Electronic Supplementary Information (ESI)

Supramolecular gelator based on benzenetricarboxamide for ionic liquids

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Abbreviations of the ionic liquids

[EtMeIm][TFSA]: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide.

[BuMeIm][TFSA]: 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide.

[HeMeIm][TFSA]: 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide.

[BuPy][TFSA]: 1-butylpyridinium bis(trifluoromethylsulfonyl)amide.

[TMPA][TFSA]: trimethylpropylammonium bis(trifluoromethylsulfonyl)amide.

[EtMeIm][CF_3SO_3]: 1-ethyl-3-methylimidazolium trifluoromethanesulfonate.

[BuMeIm][CF_3SO_3]: 1-butyl-3-methylimidazolium trifluoromethanesulfonate.

[BuMeIm][BF_4]: 1-butyl-3-methylimidazolium tetrafluoroborate.

[EtMeIm][BF_4]: 1-ethyl-3-methylimidazolium tetrafluoroborate.

[BuMeIm][PF_6]: 1-butyl-3-methylimidazolium hexafluorophosphate.

[Emim][Phe]: 1-ethyl-3-methylimidazolium α-aminohydrocinnamic acid salt.

Synthesis of gelator 1'. A solution of gelator **1** (2.14 mmol) in methanol (30 mL) was cooled to 0 °C and a NaOH aqueous solution (15 mL, 2 M) was added. The mixture was brought back to the room temperature and stirred for 22 h. A white precipitate was collected by filtration and

dissolved in diluted water (50 mL). A HCl aqueous solution (1 M) was added until the pH became below 3. After left for 5 h, a white precipitate was collected by centrifugation and dried in vacuo to obtain gelator **1'**.

Synthesis of gelator 3'. To a solution of gelator **3** (2.98 mmol) in a mixture of THF (200 mL) and diluted water (2 mL), a NaOH aqueous solution (65 mL, 2 M) was added and stirred for 30 h. The pH was adjusted to 5~6 by adding a HCl aqueous solution (2 M) and the solvent were evaporated to obtain white powder. The powder was dissolved in a NaOH aqueous solution (2 M) and the pH was adjusted to 4~5 by adding a HCl aqueous solution (2 M). A white precipitate was collected by filtration and dried in vacuo to obtain gelator **3'**.

Synthesis of gelator 4'. A solution of gelator **4** (1.69 mmol) in methanol (50 mL) was cooled to 0°C and a NaOH aqueous solution (20 mL, 2 M) was added. The mixture was brought back to the room temperature and stirred for 22 h. Water (50 mL) and a HCl aqueous solution (2 M) were added until the pH became below 3. After left for 2 h, a white precipitate was collected by centrifugation and dried in vacuo to obtain gelator **4'**.

Synthesis of gelator 5'. To a solution of gelator **5** (2.80 mmol) in mixture of 1,4-dioxane (100 mL) and diluted water (1 mL), a NaOH aqueous solution (25 mL, 2 M) was added and stirred for 30 h. The pH was adjusted to 5~6 by adding a HCl aqueous solution (2 M) and the solvent were evaporated to obtain white powder. The powder was dissolved in a NaOH aqueous solution (2 M) and the pH was adjusted to 4~5 by adding a HCl aqueous solution (2 M). A white precipitate was collected by filtration and dried in vacuo to obtain gelator **5'**.

Synthesis of gelator 6'. A solution of gelator **6** (3.69 mmol) in methanol (100 mL) was cooled to 0 °C and a NaOH aqueous solution (30 mL, 2 M) was added. The mixture was brought back to the room temperature and stirred for 22 h. Diluted water (100 mL) and a HCl aqueous solution

(2M) were added until the pH became below 3. After left for 4 h, the white precipitate was collected by centrifugation and dried in vacuo to obtain gelator **6'**.

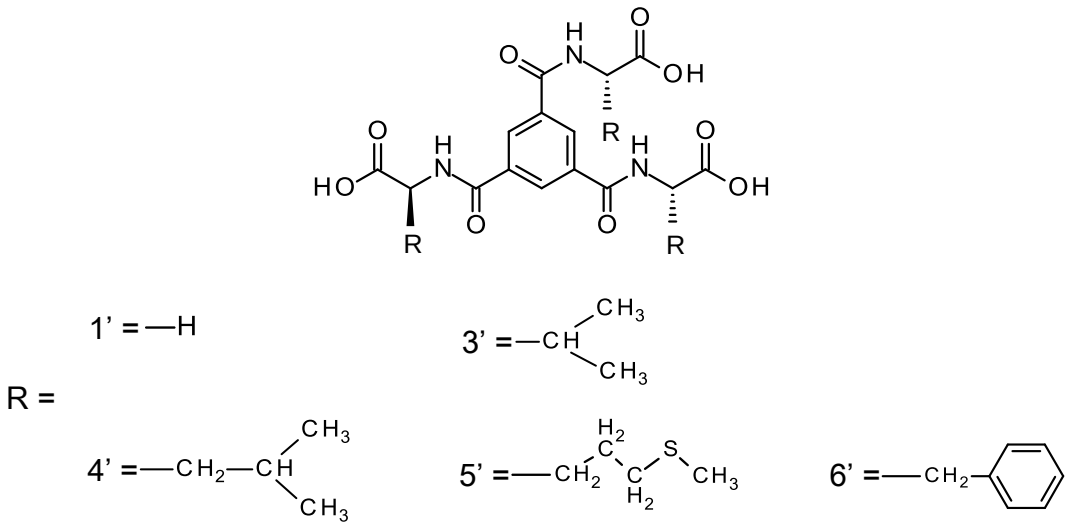

Chart S1. Molecular structures of gelators 1', 3'−6'.

Table S1. Gelation properties of gelators **1'** and **3'**–**6'** for ionic liquids, aqueous solutions, and organic solvents.

Solvent	Gelator				
	1' Gly	**3'** L-Val	**4'** L-Leu	**5'** L-Met	**6'** L-Phe
[EtMeIm][TFSA]	I	I	I	I	I
[BuMeIm][TFSA]	I	I	I	vS	I
[HeMeIm][TFSA]	I	I	I	I	I
[BuPy][TFSA]	I	I	I	I	I
[TMPA][TFSA]	I	I	I	P	I
[EtMeIm][CF_3SO_3]	S	I	I	I	S
[BuMeIm][CF_3SO_3]	I	I	I	vS	S
[EtMeIm][BF_4]	S	I	I	S	S
[BuMeIm][BF_4]	S	I	I	S	S
[BuMeIm][PF_6]	I	I	I	vS	I
[EtMeLm][Phe]	S	S	S	S	S
Deionized water	P	I	I	PG	I
HCl (aq., 0.1 M)	P	I	I	PG	I
Phosphate buffer (0.1 M, pH 7)	S	PG	S	I	I
NaCl (aq., 0.1 M)	S	S	S	S	S
Ethanol	G(2.0)	P	S	G(2.0)	S
1-Propanol	G(2.0)	I	I	S	S
Toluene	I	I	I	I	I
Ethyl acetate	I	I	I	S	I
Acetonitrile	I	I	I	S	I

G, PG, vS, P, S, and I denote gel, partial gel, viscous solution, precipitation, soluble, and insoluble, respectively; the critical gelation concentration [wt%] is given by the number in parentheses.

Characterization

Gelator **1**. Yield: 50 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 9.26(m, 1H), 8.51(t, 1H), 4.06(m, 2H), 3.67(t, 3H); IR (ATR) 3255 cm^{-1} (νN-H, amide A), 1754 cm^{-1} (νC=O, ester), 1646 cm^{-1} (νC=O, amide I), 1559 cm-1 (σN-H, amide II), ESI-MS: $[M+Na]^+$ calcd for $C_{18}H_{21}N_3NaO_9$: 446.12; found 446.0; Elemental analysis: calcd for $C_{18}H_{21}O_9N_3$: C, 51.06; H, 5.0; N, 9.93; found: C, 50.89; H, 4.89; N, 9.77.

Gelator **2**. Yield: 91 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 9.14(m, 1H), 8.50(s, 1H), 4.52(m, 1H), 3.66(s, 3H), 1.43(d, 3H); IR (ATR) 3242 cm^{-1} (νN-H, amide A), 3075 cm^{-1} (νC-H, aromatic), 1748 cm^{-1} (νC=O, ester), 1641 cm^{-1} (νC=O, amide I), 1558 cm-1 (σN-H, amide II), ESI-MS: $[M+Na]^+$ calcd for $C_{21}H_{28}N_3NaO_9$: 488.16; found: 487.96; Elemental analysis: calcd for $C_{21}H_{28}O_9N_3$: C, 54.19; H, 5.85; N, 9.03; found: C, 53.92; H, 5.62; N, 8.91.

Gelator **3**. Yield: 91 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 8.98(d, 1H), 8.43(s, 1H), 4.33(t, 1H), 3.67(s, 3H), 2.20(m, 1H), 1.01(d, 3H), 0.96(d, 3H); IR (ATR) 3238 cm^{-1} (νN-H, amide A), 3062 cm^{-1} (νC-H, aromatic), 1755 cm^{-1} (νC=O, ester), 1643 cm^{-1} (νC=O, amide I), 1555 cm-1 (σN-H, amide II), ESI-MS: $[M+Na]^+$ calcd for $C_{27}H_{39}N_3NaO_9$: 572.26; found: 572.03 ; Elemental analysis: calcd for $C_{27}H_{39}O_9N_3$: C, 59.00; H, 7.15; N, 7.65; found: C, 58.96; H, 6.97; N, 7.59.

Gelator **4**. Yield: 97 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 9.10(d, 1H), 8.49(s, 1H), 4.54(m, 1H), 3.66(s, 1H), 1.81(m, 1H), 1.72(m, 1H), 1.59(m, 1H), 0.94(d, 3H), 0.90(d, 3H); IR (ATR) 3252 cm^{-1} (νN-H, amide A), 3075 cm^{-1} (νC-H, aromatic), 1747 cm^{-1} (νC=O, ester), 1640 cm^{-1} (νC=O, amide I), 1554 cm-1 (σN-H, amide II), ESI-MS: $[M+Na]^+$ calcd for $C_{30}H_{45}N_3NaO_9$:

614.31; found: 614.07; Elemental analysis: calcd for $C_{30}H_{45}O_9N_3$: C, 60.90; H, 7.67; N, 7.10; found: C, 60.84; H, 7.41; N, 7.08.

Gelator **5**. Yield: 82 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 9.16(d, 1H), 8.51(s, 1H), 4.63(m, 1H), 3.67(s, 3H), 2.58(m, 2H), 2.07(m, 5H); IR (ATR) 3238 cm^{-1} (νN-H, amide A), 3072 cm^{-1} (νC-H, aromatic), 1747 cm^{-1} (νC=O, ester), 1640 cm^{-1} (νC=O, amide I), 1554 cm^{-1} (σN-H, amide II), ESI-MS: $[M+Na]^+$ calcd for $C_{27}H_{39}N_3NaO_9S_3$: 668.17; found: 667.92; Elemental analysis: calcd for $C_{27}H_{39}O_9N_3S_3$: C, 50.21; H, 6.09; N, 6.51; found: C, 50.17; H, 5.79; N, 6.47.

Gelator **6**. Yield: 84 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 9.18(m, 1H), 8.36(t, 1H), 7.28(m, 5H), 4.70(m, 1H), 3.64(m, 3H) 3.33(t, 1H), 3.15(m, 1H); IR (ATR) 3259 cm^{-1} (νN-H, amide A), 3073 cm^{-1} (νC-H, aromatic), 1746 cm^{-1} (νC=O, ester), 1640 cm^{-1} (νC=O, amide I), 1554 cm-1 (σN-H, amide II), ESI-MS: $[M+Na]^+$ calcd for $C_{39}H_{39}N_3NaO_9$: 716.26; found: 716.01; Elemental analysis: calcd for $C_{39}H_{39}O_9N_3$: C, 67.52; H, 5.67; N, 6.06; found: C, 67.34; H, 5.59; N, 6.11.

Compound **A**. Yield: 58 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 8.90(d, 1H), 8.47(s, 1H), 4.50(m, 1H), 1.80(m, 3H), 1.72(m, 1H), 1.61(m, 1H), 0.93(d, 3H), 0.90(d, 3H); IR (ATR) 2955 cm^{-1} (νN-H), 1734 cm^{-1} (νC=O, ester), 1457 cm-1 (σN-H), ESI-MS: $[M^+]$ calcd for $C_{30}H_{51}O_6N_3$: 549.38; found 550.16.

Gelator **1'**. Yield: 27 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ9.26(m, 1H), 8.51(t, 1H), 4.06(m, 2H), 3.67(t, 3H); IR (ATR) 3380 cm^{-1} (νN-H, amide A), 3200-2900 cm^{-1} (νO-H, carboxylic acid), 1737 cm^{-1} (νC=O, carboxylic acid), 1643 cm^{-1} (νC=O, amide I), 1539 cm-1 (σN-H, amide II), ESI-MS: $[M+Na]^+$ calcd for $C_{15}H_{15}N_3NaO_9$: 404.3; found 404.0.

Gelator **3'**. Yield: 58 %. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 12.7(s, 1H), 8.78(d, 1H), 8.40(s, 1H), 4.32(t, 1H), 2.21(m, 1H), 0.99(t, 6H); IR (ATR) 3235 cm^{-1} (νN-H, amide A), 3200-2800 cm^{-1} (νO-H, carboxylic acid), 1717 cm^{-1} (νC=O, carboxylic acid), 1636 cm^{-1} (νC=O, amide I), 1550 cm-1 (σN-H, amide II), MALDI-TOF MS: $[M]^+$ calcd for $C_{24}H_{33}O_9N_3$: 507.5; found: 508.9.

Gelator **4'**. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 8.90(s, 1H), 8.45(s, 1H), 4.50(s, 1H), 1.74(m, 2H), 1.60(m, 1H), 0.91(d, 6H); IR (ATR) 3298 cm^{-1} (νN-H, amide A), 3250-3000 cm^{-1} (νO-H, carboxylic acid), 1724 cm^{-1} (νC=O, carboxylic acid), 1647 cm^{-1} (νC=O, amide I), 1546 cm-1 (σN-H, amide II), MALDI-TOF MS: $[M]^+$ calcd for $C_{27}H_{39}O_9N_3$: 549.6; found 550.8.

Gelator **5'**. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 12.8(s, 1H), 9.00(d, 1H), 8.48(s, 1H), 4.56(m, 1H), 2.57(m, 2H), 2.07(m, 5H); IR (ATR) 3235 cm^{-1} (νN-H, amide A), 3200-2900 cm^{-1} (νO-H, carboxylic acid), 1745 cm^{-1} (νC=O, carboxylic acid), 1642 cm^{-1} (νC=O, amide I), 1537 cm-1 (σN-H, amide II), MALDI-TOF MS: $[M]^+$ calcd for $C_{24}H_{33}O_9N_3S_3$: 603.7; found 604.6.

Gelator **6'**. ^{1}H NMR: (500MHz, DMSO-d_6, TMS) δ 12.8(s, 1H), 8.98(m, 1H), 8.31(m, 1H), 7.29(m, 5H), 4.65(m, 1H), 3.20(m, 1H), 3.08(m, 1H); IR (ATR) 3335 cm^{-1} (νN-H, amide A), 3200-2900 cm^{-1} (νO-H, carboxylic acid), 1737 cm^{-1} (νC=O, carboxylic acid), 1644 cm^{-1} (νC=O, amide I), 1537 cm-1 (σN-H, amide II), MALDI-TOF MS: $[M]^+$ calcd for $C_{36}H_{33}O_9N_3$: 651.7; found 652.7.