Electronic supplementary information

3,5-Bis(trifluoromethyl)benzyl modified triazine-based covalent organic frameworks suppress the polysulfides shuttle for lithium–sulfur batteries

Chemicals:

1,3,5-tris-(4-amidophenyl) triazine (97%), and 2,5-Dihydroxy-1,4-benzenedicarboxaldehyde (97%) were obtained from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. Tetrahydrofuran (98%), mesitylene (98%), dioxane (98%), Triethylamine (98%), and 3,5-Bis(trifluoromethyl)benzoyl chloride (97%), N-methyl pyrrolidone (NMP, 99.5 %) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Polyvinylidene fluoride (PVDF), Carbon black, CNT, and Sulfur were obtained from Guangdong Canrd New Energy Technology Co., Ltd. All chemicals were used directly without purification.

Synthesis of TzDa:

TzDa was synthesized according to the literature. 1,3,5-tris-(4-amidophenyl) triazine (84.00 mg, 0.237 mmol), 2,5-Dihydroxy-1,4-benzenedicarboxaldehyde (60.00 mg, 0.361 mmol), 6M acetic acid (0.12 mL) and mesitylene/dioxane (3 mL, 1/1 in vol.) were added to a 10 mL ampoule tube. The tube was frozen at 77K, degassed by three freeze-pump-thaw cycles, sealed off, and then heated at 120 °C for 3 d. After cooling to room temperature, the product was washed with tetrahydrofuran and dried under vacuum at 80 °C for 24 h to afford red powder.

Synthesis of BTFMB-TzDa:

TzDa (400.0 mg), dry tetrahydrofuran (80.0 mL), and dry triethylamine (4.0 mL) were added into a 250 mL three-necked flask under Ar atmosphere. The mixture was stirred for 10 mins. Then 7.36 mL 3,5-Bis(trifluoromethyl)benzoyl chloride was added slowly to the flask. The resulted suspension was stirred at 60 °C for 24h. After filtration, the product was washed with tetrahydrofuran and methanol and dried under vacuum at 80 °C. BTFMB-TzDa was obtained as yellow solid. The yield is 87%.

Separator modification:

Slurry was prepared by mixing BTFMB-TzDa, carbon black, and polyvinylidene difluoride (PVDF) binder with a weight ratio of 6:3:1 in NMP. The modified separator were named BTFMB-TzDa modified separator. The separator had a diameter of 18 mm, and the mass loading of functional coating on each separator was 0.68 $mg{\cdot}cm^{-2}$.

Preparation of sulfur cathode:

Sublimed sulfur was mixed with CNT with a weight ratio of 7:3, and then heated at 155 °C for 12 h to prepare the S/C composites. The slurry containing 80 wt% S/C composites, 10 wt% Super P, and 10 wt% PVDF was coated on an aluminum foil, followed by drying under vacuum at 60 °C overnight. The cathode had a diameter of 12 mm, and the sulfur loading was about 1$mg{\cdot}cm^{-2}$.

Electrochemical measurements:

The sulfur cathode, the functional separator, and the lithium metal anode (d = 15.5 mm) were assembled into CR2032 coin batteries in a glove box filled with argon. Then, 15 µl electrolyte was added to the cell on each side, which was 1M LiTFSI in a mixture of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1, v/v) with 2 wt% LiNO3. The electrochemical performance was tested by a multichannel battery tester (Shenzhen Neware Technology Co., Ltd, China) at 25 °C. Electrochemical impedance spectroscopy (EIS) was measured in the frequency range of 1-100 kHz. Cyclic voltammetry (CV) measurements were run at 0.1 mV s^{-1} between 1.7 and 2.8 V by a CHI608D workstation.

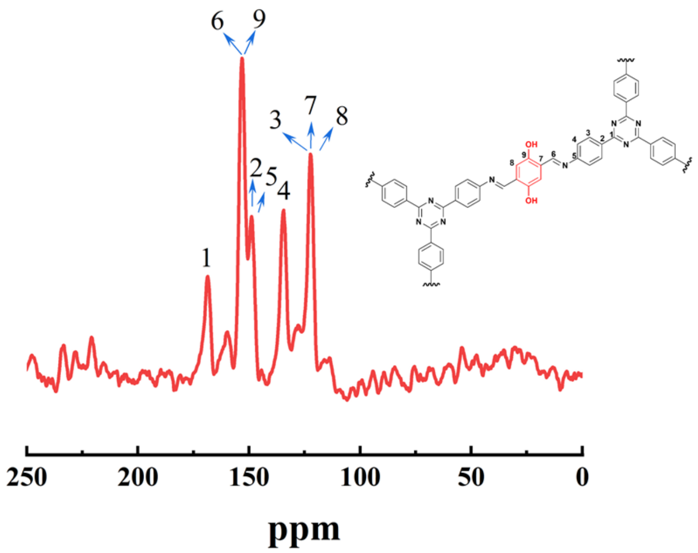

Fig. S1. Solid-state ^{13}C NMR spectrum of TzDa.

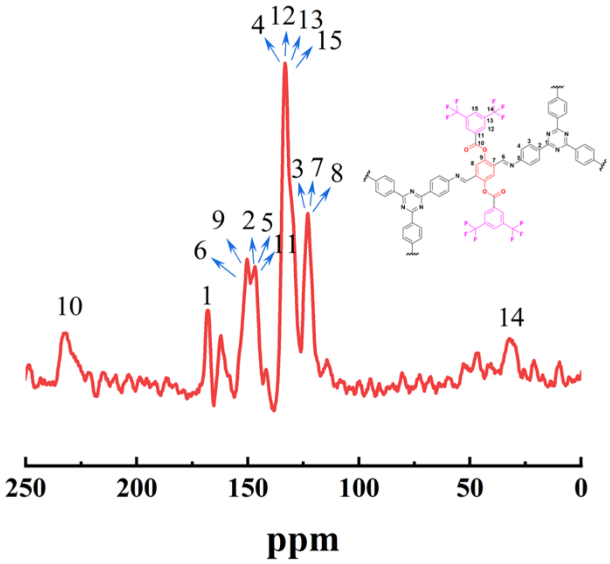

Fig. S2. Solid-state ^{13}C NMR spectrum of BTFMB-TzDa.

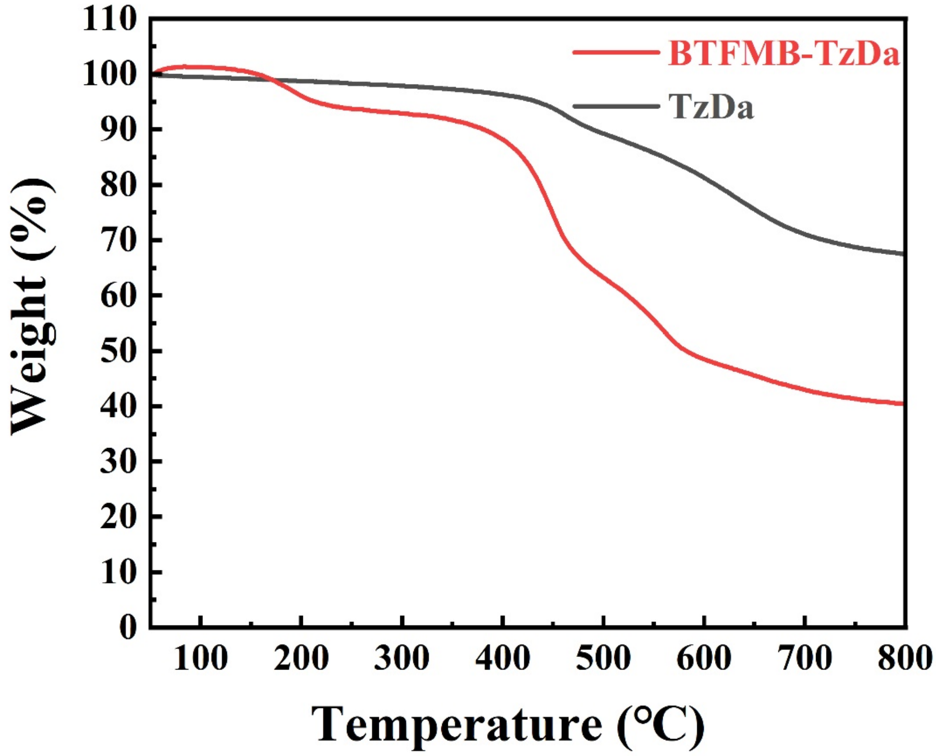

Fig. S3. Thermogravimetric curve of TzDa and BTFMB-TzDa.

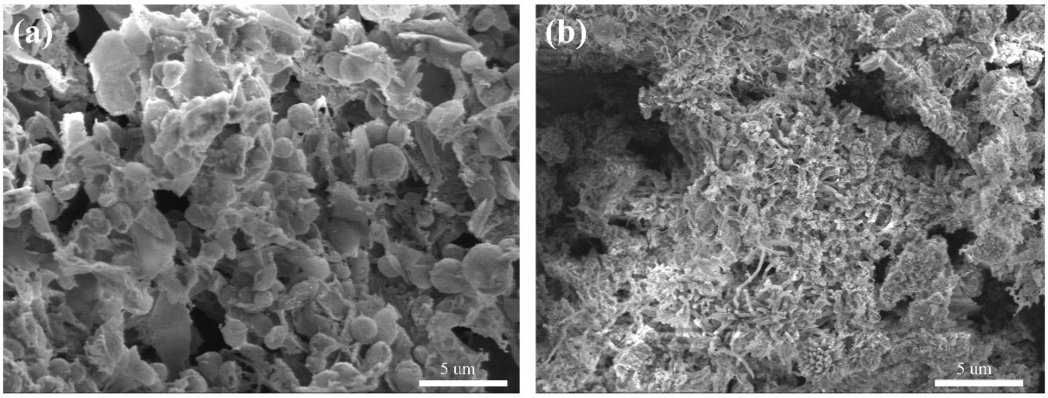

Fig. S4. SEM of (a) TzDa and (b) BTFMB-TzDa.

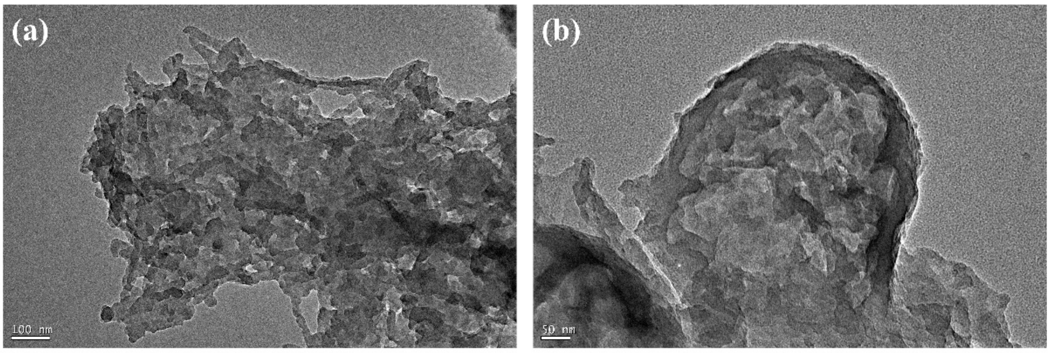

Fig. S5. TEM of (a) TzDa and (b) BTFMB-TzDa.

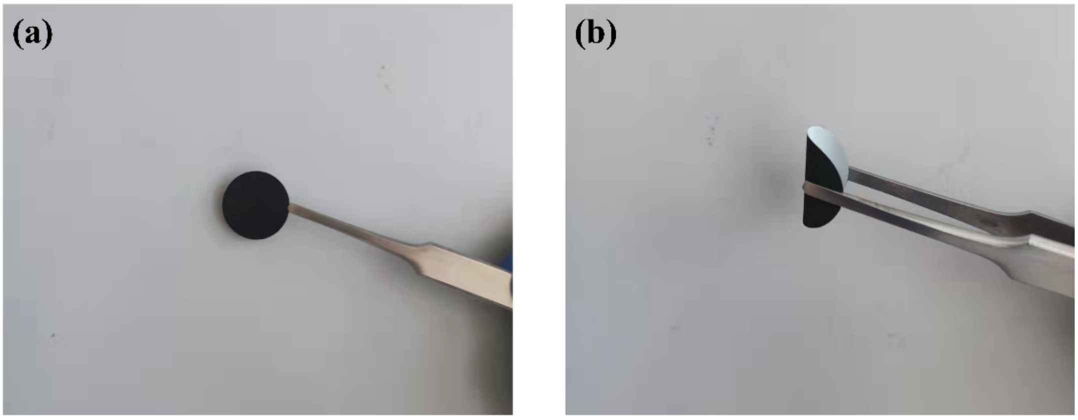

Fig. S6. Digital photographs and bending test of the BTFMB-TzDa separator.

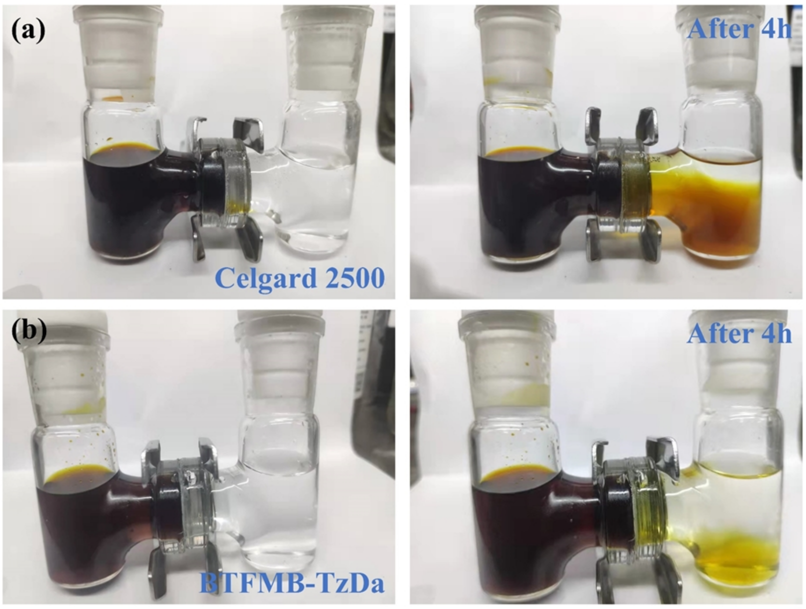

Fig. S7. Digital photographs of LiPSs permeation measurements with different modified separators: (a) Celgard 2500 and (b) BTFMB-TzDa modified separators.

(a) (b)

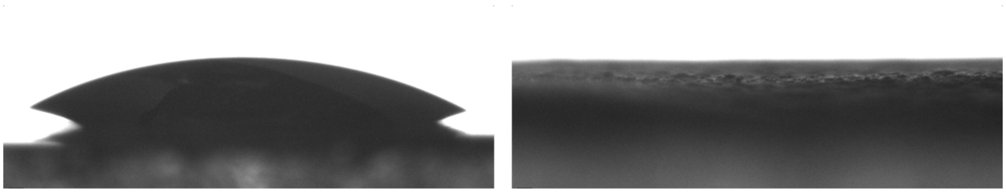

Fig. S8. Contact angles of electrolytes on the (a) Celgard 2500 and (b) BTFMB-TzDa separator.

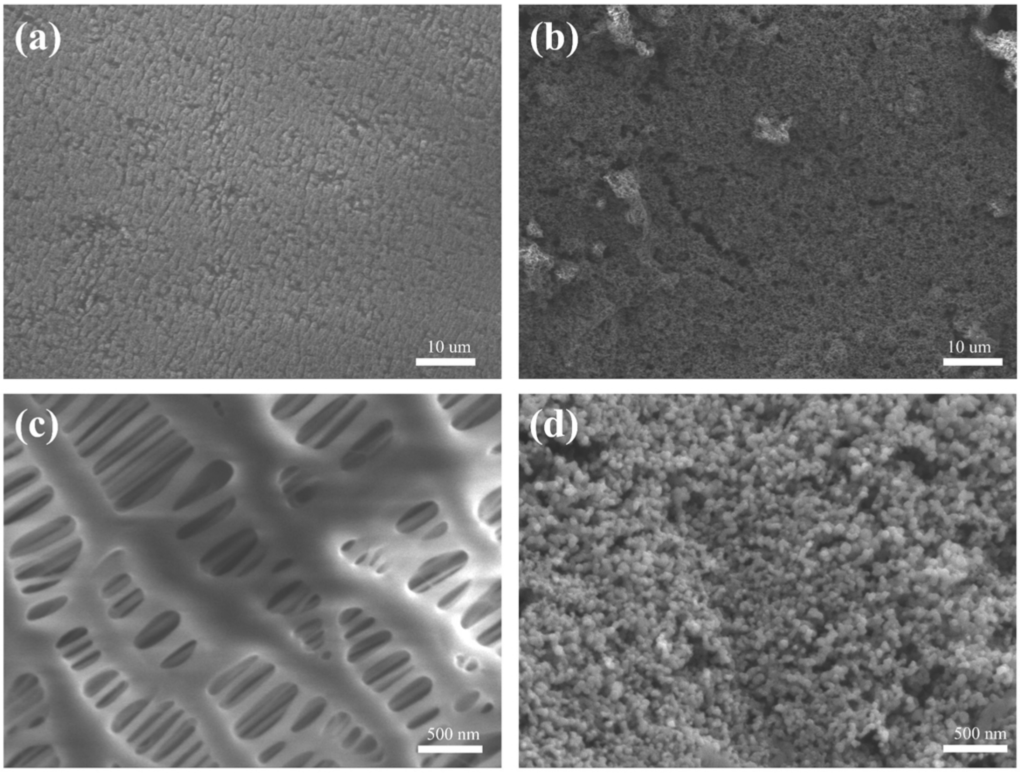

Fig. S9. SEM of (a)(c) Celgard 2500 and (b)(d) BTFMB-TzDa separator.

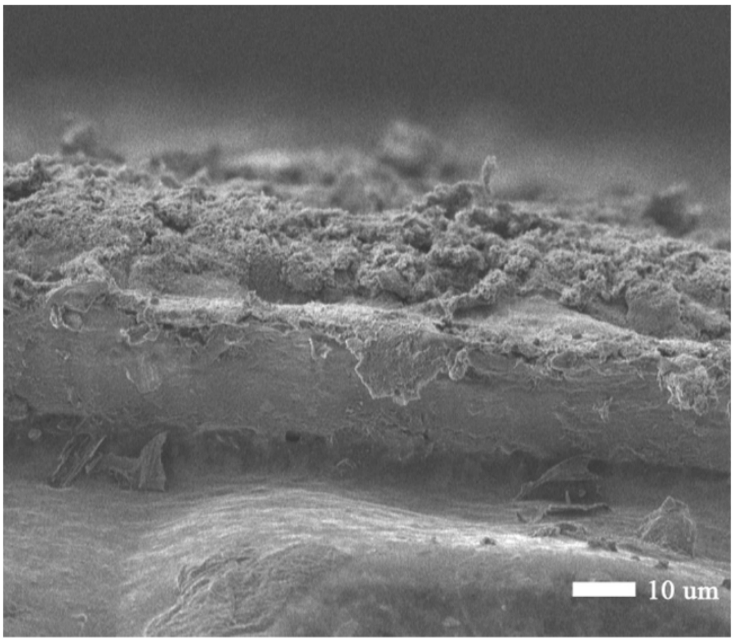

Fig. S10. SEM cross-sectional of BTFMB-TzDa separator.

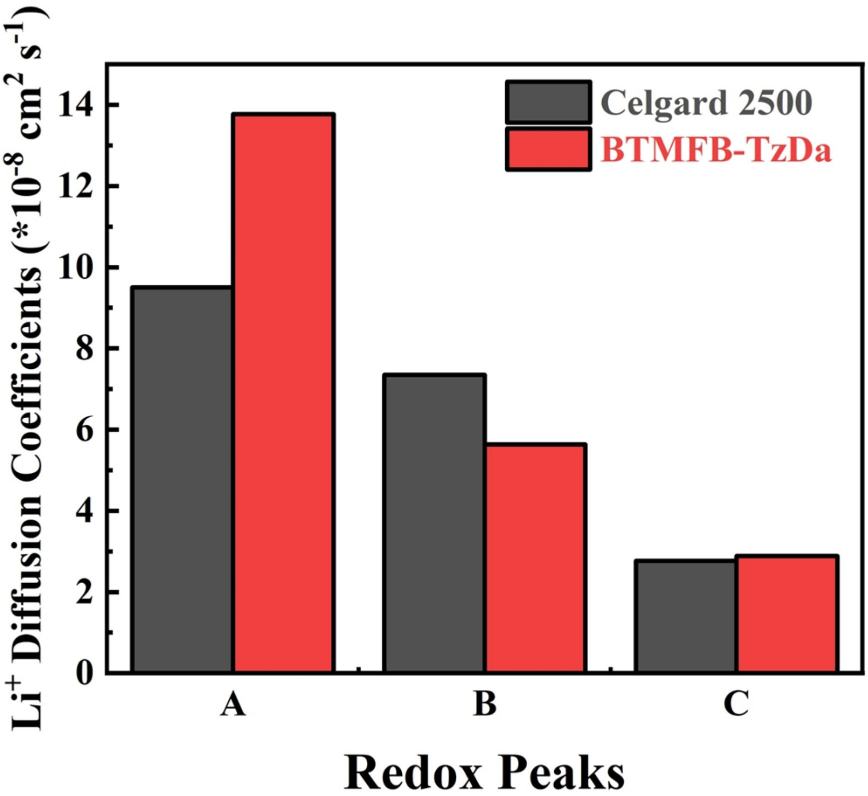

Fig. S11. Comparison of the Li^+ diffusion coefficients of the Celgard 2500 and BTMFB-TzDa.

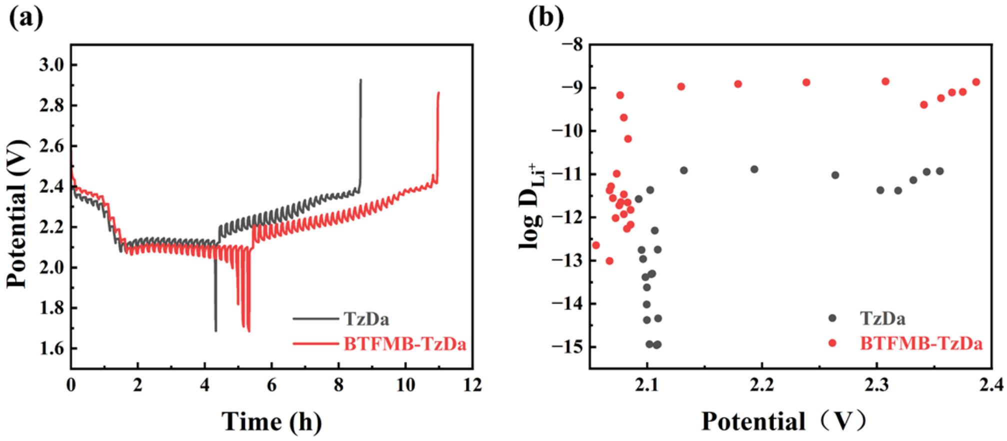

Fig. S12. (a) Galvanostatic intermittent titration (GITT) curves of different separators. (b) The Li^+ diffusion coefficients of TzDa and BTFMB-TzDa.

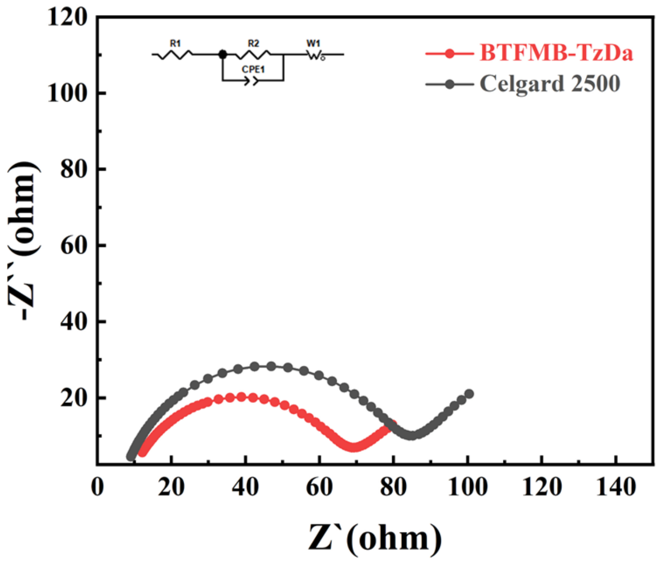

Fig. S13. EIS of the cells with Celgard 2500 and BTFMB-TzDa separator.

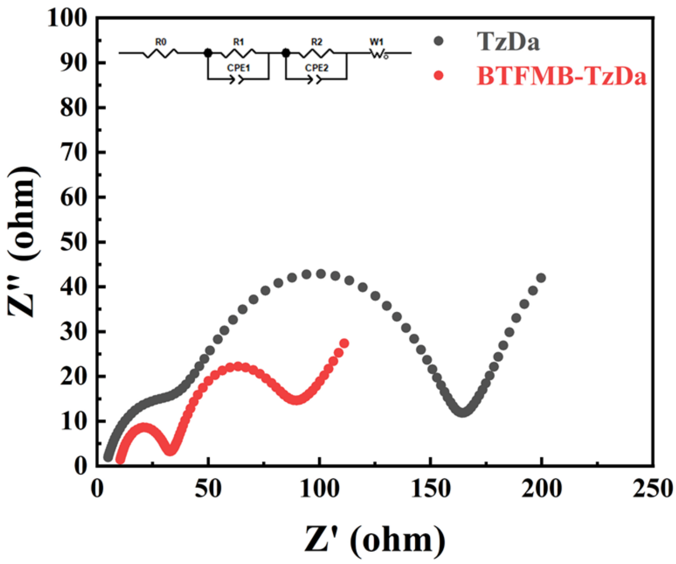

Fig. S14. EIS of the cells with Celgard 2500 and BTFMB-TzDa separator after 100 cycles.

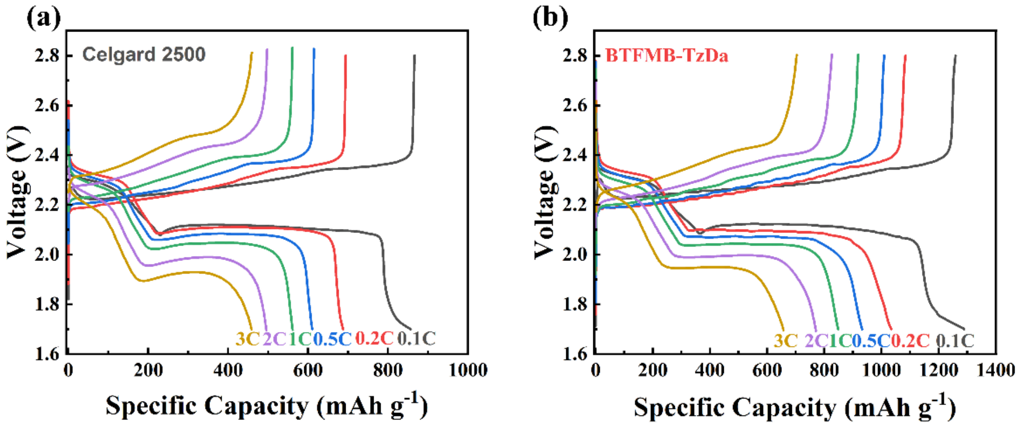

Fig. S15. Discharge–charge voltage profiles at different rate of (a) Celgard 2500 and (b) BTFMB-TzDa separator.

Table S1. Battery performance comparisons: COF modified separators for Li-S batteries.

Cathode	Sulfur content	Sulfur loading ($mg\cdot cm^{-2}$)	Capacity ($mAh\cdot g^{-1}$)	Ref.
S/CB	N/A	1.0~1.5	977 (0.2 C 100 cycles)	1
KB/S	60%	2.0	700 (1.0 C 800cycles)	2
SeS_2/CNT	60%	4.0	416 (1.0 C 800cycles)	3
S/CB	80%	1.5	534 (1.0 C 600cycles)	4
S/CNT	64%	1.3	534 (1.0 C 800cycles)	5
S/CB	80%	2.0	621 ($1A\cdot g^{-1}$ 500cycles)	6
CMK-3/S	56%	1-2	646 (1.0 C 600cycles)	7
CNT/S	76%	1.2	706 (2.0 C 2000cycles)	8
S/CB	52%	1.0	720 (0.5 C 120cycles)	9
S/CB	56%	1.0	905 (0.2 C 100cycles)	10
CNT/S	56%	5.4	638 (0.2 C 100cycles)	11
CNT/S	56%	1.0	1003 (0.2 C 100cycles)	This work
CNT/S	56%	1.0	501 (1.0 C 500cycles)	This work

References

1. Q. Xu, K. Zhang, J. Qian, Y. Guo, X. Song, H. Pan, D. Wang and X. Li, *ACS Appl. Energy Mater.*, 2019, **2**, 5793-5798.
2. Q. X. Shi, H. J. Pei, N. You, J. Wu, X. Xiang, Q. Xia, X. L. Xie, S. B. Jin and Y. S. Ye, *Chem. Eng. J.*, 2019, **375**, 121977.
3. Y. Yang, X.-J. Hong, C.-L. Song, G.-H. Li, Y.-X. Zheng, D.-D. Zhou, M. Zhang, Y.-P. Cai and H. Wang, *J. Mater. Chem. A*, 2019, **7**, 16323-16329.
4. J. Xu, S. Bi, W. Tang, Q. Kang, D. Niu, S. Hu, S. Zhao, L. Wang, Z. Xin and X. Zhang, *J. Mater. Chem. A*, 2019, **7**, 18100-18108.
5. J. Xu, F. Yu, J. Hua, W. Tang, C. Yang, S. Hu, S. Zhao, X. Zhang, Z. Xin and D. Niu, *Chem. Eng. J.*, 2020, **392**, 123694.
6. J. Wang, W. Qin, X. Zhu and Y. Teng, *Energy*, 2020, **199**, 117372.
7. Y. Cao, C. Liu, M. Wang, H. Yang, S. Liu, H. Wang, Z. Yang, F. Pan, Z. Jiang and J. Sun, *Energy Storage Mater.*, 2020, **29**, 207-215.
8. P. Li, H. Lv, Z. Li, X. Meng, Z. Lin, R. Wang and X. Li, *Adv. Mater.*, 2021, **33**, 2007803.
9. X. Deng, Y. Li, L. Li, S. Qiao, D. Lei, X. Shi and F. Zhang, *Nanotechnology*, 2021, **32**, 275708.
10. R. Wang, Q. Cai, Y. Zhu, Z. Mi, W. Weng, Y. Liu, J. Wan, J. Hu, C. Wang, D. Yang and J. Guo, *Chem. Mater.*, 2021, **33**, 3566-3574.
11. Y. Cao, H. Wu, G. Li, C. Liu, L. Cao, Y. Zhang, W. Bao, H. Wang, Y. Yao, S. Liu, F. Pan, Z. Jiang and J. Sun, *Nano Lett.*, 2021, **21**, 2997-3006.