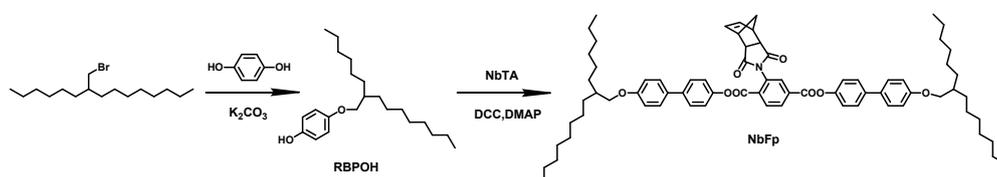


S1. The above NbTA (1.00 eq, 1.64 g, 5.00 mmol), poly(ethylene glycol) methyl ether (PEO, $M_n = 400$ g/mol, 2.20 eq, 4.40 g, 11.0 mmol), 4-dimethylaminopyridine (DMAP, 0.200 eq, 0.120 g, 1.00 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC.HCl, 2.20 eq, 2.10 g, 11.0 mmol), and 40 mL of CH_2Cl_2 were charged into a flask with a stir bar. The mixture was stirred at ambient temperature for 36 h. After the solvent was evaporated by a rotary evaporator, the remaining solution was washed with 20 mL \times 3 of 1 M HCl and 20 mL \times 3 of brine. The mixture was dried with sodium sulfate, and the solvent was evaporated. The crude product was purified by silica gel column chromatography with CH_2Cl_2 /ethanol (v/v = 20/1). Yield: 68%. The chemical structure of NbPEO was confirmed by ^1H NMR (Figure S1).

Synthesis of RBPOH. RBPOH was synthesized following the route shown in Scheme S2. 4,4'-Dihydroxybiphenyl (1.20 eq, 4.08 g, 24.0 mmol), 1-bromo-2-hexyldecane (1.00 eq, 6.10 g, 20.0 mmol), K_2CO_3 (1.20 eq, 3.30 g, 24.0 mmol), and 50 mL of *N,N*-dimethylformamide (DMF) were charged into a flask with a stir bar. The mixture was stirred at 90 °C for 12 h. The floating solid was filtered off, and the solvent was evaporated. The crude product was purified by silica gel column chromatography with CH_2Cl_2 and the product was obtained as a white powder. Yield: 52%. ^1H NMR (400 MHz, DMSO, δ , ppm): 9.43 (s, 1H), 7.44–7.48 (d, 2H), 7.38–7.42 (d, 2H), 6.92–6.97 (d, 2H), 6.78–6.83 (d, 2H), 3.83–3.87 (d, 2H), 1.69–1.77 (m, 1H), 1.18–1.46 (m, 24H), 0.82–0.88 (t, 6H).



Scheme S2. Synthesis of NbFp

Synthesis of NbFp. NbFp was synthesized with the procedure shown in Scheme S2. RBPOH (2.00 eq, 4.10 g, 10.0 mmol), NbTA (1.00 eq, 1.64 g, 5.00 mmol),

N,N'-dicyclohexylcarbodiimide (DCC, 2.00 eq, 2.06 g, 10.0 mmol), DMAP (0.200 eq, 0.120 g, 1.00 mmol), and 50.0 mL of CH₂Cl₂ were charged into a flask with a stir bar. The mixture was stirred at ambient temperature for 36 h. The floating solid was filtered off, and the solvent was evaporated. The crude product was purified by silica gel column chromatography with CH₂Cl₂/petroleum ether (v/v = 1/1), and the product was obtained as a white powder. Yield: 76%. The chemical structure of NbFp was confirmed by ¹H NMR (Figure S2).

Synthesis of the BCPs. The synthesis of PNbFp₃₁-*b*-PNbPEO₃₇ is described below as an example. Grubbs' third-generation catalyst (1 equiv, 11.8 mg, 0.0133 mmol) was added into a dry flask. After three pump-purge cycles using high-purity nitrogen, a solution of NbFp (50 equiv, 740 mg, 0.665 mmol) in 2 mL of CH₂Cl₂ was injected into the flask and the polymerization reaction was initiated. After the mixture was stirred at ambient temperature for 30 min, trace samples were taken out to conduct GPC characterization, and then a solution of NbPEO (60 equiv, 847 mg, 0.800 mmol) in 2 mL of CH₂Cl₂ was injected into the flask at once. The polymerization was quenched in 2 hours, and the solution was passed through a neutral alumina column to remove the catalyst, and then it was precipitated in 200 mL of petroleum ether to obtain the target polymer as a white solid. Yield: 80%.

2. Results

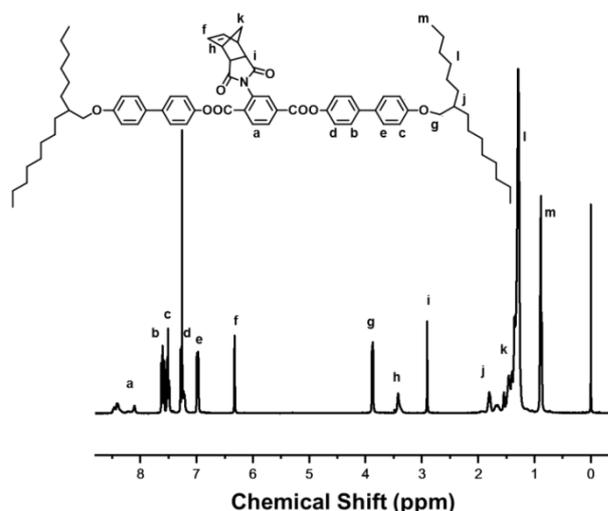


Figure S1. ^1H NMR spectrum of NbPEO in CDCl_3 .

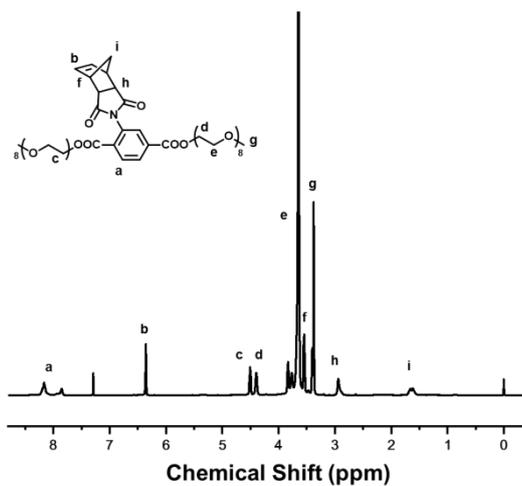


Figure S2. ^1H NMR spectrum of NbFp in CDCl_3 .

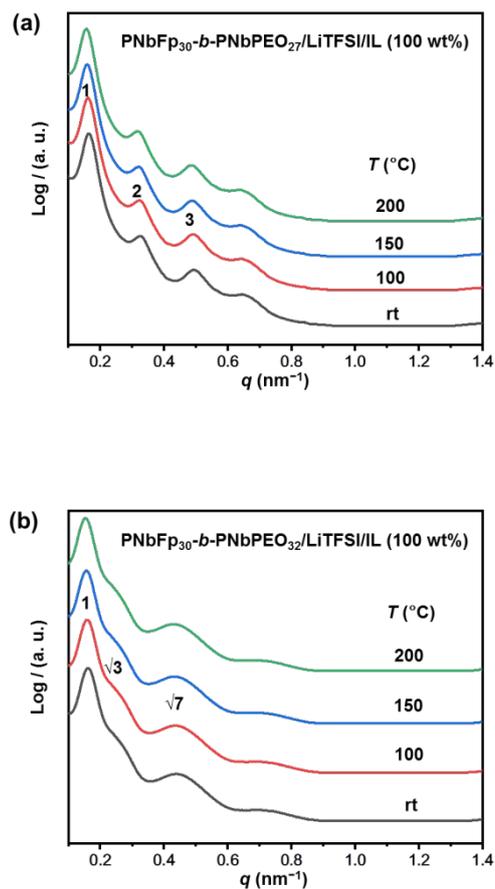


Figure S3. SAXS profiles of $\text{PNbFp}_{30}\text{-}b\text{-PNbPEO}_{27}/\text{LiTFSI}/\text{IL}$ (a) and

PNbFp₃₀-*b*-PNbPEO₃₂/LiTFSI/IL (b) complexes with 100 wt% of IL at different temperatures.

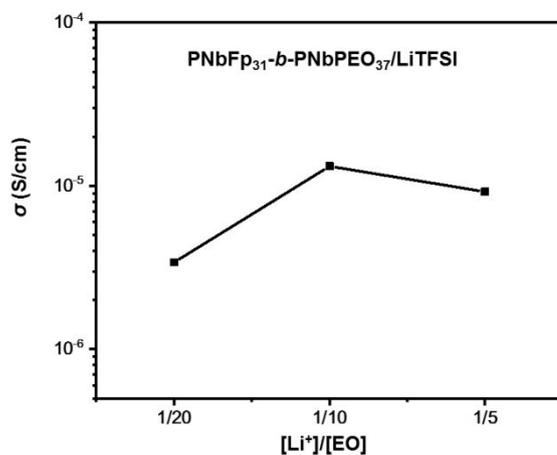


Figure S4. σ values of the PNbFp₃₁-*b*-PNbPEO₃₇/LiTFSI complexes with respect to $[Li^+]/[EO]$ ratio at ambient temperature.

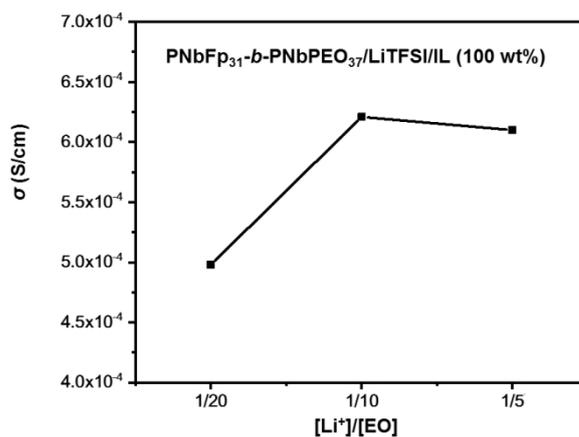


Figure S5. σ values of the PNbFp₃₁-*b*-PNbPEO₃₇/LiTFSI/IL complexes with 100 wt% of IL with respect to $[Li^+]/[EO]$ ratio at ambient temperature.

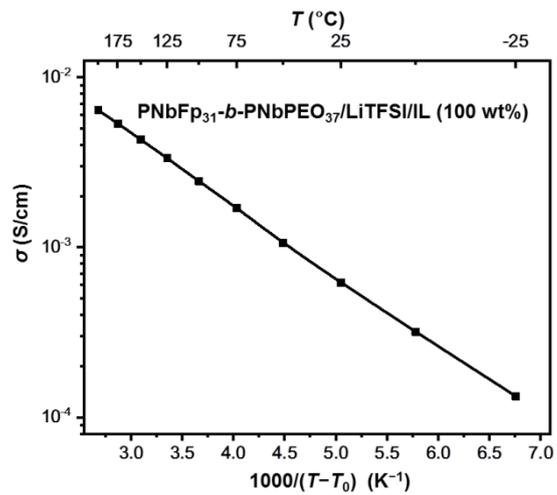


Figure S6. VTF fitting of the σ values of the PNbFp₃₁-*b*-PNbPEO₃₇/LiTFSI/IL complex with 100 wt% of IL.