# *Supporting Information*

# Facile fabrication of hybrid polymer electrolyte via initiator-free thiol-ene photopolymerization for high-performance all-solid-state lithium metal batteries

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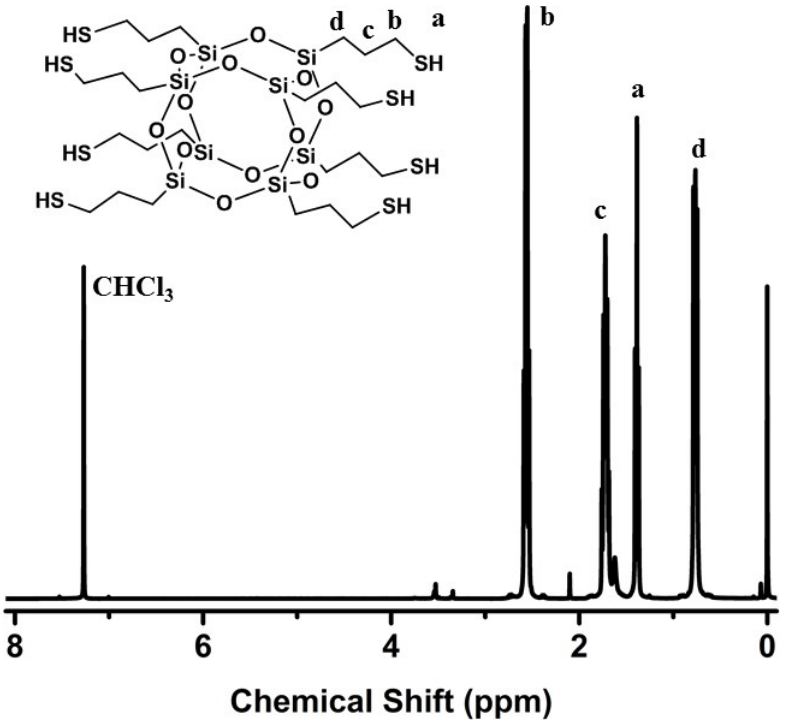


**Figure S1**. $^{1}H$ NMR spectrum of mercaptopropyl polyhedral oligometric silsesquioxane (solvent: $CDCl_3$).

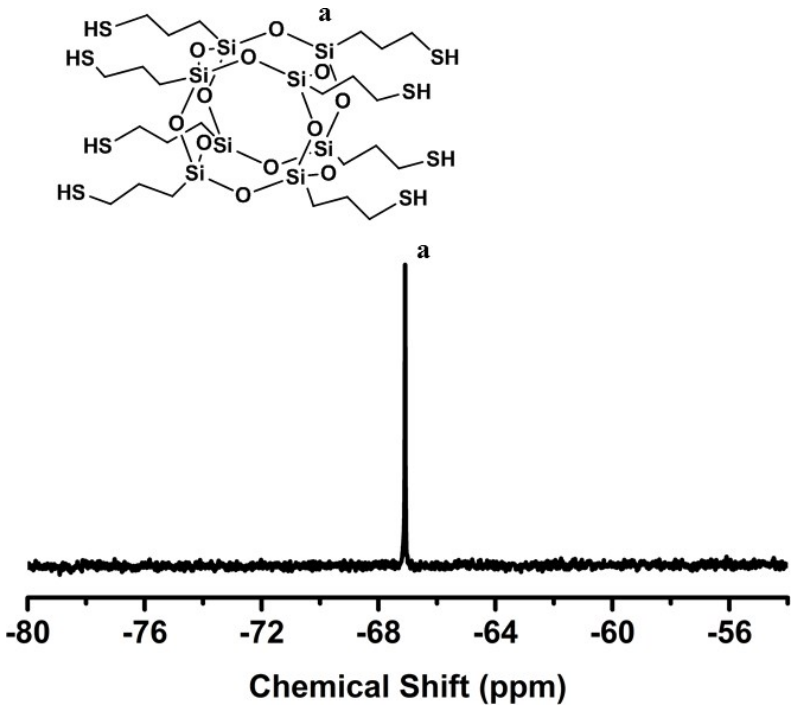


**Figure S2**. $^{29}Si$ NMR spectrum of mercaptopropyl polyhedral oligometric silsesquioxane (solvent: $CDCl_3$).

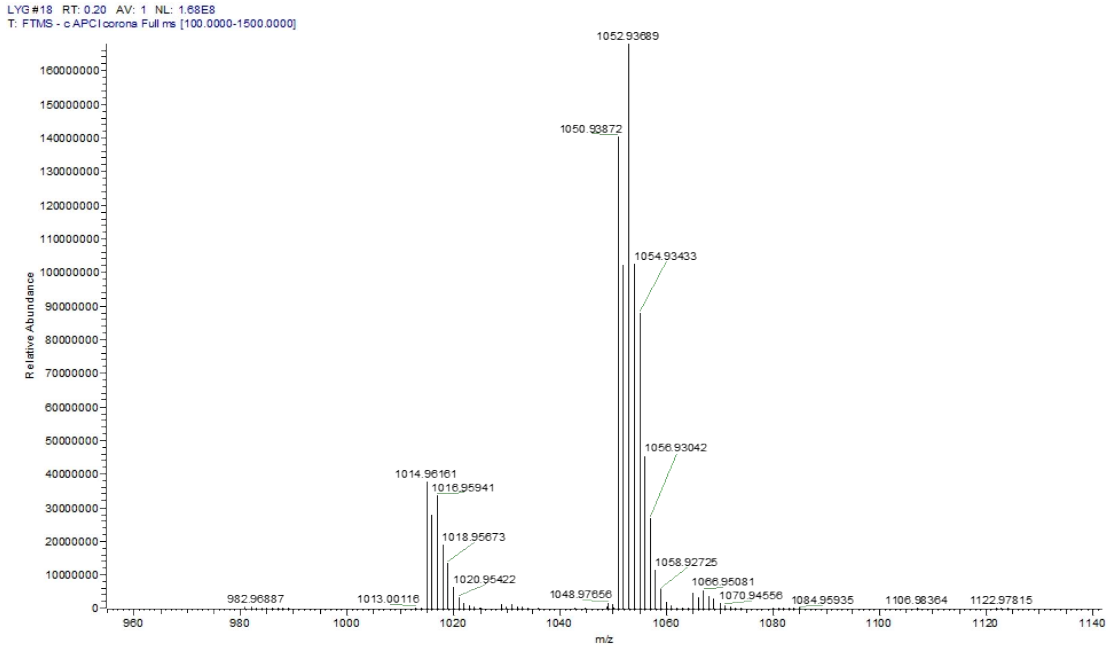


**Figure S3**. Mass spectrum of mercaptopropyl polyhedral oligometric silsesquioxane.

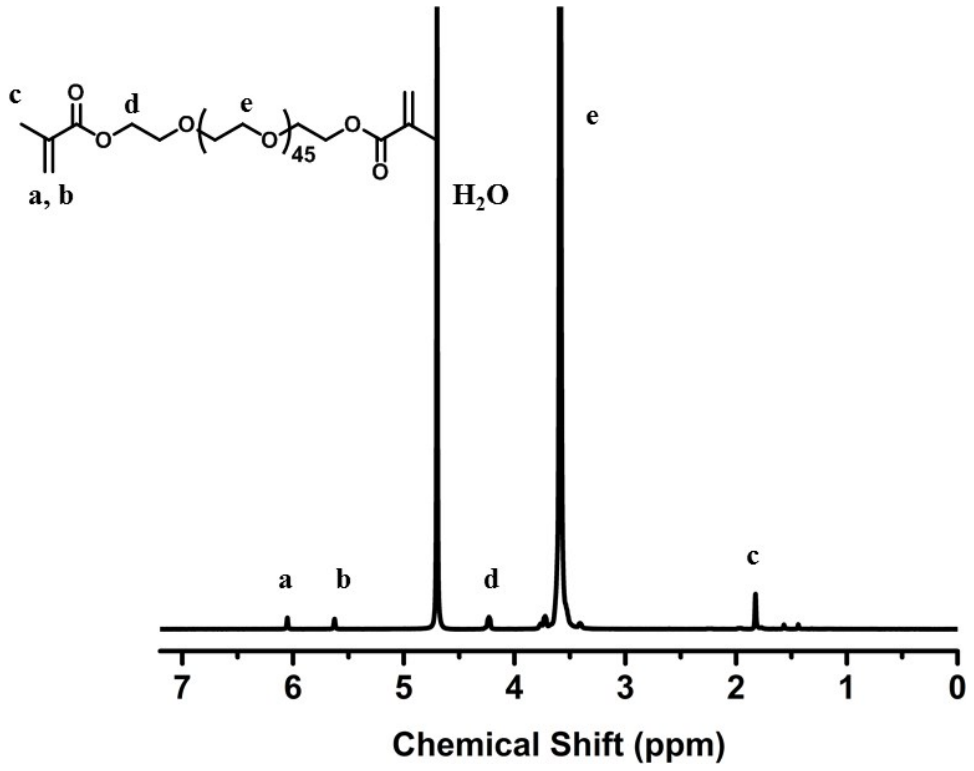


**Figure S4**. $^{1}H$ NMR spectrum of polyethylene glycol dimethacrylate Mn=2000 ($PEGDMA_{2000}$) (solvent: $D_2O$).

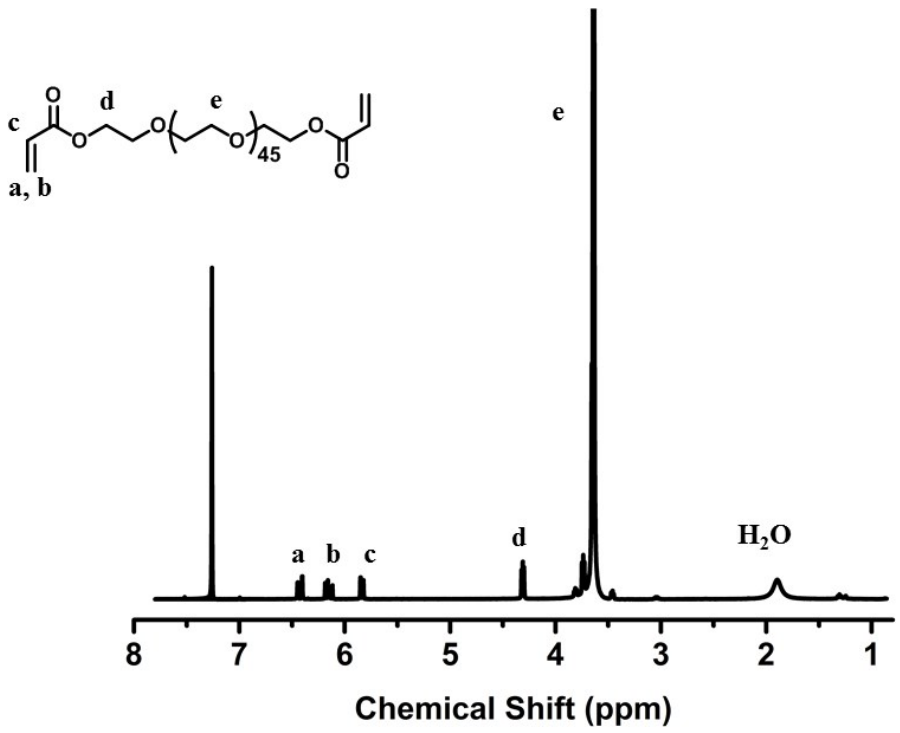


**Figure S5**. $^{1}$H NMR spectrum of polyethylene glycol dimethacrylate $M_n$=2000 ($PEGDA_{2000}$) (solvent: $CDCl_3$).

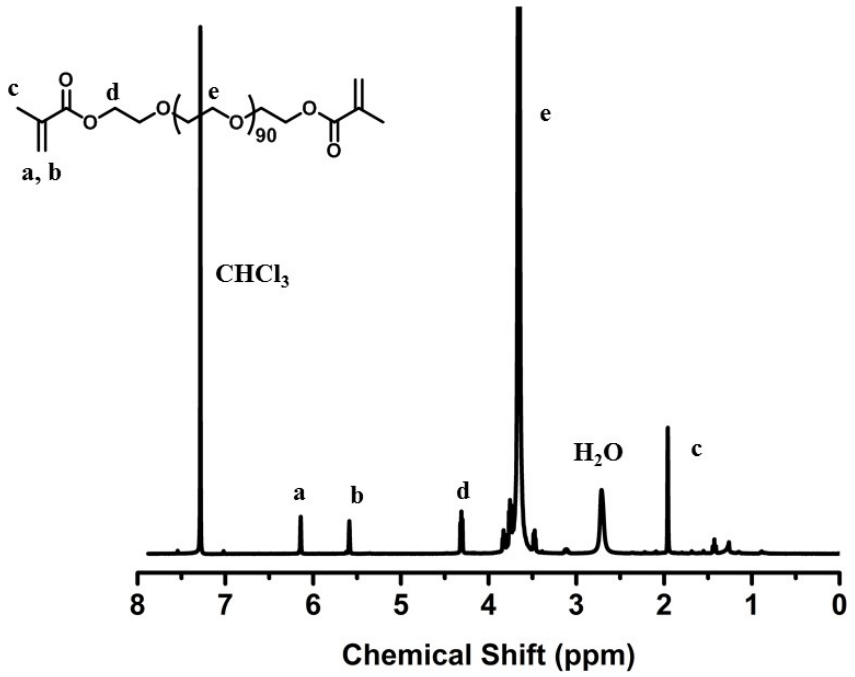


**Figure S6**. $^{1}$H NMR spectrum of polyethylene glycol dimethacrylate $M_n$=4000 ($PEGDMA_{4000}$) (solvent: $CDCl_3$).

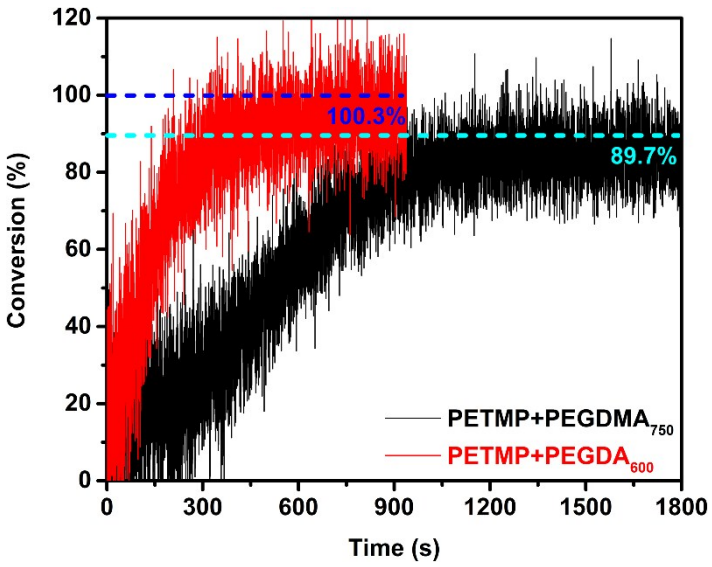


**Figure S7**. Kinetics of the initiator-free thiol-ene photopolymerization with different unsaturated bonds.

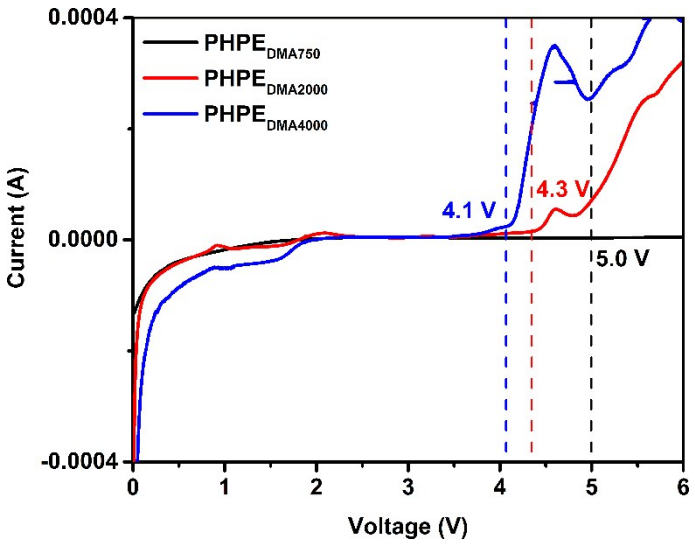


**Figure S8**. Linear sweep voltammetry (LSV) of $PHPE_{DMA750}$, $PHPE_{DMA2000}$, and $PHPE_{DMA4000}$ at 60 °C.

Table S1 VTF fitting parameters of PHPEs

| PHPEs[a] | molar ratio (EO : $Li^+$) | A | $E_a/R$ | $T_0$ |
|---|---|---|---|---|
| $PHPE_{DMA2000}$ | 12:1 | 0.00665±0.0006 | 123.7±14 | 265.9±4 |
| $PHPE_{DMA4000}$ | 12:1 | 0.0323±0.006 | 420.8±38 | 243.5±5 |
| $PHPE_{DA2000}$ | 12:1 | 0.00665±0.0006 | 1258.1±173 | 189.3±11 |
| $PHPE_{DMA750}$ | 12:1 | 0.4387±0.2 | 1061.7±508 | 197.7±37 |
| $PHPE_{DMA2000}$ | 16:1 | 0.0032±0.005 | 194.5±68 | 267.9±13 |
| $PHPE_{DMA2000}$ | 8:1 | 0.052±0.02 | 397.4±88 | 248.5±11 |