Synthesis of tetrabutylphosphonium N-trifluoromethanesulfonyleucine ([P4444][Tf-Leu])

[P4444][Tf-Leu] was synthesized and purified using the procedure reported previously.\(^1\) N-trifluoromethanesulfonyleucine methyl ester was synthesized by a reaction of trifluoromethanesulfonic anhydride with leucine methyl ester. The leucine methyl ester was suspended in dry dichloromethane, and bimolar triethylamine was then added under gentle stirring. A solution of trifluoromethanesulfonic anhydride was added to the mixture under dry N\(_2\) atmosphere at -78 °C. The resulting product was extracted to the diethyl ether and purified on silica gel (MeOH/CHCl\(_3\) = 1:5) to provide N-trifluoromethanesulfonyleucine methyl ester. Resulting trifluoromethanesulfonylestaturated leucine methyl ester was treated with 1.0 N NaOH solution at 0 °C for 10 h to hydrolyze the methyl ester group, and the sodium ions were removed by passing through a column filled with proton-exchange resign (Amberlite IRN 77). The product was washed with hexane to give N-trifluoromethanesulfonyleucine. Tetrabutylphosphonium cation ([P4444]) was coupled with the N-trifluoromethanesulfonyleucine to form the IL. Aqueous solution of [P4444][OH] was mixed with a
slightly less amount of trifluoromethanesulfonyl leucine, and the product was extracted with chloroform. After evaporation, the product was dried in vacuo for at least 24 h at 70 °C. The structure of the IL was confirmed by $^1$H NMR. $^1$H NMR (400 MHz, CDCl$_3$, δ ppm relative to TMS): 0.94(m, $J = 44.9$, 18H, CH$_2$CH$_3$), 1.39(m, $J = 185.1$, 18H, CH$_2$CH$_3$), 1.88(m, $J = 27.0$, 1H, CH$_2$CH$_3$), 2.26(m, $J = 29.3$, 8H, PCH$_2$), 3.67(q, $J = 12.8$, 1H, NCH$_2$).

Reference


$^{13}$NMR measurement of [P$_{4444}$][Tf-Leu]/water mixture

$^{13}$NMR spectroscopy for [P$_{4444}$][Tf-Leu]/water mixture was measured using a double NMR tube technique. [P$_{4444}$][Tf-Leu] was mixed with pure water to reach the water content of 31.4 wt%. The mixture was put into the inner tube, and the outer tube was filled with D$_2$O containing sodium 3-trimethylsilyl propanesulfonate (DSS) as an internal standard. $^{13}$C NMR spectrum was obtained by either JEOL JNM-ECX400 or JEOL JNM-ECX500.
Chemical shift change of carboxylic acid group on Tf-Leu after mixing with water

Fig. S1 $^{13}$C NMR spectrum of free carboxylic group on [Tf-Leu] anion after mixing with water. Blue; [H][Tf-Leu], red; [P$_{4444}$][Tf-Leu], and black; [P$_{4444}$][Tf-Leu]/[P$_{4444}$][OH] mixture at 25 °C.
Chemical shift change of carboxylic acid group on Tf-Leu anion for [P$_{4444}$][Tf-Leu] after bubbling CO$_2$ gas

Fig. S2 $^{13}$C NMR spectrum of [P$_{4444}$][Tf-Leu]/water mixture before and after CO$_2$ bubbling at 25 °C.