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Physicochemical properties of phosphonium-based and ammonium-based protic ionic liquids

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1. Pictures of as-prepared PILs and the emulsion of [Oct₃NH][TfO] dispersed in water

PIL, emulsion or Brønsted base	Melting point/°C	Picture taken at liquid state [§]
[Oct ₃ NH][TfO]	9	
[Oct ₃ PH][TfO]	51	(Not taken)
[Ph ₃ NH][TfO]	117	
[Ph ₃ PH][TfO]	125 (The observed melting point of [Ph ₃ PH][TfO] during slow heating was slightly lower than 120 °C)	

Emulsion of $[\text{Oct}_3\text{NH}][\text{TfO}]$ dispersed in water ($V([\text{Oct}_3\text{NH}][\text{TfO}]) : V(\text{water}) \approx 1:1$)	—	
Tri- <i>n</i> -octylamine	–34 (Acros Organics catalogue data)	—
Tri- <i>n</i> -octylphosphine	<20 (Sigma-Aldrich Material Safety Data Sheet)	—
Triphenylamine	125–127 (Acros Organics catalogue data)	—
Triphenylphosphine	79–81 (Alfa Aesar catalogue data)	—

§ The discoloration of some of the samples is due to impurities inherent to the preparation method.^{S1,S2} While their exact nature is not clear,^{S1} it has been observed before that they are present only in trace concentrations and we do not expect them to have an appreciable influence on our experimental results.

2. Detailed IR analysis

Fig. 3a shows that for $[\text{Oct}_3\text{NH}][\text{TfO}]$ and $[\text{Oct}_3\text{PH}][\text{TfO}]$ the peaks at 2956, 2926, 2958 cm^{-1} and 2857 cm^{-1} are ascribed to the antisymmetric and symmetric C–H vibration of the aliphatic chain, respectively.⁴⁹ For $[\text{Ph}_3\text{NH}][\text{TfO}]$ and $[\text{Ph}_3\text{PH}][\text{TfO}]$, the bands at 3062, 3034 cm^{-1} and 3088, 3065, 2997 cm^{-1} are attributed to the aromatic C–H frequencies, respectively.⁵¹

Fig. 3b confirms the formation of CF_3SO_3^- anions for the as-prepared PILs. The bands at 1289, 1255, 1275, 1273, 1251 cm^{-1} and 1027, 1031, 1023, 1029 cm^{-1} are attributed to antisymmetric and symmetric SO_3 stretching of CF_3SO_3^- , respectively.^{47,48} The peaks at 1235, 1222, 1223, 1230, 1225 cm^{-1} and 1159, 1155, 1150 cm^{-1} are assigned to symmetric and antisymmetric CF_3 stretching of CF_3SO_3^- , respectively.⁴⁸ Meanwhile, the peaks at 757 and 755 cm^{-1} are due to symmetric CF_3 bending of CF_3SO_3^- .⁴⁷

For $[\text{Oct}_3\text{NH}][\text{TfO}]$ and $[\text{Oct}_3\text{PH}][\text{TfO}]$, the strong bands at 1468, 1461 cm^{-1} (stretching of aliphatic C–C bonds in a long chain) and the weak band at 1379 cm^{-1} (characteristic of methyl groups), plus the bands at 724 and 722 cm^{-1} (methylene rocking vibration), are indicative of a long-chain linear aliphatic structure.⁴⁹ For $[\text{Ph}_3\text{PH}][\text{TfO}]$ and $[\text{Ph}_3\text{NH}][\text{TfO}]$, the bands at 747, 690 and 688 cm^{-1} are associated with the out-of-plane bending of C–H bonds on mono-substituted benzene rings,⁵⁰ while the peaks at 1584, 1587, 1482, 1481, 1445, 1442 and 1437 cm^{-1} are related with benzene ring stretching.^{50,51}

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