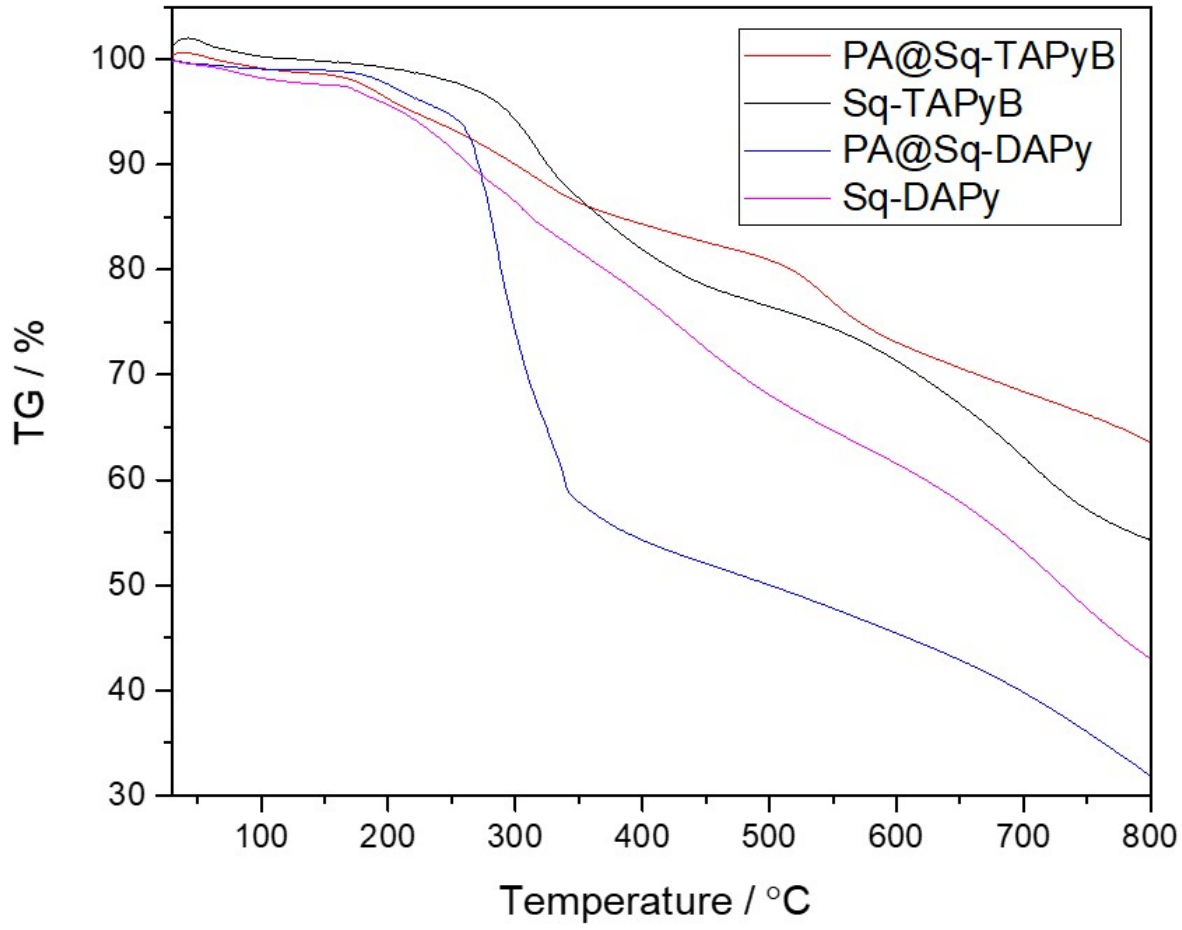

Fig. S4. Thermal gravimetry curve of samples before and after doping Sq-TAPyB (back), PA@Sq-TAPyB (red), Sq-DAPy (pink) and PA@Sq-DAPy (blue).

Section S4 XRD of the samples

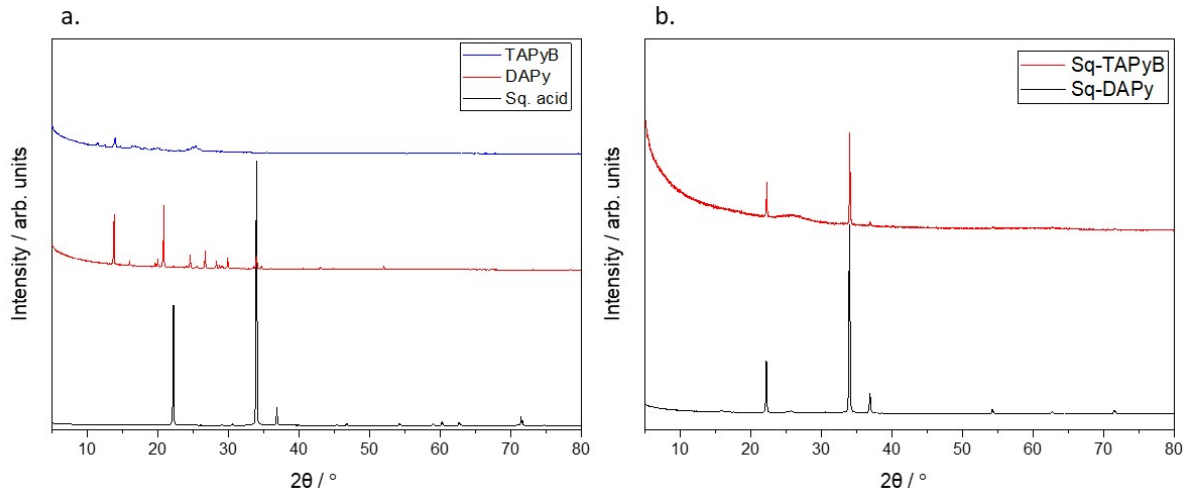

Fig. S5. XRD spectra of (a) the reactants Squaric acid (Sq. acid), 2,5-diaminopyridine (DAPy) and 5,5’,5” -(Benzene-1,3,5-triyl) tris(pyridine-2-amine) (TAPyB) and (b) products Sq-DAPy and Sq-TAPyB.

Section S5 Calculation of PA in CMP pore wall

Table 2. Calculation of PA in CMP pore wall.

Parameter	**Value**	**Calculation**
Starting wt. of Sq-TAPyB	100 mg	Given
Wt. of PA@Sq-TAPyB	127.7 mg	Given
Mol. Wt. of one pore of CMP	2036 mg/mmol	from chem draw
Mol. Wt. of H_3PO_4	97.99 mg/mmol	Given
Moles of CMP	0.0491 mmol	100/2036
Wt. of H_3PO_4	27.7 mg	127.7 – 100
Moles of H_3PO_4 in a pore	0.2826 mmol	27.7/97.99
Number of PA in one pore	5.75 ~ **6 PA/pore**	0.2826/0.04911

Section S6 Nyquist plot

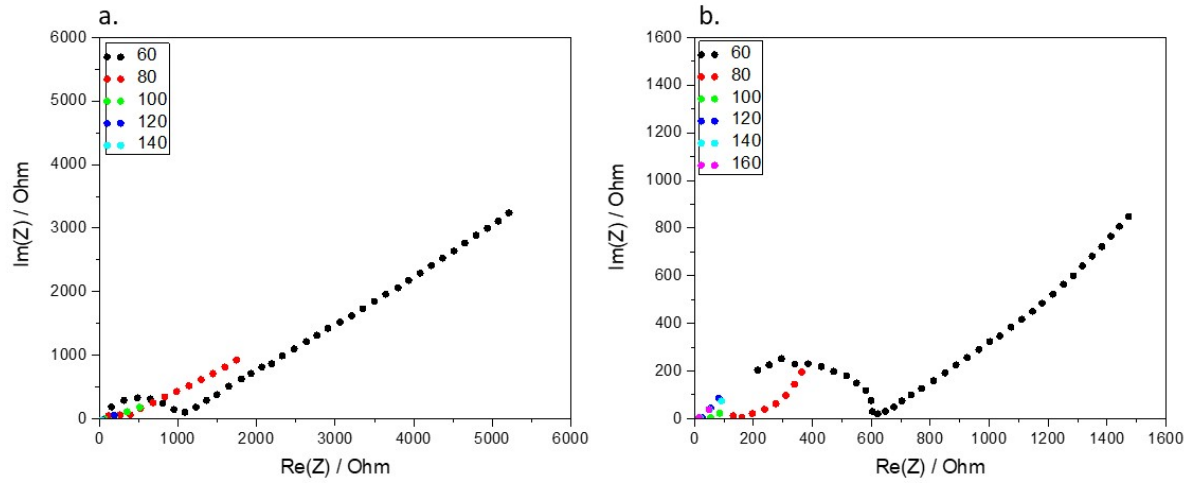

Fig. S6. Full Nyquist plot of temperature dependent proton conductivity of (a) PA@Sq-DAPy (b) PA@Sq-TAPyB.

Table 3. Temperature dependent proton conductivity values

1000/T (K^{-1})	**PA@Sq-DAPy**	**PA@Sq-TAPyB**
	Conductivity (S cm^{-1})	Conductivity (S cm^{-1})
2.309	15.92×10^{-3}	
2.421	10.22×10^{-3}	2.79×10^{-3}
2.545	5.48×10^{-3}	1.72×10^{-3}
2.681	2.30×10^{-3}	0.89×10^{-3}
2.833	1.05×10^{-3}	0.36×10^{-3}
3.003	0.27×10^{-3}	0.11×10^{-3}

Table 4. Humidity dependent proton conductivity values

Relative humidity %	**PA@Sq-DAPy**	**PA@Sq-TAPyB**
	Conductivity (S cm^{-1})	Conductivity (S cm^{-1})
90	6.79×10^{-3}	25.70×10^{-3}
80	2.15×10^{-3}	23.77×10^{-3}
60	0.18×10^{-3}	15.82×10^{-3}
40	0.04×10^{-3}	8.44×10^{-3}

Section S6 Calculation of activation energy

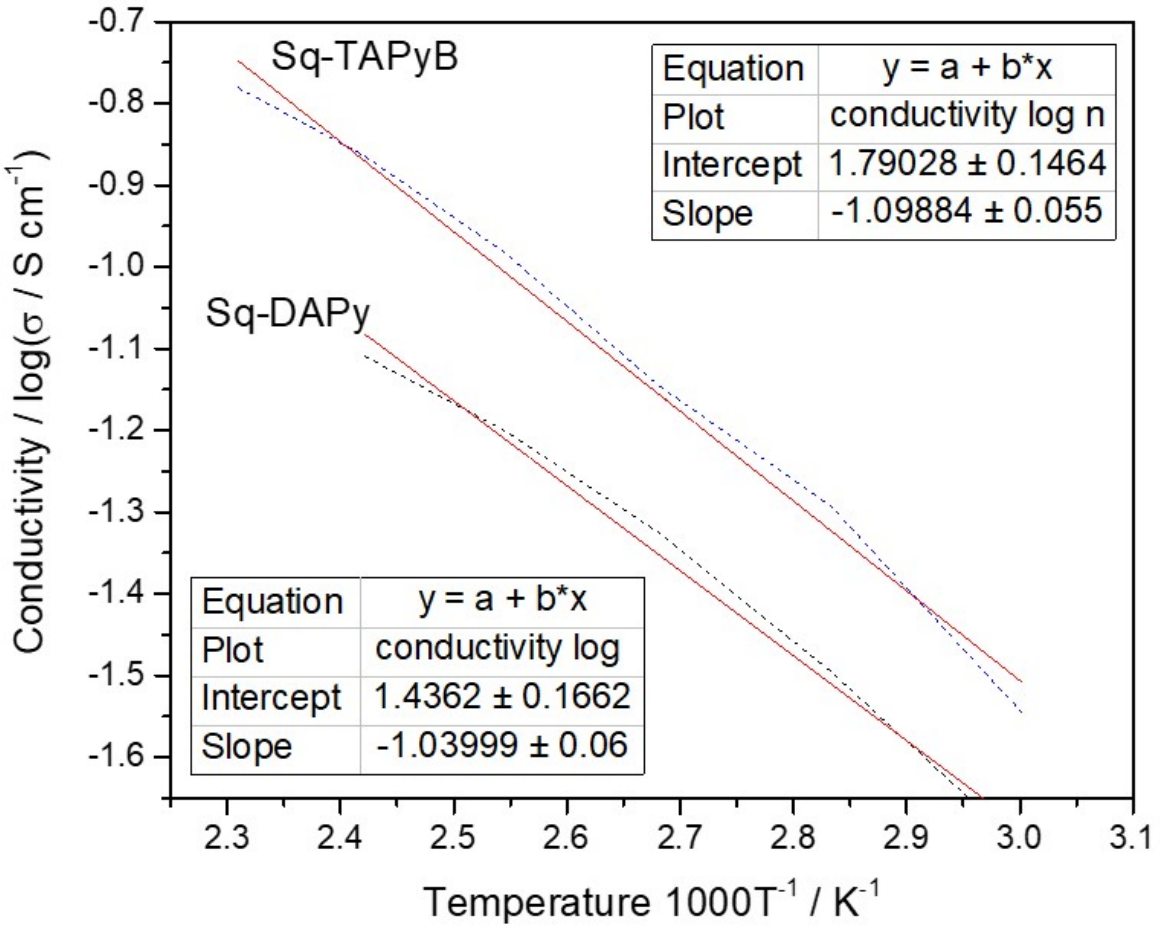

Fig. S7. Linear fit(red) of conductivity vs temperature plot to calculate slope of Sq-DAPy and Sq-TAPyB.

Slope TAPyB = -1.09884	Slope DAPy = -1.0399
E_a =Slope × R [R = 8.314 J/mol.K]	E_a =Slope × R [R = 8.314 J/mol.K]
= -0.009135 = 9.135 × 10^{-3} KJ mol^{-1}	= -0.008646 = 8.646 × 10^{-3} KJ mol^{-1}

Section S7 SEM images

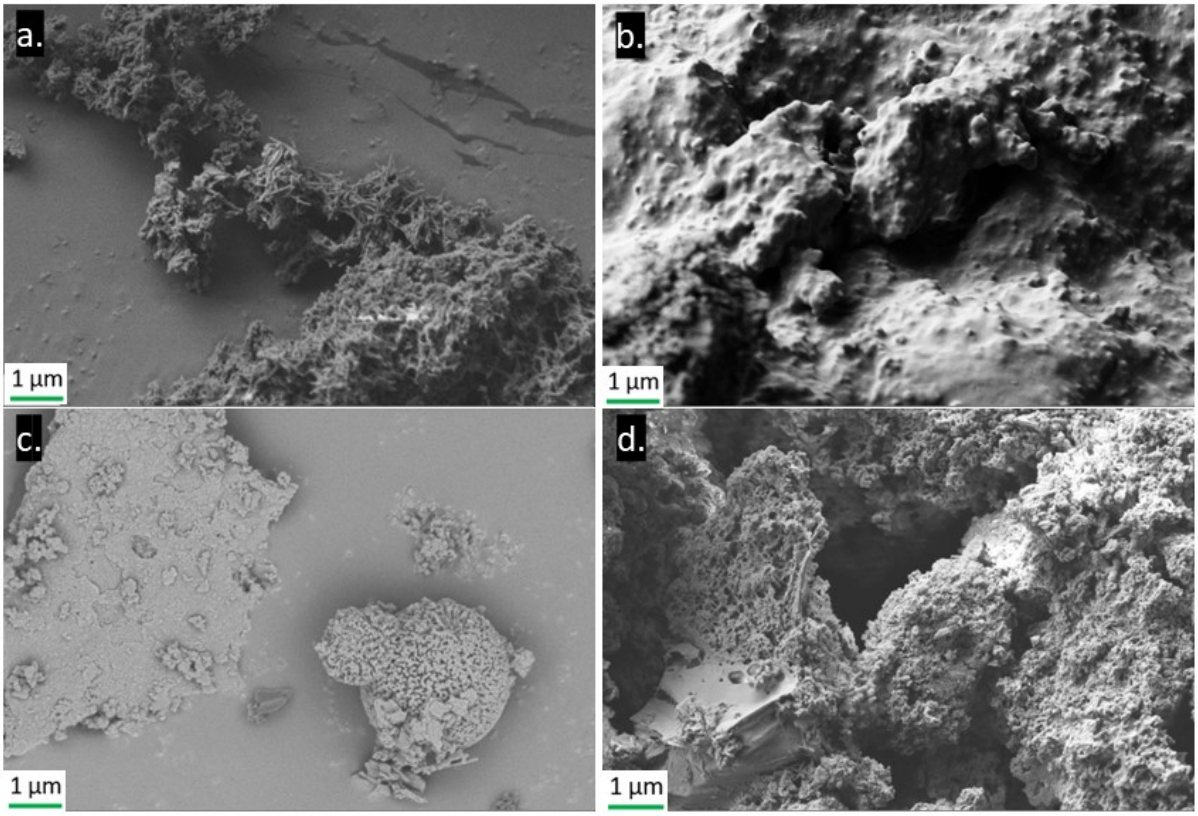

Fig. S8. SEM image of (a) Sq-TAPyB (b) PA@Sq-TAPyB (c) Sq-DAPy (d) PA@Sq-DAPy.

Section S8 EDS elemental analysis

Table 5. Results of EDS spectrum

Elements		C	N	O	Sc
Sq-	Wt. %	90.48	6.18	3.16	0.18
TAPyB	Atom. %	92.13	5.40	2.41	0.05
Sq-	Wt. %	80.96	12.48	3.76	2.8
DAPy	Atom. %	85.03	11.23	2.96	0.79