## Impact of Self-Assembled Structure on Ionic Conductivity of an Azobenzene-Containing Electrolyte

Shangming He,<sup>a</sup> Zhifan Fang,<sup>a</sup> Dong Liu,<sup>b</sup> Yun Liu,<sup>b</sup> Shichu Yang,<sup>b</sup> Hongfei Wang,<sup>b</sup> Zhihao Shen,<sup>b, \*</sup> Shuangjun Chen,<sup>a \*</sup> and Xing-He Fan<sup>b</sup>

<sup>a</sup> College of Materials Science & Engineering, Nanjing Tech University, Nanjing, 210009, China.

<sup>b</sup> Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, Center for Soft Matter Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing, 100871, China.



Figure S1. <sup>1</sup>H NMR (a), <sup>13</sup>C NMR (b), and MS (c) spectra of NbAzo.



**Figure S2**. TGA thermogram with the sample with N:P = 4:1 and  $r_{Li} = 0$ .



Figure S3. DSC thermograms of different samples with N:P = 3:1 (a), 4:1 (b), and 5:1 (c) at a scanning rate of 10  $^{\circ}$ C min<sup>-1</sup> during the first cooling (above) and second heating (below).



Figure S4. FT-IR spectra of the samples with N:P = 3:1 having different contents of the lithium salt in the range

of 1300 to 900  $cm^{-1}$  (a), 1500 to 1200  $cm^{-1}$  (b), and 1900 to 1400  $cm^{-1}$  (c).



Figure S5. FT-IR spectra of the samples with N:P = 5:1 having different contents of the lithium salt in the range of 1300 to 900 cm<sup>-1</sup> (a), 1500 to 1200 cm<sup>-1</sup> (b), and 1900 to 1400 cm<sup>-1</sup> (c).



Figure S6. FT-IR spectra of NbAzo and electrolyte samples with N:P = 3:1, 4:1, and 5:1 in the range of 3200 to

 $2400 \text{ cm}^{-1}$ .



Figure S7. EIS Nyquist curves of samples with N:P = 3:1 and  $r_{Li} = 0.05-0.10$  (a) and 0.125-0.30 (b).



Figure S8. EIS Nyquist curves of samples with N:P = 4:1 and  $r_{Li} = 0.05-0.15$  (a) and 0.20-0.35 (b).



Figure 89. EIS Nyquist curves of the sample with N:P = 5:1 and  $r_{Li} = 0.05-0.10$  (a), 0.125-0.20 (b), and

0.25–0.35 (c).