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Electronic Supporting Information

Synergistic effect of covalent bonding and physical confinement of sulfur in the pores of a microporous COF to improve cycling performance in Li-S batteries

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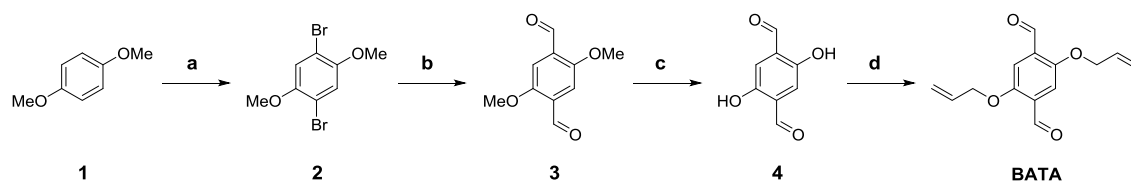
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1,4-dibromo-2,5-dimethoxybenzene (2).¹ To a solution of *p*-dimethoxybenzene (5.0 g) in anhydrous dichloromethane (25 mL) Br₂ (9.21 mL) was added dropwise at room temperature in the absence of light. The resulting mixture was stirred for 1 hour and poured into an excess amount of 1M KOH. The solution was extracted with CH₂Cl₂, washed with water, dried over MgSO₄, and the solvent was removed in vacuo. After recrystallization from ethanol **2** was obtained as a white solid (9.65 g, 90%).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.10 (s, 2H), 3.85 (s, 6H).

¹³C NMR (75 MHz, CDCl₃) δ (ppm): 150.5, 117.1, 110.5, 57.0.

2,5-dimethoxyterephthalaldehyde (3).² A solution of **2** (500 mg) in anhydrous tetrahydrofuran (THF, 8.5 mL) was cooled to -78 °C and *n*-BuLi (1.6 M in hexane, 2.3 mL) was added dropwise. After 3 hours, *N,N*-dimethylformamide (DMF, 0.6 mL) was added and the mixture stirred for 1 hour at -78 °C warmed to RT and stirred for an additional hour. The reaction was quenched with saturated ammonium chloride, THF was eliminated under reduced pressure and the resulting solution extracted with CH₂Cl₂. The organic phase was dried over MgSO₄ and the solvent removed in vacuo. The crude product was purified by column chromatography (silica gel flash, hexane/ethyl acetate 9:1) to afford a yellow solid (258 mg, 78 %).

¹H NMR (300 MHz, CDCl₃) δ (ppm): 10.49 (s, 2H), 7.45 (s, 2H), 3.94 (s, 6H).

¹³C NMR (75 MHz, CDCl₃) δ(ppm): 189.3, 155.7, 129.1, 110.9, 56.2.

2,5-dihydroxyterephthalaldehyde (4).³ To a solution of **3** (900 mg) in CH₂Cl₂ (20 mL) under Ar atmosphere BBr₃ (1M in CH₂Cl₂, 20 mL) was added dropwise at -78 °C. The solution was allowed to warm to room temperature and stirred overnight. Water (40 mL) was added to quench the reaction and the resulting mixture was extracted repeatedly with CH₂Cl₂. The organic phase was dried over MgSO₄, the solvent removed under reduced pressure and the resulting yellow solid was recrystallized three times from AcOEt yielding 696 mg (90 %) of compound **4**.

¹H NMR (300 MHz, CDCl₃) δ (ppm): 10.23 (s, 2H), 9.96 (s, 2H), 7.24 (s, 2H).

¹³C-RMN (75 MHz, DMSO-*d*₆) δ (ppm) :190.2, 152.8, 127.7, 115.17.

FTIR(CH₂Cl₂) (cm⁻¹): 3279, 3050, 2888, 1668, 1476, 1280, 1127, 888, 832, 796, 679.

2,5-bis(allyloxy)terephthalaldehyde (BATA). A mixture of **3** (200 mg) and anhydrous K₂CO₃ (520 mg) in anhydrous DMF (5.5 mL) was heated to 60 °C for 30 minutes, cooled to room temperature and allyl bromide (0.25 mL) was added. After stirring overnight water was added to precipitate the product, which was collected by filtration, washed with water and purified by column chromatography (silica gel flash, hexane/CH₂Cl₂ 8:2). **BATA** was obtained as a yellow solid (188 mg, 64%).

¹H RMN (300 MHz, CDCl₃) δ (ppm): 10.53 (s, 2H, -CHO), 7.44 (s, 2H, Ph), 6.06 (ddt, ³J_{cis}=17.1 Hz, ³J_{trans}=10.5 Hz, ³J=5.1 Hz; 2H, -CH=), 5.44 (ddt, ³J_{cis}=17.1 Hz, ²J=1.3 Hz ⁴J=1.3 Hz; 2H, =CH₂), 5.34 (ddt, ³J_{trans}=10.5 Hz, ²J=1.3 Hz, ⁴J=1.3 Hz; 2H, =CH₂), 4.67 (dt, ³J = 5.1 Hz, ⁴J = 1.3 Hz; 4H, -CH₂-).

¹³C RMN (75 MHz, CDCl₃) δ (ppm): 189.3, 154.9, 132.2, 129.5, 118.6, 112.3, 69.9.

FTIR(CH₂Cl₂) (cm⁻¹): 2872, 1679, 1482, 1423, 1409, 1263, 1214, 1128, 1096, 1000, 910, 731.

MS (ESI) $m/z = 269 [M+Na]^+$

Elemental Analysis (%) calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73; found: C, 68.16; H, 5.89; N 0.13.

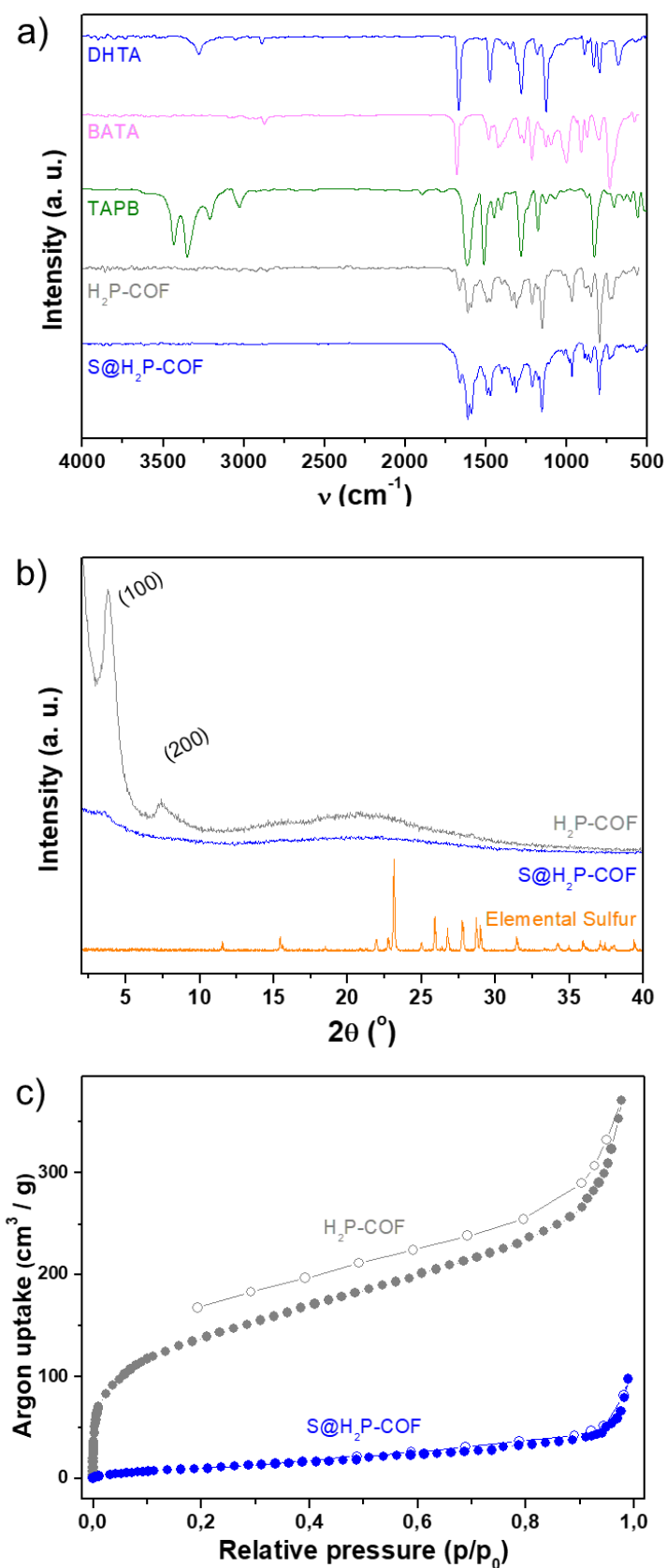


Figure S1. a) FTIR of **DHTA** and **TAPB** monomers, **H_2P-COF** and **$S@H_2P-COF$** . b) XRD of **H_2P-COF** , **$S@H_2P-COF$** and elemental sulfur. c) Argon adsorption isotherms of **H_2P-COF** and **$S@H_2P-COF$** .

XPS spectra

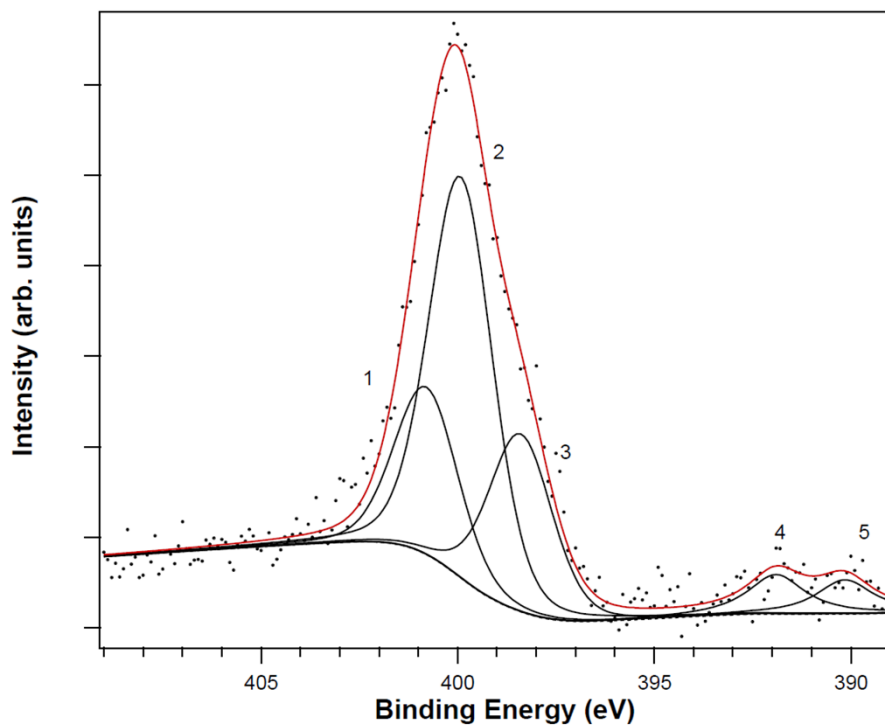


Figure S2. N 1s peak for the S@H₂P-COF sample ($h\nu = 1253.6$ eV). Numbers identify the different components (black lines): 1 (pyrrole N), 2 (imine N), 3 (aza N) and 4, 5 (Mg K α satellites). Black dots are experimental points and the red line is the results of fit.

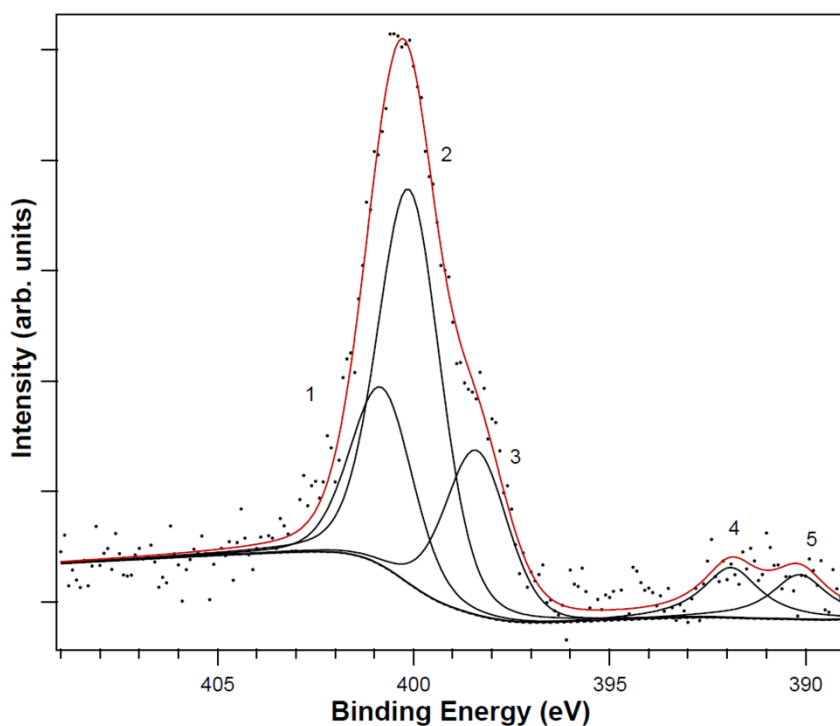


Figure S3. N 1s peak for the S@H₂P-COF-BATA sample ($h\nu = 1253.6$ eV). Numbers identify the different components (black lines): 1 (pyrrole N), 2 (imine N), 3 (aza N) and 4, 5 (Mg K α satellites). Black dots are experimental points and the red line is the results of fit.

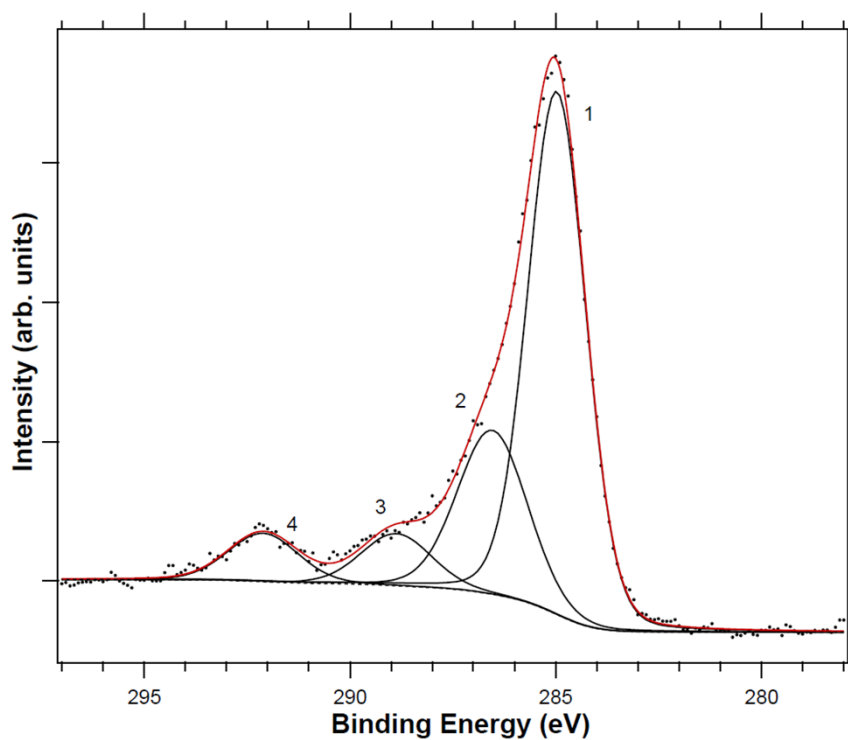


Figure S4. C 1s peak for the **S@H₂P-COF** sample ($h\nu = 1253.6$ eV). Numbers identify the different components (black lines): 1 (C=C bonds), 2 (C-N bonds type 1), 3 (C-N bonds type 2), 4 (C-F bonds from polymer). Black dots are experimental points and the red line is the results of fit.

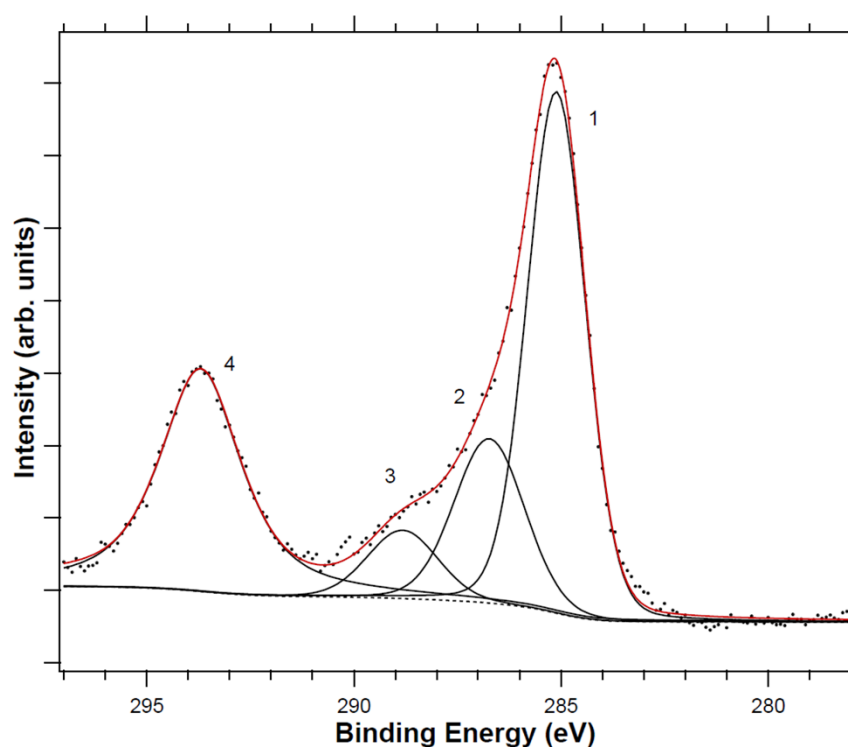


Figure S5. C 1s peak for the **S@H₂P-COF-BATA** sample ($h\nu = 1253.6$ eV). Numbers identify the different components (black lines): 1 (C=C bonds), 2 (C-N bonds type 1), 3 (C-N bonds type 2), 4 (C-F bonds from polymer). Black dots are experimental points and the red line is the results of fit.

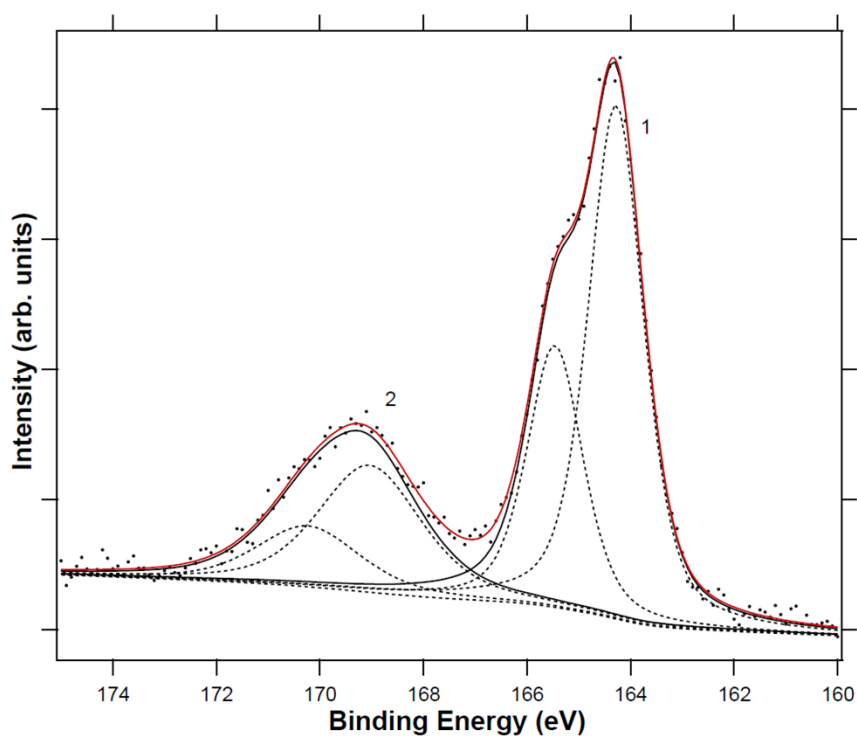


Figure S6. S 2p peak for the **S@H₂P-COF** sample ($h\nu = 1253.6$ eV). Numbers identify the different components (black lines): 1 (S-S bonds in sulfur chains) and 2 (sulfate). Each component corresponds to an S 2p doublet (dashed lines). Black dots are experimental points and the red line is the results of fit.

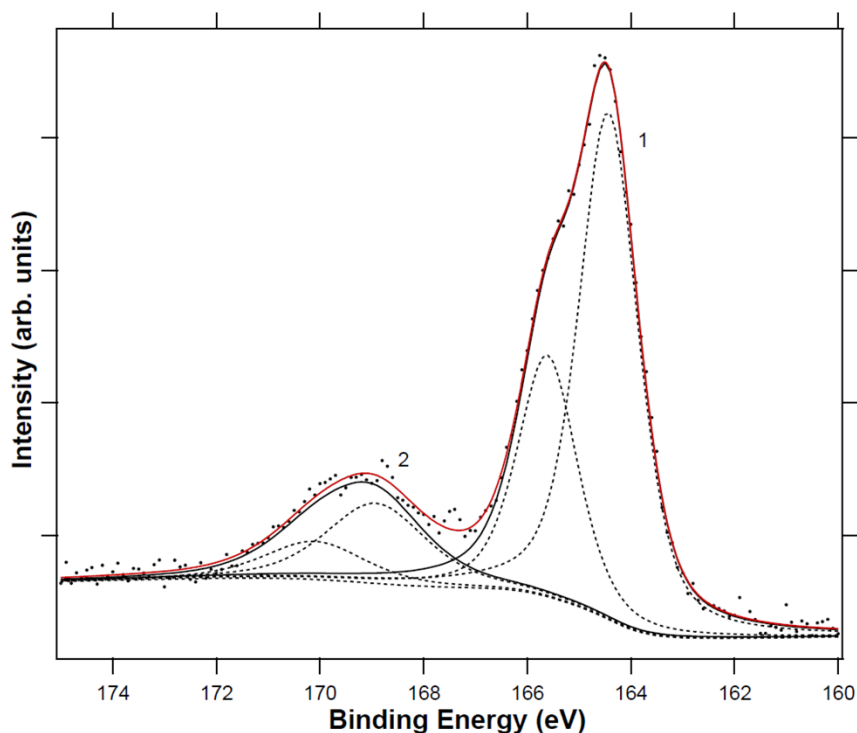


Figure S7. S 2p peak for the **S@H₂P-COF-BATA** sample ($h\nu = 1253.6$ eV). Numbers identify the different components (black lines): 1 (S-S bonds in sulfur chains) and 2 (sulfate). Each component corresponds to an S 2p doublet (dashed lines). Black dots are experimental points and the red line is the results of fit.

XPS analysis

N 1s is expected to present three different components, corresponding to pyrrole and aza nitrogen in the porphyrin, and to imine N in the **DHTA/BATA** groups. The expected binding energies and atomic proportions of each component is the same for **S@H₂P-COF** and **S@H₂P-COF-BATA** and is summarized in Table S1.

Table S1. Relative atomic fraction and reported binding energies for the different nitrogens present in porphyrin-based materials.

N species	Relative atomic fraction in S@H ₂ P-COF, S@H ₂ P-COF-BATA	BE (eV)	Ref.
Pyrrole	2	400.2	[4]
		399.7	[5]
		400.0	[5]
		400.1	[6]
Imine	3	399.0	[7]
		399.3	[7]
		399.6	[7]
Aza	2	397.9	[4]
		397.7	[5]
		398.0	[5]
		398.0	[6]

The average BE for each species is 400.0 eV (Pyrrole), 399.3 (Imine) and 397.9 (Aza). Considering the experimental resolution, only two components are distinguished in the spectra, one corresponding to pyrrole and imine N, which are split 0.7 eV, and another one for aza nitrogen (split 1.4 eV from imine N). The two components are expected to be split by 1.7 eV with an intensity ratio of 2.5 (3+2/2), in good agreement with the experimental splitting (1.6 eV) and intensity ratio (2.5).

C 1s presents three components assigned to -C=C- bonds (285.0 eV), C bonds to N type 1 (imine and pyrrole N, at 286.5 eV) and C bonds to N type 2 (aza N, 288.9 eV). Under XPS detection conditions, no C-S bonds are identified.

The fraction of S atoms bonded to C atoms is calculated considering the relative intensities of the corresponding S-C component in S 2p and the -C=C- (main) component in C 1s, taking into account the cross sections for each core level.^{5, 6, 8, 9} The result is that a fraction corresponding to 1% of C atoms are bond to sulfur atoms, in good agreement with the relative abundance of available -C= bonds in **H₂P-COF-BATA**, which is 1.4% of C atoms in the -C=C- form.

^{13}C CP-MAS NMR spectra

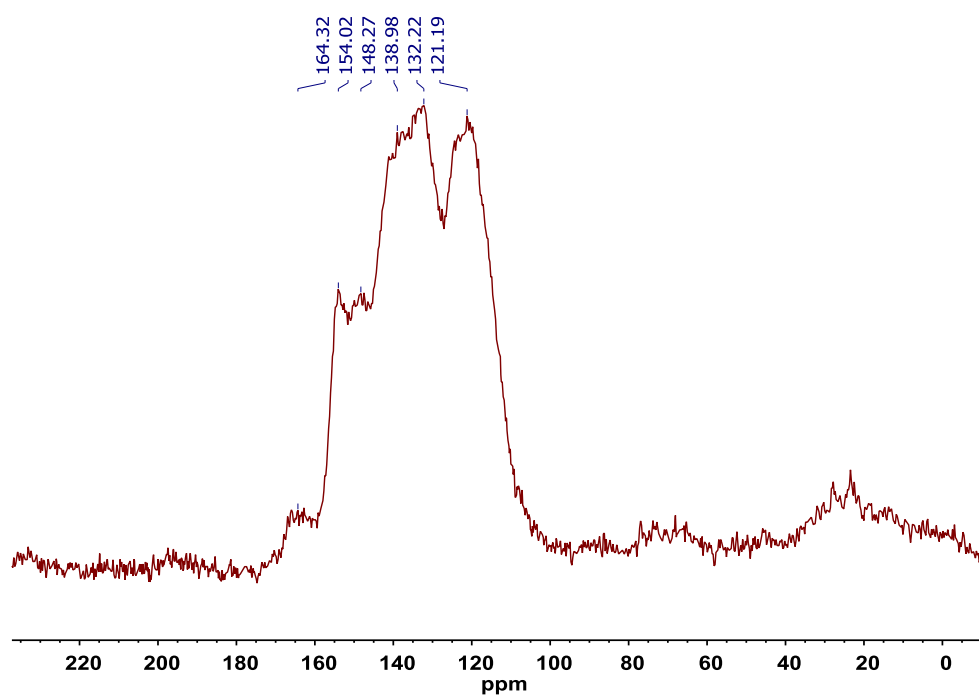


Figure S8. ^{13}C CP-MAS NMR spectrum of $\text{H}_2\text{P-COF-BATA}$.

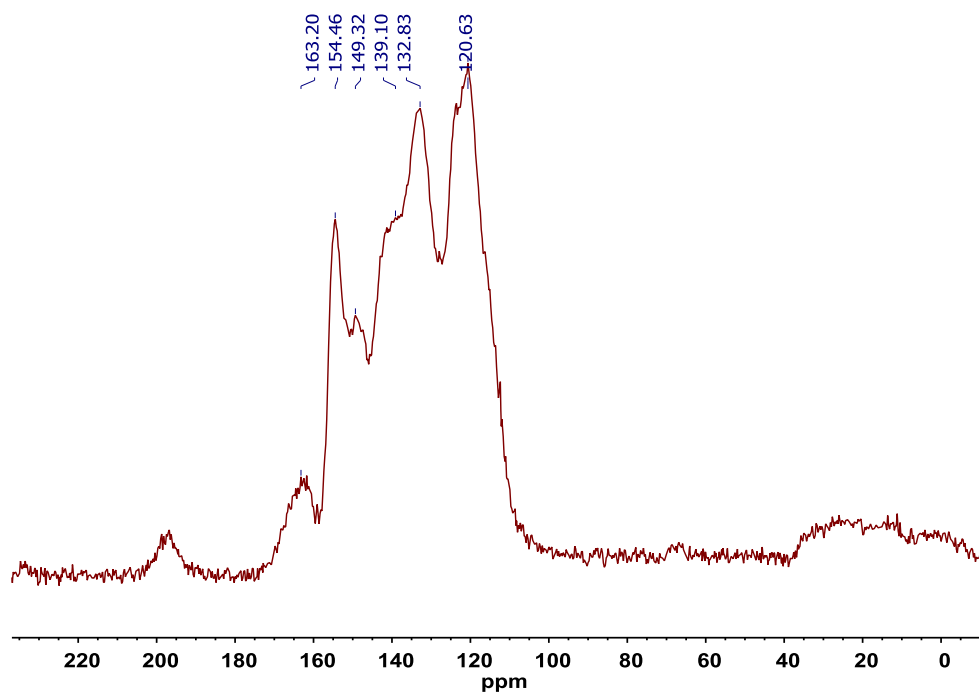


Figure S9. ^{13}C CP-MAS NMR spectrum of $\text{H}_2\text{P-COF}$.

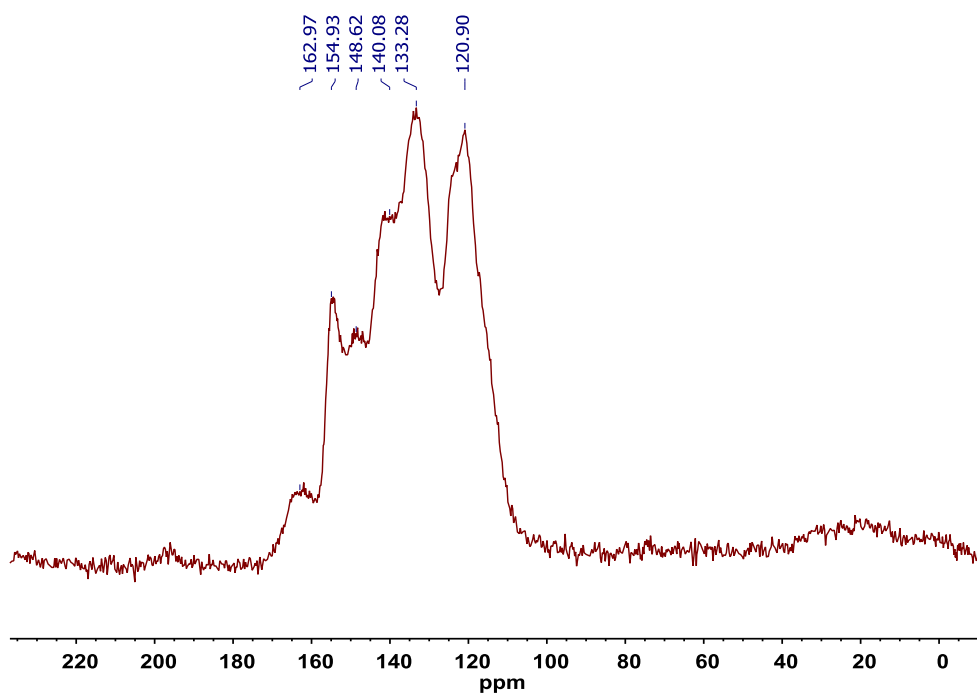


Figure S10. ^{13}C CP-MAS NMR spectrum of $\text{S@H}_2\text{P-COF-BATA}$.

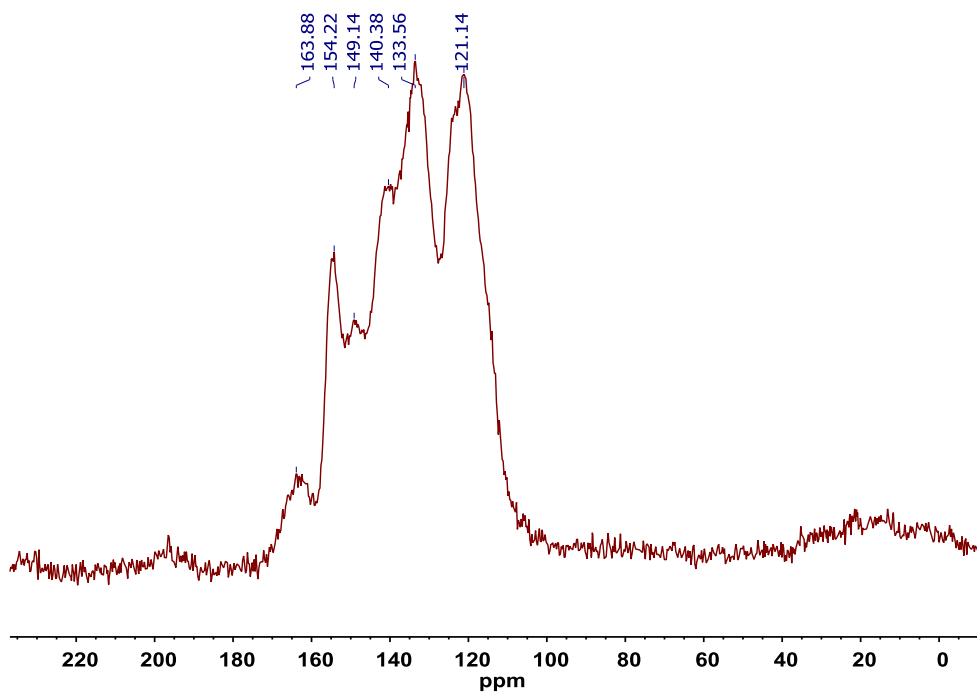
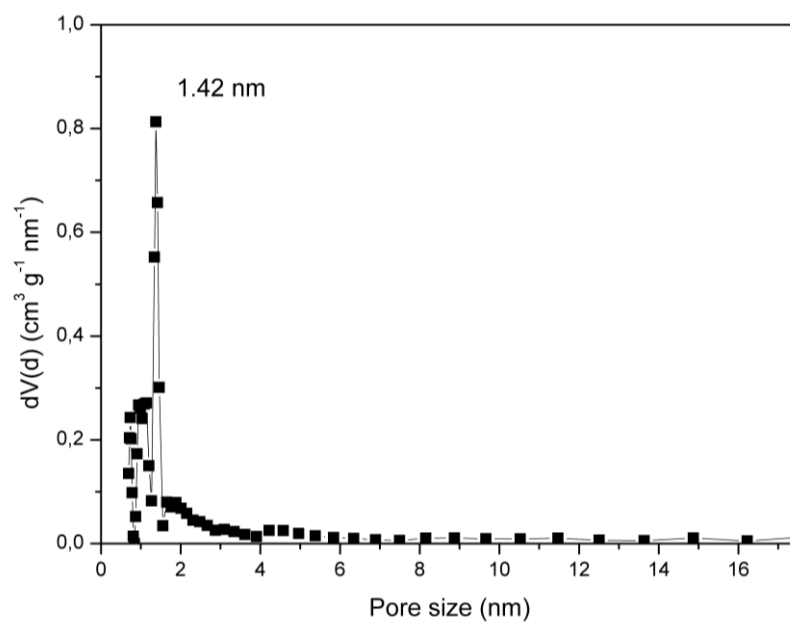


Figure S11. ^{13}C CP-MAS NMR spectrum of $\text{S@H}_2\text{P-COF}$.

Pore size distributions

a)



b)

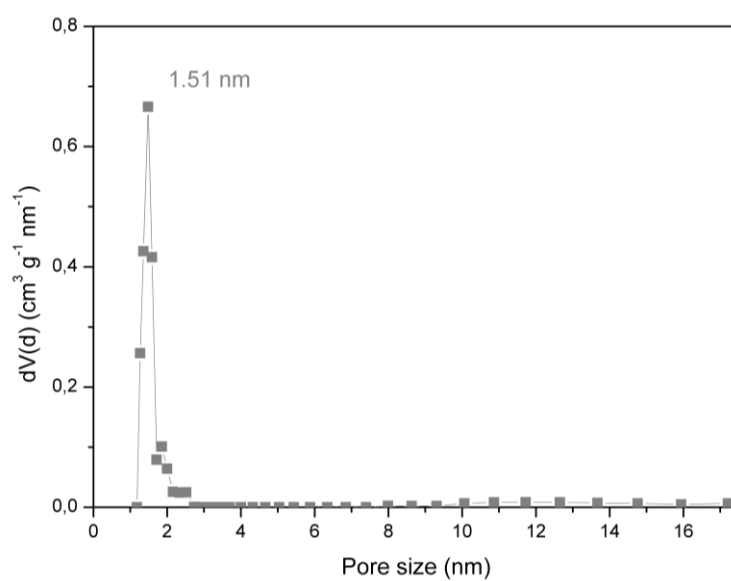


Figure S12. Pore size distribution profile of (a) H₂P-COF-BATA and (b) H₂P-COF.

Thermogravimetric analysis (TGA)

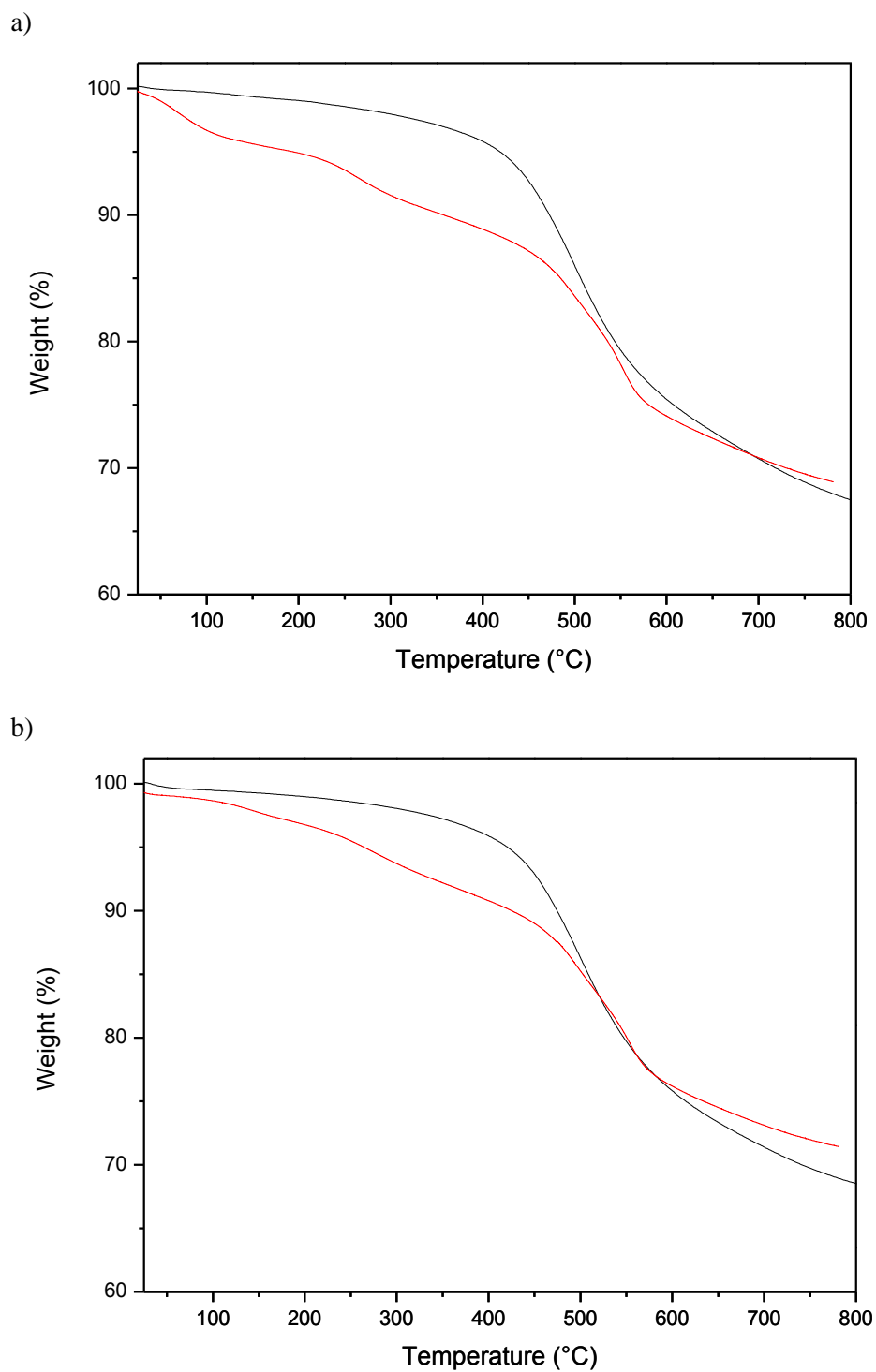
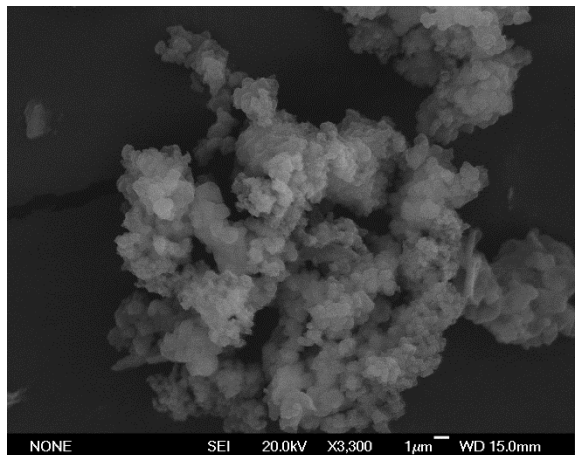


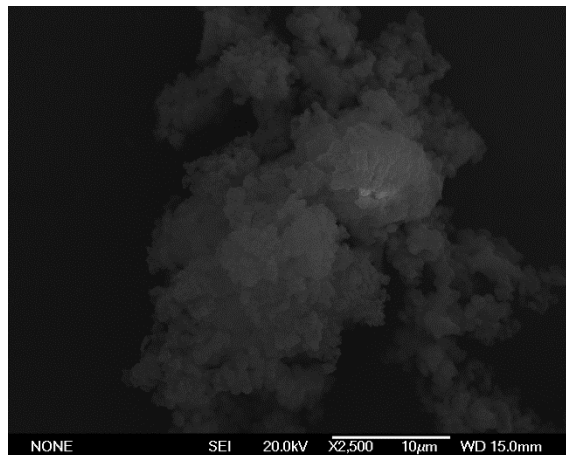
Figure S13. TGA of (a) **H₂P-COF-BATA** (black) and **S@H₂P-COF-BATA** (red); (b) **H₂P-COF** (black) and **S@H₂P-COF** (red).

Electron Microscopy Studies

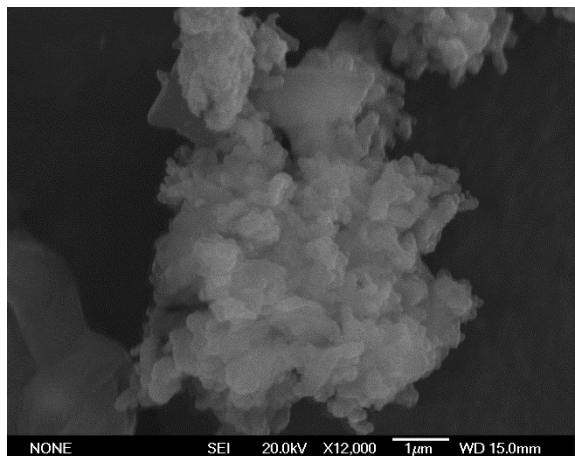
H₂P-COF-BATA



H₂P-COF



S@H₂P-COF-BATA



S@H₂P-COF

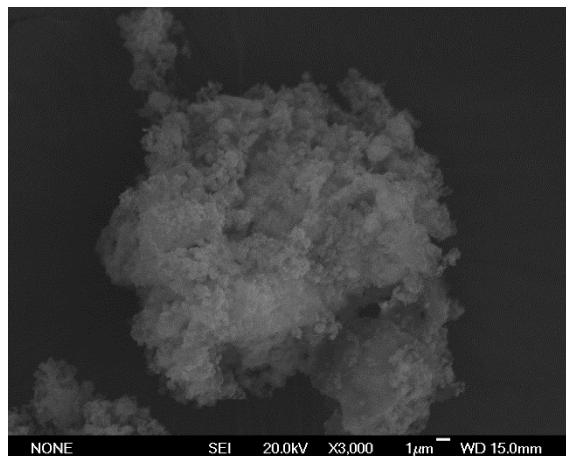


Figure S14. Scanning electron microscopy (SEM) images.

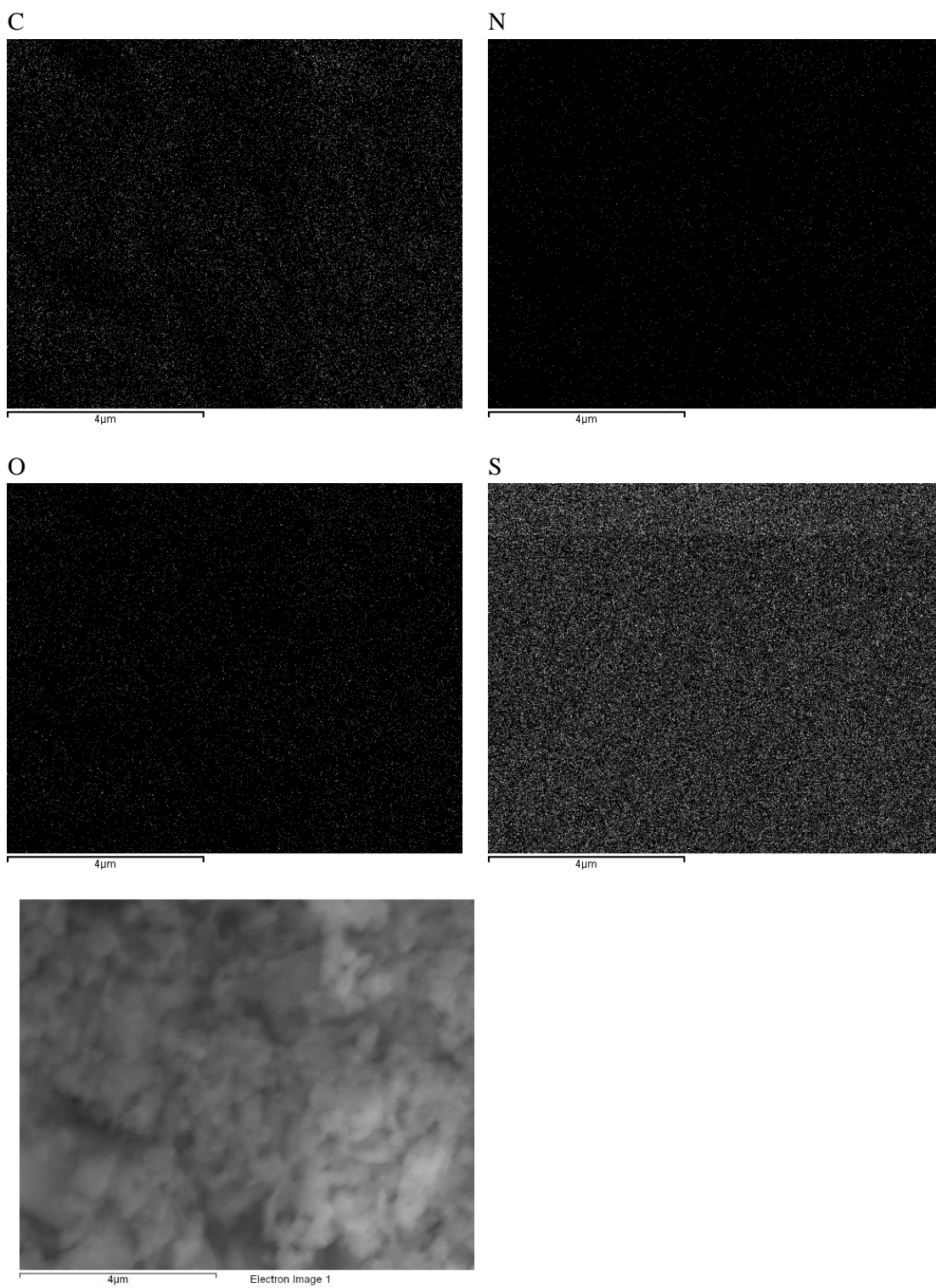


Figure S15. Elemental mapping of S@H₂P-COF-BATA.

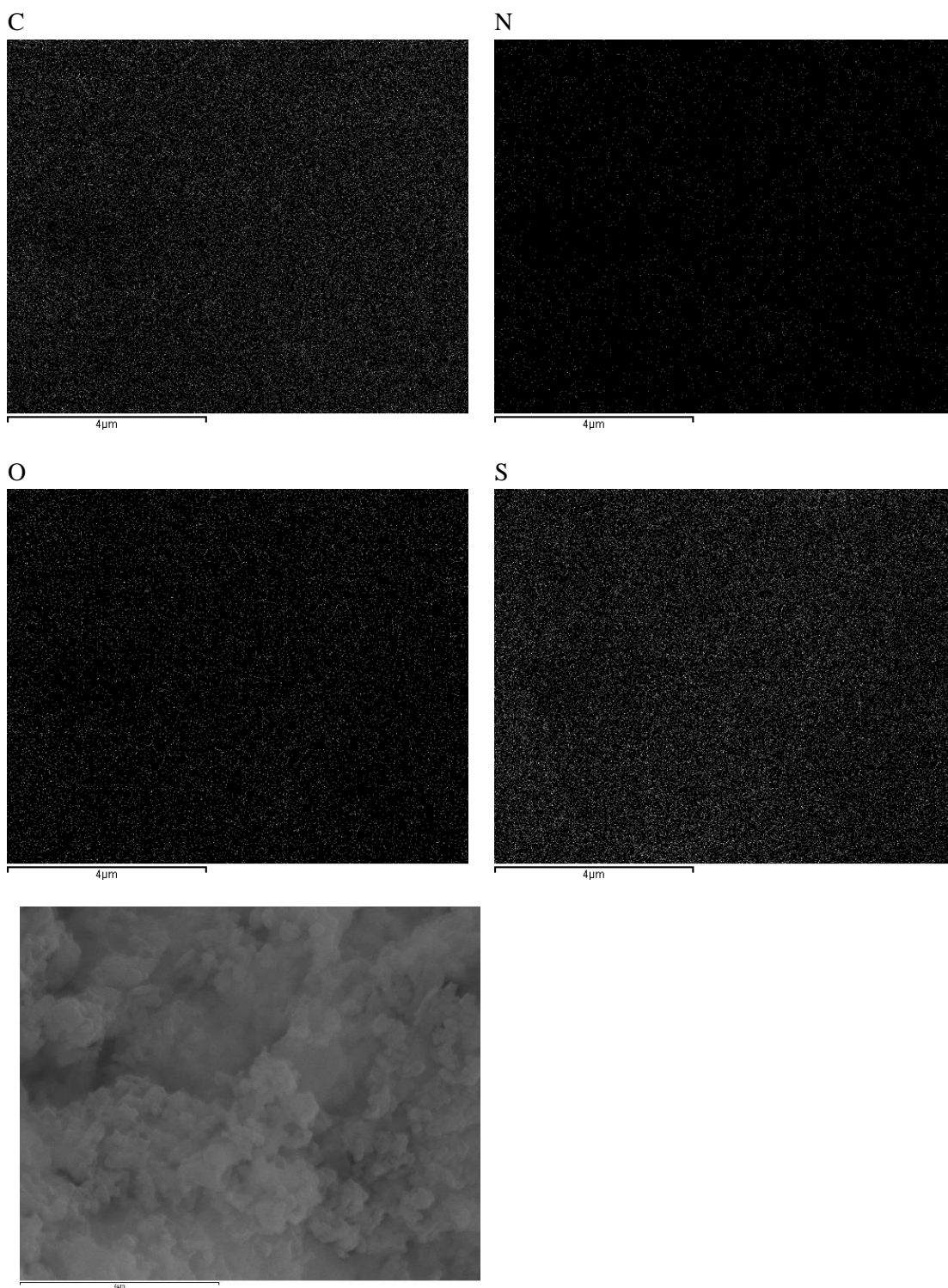


Figure S16. Elemental mapping of S@H₂P-COF-BATA.

Table S2. EIS fitting to $R_s(CPE_1[R_1W])$ equivalent circuit and D_{Li^+} for **S@H₂P-COF** and **S@H₂P-COF-BATA**.

S@H₂P-COF

	R_s (Ω)	C (F/cm)	n	R_{CT} (Ω)	W_{O-R} (Ω)	W_{O-T}	W_{O-n}	D_{Li^+} (cm/s)
Before cycling	2.30	$5.82 \cdot 10^{-5}$	0.73	15.71	$2.74 \cdot 10^7$	$2.13 \cdot 10^{12}$	0.51	$1.58 \cdot 10^{-9}$
After C rate mode	2.51	$1.24 \cdot 10^{-4}$	0.66	50.85	$1.24 \cdot 10^{10}$	$1.64 \cdot 10^{14}$	0.60	$2.20 \cdot 10^{-10}$
#100 cycle (continuous mode at 0.1 C)	4.30	$1.45 \cdot 10^{-4}$	0.58	97.52	$1.60 \cdot 10^{14}$	$1.10 \cdot 10^{20}$	0.60	$3.42 \cdot 10^{-10}$

S@H₂P-COF-BATA

	R_s (Ω)	C (F/cm)	n	R_{CT} (Ω)	W_{O-R} (Ω)	W_{O-T}	W_{O-n}	D_{Li^+} (cm/s)
Before cycling	3.31	$4.32 \cdot 10^{-5}$	0.71	24.08	$3.77 \cdot 10^8$	$8.53 \cdot 10^{13}$	0.54	$4.42 \cdot 10^{-9}$
After C rate mode	4.50	$3.22 \cdot 10^{-5}$	0.74	43.52	$6.08 \cdot 10^8$	$2.53 \cdot 10^{13}$	0.50	$1.14 \cdot 10^{-10}$
#100 cycle (continuous mode at 0.1 C)	3.83	$1.88 \cdot 10^{-4}$	0.56	69.68	$7.48 \cdot 10^7$	$7.48 \cdot 10^{13}$	0.57	$2.58 \cdot 10^{-9}$

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