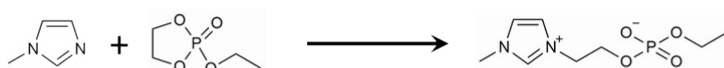


Supporting information

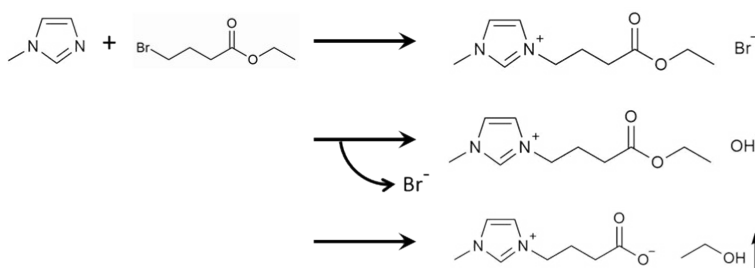
Phosphate-type zwitterionic liquid

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Synthetic scheme of C_1imC_2P (this study)



Synthetic scheme of C_1imC_3C (previous study)



Synthetic scheme of OE_2imC_3C (previous study)

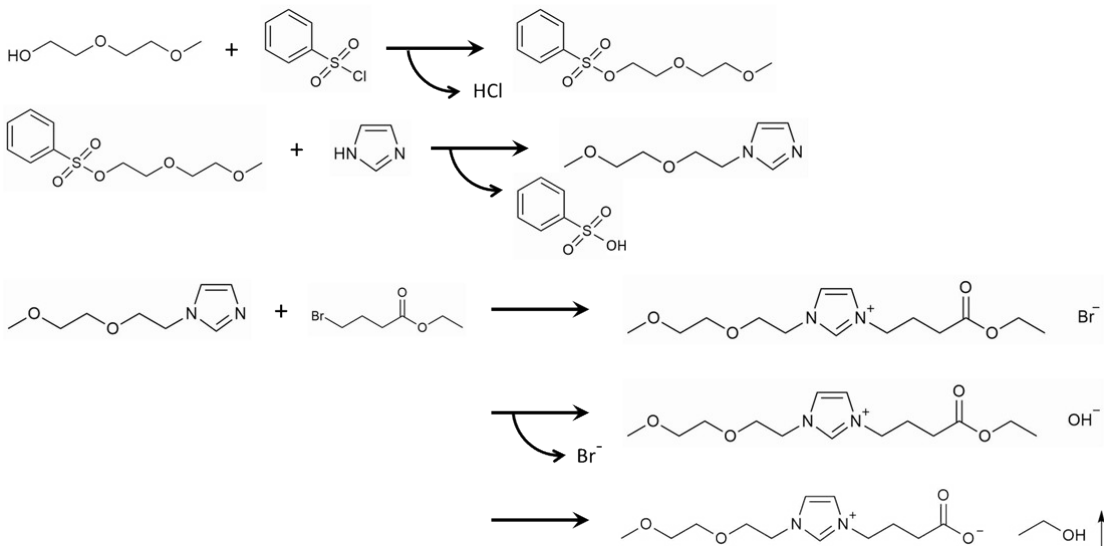


Fig. S1. Synthetic scheme of C_1imC_3C (simple synthesis, middle synthesis energy cost, high melting point, middle atom economy) and OE_2imC_3C (complicated synthesis, high synthesis energy cost, middle melting point, low atom economy), which have been developed in the previous studies.

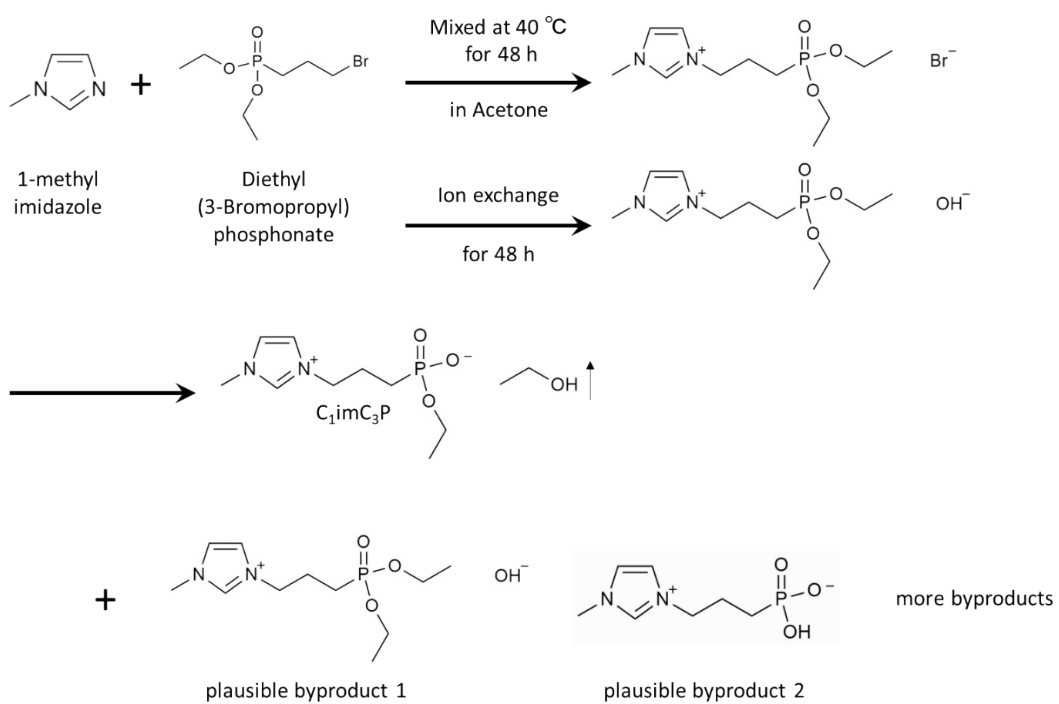


Fig. S2. Structures of the plausible byproducts.

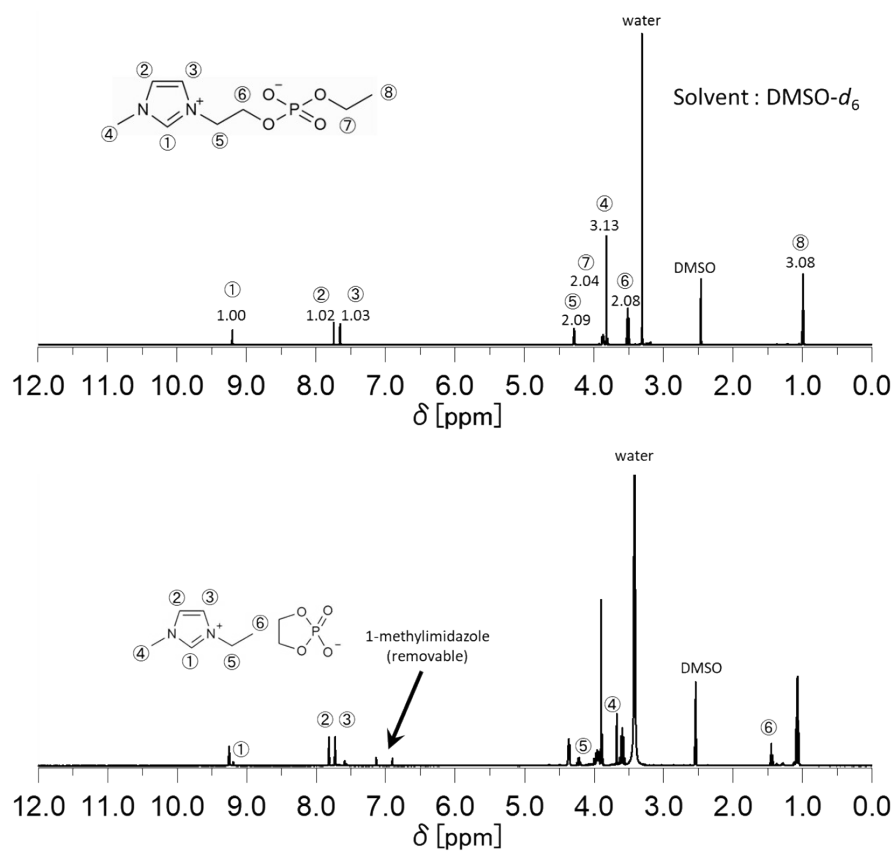


Fig. S3. Spectra of ^1H NMR of $\text{C}_1\text{imC}_2\text{C}$ and byproduct.

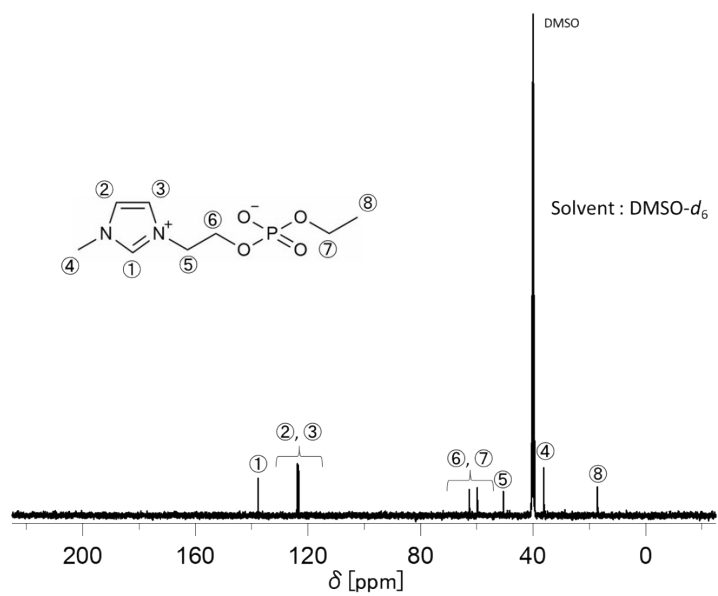


Figure S4. ^{13}C NMR spectrum of $\text{C}_1\text{imC}_2\text{P}$.

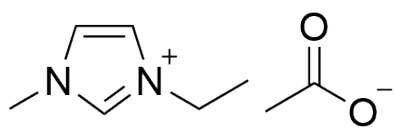


Fig. S5. Structure of [C₂mim]OAc.

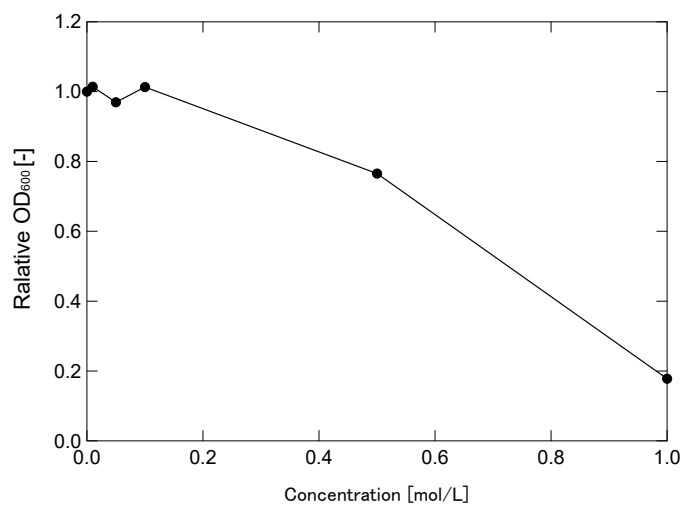


Fig. S6. Relation between relative OD₆₀₀ and C₁imC₂P concentration.

Table. S1. Various C₁imC₂P synthesis conditions and yields (Full version).

Temp. (°C)	Solvent	Molar ratio (A:B)	Time (h)	Yield (%)	Byproduct
50	THF	1:1	48	15	No
70	THF	1:1	48	16	Yes
40	DCM	1:1	48	4	No
50	toluene	1:1	48	5	Yes
70	water/ methanol	1:1	48	4	No
55	hexane	1:1	18	58	Yes
27	hexane	1:1	48	7	No
27	hexane	1:1	300	25	Yes
27	neat	1:1	24	17	No
27	neat	1:1	37	25	No
27	neat	1:1	48	25	No
27	neat	1:1	60	25	No
27	neat	1:1	125	25	Yes
27	neat	1:1	150	25	Yes
27	neat	1:1	170	25	Yes
27	neat	2:1	24	23	No
27	neat	2:1	48	33	No

Experimental

Materials and methods

1-Methylimidazole, diethyl (3-bromopropyl) phosphonate, and 2-ethoxy-1,3,2-dioxaphospholane 2-oxide were purchased from Tokyo Chemical Industry Co. Ltd. and used as received. Toluene, acetone, methanol, hexane, diethyl ether, dimethyl sulfoxide- d_6 (99.9%D), and DCM were purchased from Kanto Chemical Co., Inc., and used as received. THF was purchased from Kanto Chemical Co., Inc., and used after passing through aluminium oxide (basic, Sigma-Aldrich Co., LLC). Sodium chloride, dried yeast extract, and tryptone were purchased from Nacalai Tesque Co., Inc., and used as received.

^1H and ^{13}C NMR spectra were measured using JEOL ECA-400 and ECZ-600R spectrometers. Thermogravimetric analysis was performed using a DTG-60AH instrument (Shimadzu Co., Ltd.), and differential scanning calorimetry was performed using a DSC-60Aplus instrument (Shimadzu Co., Ltd.).

Typical Synthesis of $\text{C}_{11}\text{imC}_2\text{P}$

1-Methylimidazole (1.39 g, 0.017 mol) and 2-ethoxy-1,3,2-dioxaphospholane 2-oxide (2.58 g, 0.017 mol) were added. The mixture was then heated in an oil bath at 27 °C for 48 h. The mixture was then subjected to ion exchange with an ion exchange resin (Amberlite IRN-78, ion exchange resin, nuclear grade, Thermo Fisher Scientific) in a water/methanol mixture (1/1, v/v) to remove impurities. The solvent was then evaporated under reduced pressure. The mixture was then washed five times with excess diethyl ether, and residual ether was evaporated under reduced pressure.

^1H NMR (400 MHz; DMSO- d_6 ; $\text{Me}_4\text{-Si}$), δ = 9.20 (s, 1H, NCHN), 7.75 and 7.65 (t, J = 2.4 Hz and 2.4 Hz, 2H, NCHCHN), 4.29 (t, J = 6.8 Hz, 2H, NCH₂CH₂O), 3.885-3.855 (q, J = 5.2 Hz and 5.6 Hz, 2H, OCH₂CH₃), 3.821 (s, 3H, NCH₃), 3.51 (t, J = 9.6 Hz, 2H, NCH₂CH₂O), 1.00 (t, J = 9.2 Hz, 3H, OCH₂CH₃). ^{13}C NMR (100 MHz; DMSO- d_6 ; $\text{Me}_4\text{-Si}$), δ = 137.69, 123.74, 123.32, 62.59, 59.83, 50.61, 36.17, 58.61 and 17.1.

Fast atom bombardment ionisation mass spectrometry: 233.0695 m/z (observed) and 233.0686 m/z (calculated) as $[\text{M}+\text{H}]^-$, and 235.0847 m/z (observed) and 235.0842 m/z (calculated) as $[\text{M}-\text{H}]^+$.

Elemental analysis: $\text{C}_{11}\text{imC}_2\text{P} \cdot 1.9\text{H}_2\text{O}$ (Found: C, 35.95; H, 7.06; N, 10.17; Calculated for $\text{C}_8\text{H}_{18.8}\text{N}_2\text{O}_{5.9}$: C, 35.80; H, 7.06; N, 10.44%)

Physicochemical properties and cellulose dissolution ability of zwitterion

Differential scanning calorimetry was conducted at a heating rate of +10 °C/min and a cooling rate of -10 °C/min. Thermogravimetric analysis was conducted with a heating rate of +10 °C/min.

To investigate the cellulose dissolution ability, 1 mg (1 wt%) of cellulose was added to 100 mg of C₁imC₂P while stirring. This process was repeated until the cellulose was not dissolved. The dissolution was confirmed visually.

Rough estimation of Kamlet-Taft parameter β value

C₁imC₂P/ethanol solution of ¹H NMR was measured at room temperature. The difference between the chemical shifts of the ethanol-CH₃ and the ethanol-OH group gives the δ OH-shift. OH-shift in the C₁imC₂P/ethanol solution was 4.284.

Kamlet-Taft parameter β was estimated by approximation curve calculated from the OH shift by referring the literature (*Dialkyl Phosphate-Related Ionic Liquids as Selective Solvents for Xylan*, reported by Carmen Froschauer, Michael Hummel, Gerhard Laus, Herwig Schottenberger, Herbert Sixta, Hedda K. Weber and Gerhard Zuckerstatter, *Macromolecules*, 2012, **13**, 1973-1980).

Toxicity of zwitterions

YPD medium was prepared with 20 g/L peptone, 20 g/L glucose and 10 g/L yeast extract and autoclaved before use. Zwitterion/YPD medium (2 mL) at concentrations of 0, 0.01, 0.05, 0.1, 0.5 and 1.0 mol/L were prepared. *Kluyveromyces marxianus* (DMKU 3-1042) was precultured aerobically at 40 °C for 28 h in a 27 mL test tube containing 6 mL of YPD medium. After preculture, *Kluyveromyces marxianus* was inoculated into zwitterion/YPD medium mixtures (100 μ L per well in a 96well plate) with an initial OD₆₀₀ of 0.2, measured using a microplate spectrophotometer (Bio Tek Epoch, Agilent). The inoculated cultures were aerobically incubated at 40 °C for 6 h using an orbital shaker at 700 rpm, and the OD₆₀₀ of the solutions was measured. The toxicity of the zwitterions was evaluated based on relative growth, which is defined as the percentage of OD₆₀₀ of the zwitterion/YPD medium mixtures at 6 h compared to that of the pure medium.