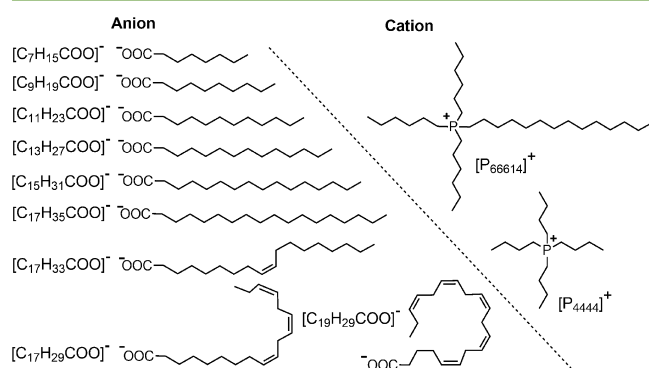




leading to a much narrower liquid range than other ILs. Additionally, those ILs are usually very hydrophilic and thus cannot easily form biphasic water–IL systems for the extraction of aqueous solutions. Only a few attempts have been made to address this problem, including the development of phosphonate ILs,<sup>14,15</sup> and it thus remains a significant challenge to enhance the basicity of ILs while simultaneously maintaining low polarity (or good lipophilicity), a wide liquid range, and a controllable phase equilibrium.

Herein, we synthesized a family of functional phosphonium ILs featuring biocompatible saturated/unsaturated long-chain fatty acid anions with the carbon number up to 20, which exhibits strong hydrogen-bond basicity, good lipophilicity, and a wide liquid range, as well as tunable hydrophilicity/hydrophobicity (Figure 1). The physicochemical properties of



**Figure 1.** Cations and anions of the LCFA-ILs.

these ILs were systematically characterized and discussed for the first time. Through the considerable electron-donating power and conformational flexibility of the incorporated long alkyl chain in the anion as well as the high asymmetry of the tetraalkylphosphonium cation and fatty acid anions, the hydrogen-bond basicities of these long-chain fatty acid ILs (LCFA-ILs) with tetraalkylphosphonium cations are among the highest of reported ILs, and their liquid range is also very wide (−90 to 300 °C). In addition, the hydrophilicity/hydrophobicity of LCFA-ILs could be readily tuned by a simple change of the side chain of the phosphonium cation, while maintaining the other characteristics such as strong hydrogen-bond basicity and good lipophilicity. Due to these unique physicochemical properties, unprecedented extraction efficiency was achieved by applying LCFA-ILs to both aqueous and nonaqueous extractions, with distribution coefficients of solutes 17–650 times higher than those in common IL-based extractions.

## EXPERIMENTAL SECTION

**Materials.** The 40% aqueous solution of tetrabutylphosphonium hydroxide ( $[P_{4444}][OH]$ ) was purchased from Tokyo Chemical Industry Co., Ltd. Acetic acid (99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. Trihexyl(tetradecyl)phosphonium bromide ( $[P_{66614}][Br]$ , 97%), butyric acid, hexanoic acid, and octanoic acid were purchased from J&K Scientific Ltd. Capric acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, and linolenic acid were purchased from Aladdin Reagent Co., Ltd. Eicosapentaenoic ethyl ester (96%) was obtained from Anti-Cancer Solution, Ltd. 1-Octyl-3-methylimidazolium hexafluorophosphates ( $[C_8mim][PF_6]$ ) and 1-octyl-3-methylimidazolium tetrafluoroborate ( $[C_8mim][BF_4]$ ) were purchased from Green Chemistry and Catalysis, LICP, CAS (>99%). The indicator probes for the Kamlet–Taft solvatochromic

experiments were 4-nitroaniline (>99%, Aldrich) and *N,N*-diethyl-4-nitroaniline (97%, Oakwood Products, Inc.). Phenol (99.5%), *p*-cresol (99%), 2,6-dimethylphenol (99%), and Sudan I (AR) were obtained from Aladdin Reagent Co., Ltd.

**Methods.** *Preparation of ILs.* Equimolar  $[P_{4444}][OH]$  (aqueous solution) and fatty acid were stirred at 45 °C for 24 h to produce the aqueous solution of tetraalkylphosphonium ILs, and then the solution was dried under high vacuum at 50 °C for 48 h. The used fatty acids include both saturated acids (acetic acid, butyric acid, hexanoic acid, octanoic acid, capric acid, lauric acid, myristic acid, palmitic acid, and stearic acid) and unsaturated acids (oleic acid and linolenic acid), having a carbon number from 2 to 20. When the unsaturated acid was used, the neutralization reaction was conducted in nitrogen atmosphere. The accurate concentration of  $[P_{4444}][OH]$  in the original aqueous solution was determined by HCl titration. The eicosapentaenoic acid ( $C_{19}H_{29}COOH$ , EPA) was prepared by a saponification reaction of eicosapentaenoic ethyl ester, following acidification according to literature.<sup>33</sup> The preparation of trihexyl-(tetradecyl)phosphonium ILs was similar to the above procedures, with the aqueous  $[P_{4444}][OH]$  solution replaced by the ethanolic solution of trihexyl(tetradecyl)phosphonium hydroxide ( $[P_{66614}][OH]$ ), which was produced by the anion-exchange of  $[P_{66614}][Br]$ . The water mass fractions of synthesized tetraalkylphosphonium and trihexyl(tetradecyl)phosphonium ILs were lower than 0.7% and 0.5%, respectively. The chemical structure of synthesized ILs was confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra and MS analysis (Supporting Information).

**Characterizations.** The Kamlet–Taft dipolarity/polarizability  $\pi^*$  and hydrogen-bond basicity  $\beta$  were measured by solvatochromic experiments,<sup>34,35</sup> using 4-nitroaniline and *N,N*-diethyl-4-nitroaniline as probe. The uncertainty of  $\pi^*$  and  $\beta$  was  $\pm 0.01$  and  $\pm 0.02$ , respectively. Differential scanning calorimetry (DSC) measurements were performed with a TA Q200 differential scanning calorimeter under a nitrogen atmosphere, within a temperature range from −90 to 150 °C at a scanning rate of 10 °C min<sup>−1</sup>. Thermal gravimetric analysis (TGA) was conducted with a PerkinElmer Pyris 1 TGA instrument at a heating rate of 10 °C min<sup>−1</sup> from 50 to 400 °C under a nitrogen atmosphere. The viscosities of ILs were measured by Brookfield LVDV-II+Pro Cone/Plate programmable viscometer, with an uncertainty of  $\pm 2\%$ .

**Liquid–Liquid Extraction.** A typical procedure is described for the extraction of phenol by  $[P_{66614}][C_7H_{15}COO]$ . At first, a known amount of phenol was dissolved in  $[P_{66614}][C_7H_{15}COO]$ -saturated water, and aliquots of this solution were contacted with an equal volume of water-saturated  $[P_{66614}][C_7H_{15}COO]$  in an Erlenmeyer flask. The flask was shaken for 45 min using a thermostatic rotary shaker at 30 °C with a speed of 200 r min<sup>−1</sup> and then settled at the same temperature to reach a phase splitting. In some cases, the phase splitting was accelerated by centrifugation with a speed of 8000 r min<sup>−1</sup> at 30 °C. Samples were taken from each of the two phases and diluted with methanol for the HPLC analysis (see the Supporting Information for details). The distribution ratio (*D*) was calculated by the following equation

$$D = C^e / C^r$$

where  $C^e$  and  $C^r$  refer to the mass fractions of solute in the extract phase (IL-rich phase) and in the raffinate phase, respectively. The uncertainties of *D* for LCFA-ILs were about 10% as a result of the very large *D* values, whereas the uncertainties of *D* for other referential extractants were within 5%.

## RESULTS AND DISCUSSION

The synthesized LCFA-ILs were easily obtained by neutralizing tetraalkylphosphonium hydroxide with long-chain fatty acids (carbon number of 8 to 20). Most of the used acids are widely present in biomass, and some are well-known natural bioactive compounds (such as EPA, a very important  $\Omega$ -3 fatty acid). Thus, the anions of LCFA-ILs are expected to have advantages

over the commonly used halogen-containing anions of ILs in terms of biodegradability and biocompatibility.

**Thermal Analysis.** All of the LCFA-ILs were obtained as transparent liquids at room temperature. DSC measurements showed that some of these LCFA-ILs exhibited a melting point ( $T_m$ ), while others had a glass transition temperature ( $T_g$ ). For the  $[P_{4444}]^+$  LCFA-ILs, the phase transition temperatures ( $T_g/T_m$ ) were far below room temperature, ranging from  $-78.1$  to  $-28.3$  °C (Table 1). The long alkyl chain is critical for the low

**Table 1.** Melting Point ( $T_m$ ), Glass Transition Temperature ( $T_g$ ), Onset Temperature of Decomposition ( $T_{onset}$ ), Hydrogen-Bond Basicity ( $\beta$ ), and Dipolarity/Polarizability ( $\pi^*$ ) of LCFA-ILs and Their Short-Chain Analogues

IL	$T_m$ (°C)	$T_g$ (°C)	$T_{onset}$ (°C)	$\beta^a$	$\pi^{*a}$
$[P_{4444}][CH_3COO]$	54.5	–	300.7	1.38	1.00
$[P_{4444}][C_3H_7COO]$	37.9	–	328.8	1.45	0.95
$[P_{4444}][C_5H_{11}COO]$	40.7	–	324.0	1.49	0.93
$[P_{4444}][C_7H_{15}COO]$	–	$-74.3$	301.3	1.55	0.86
$[P_{4444}][C_9H_{19}COO]$	–	$-78.1$	285.5	1.55	0.83
$[P_{4444}][C_{11}H_{23}COO]$	–	$-75.1$	335.0	1.61	0.81
$[P_{4444}][C_{13}H_{27}COO]$	–	$-71.2$	337.0	1.61	0.80
$[P_{4444}][C_{15}H_{31}COO]$	$-48.7$	–	306.2	1.62	0.77
$[P_{4444}][C_{17}H_{35}COO]$	$-28.3$	–	301.1	1.61	0.76
$[P_{4444}][C_{17}H_{33}COO]$	–	$-55.7$	320.6	1.65	0.69
$[P_{4444}][C_{17}H_{29}COO]^b$	–	–	314.4	1.65	0.69
$[P_{4444}][C_{19}H_{29}COO]^b$	–	–	313.0	1.65	0.68
$[P_{66614}][C_7H_{15}COO]$	$-74.6$	–	316.2	1.62	0.73
$[P_{66614}][C_9H_{19}COO]$	$-26.5$	–	265.7	1.70	0.69
$[P_{66614}][C_{11}H_{23}COO]$	$-12.9$	–	289.0	1.66	0.68
$[P_{66614}][C_{13}H_{27}COO]$	0.8	–	324.2	1.66	0.67

<sup>a</sup>Measured at 60 °C. <sup>b</sup>No featuring DSC peaks above  $-90$  °C.

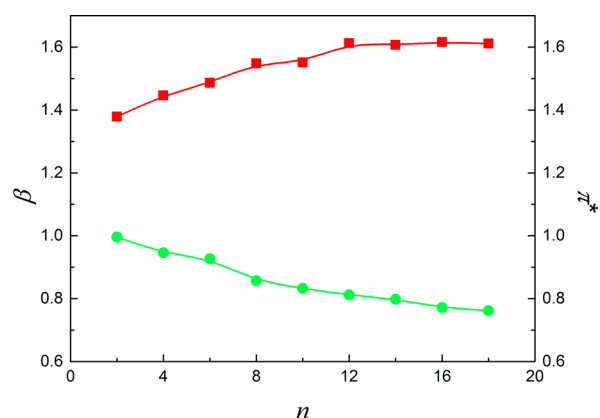
phase transition temperatures, which can lead to asymmetric ion pairs and incompact microstructures, and the structural analogues of these ILs with a short chain anion were all solid at room temperature. By comparing the phase transition temperatures of  $[P_{4444}][C_{17}H_{35}COO]$ ,  $[P_{4444}][C_{17}H_{33}COO]$ ,  $[P_{4444}][C_{17}H_{29}COO]$ , and  $[P_{4444}][C_{19}H_{29}COO]$ , we found that the phase transition temperature could be further reduced by introducing double bonds into the aliphatic chains of the anions, as was previously observed in imidazolium ILs with an unsaturated side chain.<sup>36,37</sup> The  $T_m$  of  $[P_{4444}][C_{17}H_{35}COO]$  was  $-28.3$  °C, whereas the  $T_g$  of  $[P_{4444}][C_{17}H_{33}COO]$  was  $-55.7$  °C. When more double bonds were introduced into the anion, i.e.,  $[P_{4444}][C_{17}H_{29}COO]$  and  $[P_{4444}][C_{19}H_{29}COO]$ , the scans were featureless even when the temperature decreased to  $-90$  °C. Previous work showed that a very slow scanning rate was necessary to observe the phase transition peak,<sup>36</sup> but when we decreased the scanning rate from 10 to 1 °C  $min^{-1}$ , there was still no phase transition found for  $[P_{4444}][C_{17}H_{29}COO]$  and  $[P_{4444}][C_{19}H_{29}COO]$  down to  $-90$  °C. This indicates that  $[P_{4444}][C_{17}H_{29}COO]$  and  $[P_{4444}][C_{19}H_{29}COO]$  probably have phase transition temperatures below  $-90$  °C and thus a better liquid behavior. The structure of the cation also has a significant effect on the liquid range. The  $T_m$  of  $[P_{66614}]^+$  LCFA-ILs were higher than those of  $[P_{4444}]^+$  LCFA-ILs with the same anion, but nevertheless were still lower than 1 °C. However,  $[C_{17}H_{35}COO]^-$  ILs with choline or imidazolium cations are solid at room temperature. Therefore, the high asymmetry of the tetraalkylphosphonium cation and the fatty acid anion is

essential to the broad liquid range of LCFA-ILs. The thermal stability of LCFA-ILs was determined by TGA. As shown in Table 1, the decomposition temperatures ( $T_{onset}$ ) of LCFA-ILs were between 265 to 337 °C, indicating good thermal stability. Taking both the  $T_g$  and  $T_{onset}$  into consideration, it is demonstrated that the synthesized LCFA-ILs could work as liquid materials in a very wide temperature range of approximately 300–400 °C.

#### Hydrogen-Bond Basicity and Dipolarity/Polarizability.

As discussed before, hydrogen-bond basicity is defined as a solvent's ability to donate electron density to form a hydrogen bond with protons of a solute. For example, because the oxygen atom of dimethyl sulfoxide (DMSO) can form a hydrogen bond with the hydrogen atom of the hydroxyl group of phenols or alcohols, DMSO can be viewed as a solvent with hydrogen-bond basicity. To determine the hydrogen-bond basicity of LCFA-ILs, the Kamlet–Taft solvatochromic parameter  $\beta$  was calculated for the LCFA-ILs as well as their  $C_2$ – $C_6$  analogues from the maximum absorption wavelength of two probe dyes in ILs. All of the LCFA-ILs exhibited very strong hydrogen-bond basicity, with  $\beta$  values of approximately 1.6 (Table 1). To the best of our knowledge, these  $\beta$  values are almost the largest among the reported  $\beta$  values of ILs.<sup>27</sup> Imidazolium-based chloride salts, well known as hydrogen bond basic ILs, have  $\beta$  values of only approximately 0.87,<sup>38</sup> 40–45% lower than those of LCFA-ILs, even if the much more basic imidazolium acetate and phosphate ILs only have  $\beta$  values lower than 1.4.<sup>27</sup> In fact, because the  $\beta$  values of most molecular solvents are lower than 0.9,<sup>32,39</sup> the hydrogen-bond basicities of LCFA-ILs achieve the highest level of all reported solvents. The long-chain structure of the anion is important to the strong hydrogen-bond basicity of LCFA-ILs through a considerable electron-donating effect on the charged headgroup of the anion. Besides, it was noted that  $[P_{66614}]^+$  LCFA-ILs have higher  $\beta$  values than  $[P_{4444}]^+$  LCFA-ILs with the same anion. This is because the basicity of ILs could be effectively enhanced by reducing cation–anion interactions.<sup>40</sup> We calculated the cation–anion interaction energy of LCFA-ILs with  $[C_7H_{15}COO]^-$  as the anion at the B3LYP/6-31+G(d,p) level of theory (see Supporting Information for details) and found that the interaction between  $[P_{66614}]^+$  and the  $[C_7H_{15}COO]^-$  anion (381.3  $kJ\ mol^{-1}$ ) was weaker than that between  $[P_{4444}]^+$  and the same anion (361.5  $kJ\ mol^{-1}$ ). Therefore, this work demonstrates an efficient strategy to enhance the basicity of ILs by reducing the cation–anion interactions. The effect of alkyl chain length on the hydrogen-bond basicity was also analyzed for LCFA-ILs, as well as their  $C_2$ – $C_6$  analogues (Figure 2). When the alkyl chain length was extended from  $C_2$  to  $C_{12}$ , the  $\beta$  value of the IL gradually increased. However, when the alkyl chain changed from  $C_{12}$  to  $C_{20}$ , the  $\beta$  value was almost constant, indicating the adequacy of the selected anions in this work in terms of hydrogen-bond basicity.

Another Kamlet–Taft solvatochromic parameter, the dipolarity/polarizability  $\pi^*$ , was also obtained for LCFA-ILs (Table 1), showing relatively low values (0.67–0.86) compared to most ILs (0.90–1.10).<sup>32</sup> The  $\pi^*$  of 1-butyl-3-methylimidazolium chloride ( $[C_4mim]Cl$ ) was 1.10,<sup>38</sup> much higher than those of LCFA-ILs. Increasing the alkyl chain length of anion, the  $\pi^*$  value gradually decreases. Replacing  $[P_{4444}]^+$  by  $[P_{66614}]^+$  led to lower  $\pi^*$  values. Considering that weakly polar molecular solvents generally have low  $\pi^*$  values,<sup>41</sup> these results imply that the interactions of LCFA-IL and weakly polar organic compounds are more favorable than those of common ILs. In

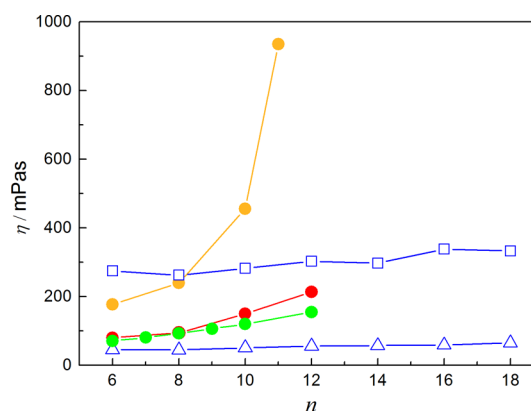


**Figure 2.** Dependence of Kamlet–Taft hydrogen-bond basicity ( $\beta$ ) and dipolarity/polarizability ( $\pi^*$ ) of  $[P_{4444}][C_{n-1}H_{2n-1}COO]$  on the carbon number of anion ( $n$ ) at 60 °C. Red stands for  $\beta$ , and green stands for  $\pi^*$ .

other words, LCFA-ILs can be considered to possess good lipophilicity.

**Viscosity.** The viscosity of solvents is crucial to mass transfer and the design of the extraction process. Compared to molecular solvents, ILs generally have a high viscosity, which has been one of the main obstacles to the practical application of ILs.<sup>42</sup> Due to the concentrated charge and enhanced electrostatic interaction between ions, ILs with a relatively strong hydrogen-bond basicity are often more viscous than other ILs. In this context, the viscosity of LCFA-ILs was determined using a cone/plate viscometer, showing values of approximately 300 mPas at 30 °C (Tables S1 and Figure S1, Supporting Information), far lower than the viscosities of imidazolium chloride ILs that are up to 20,000 mPas.<sup>43</sup> Interestingly,  $[P_{4444}][C_{17}H_{35}COO]$  has a viscosity of 59.0 mPas at 65 °C, whereas  $[P_{4444}][C_{17}H_{33}COO]$  has a viscosity of 49.0 mPas and  $[P_{4444}][C_{17}H_{29}COO]$  of 30.3 mPas at the same temperature (Figure S2, Supporting Information), showing that the unsaturation of the LCFA anion can effectively reduce the viscosity of the IL. Likewise,  $[P_{4444}][C_{19}H_{29}COO]$  has an even lower viscosity than  $[P_{4444}][C_{17}H_{29}COO]$ , despite its longer chain because of its higher degree of unsaturation. These results demonstrate that the strategy of using LCFA as an anion resource could effectively reduce the viscosity of ILs. Besides, the viscosities of all LCFA-ILs decreased exponentially when the temperature increased (Figure S1 and Table S2, Supporting Information). At 60 °C, the viscosities of LCFA-ILs were only 40–60 mPas.

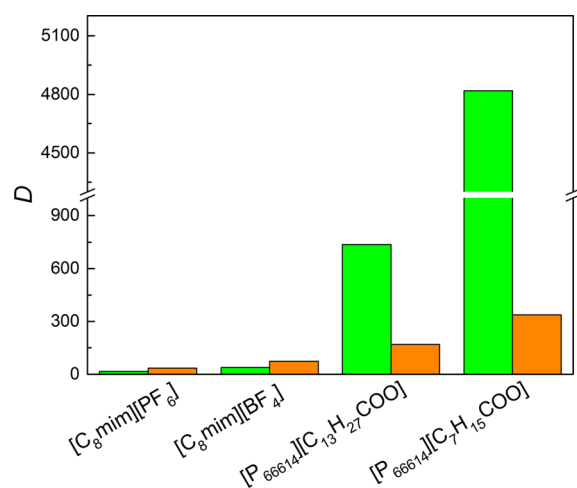
More attention was paid to another interesting observation from Table S1 of the Supporting Information that although the alkyl chain length of the studied LCFA-ILs and their short-chain analogues covered a wide range from 4 to 18, their viscosities were very similar. This is noteworthy because it is different from the well-known rule that the viscosity of ILs increases rapidly with an increase in the alkyl chain length of the cation.<sup>44,45</sup> A comparison is shown in Figure 3. For 1-alkyl-methylimidazolium tetrafluoroborate ( $[C_n\text{mim}][BF_4]$ ), when the carbon number of the alkyl chain changed from 6 to 11, the viscosity at 25 °C increased by a factor of 5.3. However, even if the carbon number of  $[P_{4444}][C_nH_{2n+1}COO]$  changed from 6 to 18, the relative standard deviation of the viscosities at 30 °C was only 9.6%. A similar result was obtained when comparing the viscosities of 1-alkyl-methylimidazolium hexafluorophosphate



**Figure 3.** Viscosity of  $[C_n\text{mim}][BF_4]$  (yellow, 25 °C),  $[C_n\text{mim}][PF_6]$  (red, 60 °C),  $[C_n\text{mim}][NTf_2]$  (green, 25 °C), and  $[P_{4444}][C_{n-1}H_{2n-1}COO]$  (blue square, 30 °C; blue triangle, 60 °C). Points of  $[C_n\text{mim}][BF_4]$  and  $[C_n\text{mim}][PF_6]$  are redrawn from ref 44 and  $[C_n\text{mim}][NTf_2]$  are redrawn from ref 45.

phosphate ( $[C_n\text{mim}][PF_6]$ ,  $n = 6, 8, 10, 12$ ) and  $[P_{4444}][C_nH_{2n+1}COO]$  at 60 °C. Even 1-alkyl-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $[C_n\text{mim}][NTf_2]$ ) ILs, which are usually regarded as low-viscous ILs, experienced increases in their viscosities at 25 °C by a factor of greater than two when the carbon number of their alkyl chain changed from 6 to 12, despite their lower viscosity values.<sup>45,46</sup> One important reason for the increase in the viscosity over the chain length of cation is that longer chain lengths give rise to increased van der Waals attractions between aliphatic alkyl chains and enhanced tail aggregation.<sup>44,47</sup> When an increase in the alkyl chain occurs in the LCFA anion, the van der Waals attractions between chains and the formation of nanoaggregates are likely to be hindered by the stronger repulsion between the charged headgroups of different anions than that between cations, so that the viscosity of the LCFA-ILs shows only a very weak dependence on the alkyl chain length. Therefore, our work indicates that the functionalization of ILs by long-chain fatty acid anions is an effective way to improve their lipophilicity without adversely affecting their transfer properties.

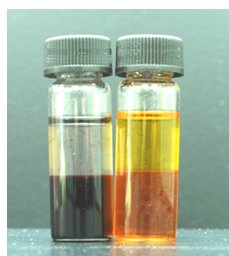
**Liquid–Liquid Extraction Using LCFA-ILs.** The above results demonstrate that the LCFA-ILs reported here are strong hydrogen-bond acceptors, lipophilic, thermally stable, low-viscosity solvents, with low-melting points. Therefore, it is expected that they can perform as efficient extractants to improve separation processes. To test this prediction, we investigated the extraction of phenol from an aqueous solution using hydrophobic LCFA-ILs as extractants. Phenolic compounds are a major class of pollutants in water, and their removal is very important in wastewater treatment. The extraction of phenolic compounds from water by hydrophobic ILs has attracted considerable attention in recent years,<sup>48–51</sup> but the type of ILs used has been very limited, as most of which were composed of fluoro-containing anions  $[PF_6]^-$ ,  $[BF_4]^-$ , and  $[NTf_2]^-$ , which are weak hydrogen-bond acceptors and may decompose to hazardous hydrogen fluoride. We found that the LCFA-ILs with  $[P_{66614}]^+$  cations are hydrophobic; therefore, they can be used as extractants in aqueous extraction. As shown in Figure 4, the distribution coefficient of phenol was 17.5 and 41.5 when using two fluoro-containing ILs as extractants. Nevertheless, surprisingly, when the LCFA-ILs were applied, unprecedented distribution coefficients of phenol were observed, up to 4818 and 735.7 in water– $[P_{66614}][C_7H_{15}COO]$



**Figure 4.** Distribution coefficients of phenol (green) and *p*-cresol (orange) in water–IL biphasic systems.

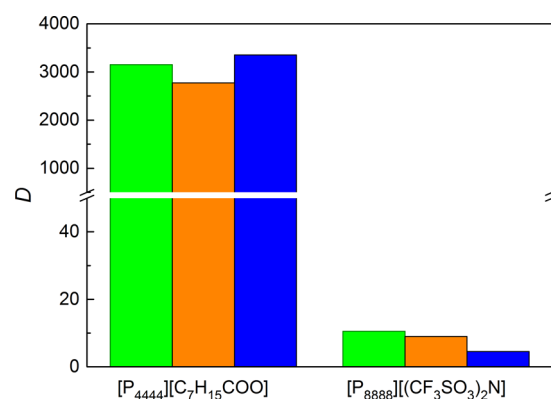
and water–[P<sub>66614</sub>][C<sub>13</sub>H<sub>27</sub>COO] biphasic systems, respectively, approximately 17–275 times higher than those obtained using fluoro-containing ILs. Not only phenol but *p*-cresol also exhibited much higher distribution coefficients in water–LCFA-IL systems than in fluoro-containing ILs (Figure 4), up to 338 and 170, respectively. Although the performance of [NTf<sub>2</sub>]<sup>−</sup> ILs was not tested in the trials shown in Figure 4, their weaker hydrogen-bond basicity relative to [PF<sub>6</sub>]<sup>−</sup> and [BF<sub>4</sub>]<sup>−</sup> ILs will probably lead to much lower extraction efficiency. In fact, it is a long-standing problem that most hydrophobic ILs have a weak hydrogen-bond basicity and strongly basic ILs are mostly hydrophilic solvents. In this work, LCFA-ILs with [P<sub>66614</sub>]<sup>+</sup> cations successfully integrated the desired hydrophobicity and hydrogen-bond basicity, providing a promising avenue for the removal of phenols and other compounds from aqueous solution.

The hydrophobicity of LCFA-ILs can be readily adjusted by changing the side chain of the cation. When the cation of the LCFA-ILs was changed from [P<sub>66614</sub>]<sup>+</sup> to [P<sub>4444</sub>]<sup>+</sup>, the LCFA-ILs changed from hydrophobic to hydrophilic, enabling them to be used in nonaqueous extraction. We selected the extraction of Sudan I, a famous pollutant,<sup>52,53</sup> from hexane as a model system to investigate the performance of LCFA-ILs in nonaqueous extraction. The used extractant was a mixture of [P<sub>4444</sub>]<sup>+</sup> LCFA-IL and a common solvent to diminish the consumption of ILs for better economy and transfer performance, as suggested in our previous work.<sup>25</sup> As shown in Figure 5, after the contact of Sudan I in hexane solution with a [P<sub>4444</sub>][C<sub>7</sub>H<sub>15</sub>COO]+DMF



**Figure 5.** Photo of equilibrated hexane–extractant biphasic systems containing Sudan I as solutes. The extractant is the [P<sub>4444</sub>][C<sub>7</sub>H<sub>15</sub>COO]+DMF mixture with a molar ratio of 1:9 (left) or pure DMF (right).

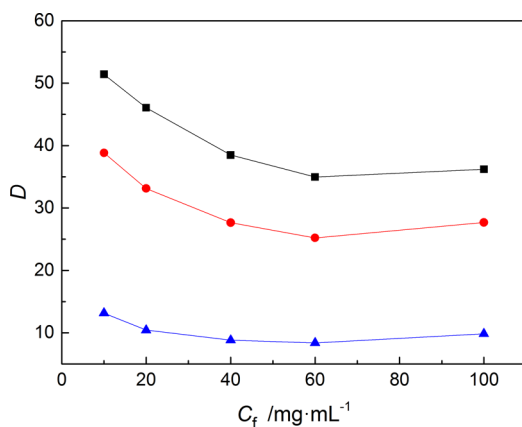
mixture (presaturated with each other), a very significant difference of phase color was observed, where the upper phase (hexane phase) was colorless and the lower phase was dark red, indicating an excellent extraction efficiency of Sudan I by the used extractant (an extraction yield of Sudan I of almost 100%). In a reference experiment using pure DMF as an extractant, the color difference between the two phases after extraction was much less significant, illustrating the key role of [P<sub>4444</sub>][C<sub>7</sub>H<sub>15</sub>COO] in the efficient extraction of Sudan I. Even if the concentration of Sudan I in oil was increased from 1.0 to 10 mg mL<sup>−1</sup>, the extraction efficiency was still very high, with distribution coefficients of approximately 3000. The consumption of DMF needed for a specific extraction yield in the presence of LCFA-IL will be dramatically lower than that in an IL-free extraction because of the enormously increased distribution coefficients (higher than 300 times) of the solute after the addition of a small amount of LCFA-IL. The LCFA-ILs also performed much better than another IL, [P<sub>8888</sub>][NTf<sub>2</sub>], which was reported for extracting Sudan I in the literature.<sup>54</sup> When the original concentration of Sudan I in hexane was 1, 5, or 10 mg mL<sup>−1</sup>, the distribution coefficients of Sudan I by [P<sub>4444</sub>][C<sub>7</sub>H<sub>15</sub>COO] were 300–650 times higher than those obtained by [P<sub>8888</sub>][NTf<sub>2</sub>] (Figure 6). Such an excellent



**Figure 6.** Distribution coefficients of Sudan I in hexane/(IL+DMF) biphasic phase at different feed concentrations: 1 mg mL<sup>−1</sup> (green), 5 mg mL<sup>−1</sup> (orange), and 10 mg mL<sup>−1</sup> (blue). Molar ratio of IL to DMF is 1:9.

extraction performance will not only benefit the removal of Sudan I by liquid–liquid extraction but will also considerably improve the efficiency of solute enrichment in sample analysis by microextraction.

The excellent extraction efficiency of LCFA-IL in nonaqueous extractions was further demonstrated in the extraction of phenols from oil, which is an important process in the coal-based chemical industry.<sup>55,56</sup> When extracting phenol from hexane (1.2 mg mL<sup>−1</sup>) by a [P<sub>4444</sub>][C<sub>7</sub>H<sub>15</sub>COO]+DMF mixture (molar ratio: 1:9) at 30 °C, the distribution coefficient of phenol was 46.4, twice as high as the distribution coefficient using pure DMF as an extractant (20.9). More significantly, when extracting 2,6-xyleneol from hexane using a [P<sub>4444</sub>][C<sub>7</sub>H<sub>15</sub>COO]+DMF mixture with different original concentrations of 2,6-xyleneol, the distribution coefficients were all approximately four times higher than those using pure DMF (Figure 7) and also exceeded those using [C<sub>4</sub>mim]Cl. Even if the original concentration of 2,6-xyleneol in hexane was as high as 100 mg mL<sup>−1</sup>, the distribution coefficient using a [P<sub>4444</sub>][C<sub>7</sub>H<sub>15</sub>COO]+DMF mixture was still higher than 30,



**Figure 7.** Distribution coefficients of 2,6-xyleneol in hexane/(IL+DMF) or hexane-DMF biphasic systems at different feed concentrations: black,  $[\text{P}_{4444}][\text{C}_7\text{H}_{15}\text{COO}]+\text{DMF}$ ; red,  $[\text{C}_4\text{mim}]\text{Cl}+\text{DMF}$ ; and blue, pure DMF. Molar ratio of IL to DMF is 1:9.

which is very favorable to reducing the extractant consumption in large-scale processes. These results of nonaqueous extractions, combined with the results of the prementioned aqueous extractions, demonstrate the excellent performance of LCFA-ILs in liquid-liquid extractions. In fact, not only great distribution coefficients can be obtained but good selectivity of target compounds over other solutes can also be achieved by LCFA-IL-based liquid-liquid extraction. For example, by comparing the distribution coefficients of phenol and *p*-cresol in water-LCFA-IL biphasic systems, the separation selectivity could be as high as 14.3, despite the similar molecular structures of these two compounds.

**Quantum Chemical Calculation.** To give more insight into the physicochemical properties of LCFA-ILs and the extraction mechanism, we carried out quantum chemical calculations at the B3LYP/6-311++(d,p) level for the IL-phenol interactions (see Supporting Information for details).  $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$  was selected as a representative LCFA-IL and was compared with a reference IL,  $[\text{C}_8\text{mim}]\text{BF}_4$ . As shown in Figure S3a of the Supporting Information, intermolecular hydrogen bonds were found between phenol and  $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$  because the distance between the two atoms of each hydrogen bond was smaller than the sum of their van der Waals radii (2.72 Å). Likewise, there are also hydrogen-bonding interactions between the phenolic H atom and the F atom of  $[\text{C}_8\text{mim}]\text{BF}_4$  (Figure S3b, Supporting Information). Nevertheless, the interaction energy of phenol with  $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$  was  $-60.89 \text{ kJ mol}^{-1}$ , much lower than that with  $[\text{C}_8\text{mim}]\text{BF}_4$  ( $-46.58 \text{ kJ mol}^{-1}$ ), indicating that  $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$  has a stronger hydrogen-bond basicity than  $[\text{C}_8\text{mim}]\text{BF}_4$ . Similar conclusions were obtained from AIM analysis.<sup>57</sup> The sum of the charge densities evaluated at the bond critical points ( $\rho_c$ ) of the intermolecular hydrogen bonds in the  $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$ -phenol complex was 0.066 au, and the corresponding value in the  $[\text{C}_8\text{mim}]\text{BF}_4$ -phenol complex was 0.043 au. Generally, a higher  $\rho_c$  implies a stronger interaction. Thus, this result also indicates that the hydrogen-bond basicity of  $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$  was much stronger than that of  $[\text{C}_8\text{mim}]\text{BF}_4$ . In fact, the  $\rho_c$  of the main hydrogen bond between  $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$  and phenol (between the anion's oxygen and hydroxyl hydrogen) was 0.059 au, far beyond the upper limit of the criterion for hydrogen bonds (0.035 au),<sup>58</sup> indicating that  $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$  has a strong

capacity for hydrogen-bonding interactions. Therefore, the strong hydrogen-bond basicity of LCFA-ILs is regarded as one important reason for the highly improved extraction performance over common ILs, while their good lipophilicity is also important.

## CONCLUSIONS

In summary, we have synthesized ILs with both strong hydrogen-bond basicity and good lipophilicity via incorporating biocompatible long-chain fatty acids anions into phosphonium ILs. These ILs not only exhibited strong hydrogen-bond basicities ( $\beta \approx 1.6$ ), achieving the highest level of all reported solvents, but also overcame several common disadvantages of traditional hydrogen-bond basic ILs such as strong polarity, difficulty of forming water-IL biphasic systems, high melting point, and high viscosity. The anion-tethered long alkyl chain plays an essential role in the unique properties of synthesized ILs. Its considerable electron-donating effect on the charged headgroup of the anion is one important reason for such strong hydrogen-bond basicity, while its conformational flexibility and asymmetry toward the cation contribute to very low solid-liquid phase transition temperatures down to  $-70$  to  $-90$  °C. Moreover, as opposed to common cation-tethered long-chain ILs, whose viscosities increase dramatically with increasing chain length, the viscosity of LCFA-ILs showed only a slight increase when the carbon number of the anion changed from 8 to 20, probably resulting from a weaker van der Waals attraction and weaker aggregate formation between the anion-tethered long alkyl chains than the cation-tethered ones. Additionally, the hydrophilicity/hydrophobicity of LCFA-ILs could be readily tuned by a simple change in the side chain of the cation.

As a result of these unique physicochemical properties, unprecedented extraction efficiency was achieved by applying LCFA-ILs to both aqueous and nonaqueous extractions. The distribution coefficients of phenol in water- $[\text{P}_{66614}][\text{C}_7\text{H}_{15}\text{COO}]$  and water- $[\text{P}_{66614}][\text{C}_{11}\text{H}_{23}\text{COO}]$  systems were 4818 and 735.7, respectively, approximately 17–275 times higher than those obtained with common hydrophobic ILs. The distribution coefficients of Sudan I in a hexane/ $([\text{P}_{4444}][\text{C}_7\text{H}_{15}\text{COO}]+\text{DMF})$  system were as high as approximately 3000, dramatically higher than those obtained with pure DMF or  $[\text{P}_{8888}][\text{NTf}_2]$ . Enhanced distribution coefficients were also observed for extracting *p*-cresol from water and 2,6-xyleneol from hexane by LCFA-ILs. These results highlight the utility of LCFA-ILs as a promising medium for the extractive separation of chemicals and also provide valuable information for the development of microextraction technologies, extractive distillations, and even homogeneous reactions.

## ASSOCIATED CONTENT

### Supporting Information

HPLC conditions, quantum chemical calculation details and results, NMR data, viscosity data, and correlations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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