Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

# Supporting Information

# Impregnation of Sulfur into a 2D Pyrene-Based Covalent Organic Framework for High-Rate Lithium-Sulfur Batteries

Yi Meng‡, Guiqing Lin‡, Huimin Ding, Huaping Liao, and Cheng Wang*

Key Laboratory of Biomedical Polymers of Ministry of Education, College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China

‡ Y. Meng and G. Lin contributed equally to this work.

*corresponding address: chengwang@whu.edu.cn

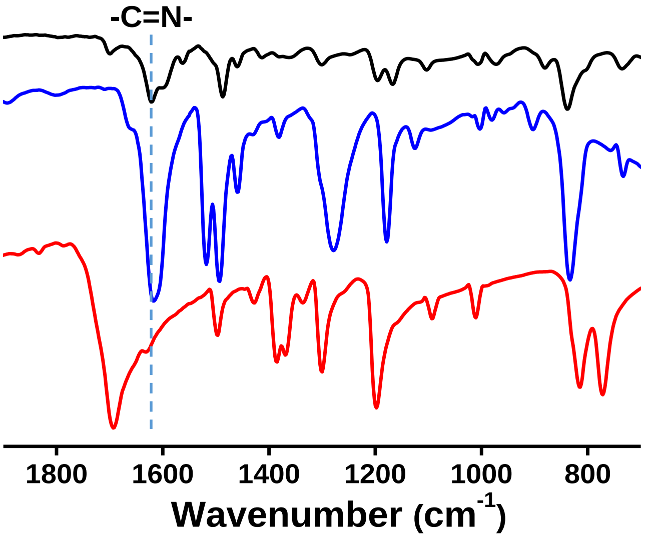

**Fig. S1** FT-IR spectra of the Py-COF (black), PyTTA (blue), and TA (red). Compared with PyTTA and TA, there is a new adsorption peak at 1620 cm$^{-1}$ belong to the stretching vibration of C=N, which indicates that there exists Sciff-based bond in Py-COF.

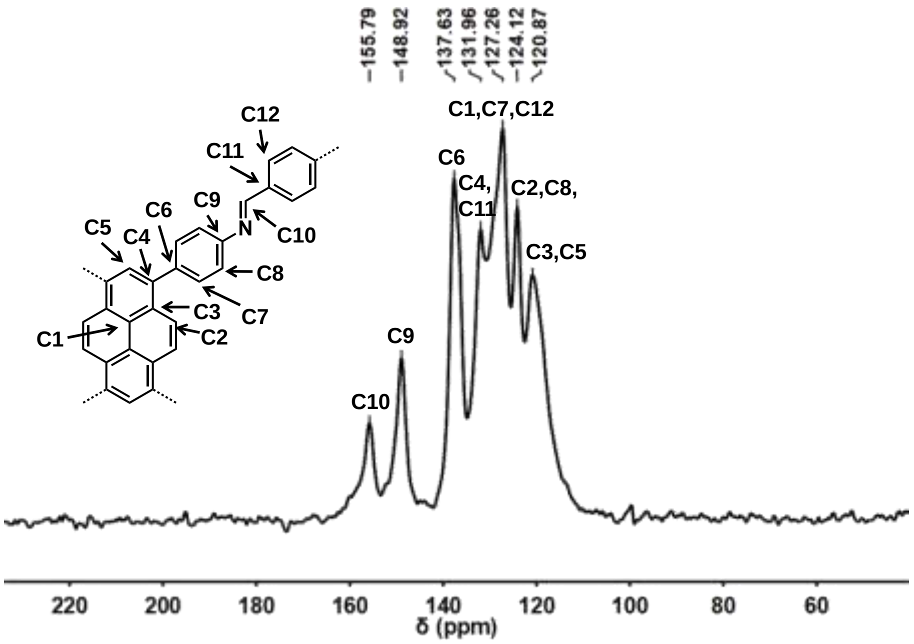

**Fig. S2** Solid NMR spectrum of Py-COF. The peak at 155.79 ppm is classified as Sciff-based carbon (C10). This data can also demonstrate the existence of Sciff-based bond in Py-COF.

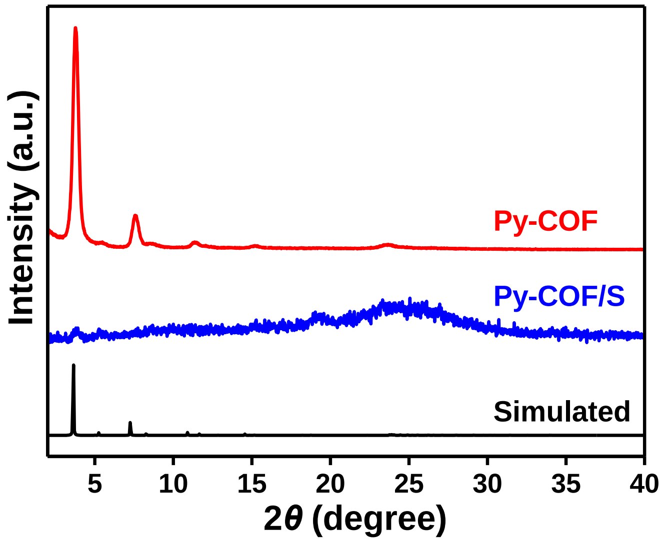

**Fig. S3** PXRD patterns of the simulated (black curve) and experimental Py-COF (red curve), Py-COF/S composite (blue curve). The PXRD pattern of Py-COF/S composite shows very week bands, which is a good sign that the sulfur is homogeneously distributed in the nanopores of Py-COF.

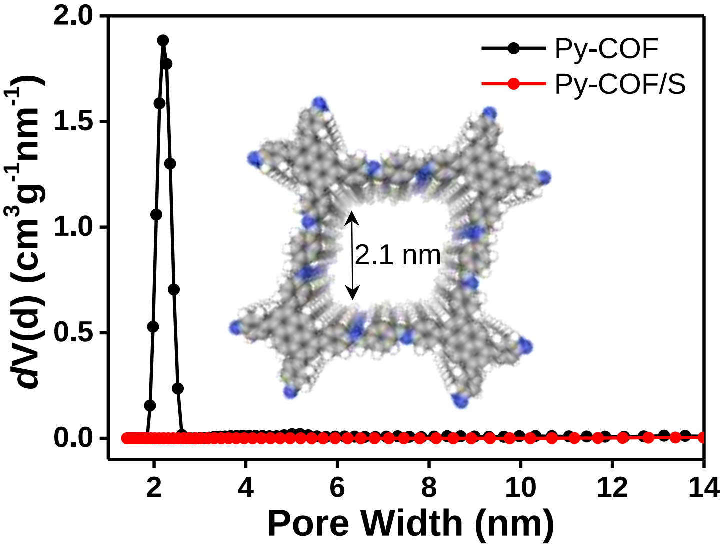

**Fig. S4** The pore size distribution curves of Py-COF and Py-COF/S composite, the inset is the simulated structure of Py-COF.

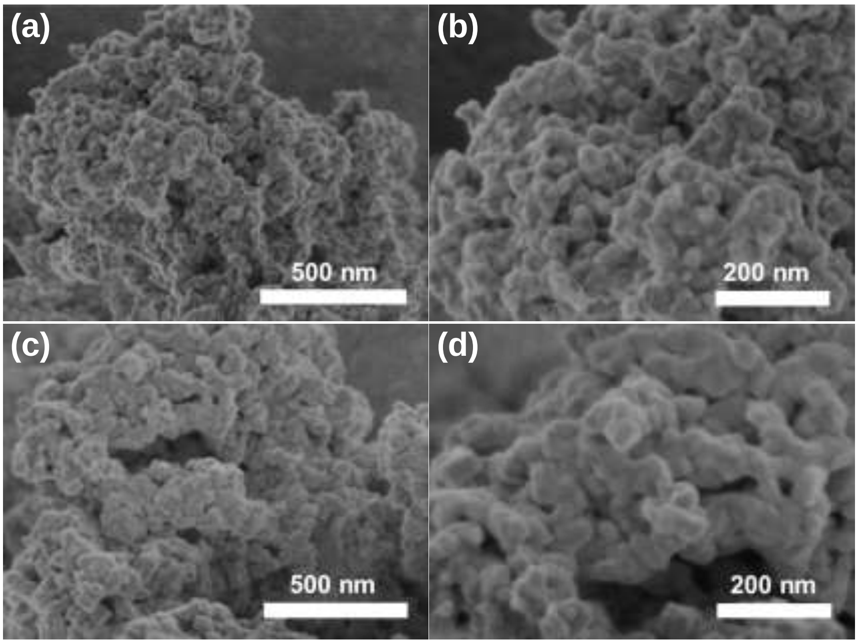

**Fig. S5** SEM images of (a, b) Py-COF and (c, d) Py-COF/S composite.

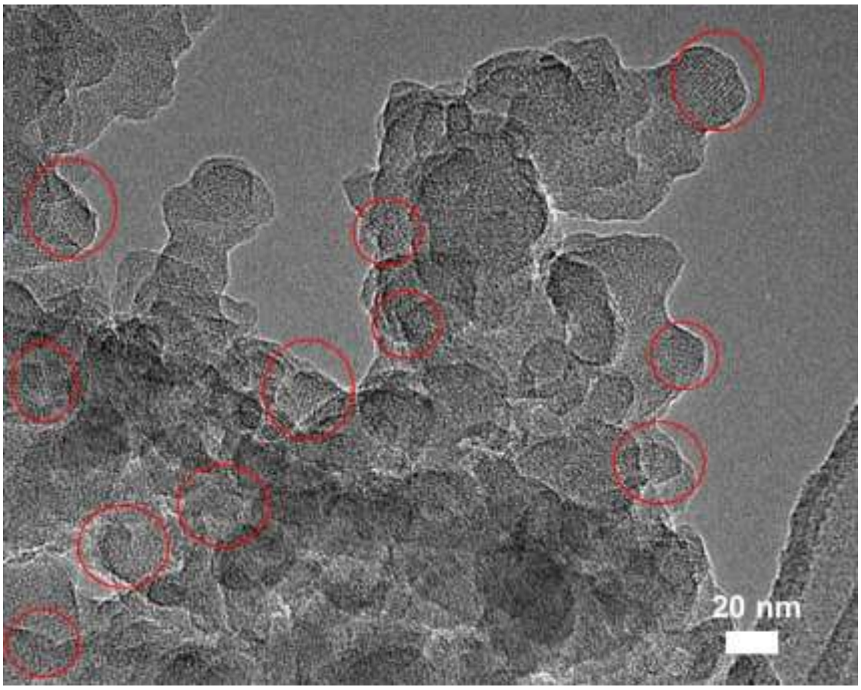

**Fig. S6** HR-TEM image of Py-COF.

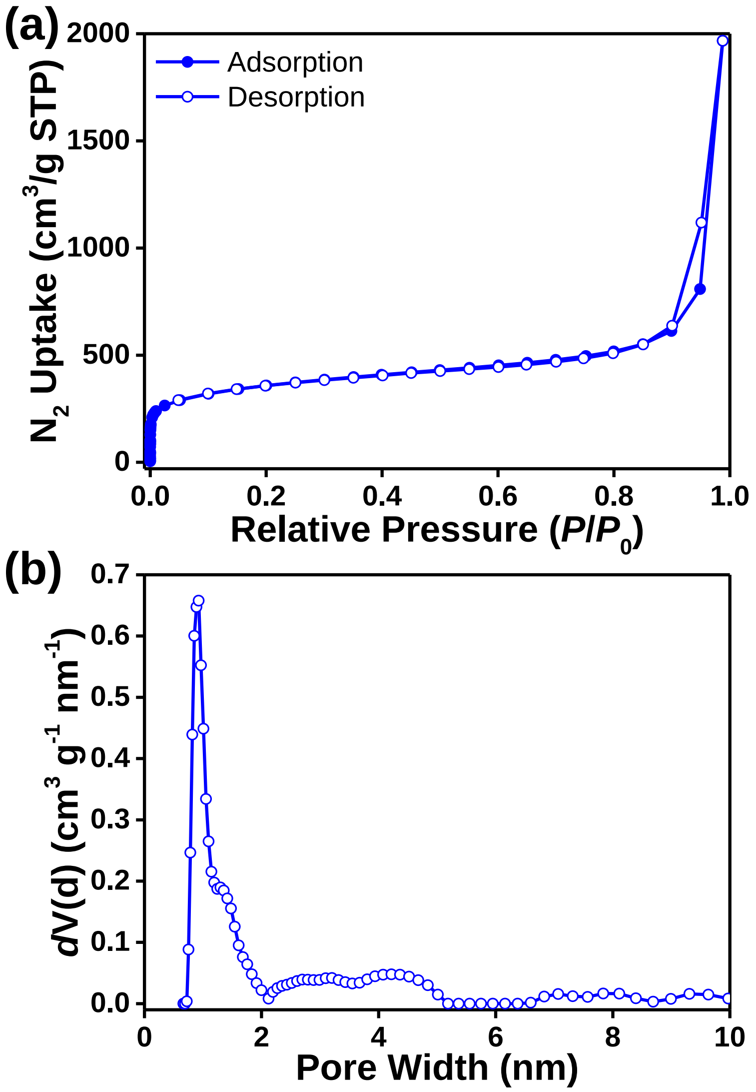

**Fig. S7** (a) $N_2$ adsorption/desorption isotherms and (b) the pore size distribution curves of BP2000.

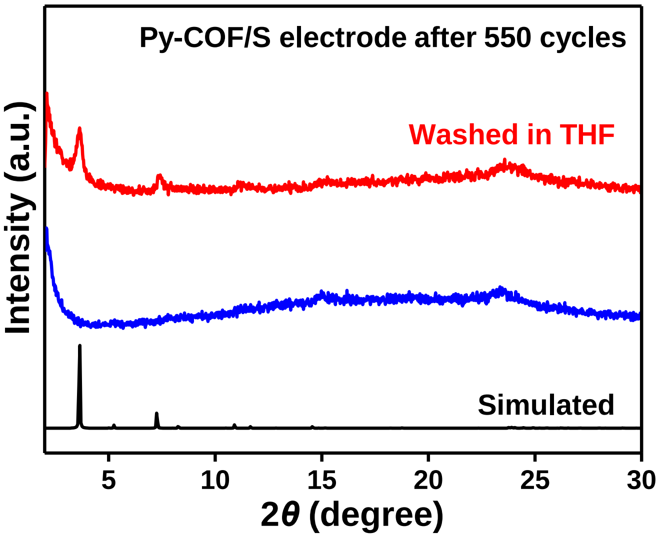

**Fig. S8** PXRD patterns of simulated Py-COF (black curve), Py-COF/S electrode after 550 cycles at rate of 5.0 C disassembled the cell (blue curve) and washed the electrode in THF (red curve).

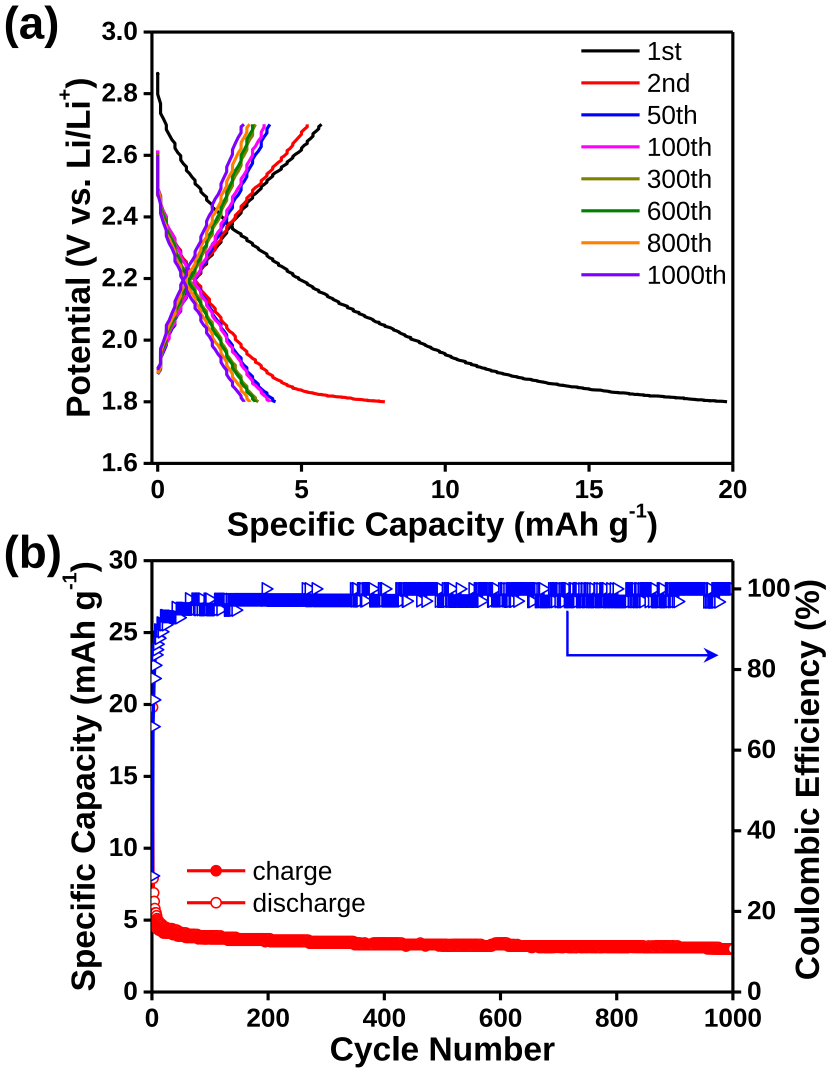

**Fig. S9** (a) Selected discharge-charge voltage-capacity profiles and (b) cycling performance of the Py-COF electrode at a current of 25 mA g$^{-1}$.

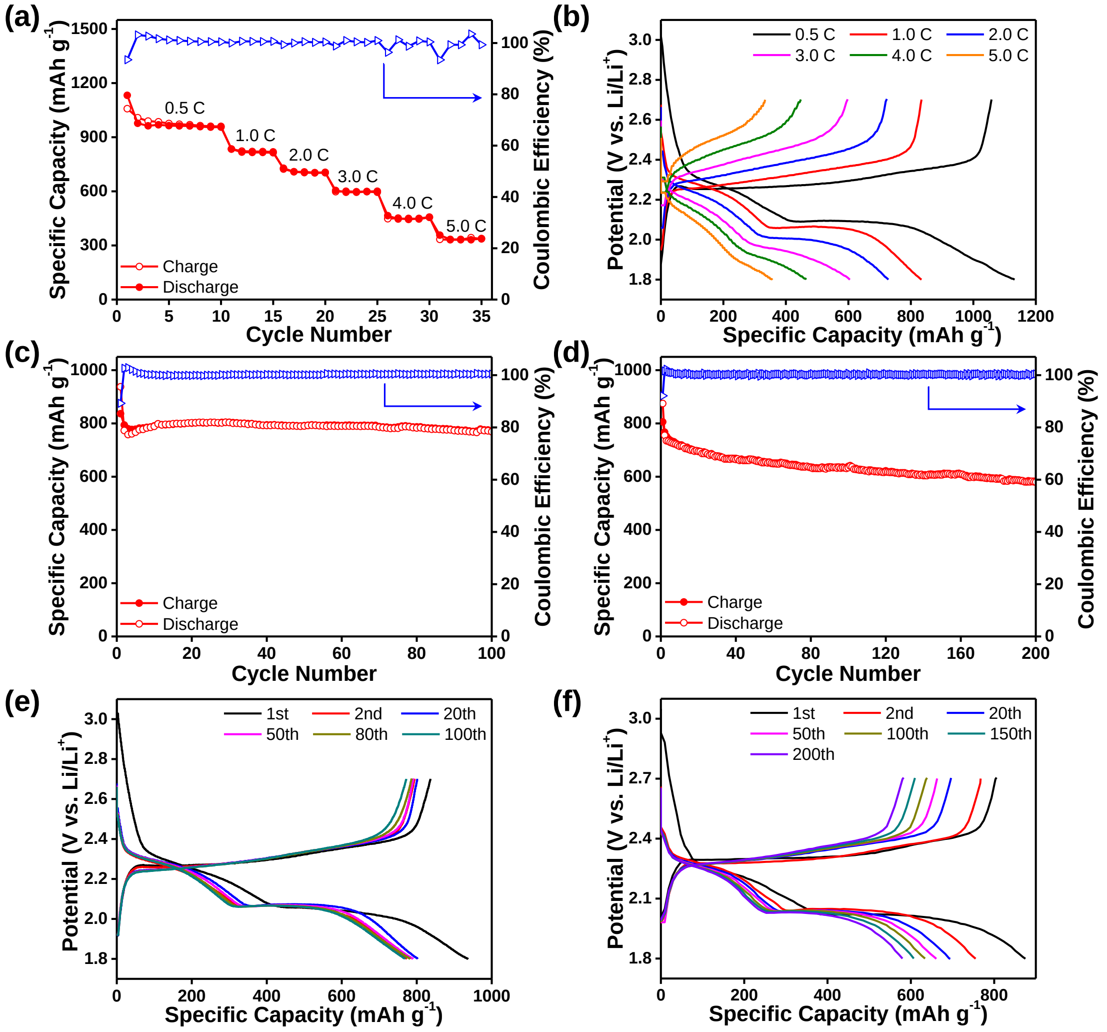

**Fig. S10** (a) Rate capability of the BP2000/S electrode at different rates, and (b) stabilized discharge/charge voltage profiles. Plots of specific capacity versus cycle number and discharge/charge voltage profiles of the BP2000/S electrode at rates of (c, e) 1.0 C and (d, f) 2.0 C.

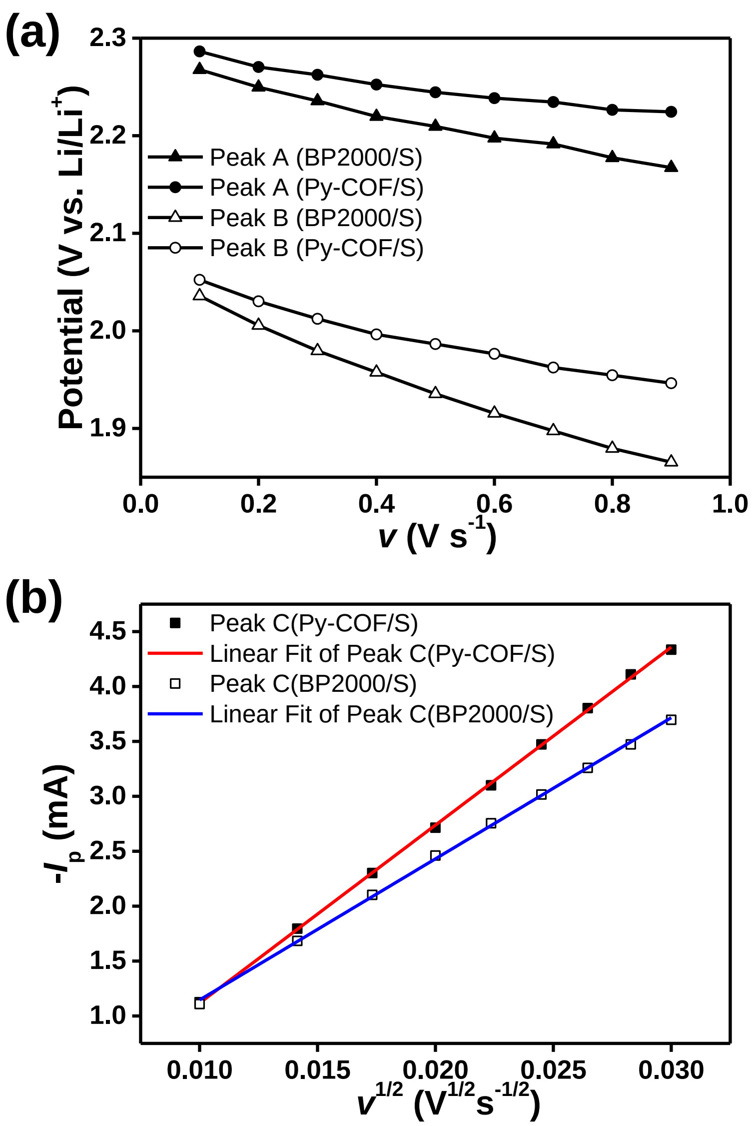

**Fig. S11** (a) Plots of peak voltage versus scan rates of cathode peaks of Py-COF/S and BP2000/S electrodes. (b) the relationship between $I_p$ and $v^{1/2}$ of the anode peak of Py-COF/S and BP2000/S electrodes.

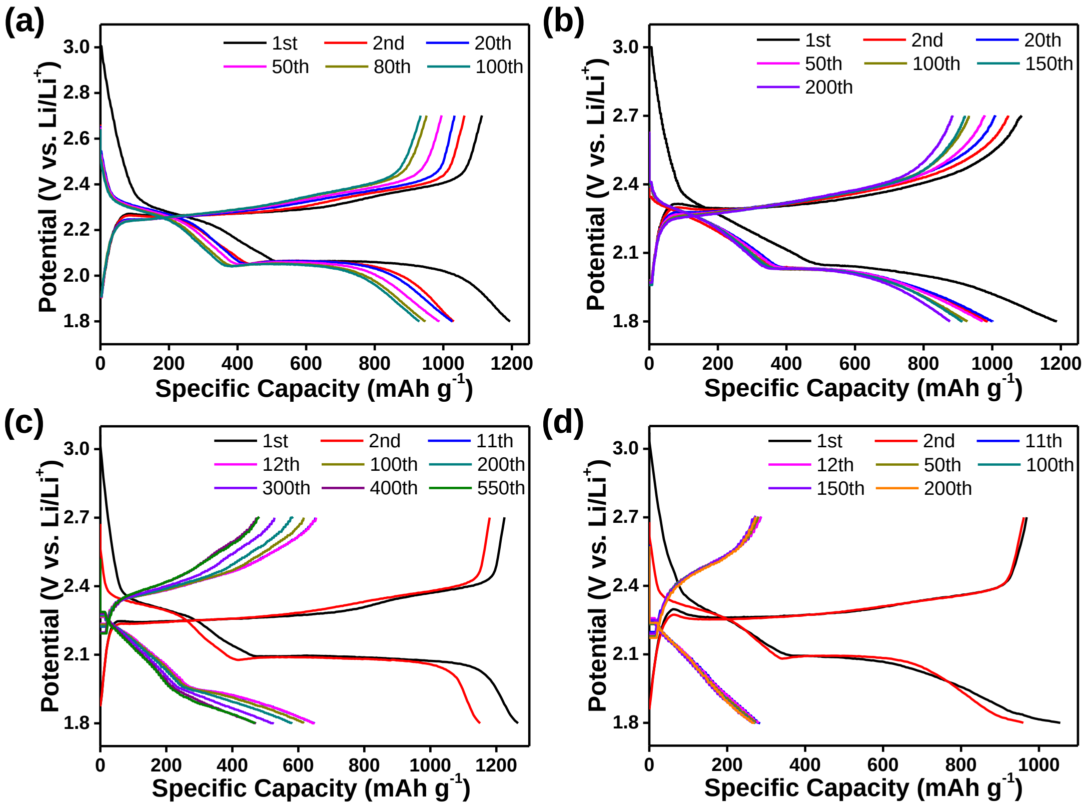

**Fig. S12** Discharge/charge voltage profiles of the Py-COF/S electrode at rate of (a) 1.0 C, (b) 2.0 C. Discharge/charge voltage profiles of the (c) Py-COF/S and (d) BP2000/S electrodes at different rates.

**Table S1** The electrode information and performances of this work and some reported results by using MOFs or COFs as host in Li-S batteries.

| Host name | Host type | Sulfur Loading (wt.%) | Rate (C) | Cycle number | Capacity Retention ($mAhg^{-1}$) | Decay Per Cycle (%) | Ref. |
|---|---|---|---|---|---|---|---|
| **MIL-100** | MOF | 48 | 0.1 | 50 | 405 | 0.99 | *J. Am. Chem. Soc.* **2011**, *133*, 16154 |
| **MIL-101** | | 58.8 | 0.8 | 100 | ~800 | 0.034 | *J. Mater. Chem. A* **2014**, *2*, 13509 |
| **ZIF-8** | | 50 | 0.5 | 300 | 553 | 0.080 | *Energy Environ. Sci.* **2014**, *7*, 2715 |
| **DUT-23** | | 60 | 0.5 | 200 | ~420 | 0.080 | *Nano Lett*. **2014,** *14*, 2345 |
| **MOF-525** | | 50 | 0.5 | 200 | 704 | 0.15 | *ACS Appl. Mater. Interfaces* **2015**, *7*, 20999 |
| **CTF-1** | COF | 34 | 0.1 | 50 | 762 | 0.72 | *J. Mater. Chem. A* **2014**, *2*, 8854 |
| **Azo-COF** | | 39 | 1.0 | 100 | 602 | 0.43 | *RSC Adv*. **2015**, *5*, 86137 |
| **Por-COF** | | 55 | 0.5 | 200 | 633 | 0.16 | *J. Mater. Chem. A* **2016**, *4*, 7416 |
| **COF-1** | | 60 | 0.5 | 200 | 770 | 0.13 | *Adv. Energy Mater.* **2016**, *6*, 1601250 |
| **TpPa-COF** | | 40 | 0.5 | 450 | 525.6 | 0.099 | *Mater. Lett.* **2018**, *213*, 143 |
| **Py-COF** | | 70 | 1.0 | 100 | 963.4 | 0.095 | This work |
| | | | 2.0 | 200 | 877.2 | 0.034 | |
| | | | 5.0 | 550 | 481.2 | 0.048 | |

**Table S2** Electrochemical performance comparison with Py-COF/S and BP2000/S electrodes at different rates.

|  | $Q_{(\text{Py-COF/S})}$ (mAh $g^{-1}$) | $Q_{(\text{BP2000/S})}$ (mAh $g^{-1}$) | $Q_{(\text{BP2000/S})}$/ $Q_{(\text{Py-COF/S})}$ (%) |
|---|---|---|---|
| 1.0 C (100th cycle) | 963.4 | 768.9 | 79.8 |
| 2.0 C (200th cycle) | 877.2 | 597.9 | 68.1 |
| 5.0 C (220th cycle) | 581.6 | 265.0 | 45.5 |

**Table S3** The apparent diffusion coefficient of Py-COF/S and BP2000/S electrodes.

|  |  | $D_{\text{Li (Py-COF/S)}}$ ($10^{-7}$ $cm^2$ $s^{-1}$) | Slope (Py-COF/S) | $D_{\text{Li (BP2000/S)}}$ ($10^{-7}$ $cm^2$ $s^{-1}$) | Slope (BP2000/S) |
|---|---|---|---|---|---|
| Peak A | 0.1-0.4 mV $s^{-1}$ | 1.931 | 72.94086 | 1.573 | 65.81688 |
|  | 0.5-0.9 mV $s^{-1}$ | 2.690 | 86.07737 | 2.047 | 75.07775 |
| Peak B | 0.1-0.4 mV $s^{-1}$ | 2.884 | 89.12826 | 2.698 | 87.58002 |
|  | 0.5-0.9 mV $s^{-1}$ | 4.050 | 105.62036 | 2.698 | 92.74025 |
| Peak C | 0.1-0.9 mV $s^{-1}$ | 9.534 | 162.0558 | 5.995 | 128.49836 |

According to the linear relation between peak currents ($I_p$) and the root of scan rates ($v^{1/2}$), the apparent diffusion coefficients of $Li^+$ ions can be estimated using the classical Randles-Sevcik equation[1]:

$$I_p = (2.99 \times 10^5)\, n^{3/2}\beta^{1/2} a C_{Li} D_{Li}^{1/2} v^{1/2}$$

where $n$ is the number of electrons per molecule during the insertion ($Li^+$, $n$=1), $a$ is the surface area of the electrode ($cm^2$), $D_{Li}$ is the apparent diffusion coefficient of the

$Li^+$ in the electrode ($cm^2\ s^{-1}$), $C_{Li}$ is the initial concentration of the $Li^+$ on the electrode ($mol\ cm^{-3}$), and $\beta$ is symmetry factor (near 0.5)[2].

## References

1. A. J. Bard and L. R. Faulkner, Electrochemical methods-fundamentals and application, Wiley, 2nd edition, 2001, Page 231.
2. F.-S. Ke, L. Huang, L. Jamison, L.-J. Xue, G.-Z. Wei, J.-T. Li, X.-D. Zhou and S.-G. Sun, *Nano Energy*., 2013, **2**, 595.