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2D Porous Porphyrin-Based Covalent Organic Framework for Sulfur Storage in Lithium-Sulfur Battery

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Section S1. Characterization of Por-COF and Por-COF/S composite

A. FT-IR Spectroscopy

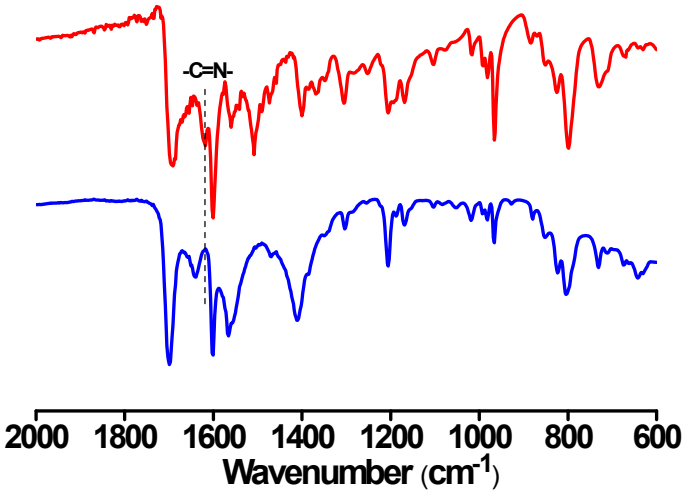

Fig. S1 FT-IR spectra of Por-COF (red curve) and *p*-Por-CHO (blue curve). The appearance of a new band at 1618 cm^{-1} in Por-COF confirmed the formation of imine linked C=N.

B. ^{13}C Solid-State NMR Spectroscopy

High resolution solid-state NMR spectrum was recorded at ambient pressure on a Bruker AVANCE III 400 MHz spectrometer using a standard CP-TOSS pulse sequence (cross polarization with total suppression of sidebands) probe with 4 mm (outside diameter) zirconia rotors. Cross-polarization with TOSS was used to acquire ^{13}C data at 100.37 MHz. The ^{13}C ninety-degree pulse widths were 4 μs. The decoupling frequency corresponded to 72 kHz. The TOSS sample-spinning rate was 5 kHz. Recycle delays was 2s. The ^{13}C chemical shifts are given relative to glycine as 176.03 ppm. ^{13}C NMR (100 MHz) δ 156.84, 150.29, 143.67, 134.69, 128.85, 120.75

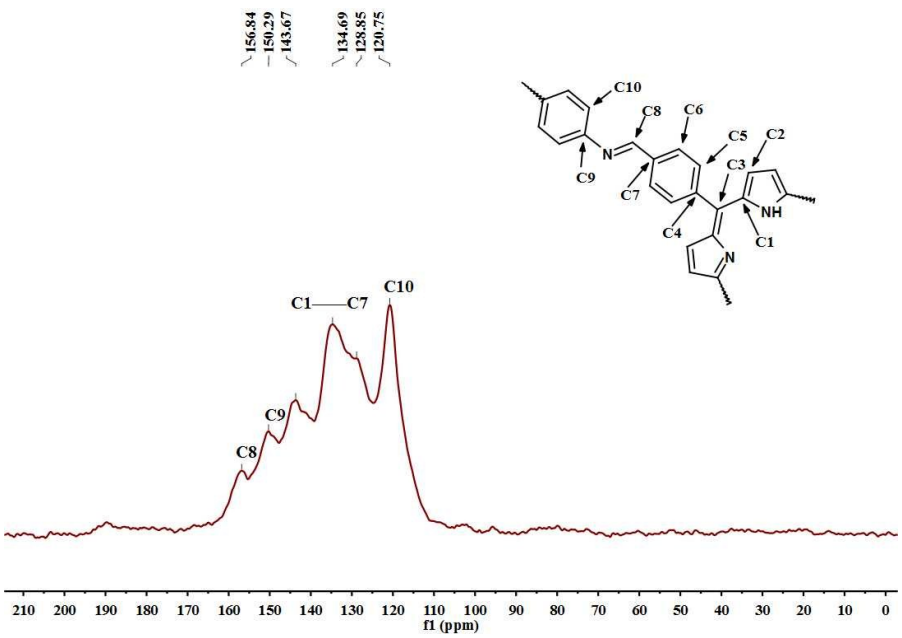

Fig. S2 Solid-state^{13}C NMR spectrum of Por-COF.

C. Thermal Gravimetric Analysis

Fig. S3 shows the TGA profiles of Por-COF under a N_2 atmosphere. Fig. S4 shows the TGA profiles of Por-COF/S composite under a N_2 atmosphere. From these data, we can calculate the weight loss in Por-COF/S composite between 200 ^oC and 400 ^oC is about 55%, which represents the amount of sulfur.

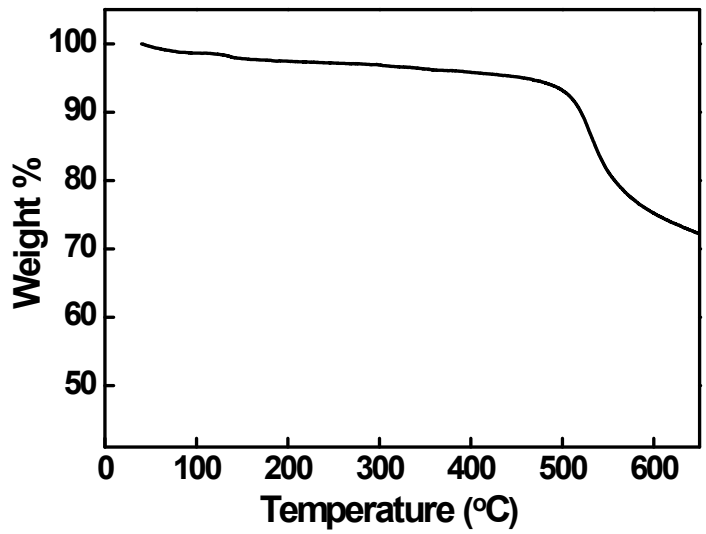

Fig. S3 TGA curves of Por-COF recorded in N_2 atmosphere.

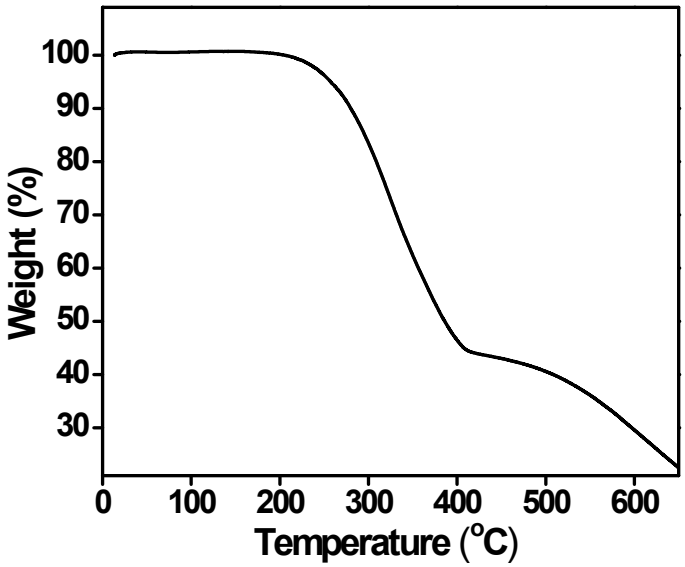

Fig. S4 TGA curve of Por-COF/S composite recorded in N_2 atmosphere

D. Powder X-ray Diffraction Analysis

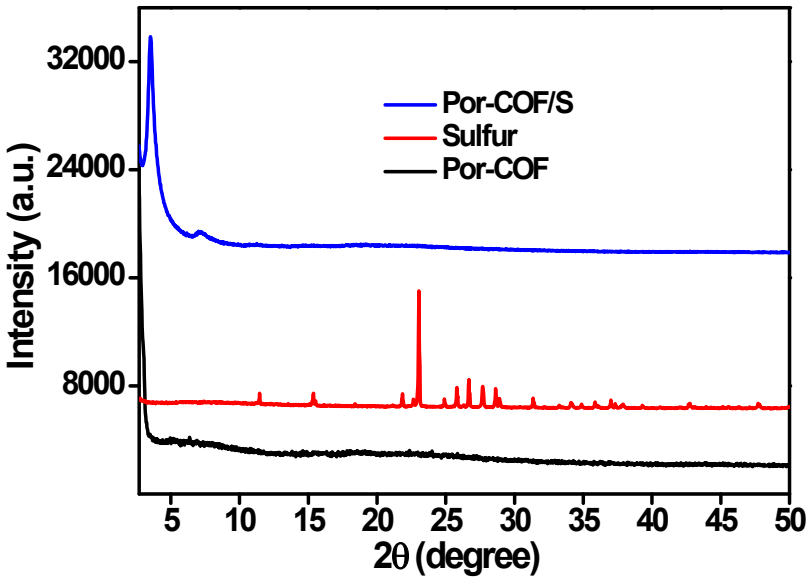

Fig. S5 Powder X-ray diffraction patterns of Por-COF (blue), sublimed sulfur (red) and Por-COF/S composite (black).

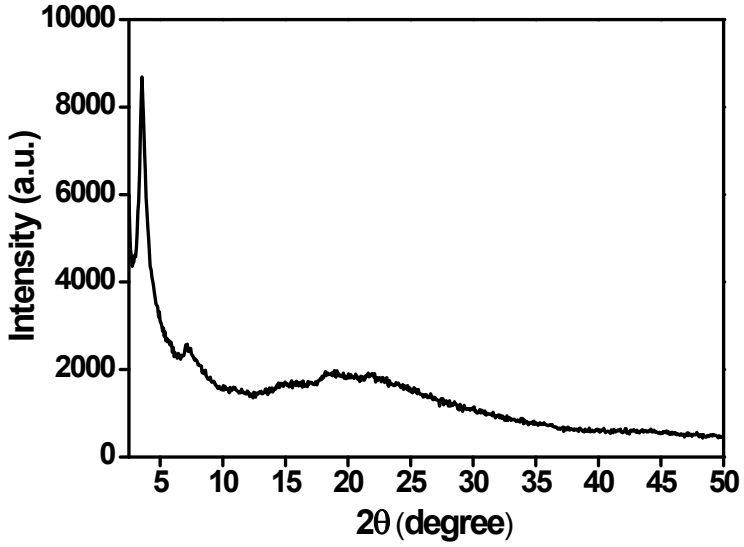

Fig. S6 The XRD spectrum of Por-COF/S composite after removing the sulfur.

E. Elemental Mapping

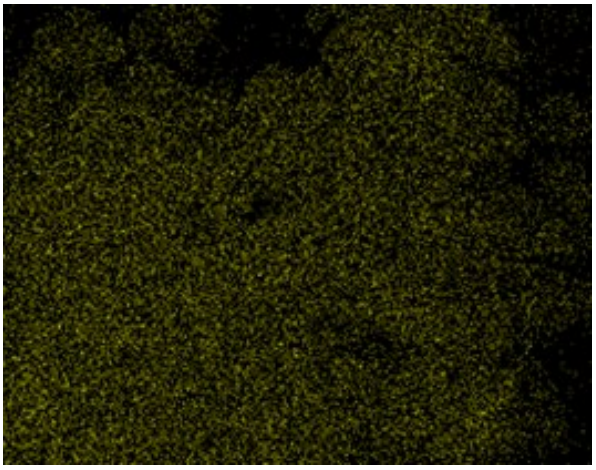

Fig. S7 The corresponding elemental mapping of sulfur for the Por-COF/S composite.

F. TEM images

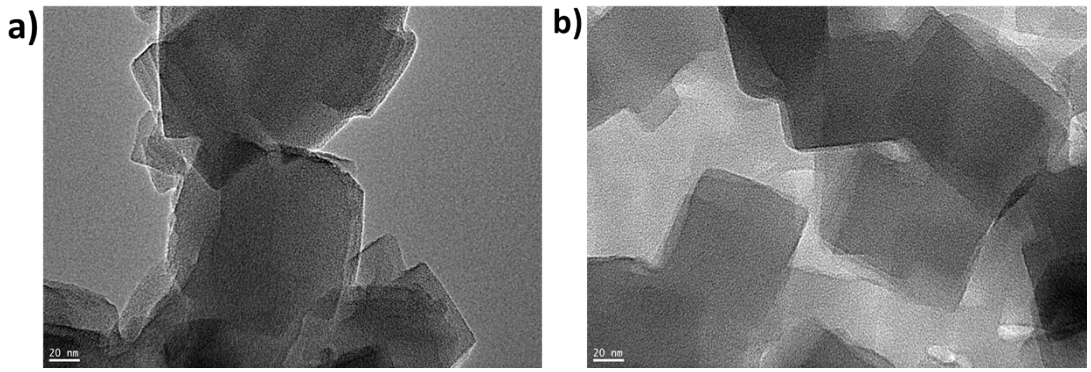

Fig. S8 a) TEM images of Por-COF; b) TEM image of Por-COF/S composite.

G. X-ray Photoelectron Spectroscopy(XPS) Analysis

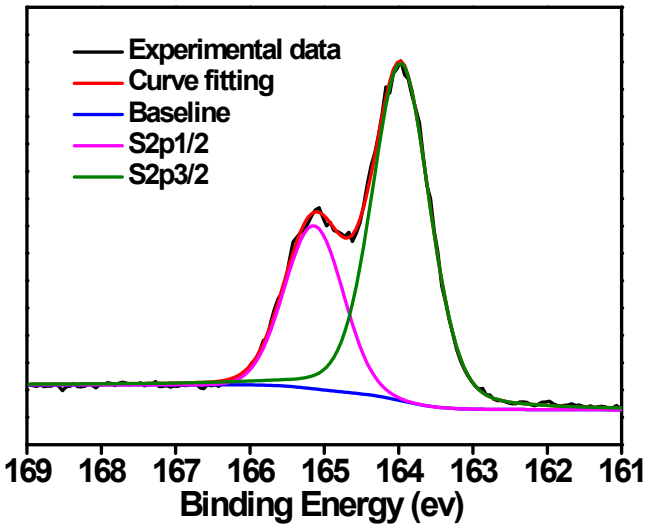

Fig. S9 XPS S2p spectra of Por-COF/S composite.

Section S2. Structure Simulation

The unit cell structures of the eclipsed AA and staggered AB stacking modes were calculated using the density-functional tight-binding method including Lennard-Jones dispersion (DFTB-D), as implemented in the DFTB+ program package. DFTB is an approximate density functional theory method based on the tight binding approach and utilizes an optimized minimal LCAO Slater-type all-valence basis set in combination with a two-center approximation for Hamiltonian matrix elements. The Coulombic interaction between partial atomic charges was determined using the self-consistent charge (SCC) formalism. Lennard-Jones type dispersion was employed in all calculations to describe van der Waals and π-stacking interactions. The lattice dimensions were optimized simultaneously with the geometry. The standard DFTB parameters for X–Y element pairs (X, Y = C, H, O and N) interactions were selected from the mio-1-1 set.

The Por-COF models were generated using Materials Studio suite of programs. Vertex positions were obtained from the Reticular Chemistry Structure Resource. Firstly, the eclipsed model was built and the symmetry of lattice was degraded to *P*1. Then the lattice model (e.g., cell parameters, atomic positions, and total energies) was fully optimized using the DFTB-D method. The slipped AA and AB conformers were obtained by the extensive energy minimizations to obtain the most stable unit cell structures with the correct space groups. The staggered arrangement for Por-COF was also examined by offsetting the alternating stacked units from the eclipsed model.

Pawley refinement was carried out using Reflex, a software package for crystal determination from XRD pattern. Unit cell dimension was set to the theoretical parameters. The Pawley refinement was performed to optimize the lattice parameters iteratively until the R_{WP} value converges and the overlay of the observed with refined profiles shows good agreement. The pseudo-Voigt profile function was used for whole profile fitting and Berrar–Baldinozzi function was used for asymmetry correction during the refinement processes. Line broadening from crystallite size and lattice strain were both considered.

Table S1. Fractional atomic coordinates for the unit cell of Por-COF after Pawley refinement

Por-COF	Space group: P_{21} a = 25.9113 Å, b = 25.3177 Å, c =7.5925 Å $\alpha = \gamma$=90.0, and β = 95.7302.		
C	0.22781	0.02174	0.12467
C	0.19934	0.06141	0.19534
C	0.14537	0.05498	0.19934
C	0.39807	0.03872	0.13246
C	0.11705	0.01057	0.11992
C	0.05968	0.00474	0.11744
C	0.28453	0.02770	0.12986
C	0.14596	0.97186	0.04342
C	0.19985	0.97631	0.05156
N	0.31088	0.99074	0.07007
C	0.38818	0.94885	0.01404
C	0.36515	0.99395	0.07408
N	0.90070	0.94059	0.11267
C	0.03317	0.95293	0.13567
C	0.05445	0.90411	0.17612
C	0.96760	0.88685	0.12884
C	0.01468	0.86383	0.16804
C	0.93336	0.29410	0.16802
C	0.93329	0.26181	0.31936
C	0.92818	0.20661	0.30431
C	0.90861	0.46184	0.11314
C	0.92132	0.18206	0.13835
C	0.91963	0.12262	0.12420
C	0.94005	0.35234	0.18369

C	0.91841	0.21410	0.98809
C	0.92526	0.26928	0.00225
N	0.95075	0.38177	0.04847
C	0.99652	0.46941	0.99491
C	0.95255	0.43741	0.05692
N	0.97952	0.05051	0.11986
C	0.96855	0.10225	0.10939
C	0.01629	0.13654	0.07582
C	0.03206	0.05034	0.09890
C	0.05522	0.10433	0.06326
H	0.53305	0.92289	0.22104
H	0.38192	0.07484	0.17871
H	0.36305	0.91427	0.96559
H	0.71195	0.03343	0.93617
H	0.61667	0.02781	0.95642
H	0.61739	0.89414	0.31353
H	0.71275	0.90453	0.31552
H	0.74123	0.08233	0.17771
H	0.81843	0.15972	0.17274
H	0.95564	0.96905	0.08597
H	0.92073	0.61229	0.29339
H	0.87356	0.43711	0.15656
H	0.03095	0.45081	0.95175
H	0.94823	0.79209	0.85743
H	0.95610	0.69519	0.87742
H	0.90118	0.69508	0.41776
H	0.89120	0.79117	0.39498
H	0.81696	0.80008	0.06495
H	0.74041	0.86226	0.06365

C	0.60999	0.96042	0.13517
C	0.63816	0.92514	0.23095
C	0.69221	0.93043	0.22924
C	0.44178	0.94743	0.01690
C	0.72046	0.96971	0.12530
C	0.77794	0.97555	0.12279
C	0.55320	0.95710	0.14511
C	0.69182	0.00374	0.02473
C	0.63793	0.99998	0.03251
N	0.52830	0.99334	0.07516
C	0.45167	0.03791	0.13146
C	0.47421	0.99190	0.07794
N	0.85679	0.04006	0.11236
C	0.80398	0.02784	0.12595
C	0.78207	0.07723	0.15317
C	0.86982	0.09397	0.12861
C	0.82206	0.11739	0.15340
C	0.93000	0.68831	0.14976
C	0.91131	0.71614	0.29358
C	0.90501	0.77024	0.28120
C	0.99696	0.52452	0.99311
C	0.91964	0.79843	0.12532
C	0.91006	0.85752	0.11848
C	0.93473	0.63119	0.16567
C	0.93756	0.77076	0.90043
C	0.94230	0.71646	0.99196
N	0.95365	0.60462	0.04106
C	0.90900	0.51696	0.11040
C	0.95347	0.54915	0.05232

N	0.85799	0.92923	0.12747
C	0.86891	0.87747	0.11219
C	0.82074	0.84314	0.08647
C	0.80528	0.92941	0.11658
C	0.78148	0.87515	0.08785
H	0.30288	0.06558	0.19023
H	0.45896	0.91208	0.96882
H	0.47685	0.07259	0.17875
H	0.12599	0.93778	0.97280
H	0.22122	0.94469	0.99640
H	0.22003	0.09741	0.25303
H	0.12503	0.08478	0.26935
H	0.09438	0.89941	0.21551
H	0.01759	0.82180	0.19585
H	0.88229	0.01125	0.09815
H	0.93547	0.36916	0.31922
H	0.03187	0.54922	0.94876
H	0.87395	0.53510	0.15065
H	0.91129	0.19570	0.85799
H	0.92428	0.29397	0.88312
H	0.93865	0.28015	0.45058
H	0.92957	0.18194	0.42305
H	0.01982	0.17958	0.05403
H	0.09533	0.11688	0.02455

Table S2. Fractional atomic coordinates for the unit cell of Por-COF with the staggered mode.

Por-COF	Space group: P_{21} a = 25.3967 Å, b = 25.3744 Å, c = 6.4174 Å

	$\alpha = \gamma = 90.0$, and $\beta = 105.0545$.		
C	0.99353	0.79056	0.19688
C	0.96703	0.80686	0.36918
C	0.91124	0.80322	0.36269
C	0.17103	0.81256	0.09720
C	0.88038	0.78313	0.18365
C	0.81989	0.77524	0.17749
C	0.05143	0.79068	0.20684
C	0.90716	0.76832	0.00909
C	0.96282	0.77203	0.01554
N	0.07266	0.76853	0.05950
C	0.13844	0.71655	0.00088
C	0.12721	0.76634	0.05799
N	0.73299	0.70207	0.14152
C	0.78811	0.72023	0.17835
C	0.80754	0.67258	0.21349
C	0.71655	0.64589	0.14270
C	0.76392	0.62738	0.19373
C	0.69632	0.06238	0.20702
C	0.68339	0.03163	0.39179
C	0.68442	0.97693	0.39782
C	0.65449	0.21396	0.03034
C	0.69732	0.95103	0.21767
C	0.69332	0.89117	0.21170
C	0.69211	0.11904	0.19893
C	0.71189	0.98229	0.03462
C	0.71178	0.03717	0.02963
N	0.71315	0.15122	0.04884
C	0.75355	0.24920	0.03061

C	0.70686	0.20465	0.03990
N	0.74443	0.82064	0.17734
C	0.74142	0.87382	0.18091
C	0.79645	0.91037	0.16978
C	0.79853	0.82155	0.16982
C	0.83169	0.87807	0.16252
H	0.27860	0.67228	0.07379
H	0.16307	0.85208	0.13557
H	0.10436	0.68071	0.96840
H	0.48884	0.80412	0.92471
H	0.39056	0.79963	0.92697
H	0.35489	0.63267	0.14968
H	0.45300	0.64096	0.19301
H	0.50527	0.82080	0.30375
H	0.58774	0.90887	0.34984
H	0.70770	0.72717	0.11072
H	0.62033	0.35556	0.20264
H	0.61803	0.17918	0.02611
H	0.79436	0.24189	0.03397
H	0.71585	0.55713	0.82540
H	0.71200	0.45831	0.83867
H	0.59246	0.43588	0.33638
H	0.59661	0.53458	0.32486
H	0.56103	0.56184	0.87570
H	0.49426	0.62718	0.85720
C	0.36546	0.71603	0.03972
C	0.38437	0.67100	0.10451
C	0.43999	0.67535	0.12478
C	0.19185	0.71201	0.99367

C	0.47908	0.72363	0.06548
C	0.53845	0.73028	0.09306
C	0.30709	0.71348	0.04312
C	0.45981	0.76707	0.98441
C	0.40438	0.76416	0.97971
N	0.29093	0.75750	0.02386
C	0.22452	0.80843	0.08158
C	0.23596	0.75806	0.03426
N	0.62472	0.80160	0.16860
C	0.56894	0.78128	0.17624
C	0.54780	0.82388	0.26235
C	0.63988	0.85560	0.22776
C	0.59080	0.86946	0.28914
C	0.65280	0.44040	0.09083
C	0.61943	0.46238	0.22269
C	0.62178	0.51789	0.21653
C	0.74773	0.30228	0.02564
C	0.65753	0.55311	0.07803
C	0.66405	0.61324	0.08811
C	0.65362	0.38291	0.10784
C	0.68892	0.53063	0.93900
C	0.68664	0.47521	0.94560
N	0.69247	0.36642	0.02222
C	0.64872	0.26711	0.02678
C	0.69538	0.31201	0.03029
N	0.61364	0.68493	0.09416
C	0.61833	0.63392	0.04446
C	0.56853	0.60303	0.94150
C	0.56211	0.68716	0.03902

C	0.53425	0.63642	0.93360
H	0.07478	0.80853	0.35029
H	0.19924	0.67259	0.95030
H	0.25843	0.84443	0.11411
H	0.88376	0.75319	0.96708
H	0.98314	0.75976	0.87913
H	0.99022	0.82165	0.51213
H	0.89108	0.81522	0.49996
H	0.84947	0.67238	0.25247
H	0.76515	0.58487	0.21430
H	0.65142	0.78029	0.11304
H	0.66981	0.13274	0.33120
H	0.78410	0.33712	0.02336
H	0.60755	0.27356	0.01883
H	0.72274	0.96291	0.89315
H	0.72280	0.06089	0.88511
H	0.67233	0.05092	0.53329
H	0.67459	0.95388	0.54428
H	0.80748	0.95513	0.16979
H	0.87630	0.89186	0.15322

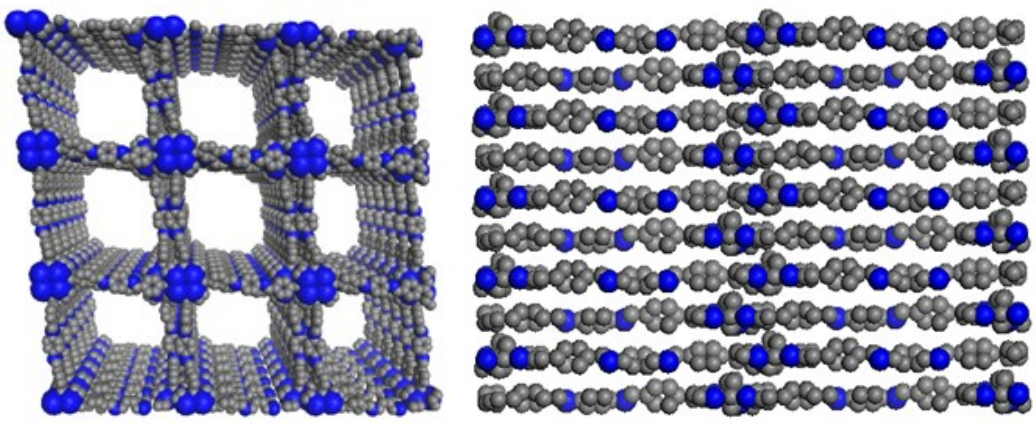

Fig. S10 Top and side views of the AA stacking structure of the Por-COF

Table S3. Fitting Parameters and Errors Obtained From the Pawley Refinement for Por-COF.

Parameter		Value	Error
Lattice	a	25.91134	±0.00081
	b	25.31766	±0.00165
	c	7.59248	±0.00028
	α	90.00000	±0.00000
	β	90.00000	±0.00000
	γ	95.73024	±0.00034
FWHM	U	0.01003	±0.03878
	V	-0.00087	±0.01000
	W	0.00193	±0.00701
Profile	NA	0.50009	±0.01407
	NB	-0.00000	±0.00056
Asymmetry Correction	P1	0.01373	±0.00065
	P2	0.00030	±0.00013
	P3	0.00187	±0.00131
	P4	0.00014	±0.00027
Crystallite Size	A	242.24340	±52.46227
	B	164.49258	±24.67361
	C	240.93709	±53.14198

Lattice Strain	A	0.01984	±0.06154
	B	0.00345	±0.14529
	C	0.01179	±0.09163

Section S3. Electrochemical Measurement

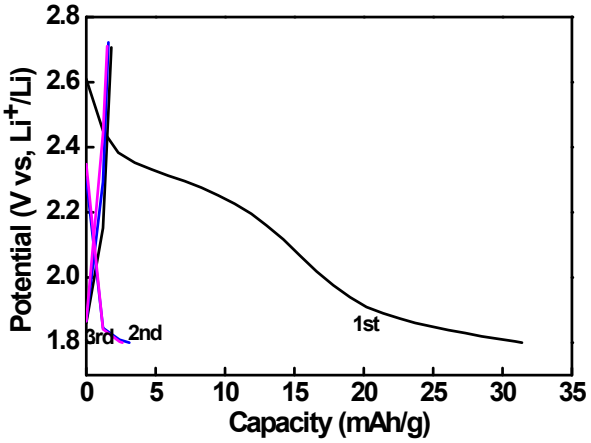

Fig. S11 The discharge and charge curves of the Por-COF substrate.