

A Green way for the synthesis of lubricating ester oil by a bi-functional ionic liquid

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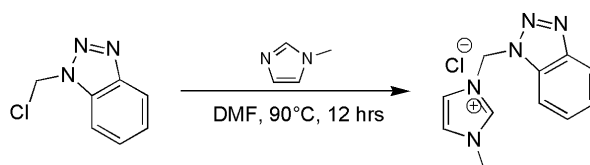
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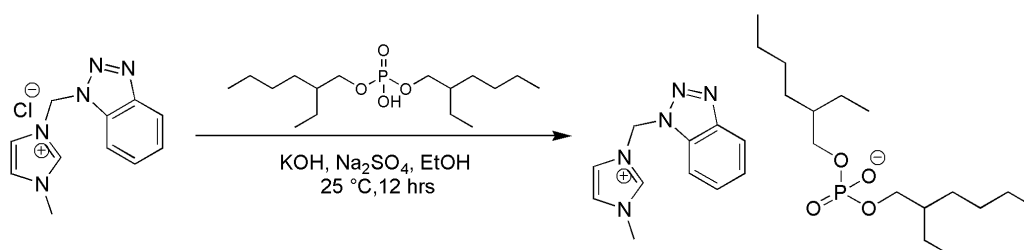
Experimental section and Fig S1, S2, S3, S4

Experimental section

Synthesis of [BTAMIM][DEHP]

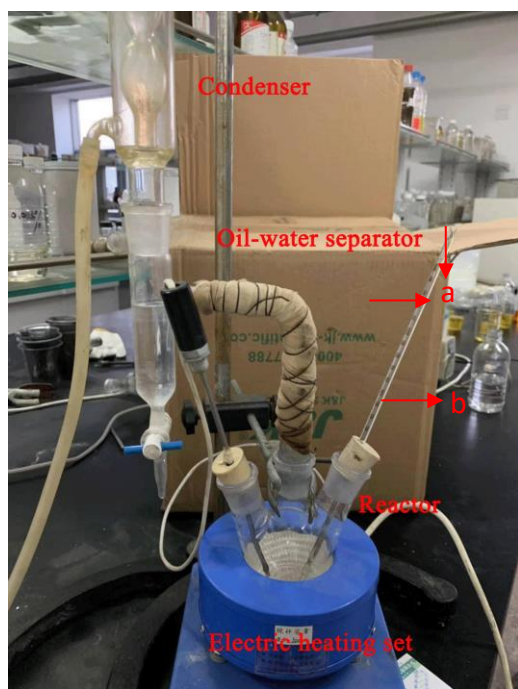


1-chloromethylbenzotriazole (298.34 mmol) was dissolved in N,N-dimethylformamide (301.32 mmol), and then the same molar amount of N-methylimidazole was added into the solution, stirring at 90 °C for 12 h. The reaction mixture was poured into methyl tert-butyl ether at 25 °C, filtered and the filter cake was dried under reduced pressure to give 1-methylbenzotriazole-3-methylimidazole chloride as a gray solid. The yield of 1-methylbenzotriazole-3-methylimidazole chloride was 95%.



To a solution of KOH (38.29 mmol) in EtOH (100 mL) was added di-(2-ethylhexyl) phosphate (38.29 mmol), the reaction was stirred at 70 °C for 2 h, 1-methylbenzotriazole-3-methylimidazole chloride (38.29 mmol) and Na₂SO₄ (76.58 mmol) was added. The mixture was stirred at 25 °C for 12 h. The reaction mixture was filtered and the filtrate concentrated under reduced pressure to give a residue. The crude product was triturated with methyl tert-butyl ether (150 mL) at 25 °C for 1 h, then filtered and the filtrate was concentrated under reduced pressure to give 1-(benzotriazole-1-methylene)-3-methylimidazole bis(2-ethylhexyl) phosphate ([BTAMIM][DEHP]) as a yellow oil. The yield of [BTAMIM][DEHP] was 87% and the ¹H NMR was applied in supplementary material.

Catalytic performance test of [BTAMIM][DEHP]



In order to provide a clear explanation by using the toluene to remove the by-product of water, a picture of the experimental device was taken as shown above. A certain amount of toluene was added into the oil-water separator until it reached the position of "a" in the picture. Under the given reaction conditions, the toluene and the by-product of water would form an azeotropic mixture. This mixture would further evaporate and reflux into the water separator to further condense into liquid water in the "a" position. The density of water is higher than that of toluene, so the condensed water stayed at the bottom of the oil-water separator, as shown in the "b" position, and the excess toluene in the oil-water separator would flow circularly into the reaction system to assist in further removing water again.

Fig S1. The experimental device

The esterification of pentaerythritol with caproic acid at a stoichiometric ratio was carried out in a 100 mL three-necked round-bottomed flask with magnetic stirring: 0.013 mol (1.770 g) pentaerythritol, and 0.052 mol (6.040 g) caproic acid (the molar ratio of pentaerythritol with caproic acid being 1:4) and catalyst ([BTAMIM][DEHP] content: 0.00013 mol (1% mol of the pentaerythritol), 0.0681 g) were introduced, and 2 mL toluene was also added as a water-removing agent to react for 7 h at 160 °C. The product was evaporated by rotation to remove the water-removal agent toluene. The acid value of the product was measured by referring to ISO 6618: 1997(E), and the degree of esterification of the product was analyzed by the acid value. The esterification rate could be calculated by the following formula:

$$Er/\% = [(1 - AN_a/AN_b) \times R/4] \times 100\%$$

Where Er represents the esterification of pentaerythritol with caproic acid, and AN_a is the acid number of the products after the reaction, AN_b is the acid number of the substrate before the reaction. R represents the molar ratio of caproic acid to pentaerythritol.

Determination of acid number:

The AN_a and AN_b were determined by titration method according to ISO 6618: 1997(E): Into a 250-ml conical flask, introduce 2.0 g sample. Add 100 ml of the titration solvent A (containing toluene: isopropyl alcohol: water at a ratio of 500:495:5) and 0.5 ml of the indicator solution (solution: 1.0 g p-naphtholbenzein in 100 mL solvent A), and without stoppering, swirl until the test portion is completely dissolved by the solvent. Add the potassium hydroxide solution (0.1 mol/L standard volumetric alcoholic solution) in increments and swirl to disperse the potassium hydroxide as necessary.

Calculate the acid number, AN , in milligrams of KOH per gram of the test sample, from the equation:

$$AN = \frac{(V_1 - V_0)c_{KOH} \times 56.1}{m}$$

V_1 is the volume, in millilitres, of potassium hydroxide solution required for titration of the test portion;

V_0 is the volume, in millilitres, of potassium hydroxide solution required for titration of the blank solution;

c_{KOH} is the concentration, in moles per litre, of the standard volumetric potassium hydroxide solution;

m is the mass, in grams, of the test portion.

Tribological performance test of [BTAMIM][DEHP]

The tribological performance test were assessed using an Optimol SRV oscillating reciprocating friction and wear tester under the conditions: load: 50N, frequency: 25Hz, temperature: 100 °C, stroke: 1mm, time: 30min and in a ball-on-block configuration. The fixed lower specimens was AISI52100 steel disc (60-64 Rockwell Hardness C, $\varnothing 24.00 \times 7.9$ mm). An AISI52100 steel ball with a diameter of 10 mm and a hardness of 58-62 HRC was rubbing against the disc. The relative humidity was 28-45%. The friction coefficient was recorded automatically by a computer connected to the SRV tester.

Fig S2

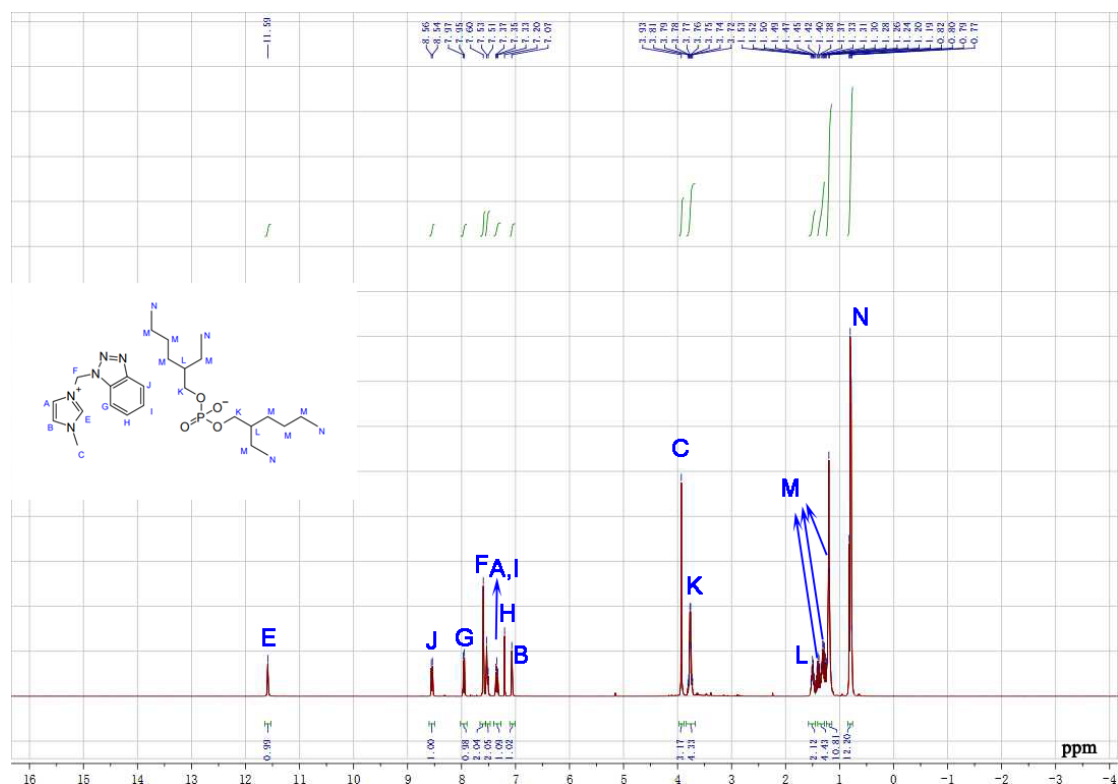


Fig S2. The ¹H NMR spectra of [BTAMIM][DEPH]

¹H NMR: (400 MHz, CHLOROFORM-d) δ = 11.59 (s, 1H), 8.56 (d, J = 8.4 Hz, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.60 (s, 2H), 7.55 - 7.51 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.20 (s, 1H), 7.07 (s, 1H), 3.98 (s, 3H), 3.81 - 3.72 (m, 4H), 1.53 - 1.45 (m, 2H), 1.31 (br dd, J = 7.0, 14.0 Hz, 4H), 1.25 - 1.14 (m, 11H), 0.85 - 0.75 (m, 12H)

Fig S3

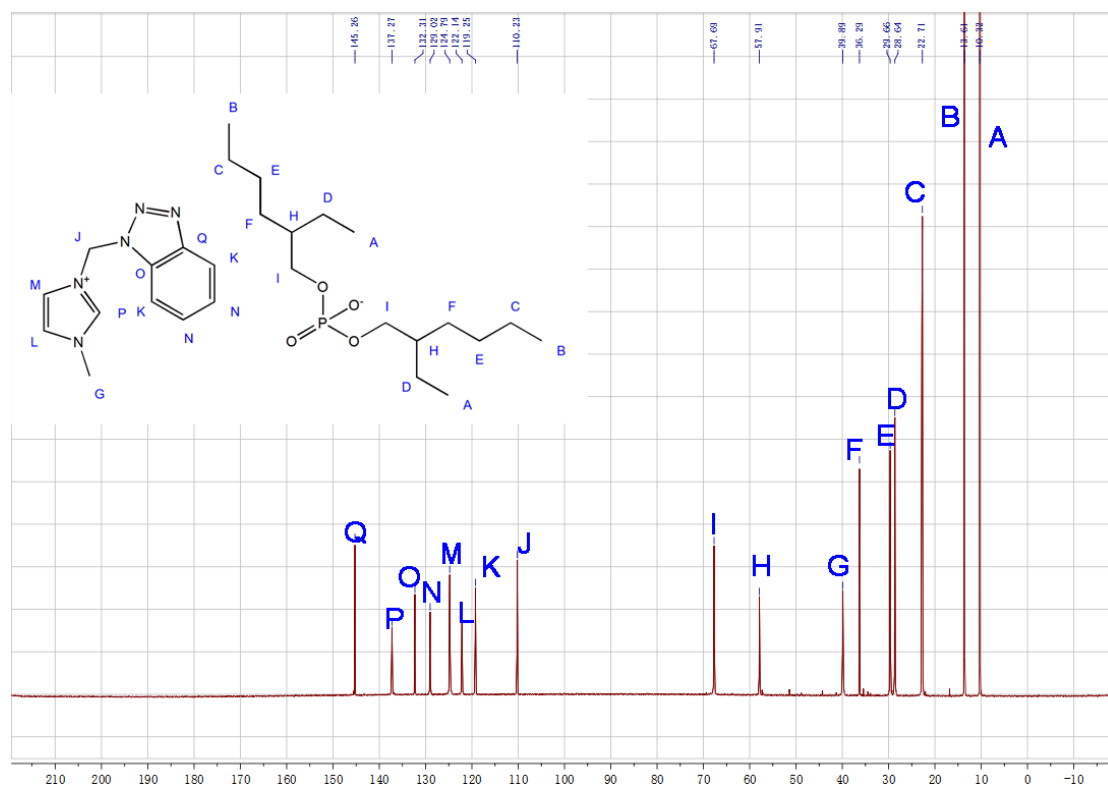


Fig S3. The ¹³CNMR spectra of [BTAMIM][DEPH]

¹³C NMR: (100 MHz, D₂O) δ = 145.26, 137.27, 132.31, 129.02, 124.79, 122.14, 119.25, 110.23, 67.69, 57.91, 39.89, 36.29, 29.66, 28.64, 22.71, 13.61, 10.32

Fig S4

NMR spectra of ester was measured using a Bruker ARX 400 spectrometer at 400 MHz (^1H). All spectra were recorded in CDCl_3 and chemical shifts (δ) are reported in ppm relative to tetramethylsilane referenced to the residual solvent peaks.

The yields were determined by ^1H NMR with triphenylmethane as internal standard of these products and were calculated by the following formula:

$$1. \text{Yield/\%} = \frac{m}{m_{\text{weighing}}} \times 100\%$$

$$2. \text{The } m \text{ was calculated by this formula: } \frac{\frac{m_{\text{triphenyl methane}}}{M_{\text{triphenyl methane}}}}{\frac{8m}{M_{\text{pentaery throtol tetra-hexanoate}}}} = \frac{n_{1\text{H}}}{n_{8\text{H}}}$$

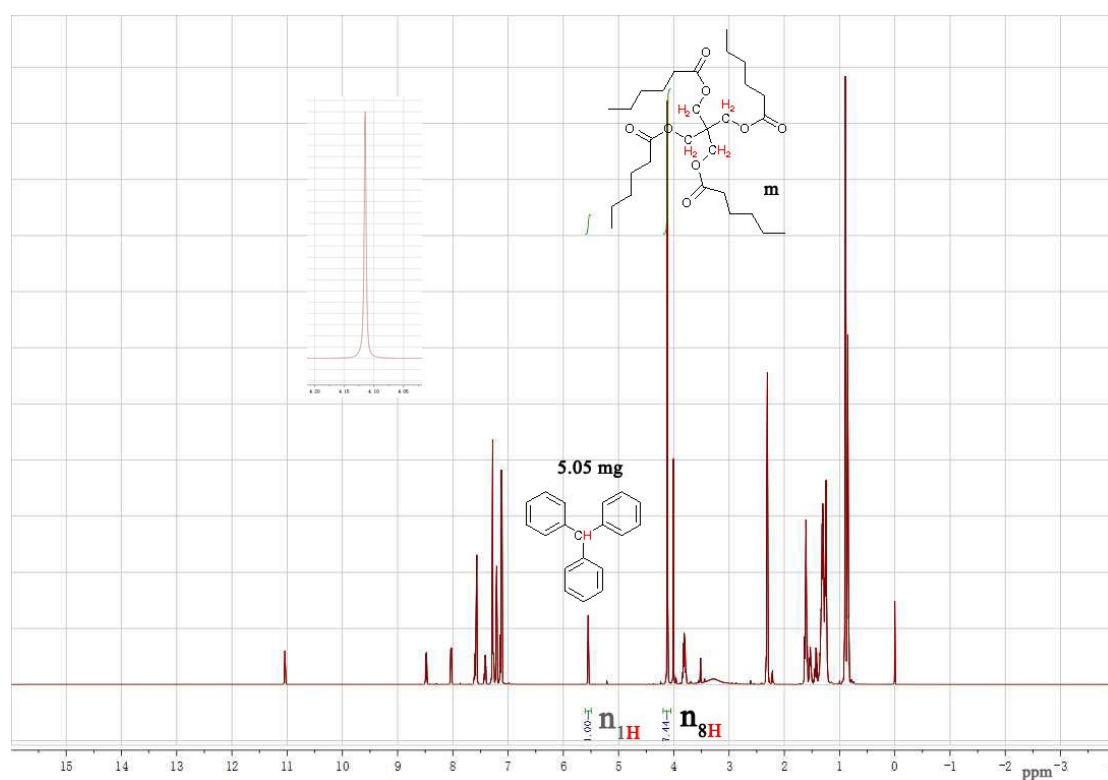


Fig S4. The ^1H NMR spectra of PETH + [BTAMIM][DEHP]