

Supplementary Information

Infrared spectroscopic study of absorption and separation of CO using copper(I)-containing ionic liquids

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Figures S1-S3: Data from high pressure IR experiments for $[C_n\text{mim}][\text{CuX}_2] + \text{CO}$ reactions.

Figures S4-S5: UV/vis spectra of solutions of Cu(II) and Cu(I) salts in MeNO_2 .

Figures S6-S7: Data from gas phase IR measurements for determination of headspace CO content.

Synthesis of 1-alkyl-3-methylimidazolium halide salts

HPIR spectroscopic data for CO uptake experiments

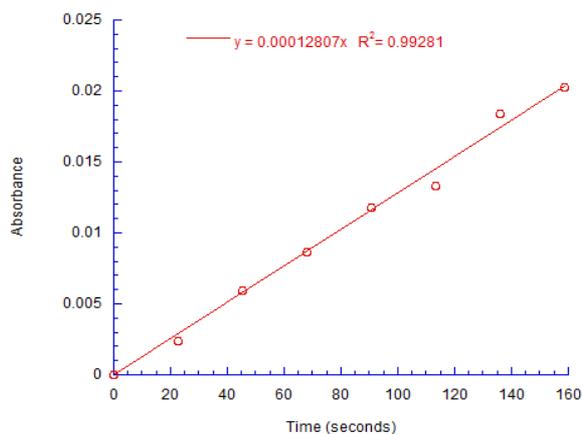


Figure S1. Plot of IR absorbance (2076 cm^{-1}) vs. time for first 160 s of CO uptake by $[\text{C}_6\text{mim}][\text{CuCl}_2]$ at $25\text{ }^\circ\text{C}$ (stirrer speed 428 rpm) with initial $p\text{CO} = 8\text{ bar}$.

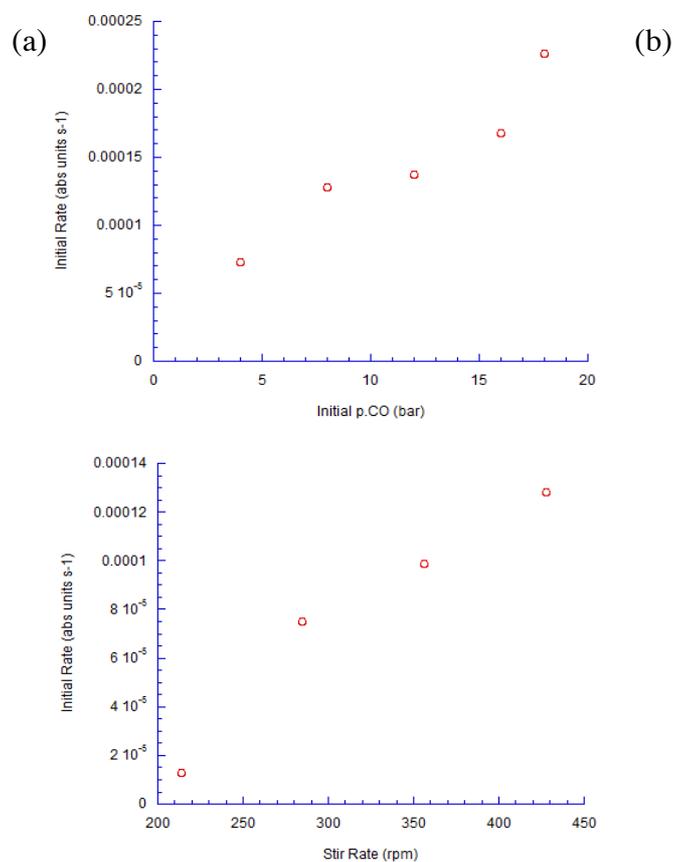


Figure S2. Initial rate of CO uptake for $[\text{C}_6\text{mim}][\text{CuCl}_2]$ at 25 °C (from slopes of absorbance vs. time plots, e.g. Fig S1) (a) vs. initial CO pressure (with stirrer speed 428 rpm) and (b) vs. stir rate (with initial $p_{\text{CO}} = 8$ bar).

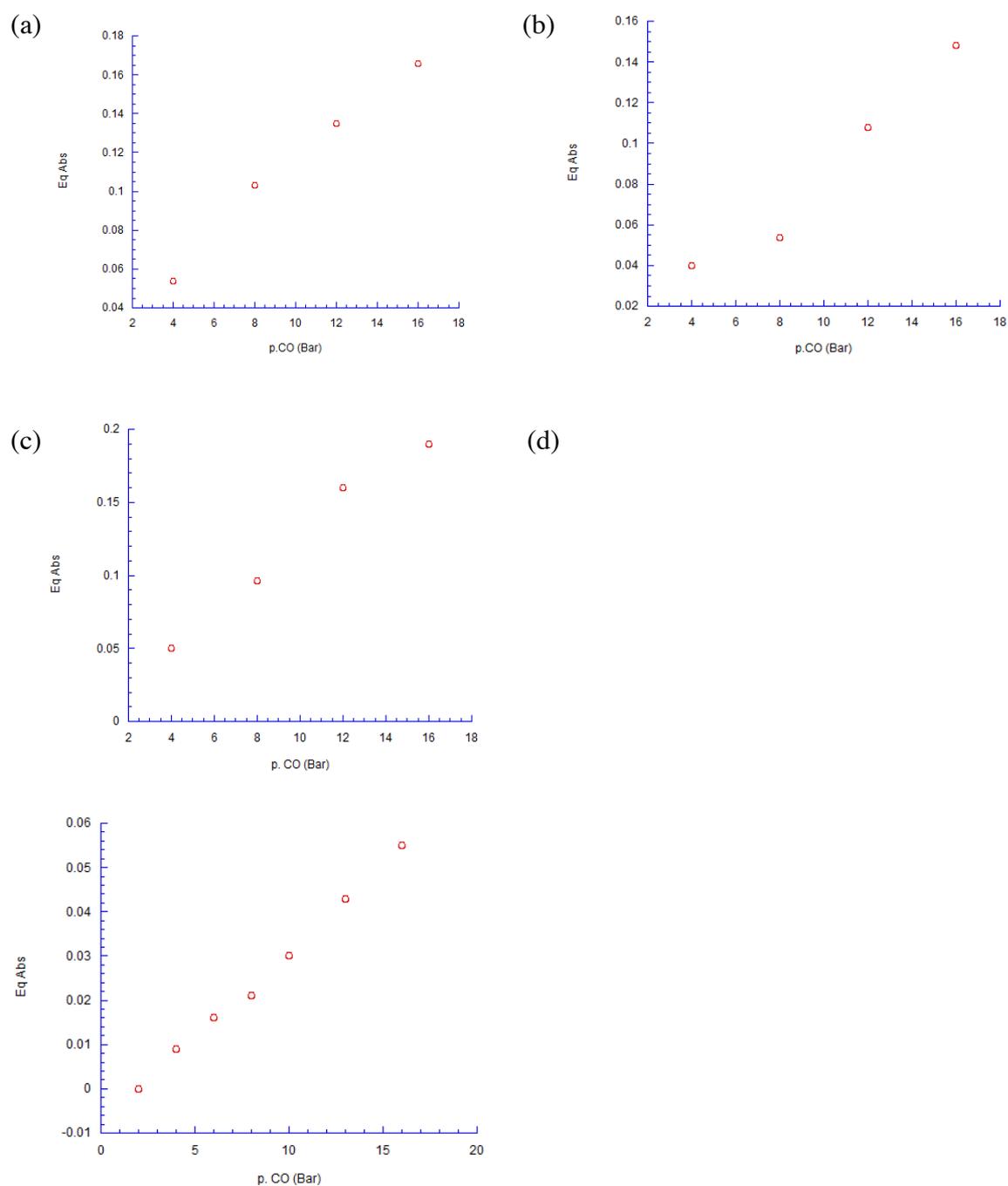


Figure S3. Plots of equilibrium $\nu(\text{CO})$ intensity vs. initial CO pressure for CO uptake at 25 °C by (a) $[\text{C}_2\text{mim}][\text{CuBr}_2]$; (b) $[\text{C}_4\text{mim}][\text{CuBr}_2]$; (c) $[\text{C}_6\text{mim}][\text{CuBr}_2]$; (d) $[\text{C}_6\text{mim}][\text{CuI}_2]$.

UV/visible spectroscopic analysis for trace Cu(II)

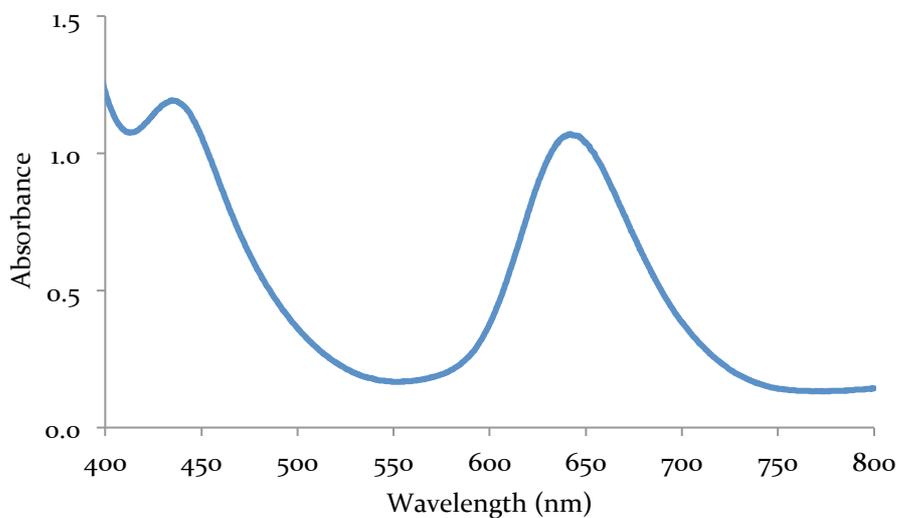


Figure S4. UV/vis spectrum of a 0.001 M solution of a 1:1 mixture of [C₆mim]Br and CuBr₂ in CH₃NO₂, showing strong absorptions due to Cu(II).

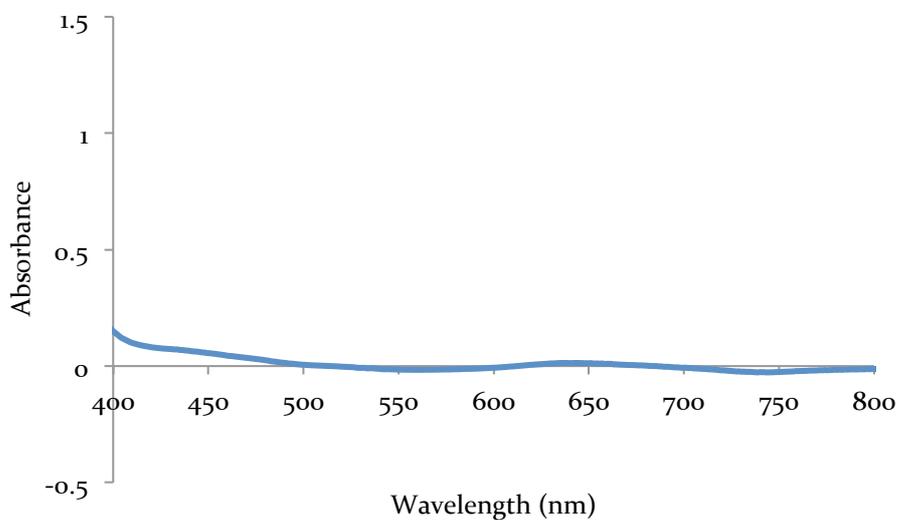


Figure S5. UV/vis spectrum of a 0.01 M solution of [C₆mim][CuBr₂] in CH₃NO₂. Note the very weak absorptions due to trace Cu(II) despite the 10x higher Cu concentration compared to Figure S4. Estimated Cu(II) content is <0.1% of total Cu.

Gas-phase IR data for quantification of CO content of gas mixtures

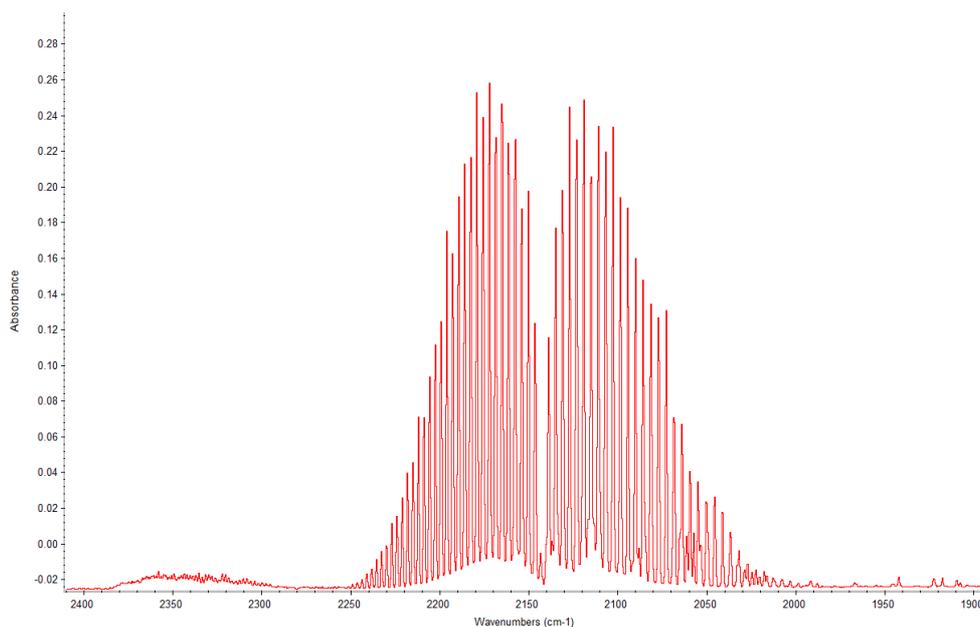


Figure S6. Example gas phase IR spectrum ($\nu(\text{CO})$ region) of CO/H₂ mixture in 10 cm gas cell.

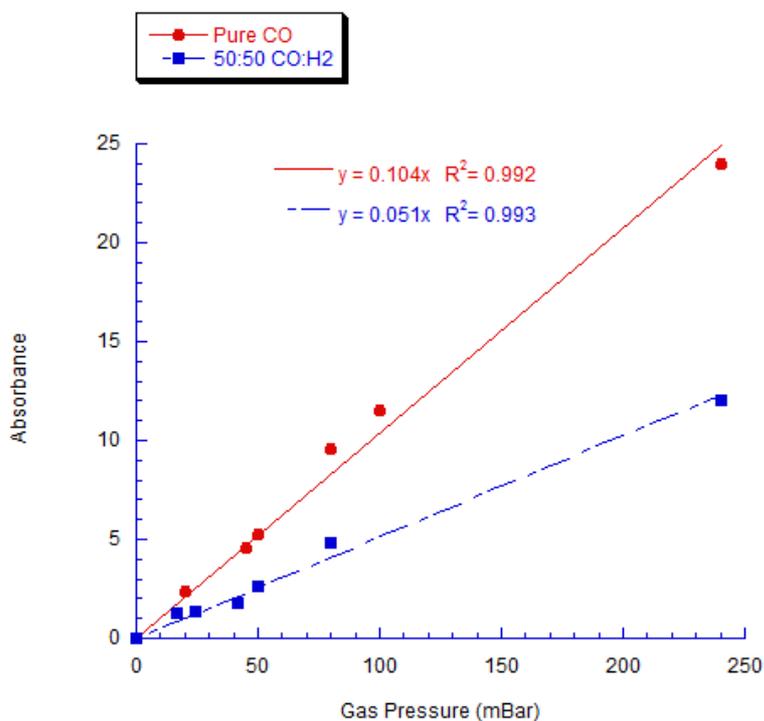


Figure S7. Beer-Lambert calibration plots for pure CO and 1:1 CO:H₂ in 10 cm gas cell. Absorbances are integrated intensities over frequency range 2250-1975 cm⁻¹.

Synthesis of 1-alkyl-3-methylimidazolium halide salts

The synthetic procedure for the 1-alkyl-3-methylimidazolium halide salts was adapted from similar methods reported in the literature.^{1,2} In a typical procedure, 1-methylimidazole or 1,2-dimethylimidazole (~ 0.250 mol) was placed into a degassed and dried round bottom flask under N₂. In the case of the chloride and bromide salts, the alkyl halide precursor was added in excess (~ 1.2 equivalents) and the reaction mixture heated to 80-90 °C overnight, with the exception being reactions involving the low-boiling bromoethane, which were carried out at 40 °C. For the iodide salts, 1 equivalent of alkyl iodide was added dropwise at 0 °C over approximately 20-30 minutes. The reaction vessel was wrapped in foil to prevent the light-induced formation of I₂. The reaction mixture was then stirred at room temperature overnight. ¹H NMR spectroscopy was used to assess complete reaction of the 1-methylimidazole. If required, a further 0.1 equivalents of the alkyl halide was added and the reaction allowed to continue for a further 6 hours under the same conditions as previously used. Unreacted alkyl halide was removed under reduced pressure and the product was dried under vacuum at 80 °C for at least 4 h. All the products were collected either as hygroscopic solids or liquids and were analysed by ¹H NMR spectroscopy, ¹³C NMR spectroscopy, electrospray mass spectrometry (ES⁺ and ES⁻) and CHN elemental analysis.

1-hexyl-3-methylimidazolium chloride [C₆mim]Cl pale yellow viscous liquid (36.65 g, 96 %).

¹H NMR (250 MHz, CDCl₃) δ/ppm, 0.75 (3H, t, 6.9 Hz), 1.15-1.30 (6H, m), 1.80 (2H, m), 4.05 (3H, s), 4.22 (2H, t, 7.4 Hz), 7.46 (1H, s), 7.65 (s, 1H), 10.50 (1H, s)

¹H NMR (250 MHz, CD₃NO₂) δ/ppm, 0.89 (3H, t, 6.9 Hz), 1.22-1.42 (6H, m), 1.94 (2H, m), 4.02 (3H, s), 4.30 (2H, t, 7.4 Hz), 7.51 (1H, s), 7.54 (s, 1H), 9.41 (1H, s)

¹³C NMR (250 MHz, CDCl₃), 13.8, 22.2, 25.7, 30.1, 30.9, 36.3, 49.8, 121.9, 123.8, 137.5

TOF MS (ES⁺): m/z 167 ([C₆mim]⁺)

Elemental analysis, calculated for C₁₀H₁₉N₂Cl: C 59.22% H 9.38% N 13.83%, found:

C 57.88% H 9.71% N 13.76%

1-ethyl-3-methylimidazolium bromide [C₂mim]Br white crystalline solid (47.96 g, 96 %).

¹H NMR (400 MHz, CDCl₃) δ/ppm, 1.6 (3H, t, 7.4Hz), 4.1 (3H, s), 4.40 (2H, q, 7.4Hz), 7.50 (1H, s), 7.52 (1H, s), 10.43 (1H, s)

^{13}C NMR (250 MHz, CDCl_3) δ /ppm, 15.57, 36.53, 45.04, 122.01, 123.64, 136.50

TOF MS (ES^+); m/z 111 ($[\text{C}_2\text{mim}]^+$), (ES^-); m/z 79 ($[\text{Br}]^-$)

Elemental analysis, calculated for $\text{C}_6\text{H}_{11}\text{N}_2\text{Br}$: C 37.72% H 5.76% N 14.67%, found: C 37.03% H 5.84% N 14.21%

1-butyl-3-methylimidazolium bromide [C_4mim] Br yellow viscous liquid (26.91 g, 98 %).

^1H NMR (250 MHz, CDCl_3) δ /ppm, 0.9 (3H, t, 7.4Hz), 1.15 (2H, m), 1.7 (2H, m), 3.90 (3H, s), 4.15 (2H, t, 7.3Hz), 4.44 (1H, s), 7.55 (1H, s), 10.10 (1H, s)

^{13}C NMR (250 MHz, CDCl_3) δ /ppm, 13.2, 19.2, 32.1, 36.7, 49.7, 122.1, 123.7, 136.9

TOF MS (ES^+), m/z 139 ($[\text{C}_4\text{mim}]^+$), (ES^-); m/z 79 ($[\text{Br}]^-$)

Elemental analysis, calculated for $\text{C}_8\text{H}_{15}\text{N}_2\text{Br}$: C 43.86% H 6.85% N 12.79%, found: C 43.09% H 6.85% N 12.53%

1-hexyl-3-methylimidazolium bromide [C_6mim] Br pale yellow liquid (29.74g, 96 %).

^1H NMR (250 MHz, CDCl_3) δ /ppm, 0.75 (3H, m), 1.1-1.3 (6H, m), 1.7-1.8 (2H, m), 4.0 (3H, s), 4.2 (2H, t, 7.3Hz), 7.4 (1H, s), 7.6 (1H, s), 9.88 (1H, s)

^1H NMR (250 MHz, CD_3NO_2) δ /ppm, 0.89 (3H, t, 6.9Hz), 1.2-1.4 (6H, m), 1.95 (2H, m), 4.01 (3H, s), 4.3 (2H, t, 7.3Hz), 7.53 (1H, s), 7.55 (1H, s), 9.22 (1H, s)

^{13}C NMR (250 MHz, CDCl_3) δ /ppm, 13.9, 22.1, 25.5, 30.25, 31.0, 36.75, 50.0, 122.0, 123.7, 137.0

TOF MS (ES^+); m/z 167 ($[\text{C}_6\text{mim}]^+$), (ES^-); (m/z) 79 ($[\text{Br}]^-$)

Elemental analysis, calculated for $\text{C}_{10}\text{H}_{19}\text{N}_2\text{Br}$: C 48.60% H 7.70% N 11.34%, found: C 47.28% H 7.73% N 11.07%

1-hexyl-3-methylimidazolium iodide [C_6mim] I , was isolated as a pale yellow liquid (yield = 31.19 g, 83 %).

^1H NMR (400 MHz, CDCl_3) δ /ppm, 0.75 (3H, m), 1.1-1.3 (6H, m), 1.85 (2H, m), 4.00 (2H, s), 4.28 (2H, t, Hz), 7.48 (1H, s), 7.58 (1H, s), 9.85 (1H, s)

^1H NMR (250 MHz, CD_3NO_2) δ /ppm, 0.90 (3H, t, 6.9 Hz), 1.3-1.4 (6H, m), 1.94 (2H, m), 4.02 (2H, s), 4.29 (2H, t, 7.3Hz), 7.51 (1H, s), 7.55 (1H, s), 8.89 (1H, s)

^{13}C NMR (250 MHz, CDCl_3) δ /ppm, 13.79, 22.15, 25.60, 30.01, 30.84, 37.00, 49.49, 122.34, 123.82, 136.25

TOF MS (ES^+); m/z 167 ($[\text{C}_6\text{mim}]^+$), (ES^-); (m/z) 127 ($[\text{I}]^-$)

Elemental analysis, calculated for $\text{C}_{10}\text{H}_{19}\text{N}_2\text{I}$: C 40.30% H 6.5% N 9.5%, found: C 40.30% H 7.05% N 9.14%

References

1. S. Liu, C. Xie, S. Yu and F. Liu, *Cat. Comm.*, 2009, **10**, 986.
2. S. V. Dzyuba and R. A. Bartsch, *J. Heterocycl. Chem.*, 2001, **38**, 265.