

## **Phenylphosphonic acid as a grain-refinement additive for stable lithium metal anode**

Pinjuan Zou<sup>a</sup>, Jun Liu<sup>a</sup>, Zhenguo Huang<sup>\*b</sup>, Renzong Hu<sup>a</sup> and Liuzhang Ouyang<sup>\*ac</sup>

<sup>a</sup> School of Materials Science and Engineering and Key Laboratory of Advanced Energy Storage Materials of Guangdong Province, South China University of Technology, Guangzhou, 510641, People's Republic of China

E-mail: meouyang@scut.edu.cn

<sup>b</sup> School of Civil and Environmental Engineering, University of Technology Sydney, Sydney, NSW, 2007 (Australia)

E-mail: zhenguo.huang@uts.edu.au

<sup>c</sup> China-Australia Joint Laboratory for Energy & Environmental Materials and Key Laboratory of Fuel Cell Technology of Guangdong Province, Guangzhou 510641, People's Republic of China

## **Experiments**

### ***Electrochemical Measurements***

The electrolyte of 1 M LiPF<sub>6</sub> EC/EMC/DMC (1:1:1 by volume) was purchased from DodoChem. Phenylphosphonic acid (PPOA, 99.8%) and Li foil with a diameter of 16 mm and a thickness of 50 μm were purchased from Shanghai Macklin and China Energy Lithium Co., respectively. All the solvents were stored in a glovebox (H<sub>2</sub>O and O<sub>2</sub> content below 0.1 ppm). Li||Li symmetric cells were assembled in CR2032 coin cells using Celgard 2320 (20 μm) separators and 40 μL electrolyte with different amount of PPOA additives (0.25, 0.5, and 1 wt%) in an Ar-filled glovebox. The Li||Li symmetrical cells were tested at either 0.5 mA cm<sup>-2</sup> or 1 mA cm<sup>-2</sup> under a deposition capacity of 1

mAh cm<sup>-2</sup>. The CE was calculated in Li||Cu half cells using the reported procedures [1, 2]. Specifically, Q<sub>T</sub> represents the initial Li plating capacity (3 mAh cm<sup>-2</sup>) at a current density of 1 mA cm<sup>-2</sup>. Then, a fixed capacity (Q<sub>C</sub>=1 mAh cm<sup>-2</sup>) was stripped and plated repeatedly at 1 mA cm<sup>-2</sup> for n cycles. Finally, a capacity retention (Q<sub>R</sub>) was obtained by recharging to a cut-off voltage of 0.5 V. The CE value can be calculated according to the equation: CE = (nQ<sub>C</sub> + Q<sub>R</sub>) / (nQ<sub>C</sub> + Q<sub>T</sub>). EIS measurements of symmetrical cells were carried out in the frequency ranging from 10<sup>5</sup> to 10<sup>-2</sup> Hz. For Li/Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> (Li||LTO) full cells, the LTO electrodes were prepared as follows. A slurry of LTO, Super C, and polyvinylidene fluoride with a mass ratio of 80:10:10 was coated on Al foils, then dried in a vacuum oven at 80 °C for 8 h, and finally punched into sheets with a diameter of 13 mm. The loading mass of electrode is about 2.5 mg cm<sup>-2</sup>. The cells were tested galvanostatically in the voltage range of 1.0-2.5 V at various rates of 0.1, 0.5, 1, 2, 5, 10, 15, 20 C (1 C=175 mA g<sup>-1</sup>).

### ***Characterizations***

The morphologies of Li metal after being cycled in different electrolytes were characterized by SEM (Hitachi SU8010) at 10 kV. The morphology evolution was observed by an optical microscope (Belona, 100X-1000X digital microscope). The <sup>13</sup>C and <sup>7</sup>Li NMR spectra were collected on Bruker Avance NEO 600. The compositions of SEI were obtained by X-ray photoelectron spectroscopy (PHI X-tool), with the spectra calibrated/referenced to carbon. Fourier transform infrared (FTIR) spectra were collected on Thermo Scientific Nicolet iS5 using the attenuated total reflection (ATR) mode. Raman spectra were obtained on a Renishaw RM 1000 microscope using a 532

nm laser. Electrochemical impedance spectroscopy (EIS) analysis was conducted on CHI600E electrochemical workstation.

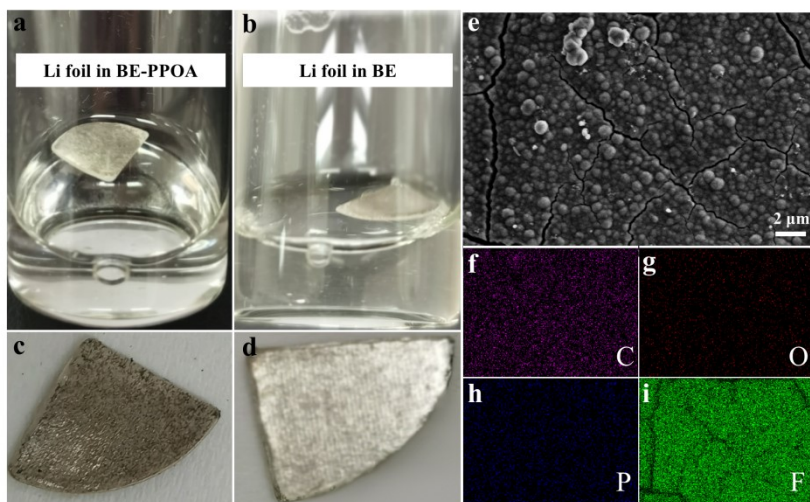


Fig. S1. Digital images of Li foil in BE-PPOA (a, c) and in BE (b, d). (e) SEM image and (f-i) elemental mappings of Li foil after immersing in PPOA-BE.

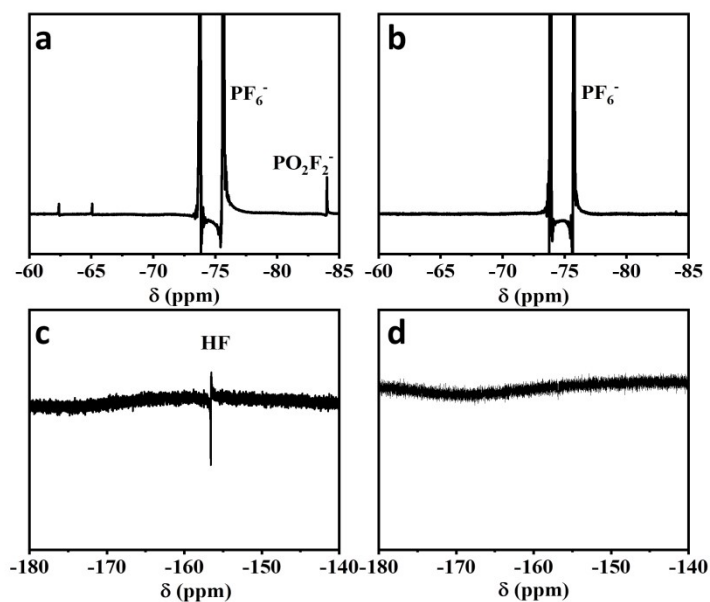


Fig. S2.  $^{19}\text{F}$  NMR spectra of (a, c) BE-PPOA and (b, d) BE

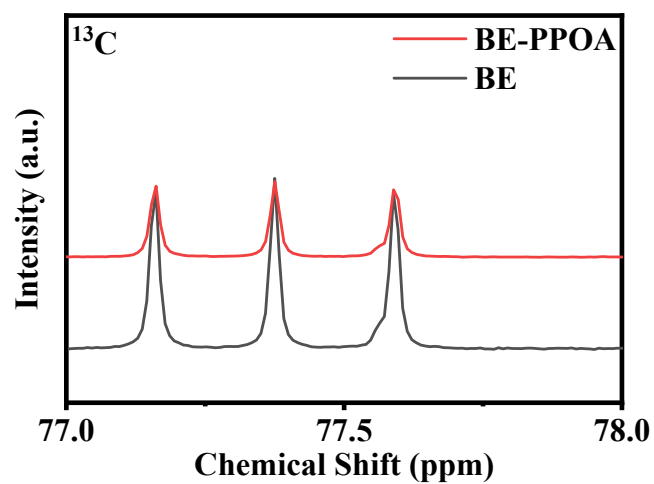


Fig. S3.  $^{13}\text{C}$  NMR spectra of  $\text{CDCl}_3$  in BE and BE-PPOA.

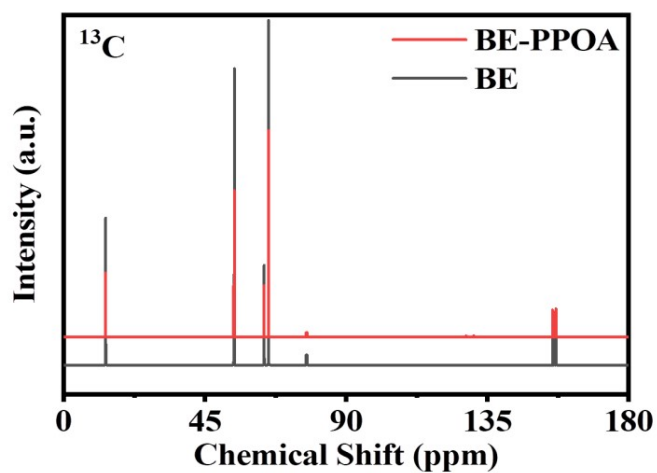


Fig. S4. Overall  $^{13}\text{C}$  NMR spectra of BE and BE-PPOA in  $\text{CDCl}_3$ .

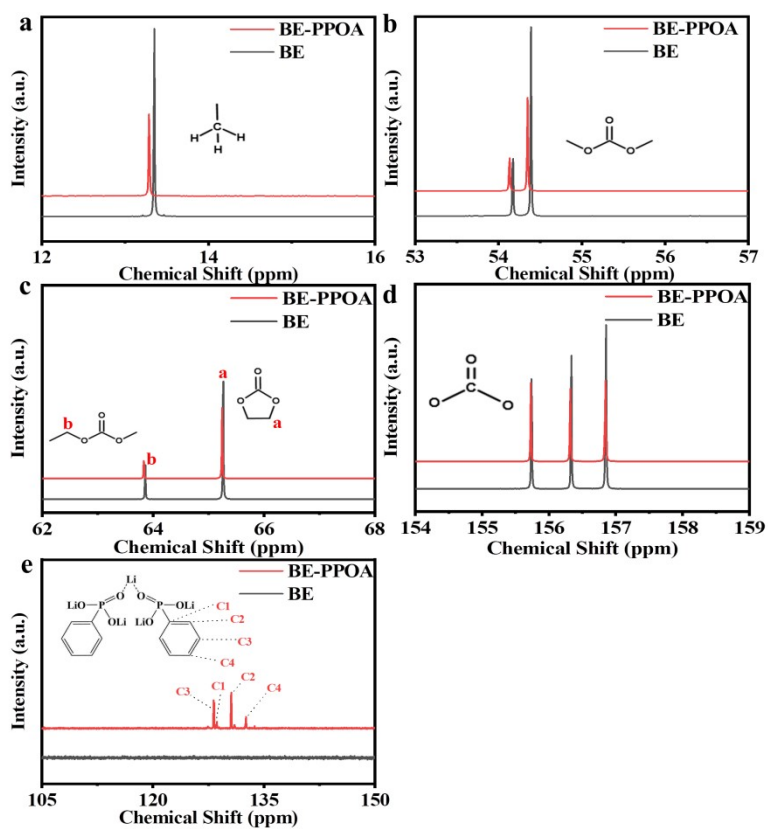


Fig. S5.  $^{13}\text{C}$  NMR resonance peak associated with different carbon in BE and BE-PPOA.

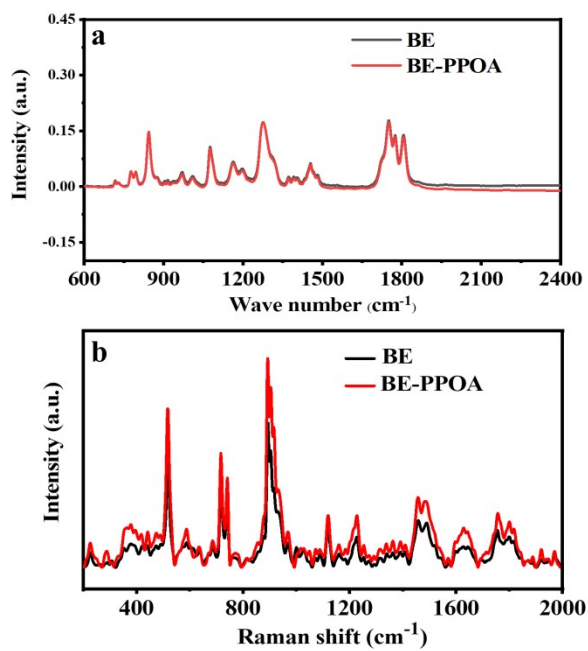


Fig. S6. (a) Fourier transform infrared (FTIR) spectra and (b) Raman spectra of BE and BE-PPOA.

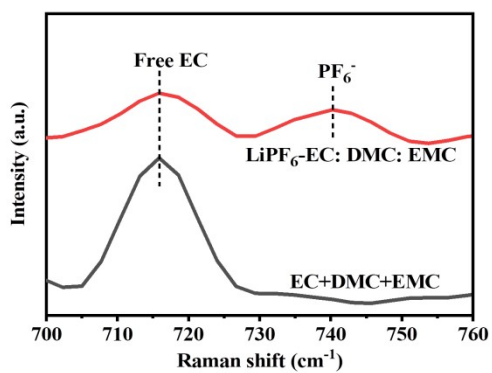


Fig. S7. Raman spectra of the mixed EC+DMC +EMC solvents and BE.

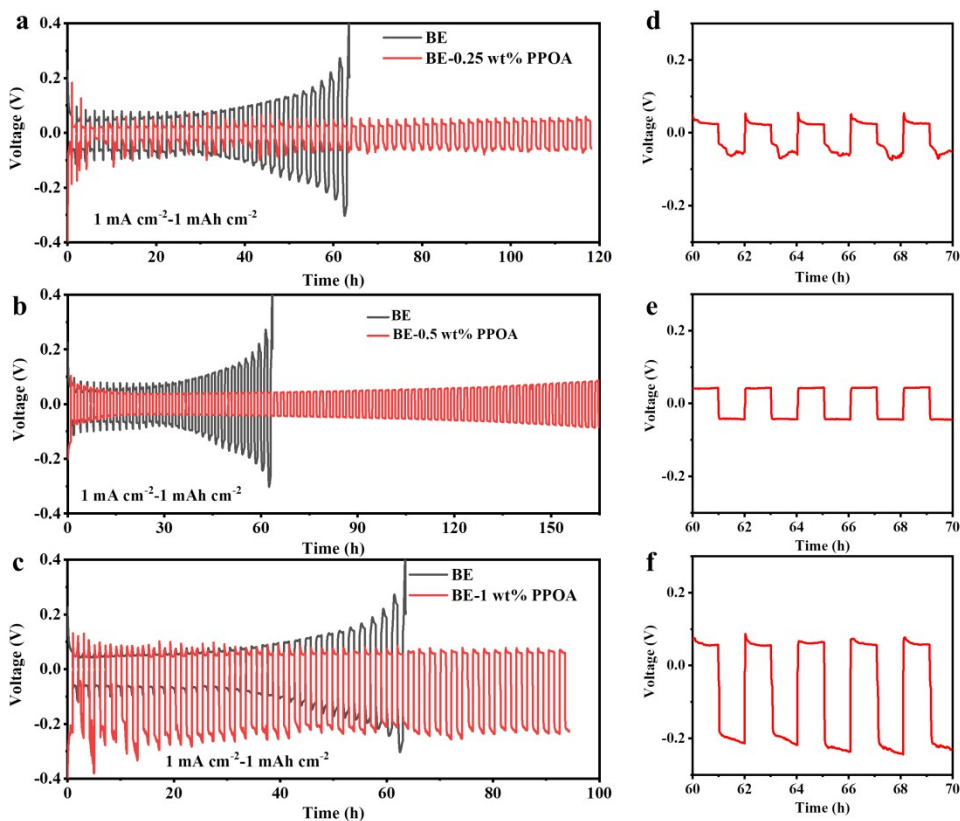


Fig. S8. Cycling stability of Li plating/stripping in BE-PPOA with different loading of PPOA at a current density of  $1 \text{ mA cm}^{-2}$  and a deposition amount of  $1 \text{ mAh cm}^{-2}$  and the enlarged views of 60<sup>th</sup> -70<sup>th</sup> hour of corresponding plating/stripping curves.

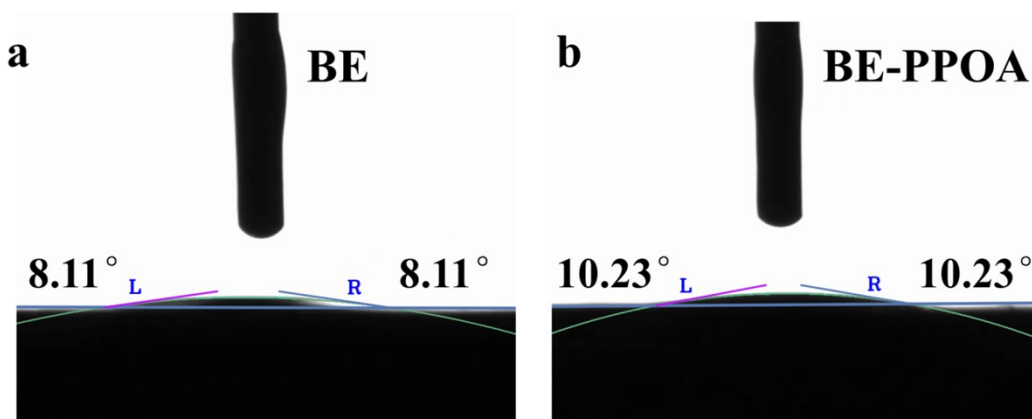


Fig. S9. Contact angles between (a) BE and (b) BE-PPOA (1 wt%) and bare Li foils.

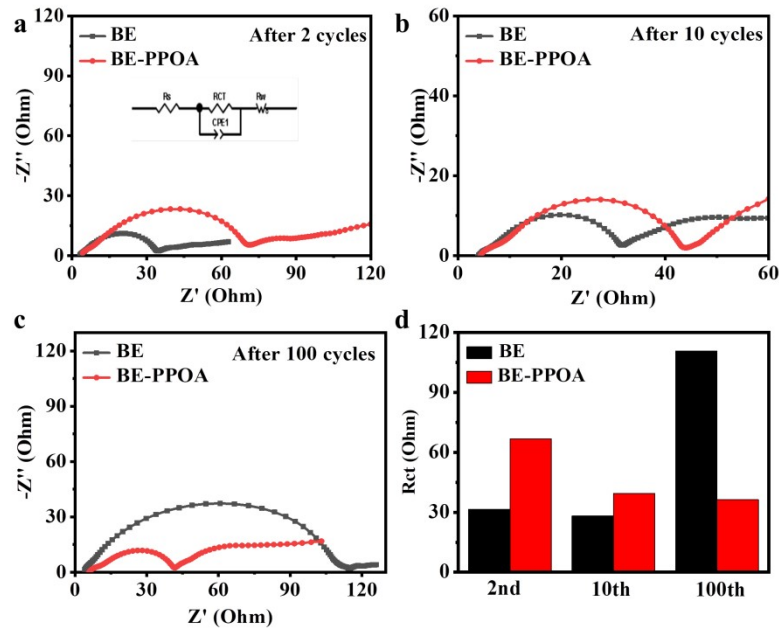


Fig. S10. EIS spectra of Li||Li symmetric cells after (a) 2, (b) 10 and (c) 100 cycles. (d) Comparison of  $R_{ct}$  after 2, 10 and 100 cycles in BE and BE-PPOA.

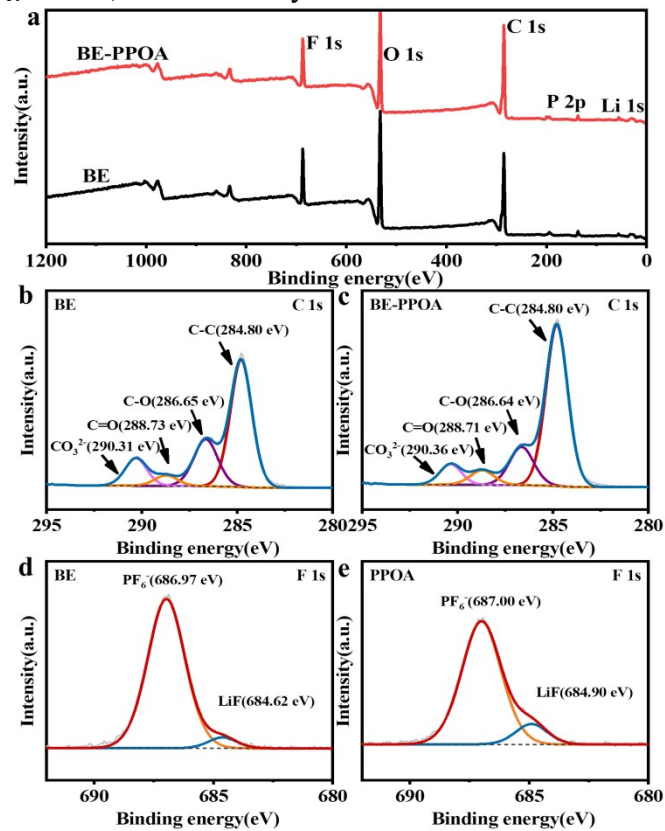


Fig. S11. (a) XPS survey spectra of the SEI films formed in different electrolytes after 20 cycles in Li||Li symmetric cells. High-resolution C 1s XPS spectra for films formed in (b) BE and (c) BE-PPOA. High-resolution F 1s XPS spectra for films formed in (d) BE and (e) BE-PPOA.



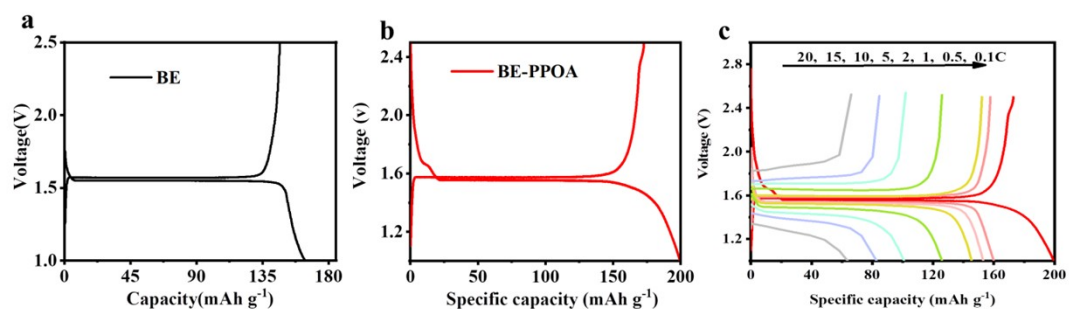


Fig. S12. The initial charge/discharge profiles of LTO||Li full cells in (a) BE and (b) BE-PPOA. (c) The charge/discharge profiles of LTO||Li full cells in BE-PPOA at different rates.

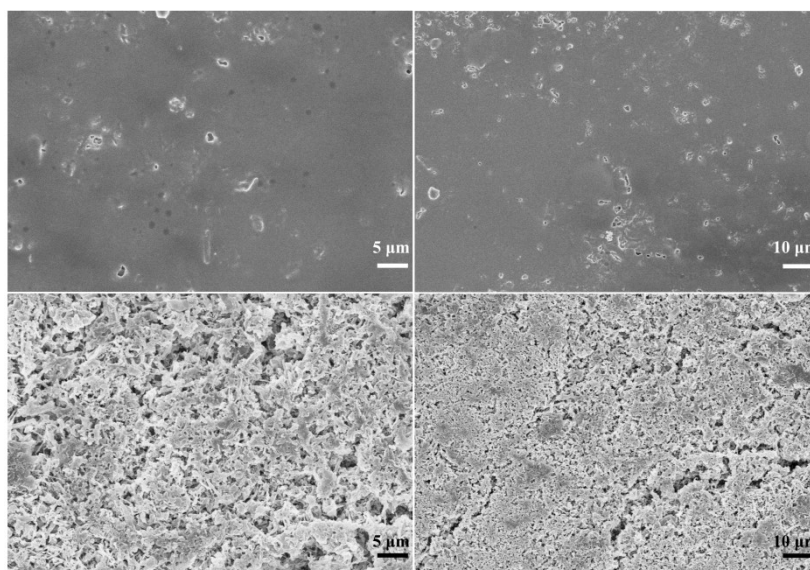


Fig. S13. The SEM images of Li metal anode in the LTO||Li cell after 100 cycles in (a, b) BE-PPOA and (c, d) BE.

## Notes and references

- [1] B. D. Adams, J. Zheng, X. Ren, W. Xu and J.-G. Zhang, *Advanced Energy Materials*, 2018, **8**, 1702097.
- [2] D. Liu, X. Xiong, Q. Liang, X. Wu and H. Fu, *Chemical Communications*, 2021, **57**, 9232-9235.