

Supporting Information

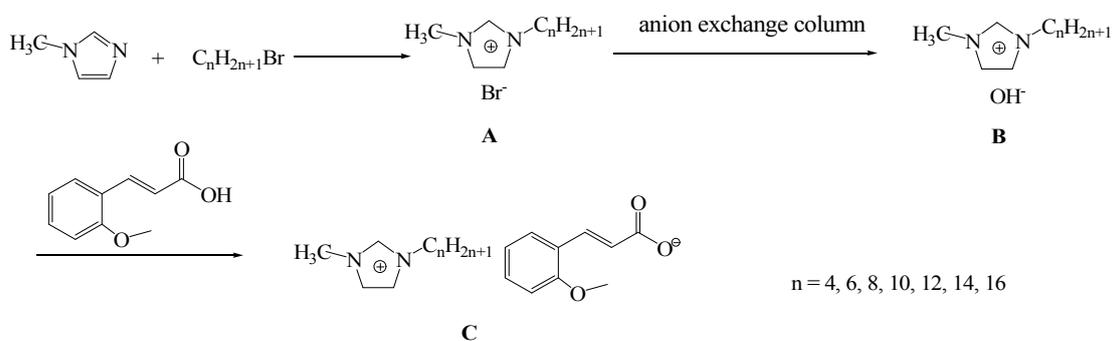
Highly Efficient Conductivity Modulation of Cinnamate-Based Light-Responsive Ionic Liquids in Aqueous Solutions

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1. Synthesis and characteristics of [C_nmim][OMCA](n = 4, 6, 8, 10, 12, 14, 16) ionic liquids



Scheme S1. Synthetic route of the photo-responsive ionic liquids

1-Methylimidazole (99%) was obtained from Shanghai Chem. Co., 1-bromobutane (99%), 1-bromohexane (99%), bromooctane (99%), 1-bromodecane (99%), 1-bromododecane (99%), 1-bromotetradecane (99%), 1-bromohexadecane (98%), trans-2-methoxycinnamic acid (98%) and anion exchange resin (Ambersep 900 OH) were purchased from Alfa Aesar. These chemicals were used without further purification.

[C_nmim]Br was prepared and purified by using the procedures described in literature.¹ Briefly, the reaction of 1-methylimidazole (0.10 mol) with an excess of 1-brominated alkanes (0.13 mol) was performed in 1,1,1-trichloroethane (100 mL) at 70°C for 48 h to obtain [C_nmim]Br. Among the products prepared, [C₄mim]Br, [C₆mim]Br, [C₈mim]Br and [C₁₀mim]Br were washed with 1,1,1-trichloroethane, and the residual solvents were removed by heating at 70 °C under vacuum. [C₁₂mim]Br was recrystallized three times from ethyl acetate and ethyl acetate/acetonitrile (3:2 by

volume), respectively. The solid [C₁₄mim]Br and [C₁₆mim]Br were recrystallized three times from ethyl acetate, and the residual solvent was removed by rotary evaporation. The resulting products were dried under vacuum for 24 h before use.

An aqueous solution of [C_nmim]Br was allowed to pass through a column filled with Ambersep 900(OH) anion exchange resin to obtain [C_nmim][OH]. Because of its limited solubility in water, aqueous ethanol solution (1:1 by volume) rather than water was used for [C₁₆mim]Br. The [C_nmim][OH] solution was then neutralized with equal molar trans-ortho-methoxycinnamic acid (H[OMCA]). After removing water by evaporation under reduced pressure, [C₄mim][OMCA] and [C₆mim][OMCA] were thoroughly washed with diethyl ether or petroleum ether, and the products were slightly brown viscous liquids. The other ionic liquids were recrystallized three times from ethyl acetate, and finally dried under vacuum for 72 h at 60 °C to obtain products as white solids. The chemical structures of these ILs were confirmed by ¹H NMR, ¹³C NMR, IR and HR- mass spectroscopy and elemental analysis. The detailed data were given below.

1-Hexadecyl-3-methylimidazolium ortho-methoxycinnate ([C₁₆mim][OMCA]):

¹H NMR (DMSO-d₆): δ =9.40 (1H, s), 7.77 (1H, d), 7.70 (1H, s), 7.44 (1H, d), 7.42 (1H, d), 7.22-7.17 (1H, m), 6.95 (1H, d), 6.88 (1H, t), 6.24 (1H, d), 4.13 (2H, t), 3.84 (3H, s), 3.78 (3H, s), 1.78-1.73 (2H, m), 1.27-1.12 (26H, m), and 0.83 (3H, t) ppm.

¹³C NMR: δ =172.0, 158.9, 139.9, 134.3, 131.0, 131.0, 130.4, 128.7, 128.0, 125.8, 124.5, 122.7, 113.5, 57.6, 50.96, 37.9, 33.6, 31.4, 31.3, 31.20 31.0, 30.8, 27.9, 24.4, and 16.2 ppm.

IR: ν = 2922, 2853, 1633, 1557, 1487, 1464, 1368, 1246, 1172, and 748 cm⁻¹.

HRMS (*m/z*): calcd for [C₂₀H₃₉N₂]⁺: 307.3108; found: 307.3119; calcd for [C₁₀H₉O₃]⁻: 177.0546; found: 177.0539.

Elemental analysis calcd (%) for C₃₀H₄₈N₂O₃: C 74.32, H 9.99, N 5.78, O 9.91; found: C 74.08, H 10.05, N 5.70, O 10.11.

1-Tetradecyl-3-methylimidazolium ortho-methoxycinnate ([C₁₄mim][OMCA]):

¹H NMR ((DMSO-d₆): δ =9.49 (1H, s), 7.78 (1H, d), 7.71 (1H, s), 7.43 (1H, d), 7.31 (1H, d), 7.22-7.18 (1H, m), 6.95 (1H, d), 6.87 (1H, t), 6.24 (1H, d), 4.13 (2H, t), 3.84 (3H, s), 3.78 (3H, s), 1.78-1.73 (2H, m), 1.29-1.11 (22H, m), and 0.80 (3H, t) ppm.

¹³C NMR: δ =172.2, 159.0, 140.1, 134.0, 131.3, 131.0, 128.7, 127.9, 125.8, 124.6, 122.7, 113.6,

57.6, 50.9, 37.8, 33.6, 31.9, 31.4, 31.3, 31.2, 31.1, 30.8, 27.9, 24.4, and 16.2 ppm.

IR: $\nu = 2959, 2873, 1631, 1595, 1557, 1487, 1463, 1359, 1244, 1173, \text{ and } 751 \text{ cm}^{-1}$

HRMS (m/z): calcd for $[\text{C}_{18}\text{H}_{35}\text{N}_2]^+$: 279.2795; found: 279.2798; calcd for $[\text{C}_{10}\text{H}_9\text{O}_3]^-$: 177.0546; found: 177.0541.

Elemental analysis calcd (%) for $\text{C}_{28}\text{H}_{44}\text{N}_2\text{O}_3$: C 73.63, H 9.72, N 6.14, O 10.52; found: C 73.52, H 9.88, N 6.20, O 10.71.

1-Dodecyl-3-methylimidazolium ortho-methoxycinnate ($[\text{C}_{12}\text{mim}][\text{OMCA}]$):

^1H NMR ((DMSO- d_6): $\delta = 9.50$ (1H, s), 7.78 (1H, d), 7.71 (1H, s), 7.45 (1H, d), 7.30 (1H, d), 7.22-7.18 (1H, m), 6.95 (1H, d), 6.87 (1H, t), 6.26 (1H, d), 4.14 (2H, t), 3.84 (3H, s), 3.78 (3H, s), 1.78-1.73 (2H, m), 1.26-1.11 (18H, m), and 0.83 (3H, t) ppm.

^{13}C NMR: $\delta = 172.2, 159.0, 139.9, 133.9, 131.4, 131.1, 128.7, 127.9, 125.8, 124.6, 122.7, 113.5, 57.6, 50.9, 37.8, 33.6, 31.4, 31.3, 31.3, 31.2, 31.0, 30.8, 27.9, 24.4, \text{ and } 16.2$ ppm.

IR: $\nu = 2923, 2853, 1633, 1557, 1487, 1464, 1368, 1246, 1172, \text{ and } 748 \text{ cm}^{-1}$

HRMS (m/z): calcd for $[\text{C}_{16}\text{H}_{31}\text{N}_2]^+$: 251.2482; found: 251.2490; calcd for $[\text{C}_{10}\text{H}_9\text{O}_3]^-$: 177.0546; found: 177.0539.

Elemental analysis calcd (%) for $\text{C}_{26}\text{H}_{40}\text{N}_2\text{O}_3$: C 72.85, H 9.41, N 6.54, O 11.20; found: C 72.69, H 9.39, N 6.48, O 11.35.

1-Decyl-3-methylimidazolium ortho-methoxycinnate ($[\text{C}_{10}\text{mim}][\text{OMCA}]$):

^1H NMR ((DMSO- d_6): $\delta = 9.52$ (1H, s), 7.78 (1H, d), 7.71 (1H, s), 7.45 (1H, d), 7.33 (1H, d), 7.23-7.19 (1H, m), 6.95 (1H, d), 6.87 (1H, t), 6.27 (1H, d), 4.14 (2H, t), 3.84 (3H, s), 3.78 (3H, s), 1.79-1.73 (2H, m), 1.30-1.12 (14H, m), and 0.83 (3H, t) ppm.

^{13}C NMR: $\delta = 172.0, 158.9, 139.9, 134.3, 131.1, 131.0, 128.7, 128.0, 125.8, 124.5, 122.7, 113.5, 57.6, 50.9, 37.9, 33.69, 31.8, 31.4, 31.3, 31.2, 31.0, 30.8, 27.9, 24.4, \text{ and } 16.2$ ppm.

IR: $\nu = 2925, 2854, 1633, 1557, 1487, 1464, 1366, 1245, 1172, \text{ and } 748 \text{ cm}^{-1}$

HRMS (m/z): calcd for $[\text{C}_{14}\text{H}_{27}\text{N}_2]^+$: 223.2169; found: 223.2152; calcd for $[\text{C}_{10}\text{H}_9\text{O}_3]^-$: 177.0546; found: 177.0539.

Elemental analysis calcd (%) for $\text{C}_{24}\text{H}_{36}\text{N}_2\text{O}_3$: C 71.95, H 9.06, N 7.00, O 11.99; found: C 71.83, H 9.07, N 7.06, O 12.15.

1-Octyl-3-methylimidazolium ortho-methoxycinnate ([C₈mim][OMCA]):

¹H NMR ((DMSO-d₆): δ = 9.72 (1H, s), 7.81 (1H, d), 7.74 (1H, s), 7.45 (1H, d), 7.33 (1H, d), 7.26-7.22 (1H, m), 6.95 (1H, d), 6.87 (1H, t), 6.28 (1H, d), 4.19 (2H, t), 3.86 (3H, s), 3.78 (3H, s), 1.80-1.68 (2H, m), 1.24-1.22 (10H, m), and 0.83 (3H, t) ppm.

¹³C NMR: δ = 172.2, 159.0, 139.9, 133.8, 131.4, 131.0, 128.7, 127.9, 125.8, 124.6, 122.7, 113.5, 57.6, 50.9, 37.9, 33.5, 31.9, 30.8, 31.0, 30.7, 27.9, 24.4, and 16.2 ppm.

IR: ν = 2956, 2856, 1637, 1558, 1495, 1467, 1365, 1242, 1171, and 773 cm⁻¹

HRMS (*m/z*): calcd for [C₁₂H₂₃N₂]⁺: 195.1856; found: 195.1849; calcd for [C₁₀H₉O₃]⁻: 177.0546; found: 177.0542.

Elemental analysis calcd (%) for C₂₂H₃₂N₂O₃: C 70.92, H 8.66, N 7.52, O 12.89; found: C 70.90, H 8.50, N 7.35, O 12.98.

1-Hexyl-3-methylimidazolium ortho-methoxycinnate ([C₆mim][OMCA]):

¹H NMR ((DMSO-d₆): δ = 9.67 (1H, s), 7.80 (1H, d), 7.73 (1H, s), 7.44 (1H, d), 7.33 (1H, d), 7.23-7.18 (1H, m), 6.95 (1H, d), 6.88 (1H, t), 6.28 (1H, d), 4.15 (2H, t), 3.86 (3H, s), 3.79 (3H, s), 1.78-1.73 (2H, m), 1.24-1.17 (6H, s), and 0.81 (3H, t) ppm.

¹³C NMR: δ = 172.2, 159.0, 140.0, 133.7, 131.5, 131.2, 128.8, 127.8, 125.8, 124.5, 122.8, 113.6, 57.6, 50.9, 37.9, 32.9, 31.8, 27.5, 24.2, and 16.1 ppm.

IR: ν = 2956, 2856, 1637, 1558, 1495, 1467, 1448, 1365, 1243, 1171, and 773 cm⁻¹

HRMS (*m/z*): calcd for [C₁₀H₁₉N₂]⁺: 167.1543; found: 167.1538; calcd for [C₁₀H₉O₃]⁻: 177.0546; found: 177.0538.

Elemental analysis calcd (%) for C₂₀H₂₈N₂O₃: C 69.72, H 8.20, N 8.14, O 13.94; found: C 69.57, H 8.50, N 8.09, O 14.05.

1-Butyl-3-methylimidazolium ortho-methoxycinnate ([C₄mim][OMCA]):

¹H NMR ((DMSO-d₆): δ = 9.62 (1H, s), 7.80 (1H, d), 7.73 (1H, s), 7.48 (1H, d), 7.40 (1H, d), 7.24 (1H, m), 6.97 (1H, d), 6.90 (1H, t), 6.35 (1H, d), 4.17 (2H, t), 3.86 (3H, s), 3.80 (3H, s), 1.74 (2H, m), 1.28-1.16 (2H, m), and 0.85 (3H, t) ppm.

¹³C NMR: δ = 172.2, 159.0, 140.0, 133.9, 131.4, 131.2, 128.8, 127.8, 125.9, 124.5, 122.8, 113.6,

57.6, 50.6, 37.9, 33.8, 21.1, and 15.5 ppm.

IR: $\nu = 2959, 2873, 1631, 1557, 1487, 1463, 1438, 1359, 1244, 1173, \text{ and } 751 \text{ cm}^{-1}$

HRMS (m/z): calcd for $[\text{C}_8\text{H}_{15}\text{N}_2]^+$: 139.1230; found: 139.1223; calcd for $[\text{C}_{10}\text{H}_9\text{O}_3]^-$: 177.0546; found: 177.0540.

Elemental analysis calcd (%) for $\text{C}_{18}\text{H}_{24}\text{N}_2\text{O}_3$: C 68.32, H 7.65, N 8.86, O 15.18; found: C 68.60, H 7.52, N 8.58, O 15.27.

2. Experiment methods

2.1. Measurements of NMR, IR, HR-Mass spectra, elemental analysis and thermal properties

^1H NMR and ^{13}C NMR spectra of the ILs were collected on a Bruker Avance-400 NMR spectrometer operating at 400 MHz and 100 MHz, respectively. IR spectra were measured on a Perkin-Elmer Spectrum 400 spectrophotometer, HR-mass spectra were obtained on a Bruker MicrOTOF II spectrometer. Elemental analysis was carried out on an Elementar Vario EL elemental analyzer. The glass transition temperature (T_g) and melting temperature (T_m) were determined by a Mettler Toledo 822e differential scanning calorimeter (DSC) at a scan rate of $5 \text{ }^\circ\text{C min}^{-1}$ and a flow rate of $20 \text{ dm}^3 \text{ h}^{-1}$. Measurements of thermal decomposition temperature (T_d) were carried out with a NETZSCH STA 449 C thermal analyzer using alumina crucibles. The sample mass was ca. 10–15 mg per-measurement, and the measurements were carried out under flowing N_2 at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

2.2. Determination of bromide content in the ILs.

Based on the procedure described by Seddon and his coworkers,² bromide contents in the ILs were determined by means of a PBr-1 bromide selective electrode (Shanghai Precision & Scientific Instrument Co. Ltd). To this end, a 232 saturated calomel reference electrode and a PHS-25 digital pH meter (both, Shanghai Precision & Scientific Instrument Co. Ltd) were used. The measurements were conducted at $25 \text{ }^\circ\text{C}$, and calibration curves were obtained from aqueous solutions of the corresponding precursor bromide ionic liquids. Triplicate measurements were performed and the reproducibility was within 2%.

2.3. Dynamic Light Scattering measurements

Dynamic light scattering (DLS) measurements were carried out using a Malvern Nano-ZS90 laser light scattering photometer. Light of $\lambda = 633 \text{ nm}$ from a solid-state He-Ne laser (4.0 mW) was

used as the incident beam. All sample solutions were filtered through a 0.22 μm hydrophilic PVDF membrane filter. All measurements were made at 25.0 $^{\circ}\text{C}$ and at 90 $^{\circ}$ scattering angle. At least three measurements were taken for each solution, and reproducibility of the aggregate size from DLS data was found to be within $\pm 3\%$.

2.4. HPLC measurements

The irradiated solutions were analyzed by using HPLC (Agilent Eclipse XDB-C18 column, 5 μm , 4.6 mm \times 150 mm) at a flow rate of 0.8 mL/min. The eluting solvent was an aqueous methanol solution (45:55 by volume) containing 1.0% acetic acid, and the column temperature was at 30 $^{\circ}\text{C}$. The peaks were detected using UV absorption at 254 nm, and cis-trans ratios of the anions were estimated from their integrated peak area ratio of HPLC.

2.5. Conductivity measurements

Conductivity measurements were performed at 298.15 K by a Wayne-Kerr 6430B Auto Balance Bridge with a resolution of $1 \times 10^{-5} \mu\text{S}\cdot\text{cm}^{-1}$, and a Shanghai DJS-1 electrode was used. The conductance cell was equipped with a water circulating jacket, and the temperature was controlled within $\pm 0.01^{\circ}\text{C}$ with a HAAKE V26 thermostat (Thermo Electron, Germany). The cell was calibrated with aqueous KCl solutions at different concentrations, and a cell constant of 1.0127 cm^{-1} was determined.

2.6. UV light irradiation experiments

IL samples were irradiated with UV light from a 300W mercury pressure short arc lamp with a filter ($<400 \text{ nm}$). Samples (30 mL) were placed in a quartz tube with a cover, and they were irradiated for a specific duration under stirring. In order to avoid overheating from the UV irradiation, the lamp was put in a well with a water circulating jacket, and the temperature was kept to be 298 K. As a comparative study, 365 nm cold light-emitting diodes (LED) were also used to irradiate some aqueous IL samples (5 mL) at 298 K under stirring. It was found from HPLC measurements that within the experimental error, the percent of trans-cis isomerization of a given IL sample in aqueous solutions was the same under irradiation of the two UV light sources. This suggests that both UV light sources could be used for conductivity modulation stimuli.

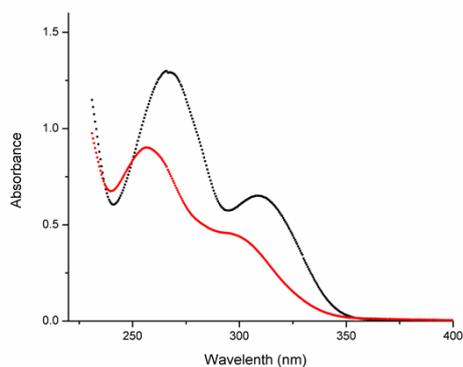


Fig. S1 UV-vis spectra of [C₁₂mim][OMCA] at the IL concentration of 1 mM in water: ●, before UV irradiation; ●, after UV irradiation.

Table S1. Bromide content in [C_nmim][OMCA] ionic liquids

IL	[Br ⁻]/mol.kg ⁻¹
[C ₄ mim][OMCA]	0.0050
[C ₆ mim][OMCA]	0.0089
[C ₈ mim][OMCA]	0.0015
[C ₁₀ mim][OMCA]	0.0016
[C ₁₂ mim][OMCA]	<0.00002
[C ₁₄ mim][OMCA]	<0.00002
[C ₁₆ mim][OMCA]	<0.00008

Table S2. Thermal properties of the [C_nmim][OMCA] ionic liquids

IL	T _m / °C	T _g / °C	T _d / °C
[C ₄ mim][OMCA]	-	-19	225
[C ₆ mim][OMCA]	-	-20	220
[C ₈ mim][OMCA]	64	-	220
[C ₁₀ mim][OMCA]	72	-	230
[C ₁₂ mim][OMCA]	68	-	240
[C ₁₄ mim][OMCA]	65	-	240
[C ₁₆ mim][OMCA]	69	-	255

References

1. P. D. María, *Angew. Chem. Int. Ed.*, 2008, **47**, 6960.
2. K. R. Seddon, A. Stark, M. Torres, *Pure Appl. Chem.*, 2000, **72**, 2275.

