Exploiting Hydrophobic Borohydride-Rich Ionic Liquids as Faster-Igniting Rocket Fuels

Tianlin Liu,^a Xiujuan Qi,^b Shi Huang,^a Linhai Jiang,^b Jianling Li,^c Chenglong Tang,^d and Qinghua Zhang^{*a}

Electronic Supplementary Information

^{a.} Research Center of Energetic Material Genome Science, Institute of Chemical Materials, China Academy of Engineering

Physics (CAEP) Mianyang, 621900, China. E-mail: qinghuazhang@caep.cn

^{b.} Southwest University of Science and Technology, Mianyang, 621900, China

^{c.} School of Power and Energy, Northwestern Polytechnical University Xi'an, China

^d State Key Laboratory of Multiphase Flows in Power Engineering, Xi'an Jiaotong University Xi'an, China

Table of Contents

1.	General information	S2
2.	Synthesis of hypergolic ionic liquids	S 5
3.	Hydrophobicity illustration of ionic liquids	S8
4.	Crystal structure data of salt 1	S9
5.	References	S10
6.	NMR Spectra	S11

1. General information

1) Materials

Ionic liquid precursors 1-ethyl-3-methylimidazolium chloride, 1-butyl-3-methylimidazolium chloride, 1-allyl-3-methylimidazolium bromide, 1-ethylpyridin-1-ium bromide, 1-butylpyridin-1-ium bromide, 1-allylpyridin-1-ium bromide, 1-allylpyridin-1-ium bromide, 1-butyl-1-methylpyrrolidin-1-ium bromide and 1-allyl-1-methylpyrrolidin-1-ium bromide were synthesized according to the reported methods.¹ Mercurous chloride was purchased from *Aladdin*; sodium cyanoborohydride, tetraphenylphosphonium bromide, tetrahydrofuran and 1,4-dioxane were purchased from J&K. Tetrahydrofuran was distilled from sodium/benzophenone before use. Other commercial reagents were used as received.

2) Product characterization

¹H and ¹³C NMR spectra were recorded on Bruker 600 AVANCE spectrometer (600 and 151 MHz, respectively) or Bruker 400 AVANCE spectrometer (400 and 101 MHz, respectively) with internal atandard (¹H NMR: DMSO at 2.50 ppm; ¹³C NMR: DMSO at 39.52 ppm). IR spectra were performed on PerkinElmer Spectrum Two IR Spectrometers. High resolution mass spectra were performed on Shimadzu LCMS-IT-TOF mass spectrometer using electrospray ionization (ESI). Elemental analysis was performed on Flash EA-1112 elemental analyzer. Thermal property measurements were performed on TGA/DSC1 and DSC1 Mettler Toledo calorimeter equipped with auto cool accessory. Densities were measured on a Micromeritics Accupyc II 1340 gas pycnometer at 25 °C. Viscosity measurements were performed on a Brook field Rheometer DV3T at 25 °C. Specific impulse data were calculated by Explo5 (version 6.02) software. Ignition photographs of ionic liquids with the oxidizer of 100% HNO₃ were recorded on high speed camera phaton v12.

3) Computational methods

Computational methods for anion/water interaction energy (E_{inter})

The structure of each complex and corresponding water and anion was optimized by DFT method at B3LYP/6-31+G(d,p) level of theory, using the Gaussian 09 program. The structures of complexes, water and anions were checked for vibrational frequencies to ensure that the optimized structures are minima on the potential-energy surface. The single point energy was conducted with MP2/6-311 ++g(d, p) method. Boys-Bernardi's counterpoise procedure (CP) to correct for basis set superposition error (BSSE) was used.

The anion/water interaction energy (E_{inter}), which is defined as the difference between the energy of the anion and water system (EA-W) and the sum of the energies of the anion (E_A) and water (E_W), can be calculated by:

$$E_{\text{inter}}(\text{kcal/mol}) = 627.51[E_{\text{A-W}}(\text{au}) - E_{\text{A}}(\text{au}) - E_{\text{W}}(\text{au})]$$
 (1)

Anion/Water Complex	E _{inter} (kcal/mol)
$[BH_3(CN)BH_2(CN)]$ - H_2O	- 5.1
[BH ₂ (CN) ₂] ⁻ - H ₂ O	- 6.1
[BH ₃ CN] ⁻ - H ₂ O	- 7.5
$[\mathrm{BH}_4]^-$ - $\mathrm{H}_2\mathrm{O}$	- 8.6

Table S1. The calculated E_{inter} of four borohydride-containing anions with H₂O



Fig. S1. Optimized structures of anion/water interaction

Computational methods for heats of formation

Theoretical calculations were performed by using the Gaussian 09 (Revision D.01) suite of programs.² For all of the new ionic liquids, geometric optimization and frequency analyses were completed by using the B3LYP functional with the 6-31+G** basis set.³ Single energy points were calculated at the MP2/6-311 + +G** level of theory. For all of the compounds, the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. Heats of formation (HOF, ΔH_f°) of all of the ionic liquids were calculated based on a Born–Haber energy cycle (Scheme S1).



Scheme S1. Born–Haber cycle for the formation of ionic liquids; the number of moles of the respective products are given by a–d.

For all the salts, calculation of the HOFs was simplified by using Equation (2),⁴ in which $\Delta H_{\rm L}$ is the lattice energy of the salts.

$$\Delta H_{\rm f}^{\circ} (\text{salts}, 298\text{K}) = \Sigma \Delta H_{\rm f}^{\circ} (\text{cation}, 298\text{K}) + \Sigma \Delta H_{\rm f}^{\circ} (\text{anion}, 298\text{K}) - \Delta H_{\rm L}$$
(2)

For 1:1 salts, and considering the nonlinear nature of the cations and anion used, ΔH_L (in kJ/mol) was predicted by using Equation (3), as suggested by Jenkins et al.,⁵ in which n_M and n_X depended on the nature of ions Mp^+ and Xq^- , respectively, and had a value of 6 for nonlinearpolyatomic ions.

$$\Delta H_{\rm L} = U_{\rm POT} + [p(n_M/2 - 2) + q(n_x/2 - 2)]RT \qquad (3)$$

The lattice-potential energy (U_{POT}) was calculated according to Equation (4),⁶ in which ρ_m is the density (in g/cm³) and M_m is the chemical formula mass of the ionic material.

$$U_{\rm POT} \,(\text{kJ/mol}) = 1981.2(\rho_{\rm m}/M_{\rm m})^{1/3} + 103.8$$
 (4)

$$\Delta H_{f(g)C}^{\circ} = \Delta H_{f(g)C}^{\circ} + IE_{C}$$
(5)
$$\Delta H_{f(g)A}^{\circ} = \Delta H_{f(g)A}^{\circ} + EA_{A}$$
(6)

The heats of formation (HOFs) of the salts were obtained by computing the component cations and anions. Specifically, the computation of HOFs for both the cations and anions was performed according to literature methods,⁷ that is, the gas-phase HOFs of the ions were determined by using Equations (5) and (6) (*IE*=ionization energy; *EA*=electron affinity). In Equations (5) and (6), additional calculations for the corresponding neutral molecules $(\Delta H_{f(g)}c^{\circ})$ and $\Delta H_{f(g)}A^{\circ}$ were performed for the atomization reaction $C_aH_bN_cO_dB_e \rightarrow aC(g) + bH(g) + cN(g) + dO(g) + eB(g)$ by using G2 theory. Based on the results from Equation (5), the HOFs of the cations were obtained by using isodesmic reactions (Table S2).

Cation	Isodesmic reaction
₽h₄₽	Ph_4P + 4 CH ₄ \longrightarrow [P(CH ₃) ₄] ⁺ + 4
	-N $+$ 2 NH ₃ $$ NH $+$ MeNH ₂ + EtNH ₂
	$-N$ $+$ 2 NH ₃ \rightarrow NH $+$ MeNH ₂ $+$ BuNH ₂
	-N $+$ 2 NH ₃ $ NH$ $+$ MeNH ₂ $+$ $NH2$
₩ N N	$ \begin{array}{c} & \oplus \\ & N $
₩ N N	$ \begin{array}{c} & & \\ & & $
₩ N N	$ \begin{array}{c} & \oplus \\ & N $
∕N⊕ ∕	$\bigwedge_{N \oplus} f + 2 NH_3 \longrightarrow \bigwedge_{N H_2} f + MeNH_2 + MeNH_2$
	$ \begin{array}{c} & & & & \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & $

Table S2. Isodesmic reactions for the HOFs calculation of nine cations

The enthalpy of reaction $(\Delta_r H^o{}_{298})$ is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero-point energies, and other thermal factors. As a result the heats of formation of all of the synthesized ionic liquids could be readily extracted. By using the calculated heats of formation and the experimentally measured densities, the specific impulses of these new hypergolic ionic liquids were calculated by using Explo5 v6.02.

 Table S3. Enthalpies of the gas-phase species of cations and anions (based on G2 method)

ions	$\Delta H_{ m f^0}$ (KJ/mol)
[P(CH ₃) ₄] ⁺	242.04
NH	726.96
₩ NH	756.36
$\bigvee_{NH_2}^{\oplus}$	581.24

[BH ₃ (CN)BH ₂ (CN)] ⁻ -141.71		
	[BH ₃ (CN)BH ₂ (CN)] ⁻	-141.71

Cation	E(MP2)	ZPE	ТСН	⊿H _{corr}	$\Delta H_{\rm f}^{\rm o}({\rm KJ/mol})$
Ph₄P	-1264.686318	0.367136	0.38894	-1264.31	711.39
	-343.6051448	0.169083	0.178439	-343.43	628.55
	-421.9984838	0.225936	0.238037	-421.77	585.78
	-381.5792238	0.173897	0.184048	-381.4	747.87
	-326.3734973	0.158887	0.167084	-326.21	682.99
₩ N	-404.7674757	0.215665	0.226629	-404.55	638.41
	-364.3473644	0.163695	0.172677	-364.18	802.83
∕N⊕ ́	-408.3446866	0.285905	0.29852	-408.06	444.86
∕_N⊕	-367.9265079	0.233941	0.244535	-367.69	604.12

Table S4. Enthalpies of the gas-phase species of cations based on isodesmic reactions.

Table S5. The calculated enthalpies of nine new ionic liquids.

HILs	$\Delta H_{\text{cation}}(\text{kJ/mol})$	$\Delta H_{\rm anion}({\rm kJ/mol})$	U _{pot} (kJ/mol)	$\Delta H_{\rm Lat}({\rm kJ/mol})$	$\Delta H_{\rm salt}({\rm kJ/mol})$
1	711.39	-141.71	382.26	387.22	182.46
2	628.5512	-141.71	439.70	444.66	42.18
3	585.7828	-141.71	423.15	428.11	15.97
4	747.872	-141.71	433.95	438.91	167.25
5	682.9898	-141.71	442.45	447.41	93.88
6	638.4115	-141.71	425.39	430.35	66.36
7	802.8257	-141.71	436.36	441.32	219.80
8	444.8636	-141.71	418.52	423.48	-120.32
9	604.1165	-141.71	428.34	433.30	29.11

2. Synthesis of hypergolic ionic liquids

1) Synthesis of Na[BH₃(CN)BH₂(CN)].

NaBH₃CN $\xrightarrow{Hg_2Cl_2, THF}$ Na[BH₃(CN)BH₂(CN)] 1,4-dioxane complex 1,4-dioxane

To a 500 mL flask was added 5.03 g NaBH₃CN (80 mmol) and dry THF (300 mL), and the mixture was cooled to 0 °C. 12.74 g Hg₂Cl₂ (27.0 mmol) was added portion-wise until the evolution of hydrogen was complete. A grey, mercury-containing slurry was formed, which was then allowed to settle out, leaving a clear supernatant liquid. This clear liquid was decanted of and evaporated to give a viscous liquid. Addition of 1,4-dioxane to the viscous liquid gave a white

precipitate. After being filtered, washed with 1,4-dioxane and dried at room temperature under vacuum, 6.89 g (62%) white powder was obtained, which was identified as a complex of Na[BH₃(CN)BH₂(CN)] \cdot 2C₄H₈O₂ by ¹H-NMR spectrum. ¹H-NMR (600 MHz, DMSO-d6): δ 3.57 (s, 16H), 2.28 – 1.38 (m, 2H), 0.85 – 0.05 (m, 3H); Anal. calcd for C₁₀H₂₁B₂N₂NaO₄: C 43.22, H 7.62, N 10.08; found: C 43.46, H 7.69, N 9.95.

2) Synthesis of cyano-bridged borohydride-rich hypergolic ionic liquids.



Scheme S2. Synthesis of new cyano-bridged borohydride-rich hypergolic ionic liquids

Synthesis of salt 1

To a 100 mL flask was added 4.19 g Ph₄PBr (10 mmol, 1.0 eq.) and 40 mL acetonitrile, and then 2.92 g Na[BH₃(CN)BH₂(CN)]·2C₄H₆O₂ (10.5 mmol, 1.05 eq.) was added subsequently into the solution. The resulting suspension solution was stirred at room temperature for 4 days. After filtration, acetonitrile was removed under vacuum. The resulting crude product was dissolved in dichloromethane (50 mL), washed with water, dried over magnesium sulphate and concentrated under reduced pressure. The ionic liquid **1** was obtained as a white solid. Yield 82%; ¹H-NMR (600 MHz, DMSO-d6): δ 7.99 – 7.95 (m, 4H), 7.85 – 7.74 (m, 16H), 2.30 – 1.37 (m, 2H), 0.77 – 0.14 (m, 3H); ¹³C-NMR (151 MHz, DMSO-d6): δ 135.8 (d, J = 2.7, 4C) 135.1(d, J = 10.5, 8C) 130.9 (d, J = 12.8, 8C) 118.2 (d, J = 88.7, 4C) ⁸; IR (KBr, cm⁻¹): 526, 689, 756, 995, 1108, 1314, 1437, 1482, 1584, 2254, 2357, 2403, 3061, 3070; HRMS (ESI) m/z: cation [M]⁺ calcd for C₂₄H₂₀P, 339.1297; found, 339.1297; anion [M]⁻ calcd for C₂H₅B₂N₂, 79.0644; found, 79.0660; Anal. calcd for C₂₆H₂₅B₂N₂P: C 74.69, H 6.03, N 6.70; found: C 74.35, H 6.11, N 6.50.

Synthesis of HILs 2-9

The same procedure as that described above for the synthesis and purification of ionic liquid **1** was used for the syntheses of other HILs **2-9**, except different ionic liquid precursors (1-ethyl-3-methylimidazolium chloride (1.47 g, 10 mmol, for **2**), (1-butyl-3-methylimidazolium chloride (1.75 g, 10 mmol, for **3**), (1-allyl-3-methylimidazolium bromide (2.03 g, 10 mmol, for **4**), 1-ethylpyridin-1-ium bromide (1.88 g, 10 mmol, for **5**), 1-butylpyridin-1-ium bromide (2.16 g, 10 mmol, for **6**), 1-allylpyridin-1-ium bromide (2.00 g, 10 mmol, for **7**), 1-butyl-1-methylpyrrolidin-1-ium bromide (2.22 g, 10 mmol, for **8**), 1-allyl-1-methylpyrrolidin-1-ium bromide (2.05 g, 10 mmol, for **9**) was used instead of tetraphenylphosphonium bromide (4.19 g, 10 mmol). The hypergolic ionic liquid **2-9** was obtained as colorless or light yellow liquid.



HIL 2 : colorless liquid, 83% yield; ¹H-NMR (600 MHz, DMSOd6): δ 9.10 (s, 1H), 7.80 – 7.52 (m, 2H), 4.19 (q, J = 7.3 Hz, 2H), 3.84 (s, 3H), 2.13 – 1.48 (m, 2H), 1.42 (t, J = 7.3 Hz, 3H), 0.70 – 0.14 (m, 3H); ¹³C-NMR (151 MHz, DMSO-d6): δ 136.66, 123.97, 122.35, 44.68, 36.15, 15.42; IR (KBr, cm⁻¹): 621, 744, 831, 1106, 1168, 1571, 2211, 2256, 2362, 2401, 2990, 3119, 3156; HRMS (ESI) m/z: cation [M]⁺ calcd for C₆H₁₁N₂, 111.0917; found, 111.0915; anion [M]⁻ calcd for C₂H₅B₂N₂, 79.0660; found: 79.0644; Anal. calcd for C₈H₁₆B₂N₄: C 50.61, H 8.49, N 29.51; found: C 50.22, H 8.55, N 29.15.



HIL **3** : colorless liquid, 79% yield; ¹H-NMR (600 MHz, DMSOd6): δ 9.10 (s, 1H), 7.87 – 7.53 (m, 2H), 4.16 (t, J = 7.2 Hz, 2H), 3.85 (s, 3H), 2.09 – 1.49 (m, 4H), 1.30 – 1.24 (m, 2H), 0.91 (t, J =7.4 Hz, 3H), 0.72 – 0.11 (m, 3H); ¹³C-NMR (151 MHz, DMSOd6): δ 136.97, 124.08, 122.72, 48.99, 36.22, 31.87, 19.24, 13.81;

IR (KBr, cm⁻¹): 622, 747, 831, 1106, 1156, 1464, 1570, 2256, 2358, 2399, 2976, 2937, 2964, 3116, 3153; HRMS (ESI) m/z cation $[M]^+$ calcd for $C_8H_{15}N_2$, 139.1230; found: 139.1230; anion $[M]^-$ calcd for $C_2H_5B_2N_2$, 79.0644; found: 79.0660; Anal. calcd for $C_{10}H_{20}B_2N_4$: C 55.12, H 9.25, N 25.71; found: C 54.78, H 9.35, N 25.45.



HIL 4 : colorless liquid, 80% yield; ¹H-NMR (600 MHz, DMSOd6):δ 9.09 (s, 1H), 7.75 – 7.59 (m, 2H), 6.13 – 5.94 (m, 1H), 5.39 – 5.35 (m, 1H), 5.30 (d, J = 17.1 Hz, 1H), 4.83 (d, J = 6.0 Hz, 2H), 3.86 (s, 3H), 2.13 – 1.41 (m, 2H), 0.71 – 0.16 (m, 3H); ¹³C-NMR (151 MHz, DMSO-d6): δ 137.09, 124.23, 122.78, 120.72,

51.32, 36.29; IR (KBr, cm⁻¹): 623, 748, 832, 945, 992, 1106, 1165, 1424, 1449, 1571, 2211, 2256, 2351, 2397, 3117, 3153; HRMS (ESI) m/z: cation $[M]^+$ calcd for $C_7H_{11}N_2$, 123.0917; found, 123.0922; anion $[M]^-$ calcd for $C_2H_5B_2N_2$, 79.0644; found, 79.0660; Anal. calcd for $C_9H_{16}B_2N_4$: C 53.55, H 7.99, N 27.75; found: C 53.20, H 8.08, N 27.55.



HIL 5 : light yellow liquid, 84% yield; ¹H-NMR (400 MHz, DMSO-d6): δ 9.09 (d, J = 6.4 Hz, 2H), 8.59 (t, J = 7.8 Hz, 1H), 8.25 - 8.05 (m, 2H), 4.63 (q, J = 7.3 Hz, 2H), 1.54 (t, J = 7.3 Hz, 5H), 0.84 - 0.05 (m, 3H).; ¹³C-NMR (101 MHz, DMSO-d6): δ 145.84, 144.98, 128.55, 56.88, 16.76; IR (KBr, cm⁻¹): 631, 681,

775, 1107, 1174, 1488, 1635, 2211, 2256, 2350, 2400, 2987, 3071, 3090, 3134; HRMS (ESI) m/z: cation $[M]^+$ calcd for $C_7H_{10}N$, 108.0808; found, 108.0803; anion $[M]^-$ calcd for $C_2H_5B_2N_2$, 79.0644; found: 79.0660; Anal. calcd for $C_9H_{15}B_2N_3$: C 57.85, H 8.09, N 22.49; found: C 57.45, H 8.21, N 22.13.



HIL 6 : light yellow liquid, 78% yield; ¹H-NMR (600 MHz, DMSO-d6): δ 9.09 (d, J = 6.1 Hz, 2H), 8.60 (t, J = 7.4 Hz, 1H), 8.27 - 8.05 (m, 2H), 4.61 (t, J = 7.5 Hz, 2H), 2.06 - 1.55 (m, 4H), 1.34 - 1.27 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H), 0.70 - 0.18 (m, 3H); ¹³C-NMR (151 MHz, DMSO-d6): δ 145.84, 145.16, 128.55, 61.17,

33.15, 19.24, 13.67; IR (KBr, cm⁻¹): 630, 682, 768, 1106, 1171, 1466, 1488, 1501, 1635, 2210, 2254, 2362, 2400, 2877, 2937, 2966, 3068, 3088, 3132; HRMS (ESI) m/z: $[M]^+$ cation calcd for C₉H₁₄N, 136.1121; found, 136.1118; anion $[M]^-$ calcd for C₂H₅B₂N₂, 79.0644; found: 79.0660; Anal. calcd for C₁₁H₁₉B₂N₃: C 61.48, H 8.91, N 19.55; found: 61.01, H 9.01, N 19.35.



HIL 7 : light yellow liquid, 83% yield; ¹H-NMR (600 MHz, DMSO-d6): δ 9.03 (d, J = 6.0 Hz, 2H), 8.62 (d, J = 6.4 Hz, 1H), 8.21 - 8.07 (m, 2H), 6.23 - 6.08 (m, 1H), 5.47 - 5.37 (m, 2H), 5.27 (d, J = 6.2 Hz, 2H), 2.06 - 1.53 (m, 2H), 0.70 - 0.16 (m, 3H); ¹³C-NMR (151 MHz, DMSO-d6): δ 146.30, 145.25, 131.87, 128.70,

122.49, 62.99; IR (KBr, cm⁻¹): 630, 684, 757, 953, 992, 1106, 1163, 1487, 1633, 2210, 2254,

2359, 2395, 2988, 3067, 3087, 3130; HRMS (ESI) m/z: $[M]^+$ cation calcd for $C_8H_{10}N$, 120.0808; found, 120.0803; anion $[M]^-$ calcd for $C_2H_5B_2N_2$, 79.0644; found, 79.0660; Anal. calcd for $C_{10}H_{15}B_2N_3$: C 60.40, H 7.60, N 21.13; found: 60.12, H 7.71, N 20.95.



HIL 8 : light yellow liquid, 80% yield; ¹H-NMR (600 MHz, DMSO-d6): δ 3.50 – 3.38 (m, 4H), 3.32 – 3.26 (m, 2H), 2.98 (s, 3H), 2.16 – 1.53 (m, 8H), 1.36 – 1.29 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H), 0.80 – 0.07 (m, 3H); ¹³C-NMR (151 MHz, DMSO-d6): δ 63.98, 63.52, 48.07, 25.42, 21.58, 19.77, 13.81; IR (KBr, cm⁻¹):

629, 928, 827, 1003, 1106, 1165, 1466, 2211, 2254, 2359, 2382, 2878, 2967; HRMS (ESI) m/z: $[M]^+$ cation calcd for C₉H₂₀N, 142.1590; found, 142.1591; anion $[M]^-$ calcd for C₂H₅B₂N₂, 79.0644; found, 79.0660; Anal. calcd for C₁₁H₂₅B₂N₃: C 59.79, H 11.40, N 19.02; found: 59.59, H 11.49, N 18.88.



HIL 9 : colorless liquid, 78% yield; ¹H-NMR (600 MHz, DMSOd6): δ 7.75 – 7.59 (m, 2H), 6.13 – 5.94 (m, 1H), 5.39 – 5.35 (m, 1H), 5.30 (d, J = 17.1 Hz, 1H), 4.83 (d, J = 6.0 Hz, 2H), 3.86 (s, 3H), 2.13 – 1.41 (m, 2H), 0.71 – 0.16 (m, 3H); ¹³C-NMR (151 MHz, DMSO-d6): δ 137.09, 124.23, 122.78, 120.72, 51.32, 36.29;

IR (KBr, cm⁻¹): 623, 748, 832, 945, 992, 1106, 1165, 1424, 1449, 1571, 2211, 2256, 2351, 2397, 3117, 3153; HRMS (ESI) m/z cation $[M]^+$ calcd for $C_8H_{16}N$, 126.1277; found, 126.1272; anion $[M]^-$ calcd for $C_2H_5B_2N_2$, 79.0644; found, 79.0660; Anal. Calcd for $C_{10}H_{21}B_2N_3$: C 58.61, H 10.33, N 20.51; found: 58.31, H 10.41, N 20.35.

3. Hydrophobicity illustration of ionic liquid 9

All the obtained HILs (1-9) showed the characteristic of water miscibility. Take HIL 9 as an example, when HIL 9 is mixed with water, a clear two-layer interface can be readily formed. Fig. S2 illustrated this two-layer formation picture. Due to the slightly lower density, the ionic liquid 9 always floats in the water, which exhibits the good hydrophobicity.



Fig. S2. Hydrophobicity illustration of HIL 9 with H_2O

4. Crystal structure data of salt 1

Single crystal X-ray diffraction data was collected on an Oxford X calibur diffratometer with Mo KR monochromated radiation (λ =0.71073 Å) at room temperature. The crystal structures were solved by direct methods. The structures were refined on F2 by full-matrix least-squares methods using the SHELXTL program package.⁹ All non-hydrogen atoms were refined anisotropoically.

CCDC	1424782
Formula	C ₂₆ H ₂₅ N ₂ PB ₂
Mr	418.07
crystal system	Monoclinic
space group	$P2_1/c$
<i>a</i> [Å]	9.8180(6)
<i>b</i> [Å]	18.2883(13)
<i>c</i> [Å]	13.7042(7)
α [Å]	90.00
β [Å]	97.628(5)
γ [Å]	90.00
<i>V</i> [Å ³]	2438.9(3)
Ζ	4
<i>T</i> [K]	293
$\rho_{calcd} [Mg \cdot m^{-3}]$	1.139
M [mm ⁻¹]	0.127
F(000)	880
heta [°]	3.423 to 26.371
index range	$-13 \le h \le 13$
	$-24 \leq k \leq 24$
	$-12 \le 1 \le 12$
reflections collected	14613
independent reflections (R_{int})	4973
data/restraints/paraneters	4973/0/281
GOF on F ²	0.982
$R_1 [I \ge 2\sigma(I)]$	0.0725
<i>wR</i> ₂ [Ι>2σ(Ι)]	0.1369
$R_1(\text{all data})$	0.1777
$wR_2(all data)$	0.2096
largest diff. peak and hole [e Å ⁻³]	0.313 and -0.173

Table S6. crystallographic data for ionic salt 1

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5. References

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6. NMR Spectra

7.98 7.97 7.77 7.77 7.77 7.75 7.75	-3.33	-2.50	-1.92 -1.72	∠0.68 _0.54 _0.38 _0.23



¹H-NMR spectrum of ionic salt 1



¹³C-NMR spectrum of ionic salt 1

-9.10 -9.10 7.75 7.75 7.74 7.0207.020



¹³C-NMR spectrum of ionic liquid **2**

-9.104.17 4.16 4.15 3.85 7.75 7.73 7.72 7.68 7.67 -2.50 ⊖ BH₃CNBH₂CN 111 20- 0.0 2.03 Å F00. -96. 2.02≠ 3.04≠ 5.0 4.5 4.0 3.5 3.0 2.5 2.0 f1 (ppm) 10.5 10.0 9.5 9.0 6.0 5.5 8.5 8.0 7.5 7.0 6.5 ¹H-NMR spectrum of ionic liquid **3** -137.0~124.1 ~122.7 -49.0-36.2 -31.9 -19.2 -13.8 ⊖ BH₃CNBH₂CN 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 f1 (ppm)















$\begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & \begin{array}{c} & 0.04 \\ & 0.03 \\ & 0.04 \\ & 0.$



155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 f1 (ppm)

¹³C-NMR spectrum of ionic liquid 7

$\begin{array}{c} 3.48\\ 3.47\\ 3.46\\ 3.42\\ 3.41\\ 3.42\\ 3.33\\ 3.31\\ 3.29\\ 3.32\\ 3.32\\ 3.32\\ 3.32\\ 3.32\\ 0.32\\ 0.32\\ 0.93\\ 0.93\\ 0.93\\ 0.93\\ 0.37\\ 0.032\\ 0.037\\ 0.032\\ 0.032\\ 0.037\\ 0.$



¹³C-NMR spectrum of ionic liquid 8



