Electronic Supplementary Material (ESI) for Chemical Communications. This journal is © The Royal Society of Chemistry 2022

Supporting Information

Keggin-type polyoxometalate-based crown ether complex for lithium-sulfur

batteries

Guang Yang,‡^a Yuchao Wu,‡^a Zengxiang Lv,^a Xinyuan Jiang,^a Jianhang Shi,^a Yuzhen Zhang,^c Ming Chen,^a Lubin Ni,*^a Guowang Diao*^a and Yongge Wei*^b

^aSchool of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, 225002, Jiangsu, People's Republic of China. E-mail: <u>lbni@yzu.edu.cn</u>

^bKey Lab of Organic Optoelectronics & Molecular Engineering of Ministry of Education, Department of Chemistry, Tsinghua University, Beijing 100084, PR China. E-mail: <u>yonggewei@tsinghua.edu.cn</u>

^cSchool of Chemistry and Chemical Engineering, Guangxi Minzu University, No. 158, Daxue West Road, Nanning, Guangxi 530006, China.

‡ These authors contributed equally.

Table of Contents

S1 Experimental Section	
-------------------------	--

S1 Experimental Section

S1.1 Materials and characterizations

Phosphotungstic acid H₃PW₁₂O₄₀ xH₂O was purchased from Shanghai Chemical Reagents Company (Shanghai, China). 18-crown-6 was purchased from Shanghai Aladdin Biochemical Technology (Shanghai, China). Lithium sulfide (Li₂S) was purchased from Sigma Aldrich (USA). Other chemicals and solvents were reagent grade and commercially available. Elemental analyses (C, H, N) were performed using an EA 1110 elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Bruker TENSOR27. The UV-Vis spectra were recorded on a Shimadzu UVmini-1280 spectrophotometer. Raman spectroscopy was conducted on a Renishaw inVia with a green Spectra Physics Argon laser with a wavelength of 524.5 nm and 50 mW capacity. Powder X-ray diffraction (PXRD) data were performed on a D8 advance super speed powder diffractometer (Bruker) with a graphite monochromator and Cu Ka radiation (0.1541 nm). Thermogravimetric Analysis (TGA) measurements were conducted on a Netzsch TG209 F3 between 25 and 800 °C with a heating rate of 10 °C min⁻¹. Scanning Electron Microscope (SEM) was performed on a Zess supra-55VP (Germany) instrument. The Xray photoelectron spectroscopy (XPS) experiment was performed on a Thermo Escalab 250 system using Al K α radiation (hv = 1486.6 eV) and the chamber pressure was kept below 2×10^{-9} Torr.

S1.2 Synthetic methods

Synthesis of Li₃Cl[(HPW₁₂O₄₀)(H₂₄C₁₂O₆)₃(CH₃CN)₂] {CR-PW₁₂}

720 mg (0.25 mmol) of Keggin-type $H_3PW_{12}O_{40}$ was dissolved in 150 mL of acetonitrile (CH₃CN), and this was then heated to 70 °C under stirring. After 30 min, 53 mg (1.25

mmol) of lithium chloride (LiCl) and 330 mg (1.25 mmol) of 18-crown-6 ($[C_2H_4O]_6$) were added in individual portions. The mixture was left to stir for 30 min, followed by cooling to room temperature and filtration. The slow evaporation of the solution afforded colorless block-like crystals. Yield: 0.833 g, 88.0 % based on W. FT-IR (cm⁻¹): 2879 (m), 1979 (w), 1656 (w), 1471 (vs), 1353 (vs), 1290 (w), 1251 (w), 1082 (vs), 981 (s), 899 (vs), 816 (vs), 592 (w), 509 (w). Raman(cm⁻¹): 2918 (s), 1475 (vs), 1007 (vs), 923 (w), 521 (s). Elemental analysis [found (calculated)]: C, 11.54 (12.61); H, 2.21 (2.06); N, 0.50 (0.73).

S1.3 Single-crystal X-ray diffraction

Data collections were performed at 298(2) K on a Bruker D8-quest CCD diffractometer using graphite-monochromated Mo K_{α} radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods (SHELXTL-2014/7) and refined by full-matrix-block least squares methods on F^2 . All calculations were performed using the SHELXTL-2014/7 program package.^[S1] Further details on the crystal structure data can be obtained from the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB21EZ, UK) via http://www.ccdc.cam.ac.uk (fax +44-1223-336-033; e-mail deposit@ccdc.cam.ac.uk), on quoting the depository number CCDC-2163843 for {CR-PW₁₂}.

S1.4 Lithium polysulfide (LiPSs) adsorption test

Lithium polysulfide solution (mainly Li_2S_4 , 0.04 M) was prepared by adding 184 mg of Li_2S (4.0 mmol) and 384 mg of sulfur (12 mmol) into 100 mL of DME solution with

vigorous stirring, according to previous literatures. ^[S2, S3] Diluted Li_2S_4 test solution was prepared by mixing 0.5 mL of 0.04 M Li_2S_4 in DME and 6.5 mL of DME. 100 mg of {**CR-PW**₁₂} materials were added to 7.0 mL of Li_2S_4 /DME solutions separately. The reaction mixture was stirred for an additional 2 hours. All experiments were done in an argon-filled glove box. All supernatants after treatment with various sulfur hosts were analyzed by UV-Vis spectroscopy.

S1.5 Computational methods

The conformational analyses of the molecular systems described in this study, including structural and orbital arrangements as well as property calculations, were carried out using the GAUSSIAN09 software packages.^[S4] Structural computations of **18-crown-6** and Li_2S_x (x= 2, 4, and 6) molecules were performed using the M062X ^[S5] density functional method with def2tzvp ^[S6] basis set for **18-crown-6**. The binding energy is calculated as E_b = $E_{\text{Li2Sx}} + E_{\text{CR}} - E_{\text{CR-Li2Sx}}$ where $E_{\text{CR-Li2Sx}}$ is the energy of the interaction system of Li_2S_x with POM; E_{Li2Sx} and E_{POM} are the energies of the free Li_2S_x and POM cluster, respectively.

S1.6 Cell assembly and electrochemical measurements

The **CR-6-PW**₁₂@**S** composite cathode was synthesized by mixing {**CR-PW**₁₂} and sublimed sulfur via ball mill method in a weight ratio of 3:7. For the fabrication of cathode slurry, 70 wt % of active substances (**CR-PW**₁₂@**S**), 20 wt % of Super P li (TIMCAL) and 10 wt % of binder poly(vinylidene fluoride) (PVDF, HSV900) were mixed by ball mill method and dispersed in N-methyl pyrrolidone (NMP) to form a slurry and then coated on carbon paper current collector (GDL 28 AA, SGL), cut into disks with diameter of 16 mm after drying at 60 °C for 12 h with a low sulfur mass loading of ~1.2 mg cm⁻² and a high sulfur mass loading of ~4.0 mg cm⁻². CR2032-type coin cells were assembled in an Arfilled glovebox with lithium metal as a counter electrode and Celgard 2500 microporous polypropylene (PP) separator. The liquid electrolyte was composed of 1.0 M lithium bis(trifluoromethylsulphonyl)imide (LiTFSI) and 1 wt% LiNO₃ in a mixed solvent with dimethoxymethane (DME) and 1,3-dioxolane (DOL) (1:1 by volume). The ratio of electrolyte to sulfur (E/S) in the battery is stringently controlled at 12 mL g⁻¹ for performance evaluation. Galvanostatic charge/discharge tests were carried out by Neware CT 4008 (5 V, 50 mA, Neware, China) with a voltage window of 2.8–1.7 V at room temperature. Electrochemical impedance spectra (EIS) and cyclic voltammetry (CV) were tested on an electrochemical workstation (1010 E, Gamry, America). CV curves were performed in the potential range of 1.7–2.8 V at a scan rate of 0.10 mV s⁻¹, and the EIS was measured at a frequency from 100 kHz to 10 mHz at open-circuit potential.

Compound	Li ₃ Cl[(HPW ₁₂ O ₄₀)(H ₂₄ C ₁₂ O ₆) ₃ (CH ₃ CN) ₂]
empirical formula	$C_{40}H_{79}ClLi_{3}N_{2}O_{58}PW_{12}$
formula weight (g·mol ⁻¹)	3809.48
temperature (K)	293(2)
wavelength (Å)	0.71073
crystal system, S. G.	Monoclinic, C2/m
a (Å)	25.536(3)
b (Å)	13.4053(14)
c (Å)	20.948(2)
a(deg)	90
β(deg)	140.504(2)
γ (deg)	90
volume (Å ³)	4560.8(8)
Z	2
Abs coefficient (mm ⁻¹)	15.205
d (calcd.) (Mg \cdot m $^{-3}$)	2.371
F(000)	3450
crystal size (mm ³)	0 18×0 100×0 08
goodness-of-fit on F ²	1.055
Reflections collected / unique	22224/5433
R(int)	0.0420
$R_1[I > 2\sigma(I)]$	0.0624
wR_2 indices $[I > 2\sigma(I)]$	0.1109

 Table S1. Crystal data and structure refinement for {CR-PW12}.

 $R_1 = \sum (F_o - F_c) / \sum F_o$ and $wR_2 = \{ \sum w (F_o^2 - F_c^2)^2 / \sum (F_o^2)^2 \}^{1/2}$

•	W(1)-O(3)	1.674(11)	O(14)-C(5)	1.454(18)
	W(1)-O(4)	1.860(7)	O(14)-C(6)	1.460(17)
	W(1)-O(4)#1	1.860(7)	O(15)-C(4)#1	1.421(14)
	W(1)-O(8)	1.907(7)	O(15)-C(4)	1.421(14)
	W(1)-O(8)#1	1.907(7)	O(16)-C(3)#1	1.419(18)
	W(1)-O(12)	2.465(11)	O(16)-C(3)	1.419(18)
	W(1)-O(12)#1	2.465(11)	O(17)-C(8)	1.448(16)
	W(2)-O(1)	1.676(7)	O(17)-C(9)	1.462(19)
	W(2)-O(8)	1.875(8)	O(18)-C(7)	1.421(18)
	W(2)-O(5)	1.881(7)	O(18)-C(7)#4	1.421(18)
	W(2)-O(6)#2	1.901(7)	C(1)-C(4)	1.434(19)
	W(2)-O(7)	1.903(8)	C(2)-C(5)	1.46(2)
	W(2)-O(11)#1	2.436(11)	C(3)-C(6)	1.43(2)
	W(3)-O(2)	1.676(7)	C(7)-C(8)	1.40(2)
	W(3)-O(6)	1.874(7)	C(9)-C(9)#5	1.42(3)
	W(3)-O(7)	1.878(8)	C(10)-N(1)	1.134(18)
	W(3)-O(9)	1.895(7)	C(10)-C(11)	1.507(18)
	W(3)-O(4)#3	1.923(8)	P(1)-O(12)#2	1.472(11)
	W(3)-O(11)#1	2.434(10)	P(1)-O(12)	1.472(11)
	W(4)-O(10)	1.686(9)	P(1)-O(11)	1.566(11)
	W(4)-O(9)	1.883(8)	P(1)-O(11)#2	1.566(11)
	W(4)-O(9)#1	1.883(8)	P(1)-O(11)#1	1.566(11)
	W(4)-O(5)#1	1.907(8)	P(1)-O(11)#3	1.566(11)
	W(4)-O(5)	1.908(8)	O(11)-O(12)#3	1.742(15)
	W(4)-O(11)#1	2.498(11)	O(11)-O(12)#1	1.773(15)
	W(4)-O(11)	2.498(11)	O(12)-O(12)#1	1.61(2)
	P(1)-O(12)#3	1.472(11)	O(13)-C(2)	1.409(16)
	P(1)-O(12)#1	1.472(11)	O(13)-C(1)	1.455(14)

Table S2. Selected bond lengths [A] for $\{CR-PW_{12}\}$.



Fig. S1 The structural characterization of $\{CR-PW_{12}\}$: (a) The comparison chart of theoretical and experimental values of X-ray powder diffraction (PXRD). (b, c) FT-IR and Raman spectra of 18-Crown-6, $\{CR-PW_{12}\}$, and $H_3P_{12}O_{40}$ $\{PW_{12}\}$. (d) The thermogravimetric analysis comparison chart of 18-Crown-6, $\{CR-PW_{12}\}$, and $\{PW_{12}\}$.

The FT-IR spectrum of {**CR-PW**₁₂} displays the characteristic W-O asymmetrical vibration peaks at 977 (s), 929 (s) and 790 (s) cm⁻¹ due to terminal v_{as} (W-O_t), cornersharing v_{as} (W-O_b) and edge-sharing v_{as} (W-O_c) of the {**PW**₁₂} cluster, respectively.^[S7] The vibration bands at around 2900-3000; 1470; 1356; and 1297 and 1246 cm⁻¹ can be assigned to v_{as} (CH₂) and v_{as} (CH₃, CH₃CN); δ (CH₂)/scissoring; ω (CH₂)/wagging; and τ (CH₂)/twisting of [Li(18-crown-6)Cl] and [Li(18-crown-6)](CH₃CN)⁺ supramolecular cations, respectively. The sharp peaks observed at about 1110 cm-1 correspond to v_{as} (C–O–C) of the 18-crown-6 ring.^[S7]

Thermogravimetric (TG) measurement of complex {**CR-PW**₁₂} exhibited one weight loss of about 21.5 % due to the decomposition of three 18-crown-6 and one acetonitrile molecules (21.9 % estimated, Fig. S1d). The decomposition of the supramolecular POM complex occurred between 385 and 800 °C (Fig. S1).



Fig. S2 (a) Powder X-ray powder diffraction patterns of $CR-PW_{12}@S$. (b) The thermogravimetric analysis curves of $CR-PW_{12}@S$ composite and $\{CR-PW_{12}\}$.



Fig. S3 (a) Optimized structures of $\{18$ -crown-6/Li₂S₆ $\}$ complex and (b) together with electrostatic potential map (ESPs). (c, d) Frontier molecular orbital diagrams (Color codes: red, oxygen; purple, lithium; white, hydrogen; yellow, sulfur; gray, carbon).



Fig. S4 (a, b) Cyclic voltammograms of bare Crown-6 and $\{CR-PW_{12}\}$ electrodes. (c, d) Initial four CV curves of $CR-PW_{12}$ and S cathode materials.

Sample	χ^2	$R_s(\Omega)$	$R_{surf}(\Omega)$	$R_{ct}(\Omega)$
Complex@ S	2.95E-04	7.06	21.38	12.37

Table S3. Equivalent circuit parameters for CR-PW₁₂@S electrode.



Fig. S5 (a) CV curves of the **CR-PW**₁₂**@S** and pure S cathodes in the ¹st cycle. (b) Nyquist plots at open circuit voltage (OCV). (c) PITT profiles. (d) Initial galvanostatic charge/discharge voltage curves. (e) Charge–discharge profiles.



Fig. S6 Morphology characterization of the CR-PW₁₂@S after cycling. (a, b) SEM and elemental mappings of CR-PW₁₂@S cathode over 100 cycles at 1.0 C



Fig. S7 Structural characterization of the CR-PW₁₂@S after cycling. (a) FT-IR spectra and (b) Powder X-ray powder diffraction patterns of CR-PW₁₂@S electrode before cycling and after 50 cycles at 1.0 C.

Material	Cyclic performance	Rate performance	Reference
K ₃ PW ₁₂ O ₄₀ /S	560.4 mAh/g after 250 cycles at 2 C	1270.3 mAh/g at 0.1 C 416.5 mAh/g at 5 C	S8
PVIMo-ZnPOM/C/S	1060 mAh/g after 120 cycles at 1 C	1450 mAh/g at 0.5 C 900 mAh/g at 5 C	S9
$\{Co_4W_{18}\}/rGO/S$	670 mAh/g after 1000 cycles at 2 C	1426 mAh/g at 0.05 C 644 mAh/g at 5 C	S10
AgPW ₁₁ /S	810 mAh/g after 300 cycles at 2 C	1580 mAh/g at 0.1 C 600 mAh/g at 5 C	S11
rGO-CNT/PW ₁₂ @S	530 mAh/g after 1000 cycles at 3 C	1425 mAh/g at 0.1 C 573 mAh/g at 5 C	S12
rGO@β-CDP@S	270 mAh/g after 1000 cycles at 3 C	1329 mAh/g at 0.1 C 387 mAh/gat 5 C	S13
GO-S-Amy	430 mAh/g after 100 cycles at 0.5 C	817 mAh/g at 0.125 C 596 mAh/g at 0.5 C	S14
S-PPy/G	${\sim}750$ mAh/g after 60 cycles at 160 mA/g	~833 mAh/g at 0.1 C 325 mAh/g at 1 C	S15
C ₆₀ -S	691 mAh/g after 350 cycles at 0.2 C	1286 mAh/g at 0.1 C 530 mAh/gat 2 C	S16
CR-PW ₁₂ @S	500 mAh/g after 300 cycles at 3 C	1437 mAh/g at 0.1 C 650 mAh/gat 5 C	This work

Table S4. Comparison of the electrochemical performance of Li-S batteries with other similar supramolecule or polyoxometalate-based cathode composites.

Reference

- 1. G. M. Sheldrick "SHELXTL Version 2014/7." Programs for the Determination of Small and Macromolecular Crystal Structures by Single Crystal X-ray and Neutron Diffraction" University of Göttingen Germany. URL http://shelx. uni-ac. gwdg. de/SHELX/index. php (2014).
- L. Ji, M. Rao, S. Aloni, L. Wang, E. J. Cairns and Y. Zhang, *Energy Environ. Sci.* 2011, 4, 5053–5059.
- Z. Yuan, H. J. Peng, T. Z. Hou, J. Q. Huang, C. Chen, D. W. Wang, X. B. Cheng, F. Wei and Q. Zhang, *Nano Lett.*, 2016, 16, 519–527.
- 4. Gaussian 09, Revision A.02, Frisch, M. J. et al. Gaussian, Inc., Wallingford CT, 2016.
- 5. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215–241.
- 6. Pritchard, P. Benjamin, Altarawy, Doaa, Didier, Brett, Gibsom, D. Tara, Windus and L. Theresa, *J. Chem. Inf. Model.* 2019, **59**, 4814–4820.
- J, Shi, H. Zhang, P. Wang, P. Wang, J. Zha, Y. Liu, J. Gautam, L. N. Zhang, Y. Wang, J. Xie, L. Ni, G. Diao and Y. Wei, *CrystEngComm*, 2021, 23, 8482–8489.
- 8. N. Yan, W. Zhang, J. Shi, Y. Liu and H. Cui, Mater. Lett., 2018, 229, 198-201.
- 9. V. Singh, A. K. Padhan, S. D. Adhikary, A. Tiwari, D. Mandal and T. C. Nagaiah, J. Mater. Chem. A, 2019, 7, 3018–3023.
- 10. J. Lei, X. X. Fan, T. Liu, P. Xu, Q. Hou, K. Li, R. M. Yuan, M. S. Zheng, Q. F. Dong and J. J. Chen, *Nat. Commun.*, 2022, **13**, 202.
- 11. J. C. Ye, J. J. Chen, R. M. Yuan, D. R. Deng, M. S. Zheng, L. Cronin and Q. F. Dong, *J. Am. Chem. Soc.*, 2018, **140**, 3134–3138.
- 12. L. B. Ni, G. Yang, Y. Liu, Z. Wu, Z. Y. Ma, C, Shen, Z. X. Lv, Q. Wang, X. X. Gong, J. Xie, G. W. Diao and Y. G. Wei, *ACS Nano*, 2021, **15**, 12222–12236.
- 13. L. B. Ni, G. Yang, Q. Wang, S. Q. Duan, C, Shen, J. Xie, G. S. Niu, H. Li, M. Chen and G. W. Diao, *Energy Storage Mater.*, 2019, **21**, 378–389.
- 14. W. D. Zhou, H. Chen, Y. C. Yu, D. L. Wang, Z. M. Cui, F. J. DiSalvo and H. D. Abruña, ACS Nano, 2013, 7, 8801–8808.
- 15. W. Wang, G. G. Li, Q. Wang, G. R. Li, S.H. Ye and X. P. Gao, J. Electrochem. Soc., 2013, 160, A805–A810.
- J. Xiang, W. Shen, Z. Guo, J. Meng, L. Yuan, Y. Zhang, Z. Cheng, Y. Shen, X. Lu and Y. Huang, Angew. Chem. Int. Ed., 2021, 60, 14313–14318.