Supplementary Materials for

Switchable oil-water phase separation of ionic liquids based microemulsions by CO₂

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References
Experimental Section

1. NMR and IR data of the ILs

![Diagram of ILs with numbering of carbon atoms]

Numbering of the position of carbon atoms in the anions and cations of the ILs

[C₈DMEA][Im]: ¹H NMR (D₂O, TMS): δ 0.75 (t, 3H, CH₃), 1.24 (m, 13H, CH₂ and CH₃), 1.62 (m, 2H, CH₂), 2.89 (s, 6H, CH₃), 3.11 (t, 2H, CH₂), 3.24 (m, 2H, CH₂), 7.02 (s, 2H, Im C4 and C5), 7.64 (s, 1H, Im C2) ppm; ¹³C NMR (D₂O, TMS): δ 7.35 (C6), 13.47 (C16), 21.69 (C15), 22.01 (C10), 25.48 (C11), 28.18 (C12), 28.22 (C13), 31.02 (C14), 49.75 (C8), 49.80 (C8), 59.32 (C7), 63.36 (C9), 122.50 (C4), 122.55 (C5), 137.69 (C2) ppm; IR: ν 3070, 2955, 2925, 2856, 1707, 1634, 1446, 1378, 1289, 1215, 1150, 1076, 1022, 979, 920, 820, 757, 724 cm⁻¹.

[C₁₀DMEA][Im]: ¹H NMR (D₂O, TMS): δ 0.76 (t, 3H, CH₃), 1.19 (m, 17H, CH₂ and CH₃), 1.63 (m, 2H, CH₂), 2.91 (s, 6H, CH₃), 3.12 (t, 2H, CH₂), 3.25 (m, 2H, CH₂), 7.03 (s, 2H, Im C4 and C5), 7.66 (s, 1H, Im C2) ppm; ¹³C NMR (D₂O, TMS): δ 7.39 (C6), 13.77 (C18), 21.90 (C17), 22.43 (C10), 25.80 (C11), 28.68 (C12), 29.03 (C15), 29.09 (C13), 29.18 (C14), 31.65 (C16), 49.85 (C8), 49.85 (C8), 59.24 (C7), 63.11 (C9), 122.49 (C4), 122.54 (C5), 137.96 (C2) ppm; IR: ν 3152, 2923, 2854, 1577, 1467, 1381, 1323, 1024, 900, 870, 817, 721 cm⁻¹.
[C_{12}DMEA][Im]: ¹H NMR (D₂O, TMS): δ 0.81 (t, 3H, CH₃), 1.21 (m, 21H, CH₂ and CH₃), 1.48 (m, 2H, CH₂), 2.79 (m, 6H, CH₃), 2.94 (t, 2H, CH₂), 3.11 (m, 2H, CH₂), 6.93 (s, 2H, Im C4 and C5), 7.57 (s, 1H, Im C2) ppm; ¹³C NMR (D₂O, TMS): δ 7.39 (C6), 13.88 (C20), 22.00 (C19), 22.62 (C10), 25.99 (C11), 28.98 (C12), 29.40 (C17), 29.45 (C13), 29.58 (C14), 29.70 (C15), 29.73 (C16), 31.92 (C18), 48.83 (C8), 48.83 (C8), 59.14 (C7), 62.93 (C9), 122.53 (C4 and C5), 138.11 (C2) ppm; IR: v 3100, 2923, 2854, 1635, 1579, 1467, 1381, 1323, 1294, 1248, 1092, 1024, 977, 909, 818, 743 cm⁻¹.

[C_{14}DMEA][Im]: ¹H NMR (D₂O, TMS): δ 0.81 (t, 3H, CH₃), 1.23 (m, 25H, CH₂ and CH₃), 1.51 (m, 2H, CH₂), 2.83 (s, 6H, CH₃), 2.97 (t, 2H, CH₂), 3.13 (m, 2H, CH₂), 6.96 (s, 2H, Im C4 and C5), 7.60 (s, 1H, Im C2) ppm; ¹³C NMR (D₂O, TMS): δ 7.42 (C6), 13.88 (C22), 22.01 (C21), 22.63 (C10), 26.00 (C11), 28.99 (C12), 28.99 (C19), 29.41 (C13), 29.45 (C14), 29.59 (C15), 29.70 (C16), 29.74 (C17), 29.74 (C18), 31.93 (C20), 49.84 (C8), 49.84 (C8), 59.15 (C7), 62.94 (C9), 122.90 (C4 and C5), 139.01 (C2) ppm; IR: v 3106, 2923, 2853, 1578, 1467, 1385, 1323, 1248, 1141, 1092, 1022, 910, 819, 744, 722 cm⁻¹.

[C_{16}DMEA][Im]: ¹H NMR (D₂O, TMS): δ 0.81 (t, 3H, CH₃), 1.22 (m, 29H, CH₂ and CH₃), 1.62 (m, 2H, CH₂), 2.96 (s, 6H, CH₃), 3.13 (m, 2H, CH₂), 3.28 (m, 2H, CH₂), 7.03 (s, 2H, Im C4 and C5), 7.68 (s, 1H, Im C2) ppm; ¹³C NMR (D₂O, TMS): δ 7.42 (C6), 13.82 (C24), 22.04 (C23), 22.61 (C10), 26.02 (C11), 29.05 (C12), 29.05 (C21), 29.46 (C13), 29.54 (C14), 29.70 (C15), 29.70 (C16), 29.79 (C17), 29.79 (C18), 29.89 (C19), 29.92 (C20), 31.94 (C22), 50.06 (C8), 50.06 (C8), 59.09 (C7), 62.75 (C9), 121.54 (C4 and C5), 136.02 (C2) ppm; IR: v 3080, 2918, 2851, 1633, 1468, 1379, 1338, 1295, 1151, 1076, 1023, 979, 924, 836, 759, 720 cm⁻¹.

[C₅DMEA][Pyr]: ¹H NMR (D₂O, TMS): δ 0.77 (t, 3H, CH₃), 1.22 (m, 13H, CH₂ and CH₃), 1.62 (m, 2H, CH₂), 2.90 (s, 6H, CH₃), 3.13 (t, 2H, CH₂), 3.22 (m, 2H, CH₂), 6.32 (s, 1H, Pyr C4), 7.57 (s, 2H, Pyr C3 and C5) ppm; ¹³C NMR (D₂O, TMS): δ 7.34 (C6), 13.66 (C16), 21.75 (C15), 22.24 (C10), 25.63 (C11), 28.44 (C12), 28.54 (C13), 31.29 (C14), 49.76 (C8), 49.76 (C8), 59.30 (C7), 63.07 (C9), 104.03 (C4), 134.88 (C3 and C5) ppm; IR: v 3022, 2925, 2856, 1636, 1462, 1349, 1281, 1208,
1141, 1065, 1008, 980, 916, 841, 736 cm\(^{-1}\).

\[\text{[C}_{10}\text{DMEA][Pyr]}\]: \(^1\text{H}\) NMR (D\(_2\)-O, TMS): \(\delta\) 0.77 (t, 3H, CH\(_3\)), 1.19 (m, 17H, CH\(_2\) and CH\(_3\)), 1.61 (m, 2H, CH\(_2\)), 2.89 (s, 6H, CH\(_3\)), 3.11 (t, 2H, CH\(_2\)), 3.23 (m, 2H, CH\(_2\)), 6.31 (s, 1H, Pyr C4), 7.61 (s, 2H, Pyr C3 and C5) ppm; \(^{13}\text{C}\) NMR (D\(_2\)-O, TMS): \(\delta\) 7.38 (C6), 13.85 (C18), 21.89 (C17), 22.55 (C10), 25.87 (C11), 28.83 (C12), 29.22 (C15), 29.28 (C13), 29.36 (C14), 31.81 (C16), 49.82 (C8), 49.82 (C8), 59.14 (C7), 62.87 (C9), 103.70 (C4), 134.89 (C3 and C5) ppm; IR: \(\nu\) 3050, 2923, 2854, 1714, 1636, 1464, 1378, 1350, 1281, 1213, 1143, 1011, 916, 842, 812, 736 cm\(^{-1}\).

\[\text{[C}_{12}\text{DMEA][Pyr]}\]: \(^1\text{H}\) NMR (D\(_2\)-O, TMS): \(\delta\) 0.84 (t, 3H, CH\(_3\)), 1.24 (m, 21H, CH\(_2\) and CH\(_3\)), 1.44 (m, 2H, CH\(_2\)), 2.80 (s, 6H, CH\(_3\)), 2.89 (t, 2H, CH\(_2\)), 3.10 (m, 2H, CH\(_2\)), 6.18 (m, 1H, Pyr C4), 7.53 (d, 2H, Pyr C3 and C5) ppm; \(^{13}\text{C}\) NMR (D\(_2\)-O, TMS): \(\delta\) 7.41 (C6), 13.88 (C20), 21.99 (C19), 22.63 (C10), 25.99 (C11), 28.98 (C12), 29.41 (C17), 29.45 (C13), 29.58 (C14), 29.70 (C15), 29.74 (C16), 31.93 (C18), 49.85 (C8), 49.85 (C8), 59.14 (C7), 62.90 (C9), 103.72 (C4), 138.16 (C3 and C5) ppm; IR: \(\nu\) 3032, 2923, 2853, 1635, 1465, 1378, 1351, 1280, 1213, 1143, 1014, 917, 842, 812, 738 cm\(^{-1}\).

\[\text{[C}_{14}\text{DMEA][Pyr]}\]: \(^1\text{H}\) NMR (D\(_2\)-O, TMS): \(\delta\) 0.84 (t, 3H, CH\(_3\)), 1.24 (m, 25H, CH\(_2\) and CH\(_3\)), 1.46 (m, 2H, CH\(_2\)), 2.81 (s, 6H, CH\(_3\)), 2.91 (t, 2H, CH\(_2\)), 3.10 (m, 2H, CH\(_2\)), 6.21 (m, 1H, Pyr C4), 7.55 (m, 2H, Pyr C3 and C5) ppm; \(^{13}\text{C}\) NMR (D\(_2\)-O, TMS): \(\delta\) 7.42 (C6), 13.89 (C22), 21.96 (C21), 22.65 (C10), 25.99 (C11), 29.01 (C12), 29.01 (C19), 29.46 (C13), 29.50 (C14), 29.63 (C15), 29.63 (C16), 29.75 (C17), 29.79 (C18), 31.97 (C20), 49.87 (C8), 49.87 (C8), 59.11 (C7), 62.77 (C9), 103.53 (C4), 134.80 (C3 and C5) ppm; IR: \(\nu\) 3070, 2922, 2853, 1640, 1465, 1394, 1351, 1308, 1282, 1216, 1144, 1014, 918, 844, 737 cm\(^{-1}\).

\[\text{[C}_{18}\text{DMEA][Pyr]}\]: \(^1\text{H}\) NMR (D\(_2\)-O, TMS): \(\delta\) 0.82 (t, 3H, CH\(_3\)), 1.22 (m, 29H, CH\(_2\) and CH\(_3\)), 1.53 (m, 2H, CH\(_2\)), 2.91 (s, 6H, CH\(_3\)), 3.04 (t, 2H, CH\(_2\)), 3.20 (m, 2H, CH\(_2\)), 6.26 (m, 1H, Pyr C4), 7.58 (m, 2H, Pyr C3 and C5) ppm; \(^{13}\text{C}\) NMR (D\(_2\)-O, TMS): \(\delta\) 7.41 (C6), 13.83 (C24), 22.00 (C23), 22.63 (C10), 25.98 (C11), 29.04 (C12), 29.04 (C21), 29.49 (C13), 29.49 (C14), 29.54 (C15), 29.54 (C16), 29.71 (C17), 29.71 (C18), 29.82 (C19), 29.95 (C20), 31.97 (C22), 50.04 (C8), 50.04 (C8), 59.08 (C7), 62.72
(C9), 104.49 (C4), 133.88 (C3 and C5) ppm; IR: v 3020, 2917, 2850, 1632, 1468, 1377, 1281, 1143, 1007, 990, 927, 889, 838, 752 cm\(^{-1}\).

\textbf{[C\_9DMEA][Triz]}: \(^1\)H NMR (D\(_2\)O, TMS): \(\delta\) 0.77 (t, 3H, CH\(_3\)), 1.20 (m, 13H, CH\(_2\) and CH\(_3\)), 1.60 (m, 2H, CH\(_2\)), 2.87 (s, 6H, CH\(_3\)), 3.10 (t, 2H, CH\(_2\)), 3.22 (m, 2H, CH\(_2\)), 8.03 (s, 2H, Triz C3 and C5) ppm; \(^{13}\)C NMR (D\(_2\)O, TMS): \(\delta\) 7.34 (C6), 13.56 (C16), 21.71 (C15), 22.10 (C10), 25.53 (C11), 28.26 (C12), 28.32 (C13), 31.11 (C14), 49.74 (C8), 49.74 (C8), 59.29 (C7), 63.33 (C9), 149.61 (C3 and C5) ppm; IR: ν 3073, 2925, 2857, 1644, 1470, 1378, 1240, 1183, 1142, 1020, 962, 849, 814, 723, 683 cm\(^{-1}\).

\textbf{[C\_10DMEA][Triz]}: \(^1\)H NMR (D\(_2\)O, TMS): \(\delta\) 0.79 (t, 3H, CH\(_3\)), 1.20 (m, 17H, CH\(_2\) and CH\(_3\)), 1.58 (m, 2H, CH\(_2\)), 2.86 (s, 6H, CH\(_3\)), 3.07 (t, 2H, CH\(_2\)), 3.20 (m, 2H, CH\(_2\)), 8.02 (s, 2H, Triz C3 and C5) ppm; \(^{13}\)C NMR (D\(_2\)O, TMS): \(\delta\) 7.38 (C6), 13.82 (C18), 21.91 (C17), 22.49 (C10), 25.84 (C11), 28.75 (C12), 29.12 (C15), 29.17 (C13), 29.26 (C14), 31.72 (C16), 49.82 (C8), 49.82 (C8), 59.25 (C7), 63.12 (C9), 149.56 (C3 and C5) ppm; IR: ν 3053, 2920, 2837, 1643, 1455, 1387, 1220, 1153, 1112, 1020, 972, 936, 849, 804, 723, 683 cm\(^{-1}\).

\textbf{[C\_12DMEA][Triz]}: \(^1\)H NMR (D\(_2\)O, TMS): \(\delta\) 0.83 (t, 3H, CH\(_3\)), 1.24 (m, 21H, CH\(_2\) and CH\(_3\)), 1.52 (m, 2H, CH\(_2\)), 2.82 (s, 6H, CH\(_3\)), 2.99 (t, 2H, CH\(_2\)), 3.15 (m, 2H, CH\(_2\)), 8.00 (s, 2H, Triz C3 and C5) ppm; \(^{13}\)C NMR (D\(_2\)O, TMS): \(\delta\) 7.41 (C6), 13.87 (C20), 22.01 (C19), 23.42 (C10), 26.00 (C11), 28.99 (C12), 29.41 (C17), 29.46 (C13), 29.59 (C14), 29.70 (C15), 29.74 (C16), 31.92 (C18), 49.87 (C8), 49.87 (C8), 59.21 (C7), 63.01 (C9), 148.76 (C3 and C5) ppm; IR: ν 3025, 2923, 2854, 1582, 1470, 1380, 1271, 1242, 1143, 1063, 1022, 962, 928, 854, 814, 722, 683 cm\(^{-1}\).

\textbf{[C\_14DMEA][Triz]}: \(^1\)H NMR (D\(_2\)O, TMS): \(\delta\) 0.82 (t, 3H, CH\(_3\)), 1.23 (m, 25H, CH\(_2\) and CH\(_3\)), 1.55 (m, 2H, CH\(_2\)), 2.84 (s, 6H, CH\(_3\)), 3.02 (t, 2H, CH\(_2\)), 3.18 (m, 2H, CH\(_2\)), 8.00 (s, 2H, Triz C3 and C5) ppm; \(^{13}\)C NMR (D\(_2\)O, TMS): \(\delta\) 7.34 (C6), 13.87 (C22), 21.95 (C21), 22.63 (C10), 25.97 (C11), 29.01 (C12), 29.01 (C19), 29.48 (C13), 29.52 (C14), 29.68 (C15), 29.80 (C16), 29.89 (C17), 29.89 (C18), 31.96 (C20), 49.77 (C8), 49.77 (C8), 59.07 (C7), 62.87 (C9), 149.78 (C3 and C5) ppm; IR: ν 3050, 2923, 2854, 1583, 1469, 1379, 1270, 1240, 1184, 1142, 1022, 962, 928, 851, 814, 721, 684 cm\(^{-1}\).

\textbf{[C\_16DMEA][Triz]}: \(^1\)H NMR (D\(_2\)O, TMS): \(\delta\) 0.77 (t, 3H, CH\(_3\)), 1.18 (m, 29H, CH\(_2\)
and CH₃), 1.36 (m, 2H, CH₂), 2.68 (s, 6H, CH₃), 2.81 (t, 2H, CH₂), 2.98 (m, 2H, CH₂), 7.88 (s, 2H, Triz C3 and C5) ppm; ¹³C NMR (D₂O, TMS): δ 7.37 (C6), 13.88 (C24), 21.97 (C23), 22.66 (C10), 26.00 (C11), 29.07 (C12), 29.07 (C21), 29.54 (C13), 29.54 (C20), 29.59 (C14), 29.59 (C19), 29.76 (C15), 29.76 (C18), 29.87 (C16), 30.01 (C17), 32.00 (C22), 49.79 (C8), 49.79 (C8), 59.06 (C7), 62.83 (C9), 149.57 (C3 and C5) ppm; IR: ν 3020, 2917, 2850, 1629, 1470, 1375, 1337, 1235, 1186, 1140, 1024, 971, 930, 838, 719, 684 cm⁻¹.

2. Determination of bromide content in the ILs.

Bromide contents in the ILs were determined by means of a Br⁻ selective electrode (Shanghai Precision & Scientific Instrument Co. Ltd) coupled with a 6802 saturated calomel electrode, and a PHSJ-4F digital pH meter was used to measure the potentials. The measurements were conducted at 25 ± 0.1 °C, and calibration curves were obtained from the potential values against concentrations of aqueous solutions of the corresponding precursor bromide ionic liquids. Each experiment was performed in triplicate, and the reproducibility was within 2%.

3. Analysis of the composition of the aqueous phase after phase separation.

The concentration of the residual ILs in the aqueous solution after phase separation was determined by spectrophotometric method.¹¹⁻³ Briefly, we prepared a given concentration of aqueous IL solutions saturated with CO₂ at 25 °C as mother-liquid of sample firstly. Then, a series of different concentrations of the ILs-CO₂ aqueous solutions were obtained by diluting the above sample solution under an atmosphere of carbon dioxide. The absorbance of each of them was measured in a 1 cm cell, and then standard curve was established through fitting the absorbance intensity with different concentrations of IL. Taking [C₁₂DMEA][Im] as an example, a series of standard solutions of the IL reacted with CO₂ were prepared and their absorbance intensity was measured at 206 nm, respectively. The absorbance intensity of [C₁₂DMEA][Im] was obtained as a linear function of the IL content in water (Figure S16). Thus, the content of the residual [C₁₂DMEA][Im] in the aqueous solution after phase separation could be read from the standard curve by measuring its corresponding absorbance intensity.
Tables S1-S2

**Table S1.** The droplet size of n-pentanol/[C\textsubscript{12}DMEA][Im]/H\textsubscript{2}O microemulsions as a function of water content at 25 °C.

<table>
<thead>
<tr>
<th>microemulsion</th>
<th>R</th>
<th>Size distribution (nm)</th>
<th>Mean (nm)</th>
<th>PDI</th>
<th>Number (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentanol/[C\textsubscript{12}DMEA][Im]/H\textsubscript{2}O</td>
<td>9.28</td>
<td>1.5 ~ 2.7</td>
<td>2.0</td>
<td>0.209</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>19.30</td>
<td>4.2 ~ 8.7</td>
<td>5.6</td>
<td>0.176</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>31.38</td>
<td>6.5 ~ 15.7</td>
<td>8.7</td>
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<td>43.26</td>
<td>7.5 ~ 15.7</td>
<td>10.1</td>
<td>0.124</td>
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<tr>
<td></td>
<td>57.01</td>
<td>7.9 ~ 28.2</td>
<td>15.7</td>
<td>0.222</td>
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</table>

**Table S2.** Yields for the reactions of aromatic aldehydes with malononitrile in [C\textsubscript{12}DMEA][Im] based microemulsions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R\textsuperscript{a}</th>
<th>Yield (%)\textsuperscript{b}</th>
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<td><img src="image1.png" alt="Chemical Structure" /></td>
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</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Chemical Structure" /></td>
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</tr>
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<td><img src="image4.png" alt="Chemical Structure" /></td>
<td>94.5</td>
</tr>
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<td>96.2</td>
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<tr>
<td>7</td>
<td><img src="image7.png" alt="Chemical Structure" /></td>
<td>98.7</td>
</tr>
</tbody>
</table>

\[a\] All of these reactions were performed with aldehyde (1.05 mmol) and malononitrile (1.00 mmol) in 1.5 mL of microemulsion at 25 °C for 1h.

\[b\] Determined by \textsuperscript{1}H NMR using anisole as an internal standard.
Figures S1-S27

**Figure S1.** Phase diagrams of the n-pentanol/[C₉DMEA][Pyr] (n = 8, 10, 12, 14, 16)/H₂O microemulsions (in mass fraction) at 25.0 °C.

**Figure S2.** Phase diagrams of the n-pentanol/[C₉DMEA][Triz] (n = 8, 10, 12, 14, 16)/H₂O microemulsions (in mass fraction) at 25.0 °C.

**Figure S3.** Phase diagrams of the n-pentanol/[C₁₂DMEA][Im]/H₂O (black), n-pentanol/[C₁₂DMEA][Pyr]/H₂O (red) and n-pentanol/[C₁₂DMEA][Triz]/H₂O microemulsions (blue) at 25.0 °C.
Figure S4. Electrical conductivity of the n-pentanol/[C12DMEA][Im]/H2O microemulsion as a function of water content (W0) at different I values as stated at 25.0 °C.

Figure S5. Electrical conductivity of the n-pentanol/[C12DMEA][Pyr]/H2O microemulsion as a function of water content (W0) at different I values as stated at 25.0 °C.
Figure S6. Phase diagram of the n-pentanol/[C_{12}DMEA][Pyr]/H_{2}O microemulsion at 25.0 °C with different types of microstructure; Circles (pink and blue) were results from DLS measurements.

Figure S7. Electrical conductivity of the n-pentanol/[C_{12}DMEA][Triz]/H_{2}O microemulsion as a function of water content (W_0) at different I values as stated at 25.0 °C.
Figure S8. Phase diagram of the n-pentanol/[C_{12}DMEA][Triz]/H_{2}O microemulsion with different types of microstructure at 25.0 °C; Circles (pink and blue) were results from DLS measurements.

Figure S9. SAXS curves of the n-pentanol/[C_{12}DMEA][Im]/H_{2}O microemulsion droplets at I = 9.0 (n-pentanol/[C_{12}DMEA][Im], 9:1, w/w) and different R values (R = H_{2}O/[C_{12}DMEA][Im] molar ratio) as stated.

Figure S10. Size distribution of the n-pentanol/[C_{12}DMEA][Im]/H_{2}O microemulsion droplets (n-pentanol/H_{2}O, 4 : 1, w/w) at different R (molar ratio of H_{2}O to [C_{12}DMEA][Im]) values.
Figure S11. Size distribution of the n-pentanol/[C_{12}DMEA][Pyr]/H_{2}O microemulsion droplets (n-pentanol/[C_{12}DMEA][Pyr], 11.3 : 1.0, w/w) and different $R_1$ (molar ratio of H_{2}O to [C_{12}DMEA][Pyr]) values.

Figure S12. Size distributions of the n-pentanol/[C_{12}DMEA][Pyr]/H_{2}O microemulsion droplets (n-pentanol/H_{2}O, 4 : 1, w/w) at different $R_1$ (molar ratio of H_{2}O to [C_{12}DMEA][Pyr]) values.

Figure S13. Linear correlation of size of the n-pentanol/[C_{n}DMEA][Pyr] (n= 8, 10, 12, 14, 16)/H_{2}O microemulsion droplets with the $R_1$ values (molar ratio of H_{2}O to [C_{12}DMEA][Pyr]) at 25.0 °C.
Figure S14. Size distribution of the n-pentanol/[C\textsubscript{12}DMEA][Triz]/H\textsubscript{2}O microemulsion droplets (n-pentanol/[C\textsubscript{12}DMEA][Triz], 8.8:1.0, w/w) and different $R_2$ values (molar ratio of H\textsubscript{2}O to [C\textsubscript{12}DMEA][Triz]) values.

![Size distribution of the n-pentanol/[C\textsubscript{12}DMEA][Triz]/H\textsubscript{2}O microemulsion droplets](image1)

Figure S15. Size distribution of the n-pentanol/[C\textsubscript{12}DMEA][Triz]/H\textsubscript{2}O microemulsion droplets (n-pentanol/H\textsubscript{2}O, 4:1, w/w) at different $R_2$ values (molar ratio of H\textsubscript{2}O to [C\textsubscript{12}DMEA][Triz]).

![Size distribution of the n-pentanol/[C\textsubscript{12}DMEA][Triz]/H\textsubscript{2}O microemulsion droplets](image2)

Figure S16. Linear correlation of size of the n-pentanol/[C\textsubscript{n}DMEA][Triz] (n= 8, 10, 12, 14, 16)/H\textsubscript{2}O microemulsion droplets with the $R_2$ values at 25.0 °C.

![Linear correlation of size of the n-pentanol/[C\textsubscript{n}DMEA][Triz]/H\textsubscript{2}O microemulsion droplets](image3)
**Figure S17.** Linear change of absorbance intensity with concentrations of [C12DMEA][Im]-CO2 in water at 206 nm.

**Figure S18.** $^{13}$C NMR spectra of [C12DMEA][Pyr] in the n-pentanol/[C12DMEA][Pyr]/H2O microemulsion system before bubbling of CO2 and after bubbling of N2 as well as in the aqueous solution after phase separation.

**Figure S19.** $^{13}$C NMR of [C12DMEA][Triz] in the n-pentanol/[C12DMEA][Triz]/H2O microemulsions system before bubbling of CO2 and after bubbling of N2 as well as in the aqueous solution after phase separation.
**Figure S20.** Change in size of the n-pentanol/[C\textsubscript{12}DMEA][Im]/H\textsubscript{2}O system with increasing concentrations of sodium bicarbonate.

**Figure S21.** \textsuperscript{1}H NMR spectrum of 2-benzylidenemalonitrile in CDCl\textsubscript{3}.

**Figure S22.** The reusability of [C\textsubscript{12}DMEA][Im] based microemulsion in the reaction of benzaldehyde and malononitrile (1, 97.2%; 2, 96.2%; and 3, 94.5%).
Figure S23. $^1$H NMR spectrum of 3-(2,2-dicyanovinyl)phenyl nitrate in CDCl$_3$.

Figure S24. $^1$H NMR spectrum of 4-(2,2-dicyanovinyl)phenyl nitrate in CDCl$_3$.

Figure S25. $^1$H NMR spectrum of 2-(4-methylbenzylidene)malononitrile in CDCl$_3$. 
Figure S26. $^1$H NMR spectrum of 2-(4-fluorobenzylidene)malononitrile in CDCl$_3$.

Figure S27. $^1$H NMR spectrum of 2-(furan-2-ylmethylene)malononitrile in CDCl$_3$.

References

