Electronic supplementary information

Light-Modulated Aggregation Behavior of Some Unsubstituted Cinnamate-Based Ionic Liquids in Aqueous Solutions

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Synthesis and characteristics of [Cn mim][CA](n = 4, 6, 8, 10, 12) ionic liquids

1-dodecyl-3-methylimidazolium ortho-methoxycinnate ([C12 mim][CA]):

1H NMR ((DMSO-d6): δ = 9.79 (1H, s), 7.84 (1H, s), 7.76 (1H, s), 7.43 (2H, d), 7.30 (2H, t), 7.22 (1H, t), 7.03 (1H, d), 6.35 (1H, d), 4.17 (2H, t), 3.88 (3H, s), 1.76 (2H, m), 1.19 (2H, m), 0.84 (3H, t) ppm.

13C NMR: δ = 169.7, 137.9, 137.6, 134.6, 132.2, 129.0, 128.0, 127.2, 124.0, 122.7, 49.1, 36.1, 31.8, 30.0, 29.5, 29.5, 29.4, 29.3, 29.2, 28.9, 26.0, 22.6, 14.4 ppm.

HRMS: calcd for [C16H31N2]+: 251.2482; found: 251.2476; calcd for [C10H9O3]−: 147.0441; found: 147.0442

1-decyl-3-methylimidazolium cinnate ([C10 mim][CA]):

1H NMR ((DMSO-d6): δ = 9.87 (1H, s), 7.86 (1H, s), 7.78 (1H, s), 7.44 (2H, d), 7.30 (2H, t), 7.22
(1H, t), 7.06 (1H, d), 6.38 (1H, d), 4.17 (2H, t), 3.88 (3H, s), 1.74 (2H, m), 1.19 (2H, m), 0.82 (3H, t) ppm.

$^{13}$C NMR: $\delta = 170.0, 138.0, 137.5, 135.0, 131.7, 129.0, 128.1, 127.2, 124.0, 122.7, 49.1, 36.0, 31.8, 30.0, 29.4, 29.3, 29.2, 28.9, 26.0, 22.6, 14.4$ ppm.

HRMS: calcd for $[C_{14}H_{27}N_2]^+ : 223.2169$; found: 223.2151; calcd for $[C_{10}H_{9}O_3]^-$: 147.0441; found: 147.0449.

1-octyl-3-methylimidazolium cinnate ([C$_8$mim][CA]):

$^1$H NMR ((DMSO-d$_6$): $\delta = 9.41$ (1H, s), 7.77 (1H, s), 7.70 (1H, s), 7.45 (2H, d), 7.31 (2H, t), 7.23 (1H, t), 7.08 (1H, d), 6.39 (1H, d), 4.14 (2H, t), 3.84 (3H, s), 1.74 (2H, m), 1.20 (2H, m), 0.82 (3H, t) ppm.

$^{13}$C NMR: $\delta = 171.8, 139.9, 139.3, 136.8, 133.7, 130.8, 129.9, 129.0, 125.8, 124.6, 50.9, 37.9, 33.5, 31.9, 30.8, 31.0, 27.9, 24.4, 16.2$ ppm.

HRMS: calcd for $[C_{12}H_{25}N_2]^+$: 195.1856; found: 195.1843; calcd for $[C_{10}H_{9}O_3]^-$: 147.0441; found: 147.0448.

1-hexyl-3-methylimidazolium cinnate ([C$_6$mim][CA]):

$^1$H NMR ((DMSO-d$_6$): $\delta = 9.81$ (1H, s), 7.85 (1H, s), 7.77 (1H, s), 7.44 (2H, d), 7.31 (2H, t), 7.23 (1H, t), 7.04 (1H, d), 6.37 (1H, d), 4.17 (2H, t), 3.88 (3H, s), 1.75 (2H, m), 1.22 (2H, m), 0.81 (3H, t) ppm.

$^{13}$C NMR: $\delta = 170.0, 137.9, 137.5, 134.9, 131.9, 129.0, 128.1, 127.2, 124.0, 122.7, 49.1, 36.1, 31.0, 29.9, 25.7, 22.4, 14.3$ ppm.

HRMS (m/z): calcd for $[C_{10}H_{19}N_2]^+$: 167.1543; found: 167.1553; calcd for $[C_{10}H_{9}O_3]^-$: 147.0441; found: 147.0454.

1-butyl-3-methylimidazolium cinnate ([C$_4$mim][CA]):

$^1$H NMR ((DMSO-d$_6$): $\delta = 9.84$ (1H, s), 7.85 (1H, s), 7.78 (1H, s), 7.44 (2H, d), 7.31 (2H, t), 7.23 (1H, t), 7.04 (1H, d), 6.37 (1H, d), 4.18 (2H, t), 3.88 (3H, s), 1.74 (2H, m), 1.23 (2H, m), 0.86 (3H, t) ppm.

$^{13}$C NMR: $\delta = 172.0, 140.2, 139.7, 136.9, 134.3, 131.2, 130.3, 129.4, 126.2, 124.9, 51.0, 38.3, 34.1, 21.5, 15.9$ ppm.

HRMS (m/z): calcd for $[C_{9}H_{13}N_2]^+$: 139.1230; found: 139.1239 calcd for $[C_{10}H_{9}O_3]^-$: 147.0441; found: 147.0449.
Table S1. Bromide content in [Cₙmim][CA] ionic liquids

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<th>IL</th>
<th>[Br⁻]/mol.kg⁻¹</th>
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<tr>
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Fig. S1 UV-vis spectra of aqueous trans- cinnamic acid (H[CA])

at the concentration of 1 mM before and after irradiation

¹H -NMR spectra for [Cₙmim][CA] ionic liquids:
$^{13}$C-NMR spectra for $[\text{C}_n\text{mim}][\text{CA}]$ ionic liquids:

- **C12mimCA+DMSO**
- **C10mimCA+DMSO**
C4mimCA

f1 (ppm)