

# **Electronic Supplementary Information**

## **Empirical Study of Physicochemical and Spectral Properties of Cu<sup>II</sup>-Containing Chelate-Based Ionic Liquids**

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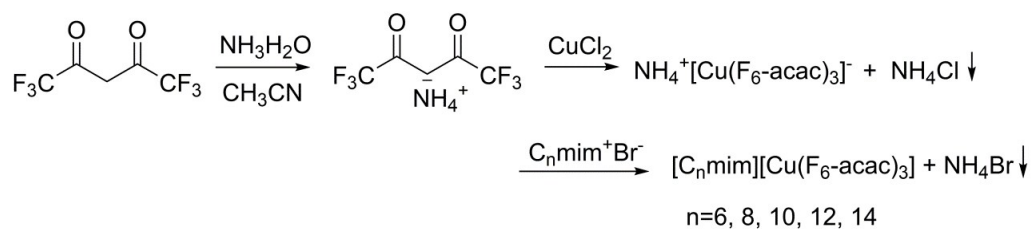
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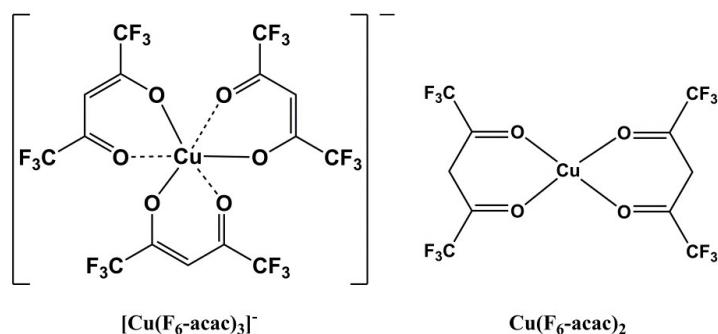
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## Scheme and Figure

**Scheme S<sub>1</sub>.** A brief method for the synthesis of chelate-based ILs.



**Figure S<sub>1</sub>.** The structure of  $[\text{Cu}(\text{F}_6\text{-acac})_3]^-$  and  $\text{Cu}(\text{F}_6\text{-acac})_2$ .



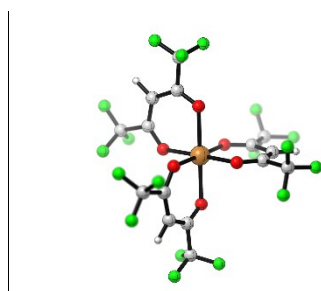
## Calculation Section

### Cartesian Coordinates and Energies

G: Sum of RI-(U)BP86/SVP Gibbs free energy corrections.

All energies are given in Hartree.

**$[\text{Cu}(\text{F}_6\text{-acac})_3]^-$**



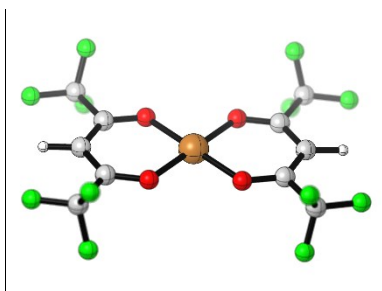
G = -4460.462656

0 imaginary frequencies

|   |           |           |            |
|---|-----------|-----------|------------|
| C | 2.2196409 | 1.5171398 | -3.3225369 |
| C | 1.3148109 | 1.5878198 | -2.0630779 |
| O | 1.1922629 | 0.4574168 | -1.5012279 |
| C | 0.7717489 | 2.8398858 | -1.7235669 |

|    |            |            |            |
|----|------------|------------|------------|
| C  | -0.0640821 | 3.0613558  | -0.5902849 |
| O  | -0.4579281 | 2.2417488  | 0.2657911  |
| C  | -0.5521001 | 4.5222278  | -0.3530549 |
| F  | 2.3874639  | 2.7190578  | -3.9367969 |
| F  | 3.4515749  | 1.0590648  | -2.9999739 |
| F  | 1.6958419  | 0.6706548  | -4.2391189 |
| F  | -0.0453551 | 5.0062168  | 0.8082901  |
| F  | -0.1899481 | 5.3916868  | -1.3373829 |
| F  | -1.9002151 | 4.5668998  | -0.2580169 |
| C  | 0.3535039  | -4.4269242 | -0.8451119 |
| C  | -0.1384461 | -2.9484522 | -0.8314789 |
| O  | 0.5218359  | -2.1952102 | -0.0852319 |
| C  | -1.2642491 | -2.6373762 | -1.6479689 |
| C  | -1.8406251 | -1.3571482 | -1.7363069 |
| O  | -1.5225021 | -0.2686102 | -1.1689469 |
| C  | -3.0743921 | -1.1925942 | -2.6646319 |
| F  | 0.2687709  | -4.9640962 | 0.3965631  |
| F  | -0.3550321 | -5.2384122 | -1.6791019 |
| F  | 1.6490469  | -4.4946162 | -1.2299059 |
| F  | -4.1511991 | -0.7774822 | -1.9578269 |
| F  | -2.8317821 | -0.2671062 | -3.6215139 |
| F  | -3.4310241 | -2.3415662 | -3.2996289 |
| C  | 2.9379779  | 0.4531658  | 3.2577321  |
| C  | 1.5776569  | 0.1693738  | 2.5670241  |
| O  | 1.6111159  | 0.3324968  | 1.3162771  |
| C  | 0.4925099  | -0.2235362 | 3.3819411  |
| C  | -0.7872241 | -0.4902022 | 2.8473231  |
| O  | -1.1698291 | -0.4402512 | 1.6456561  |
| C  | -1.9178091 | -0.8881852 | 3.8326921  |
| F  | 3.8993409  | -0.3571992 | 2.7641951  |
| F  | 3.3227989  | 1.7310938  | 3.0418961  |
| F  | 2.9002039  | 0.2643848  | 4.6037551  |
| F  | -2.8833341 | 0.0584408  | 3.8504051  |
| F  | -2.4884561 | -2.0534562 | 3.4592151  |
| F  | -1.4794151 | -1.0419442 | 5.1106171  |
| Cu | 0.0321879  | 0.0222078  | 0.0901951  |
| H  | -1.7138871 | -3.4412502 | -2.2407139 |
| H  | 1.0108699  | 3.6929998  | -2.3676769 |
| H  | 0.6476719  | -0.3197202 | 4.4615151  |

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**Cu(F<sub>6</sub>-acac)<sub>2</sub>**



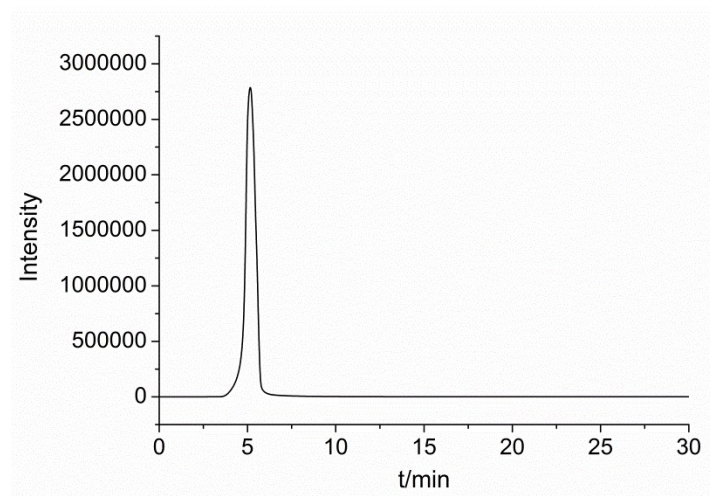
G = -3520.435019

0 imaginary frequencies

|    |            |            |            |
|----|------------|------------|------------|
| C  | 3.3043717  | 1.1914928  | -2.4299293 |
| C  | 1.8245337  | 1.0094968  | -1.9966493 |
| O  | 1.6993407  | 0.4107598  | -0.8827493 |
| C  | 0.8038997  | 1.4980498  | -2.8360783 |
| C  | -0.5542953 | 1.3529898  | -2.4903453 |
| O  | -1.0411773 | 0.8056748  | -1.4520123 |
| C  | -1.6374403 | 1.9078478  | -3.4546693 |
| F  | 3.4111197  | 1.8352958  | -3.6131903 |
| F  | 3.9697987  | 1.9050018  | -1.5016773 |
| F  | 3.8969927  | -0.0118532 | -2.5514103 |
| F  | -2.3924573 | 2.8231968  | -2.8180943 |
| F  | -1.0937753 | 2.4933618  | -4.5446913 |
| F  | -2.4371863 | 0.9069928  | -3.8701223 |
| C  | -3.3042773 | -1.1883362 | 2.4316347  |
| C  | -1.8246043 | -1.0106262 | 1.9960717  |
| O  | -1.6996373 | -0.4182452 | 0.8787167  |
| C  | -0.8038433 | -1.4962082 | 2.8370177  |
| C  | 0.5541587  | -1.3559992 | 2.4886737  |
| O  | 1.0409237  | -0.8149662 | 1.4470007  |
| C  | 1.6374117  | -1.9084642 | 3.4542837  |
| F  | -3.9720813 | -1.9041672 | 1.5069937  |
| F  | -3.4107823 | -1.8273492 | 3.6175857  |
| F  | -3.8945253 | 0.0165978  | 2.5492037  |
| F  | 1.0938147  | -2.4910522 | 4.5460157  |
| F  | 2.3921907  | -2.8255012 | 2.8200267  |
| F  | 2.4373007  | -0.9065912 | 3.8670717  |
| Cu | -0.0001673 | -0.0046022 | -0.0025553 |
| H  | 1.0705727  | 1.9974908  | -3.7736853 |
| H  | -1.0701793 | -1.9902872 | 3.7775627  |

## Experimental Section

**Figure S<sub>2</sub>.** HPLC of the IL [C<sub>10</sub>mim][Cu(F<sub>6</sub>-acac)<sub>3</sub>] (with acetonitrile as the solvent).



**Table S<sub>1</sub>.** Copper contents in the ILs.

| Entry | ILs(n) | Exp(%) | Cal(%) | δ%   |
|-------|--------|--------|--------|------|
| 1     | 6      | 7.58   | 7.46   | 1.60 |
| 2     | 8      | 6.93   | 7.22   | 4.00 |
| 3     | 10     | 6.81   | 7.00   | 2.70 |
| 4     | 12     | 6.50   | 6.79   | 4.20 |
| 5     | 14     | 6.27   | 6.59   | 4.80 |

Exp(%) refers to the experimental results from AAS; Cal(%) refers to the theoretical calculation results; δ% refers to standard deviation.

**Table S<sub>2</sub>.** Density,  $\rho$  (g·cm<sup>-3</sup>), Viscosity,  $\eta$  (mPa·s), Conductivity,  $\kappa$  (μS·cm<sup>-1</sup>), and Surface Tension,  $\gamma$  (mN·m<sup>-1</sup>), of [C<sub>n</sub>mim][Cu(F<sub>6</sub>-acac)<sub>3</sub>] (n = 6, 8, 10, 12, 14) at 298.15 to 323.15 K

| n | T/K    | $\rho$ | $\eta$ | $\kappa$ | $\gamma$ |
|---|--------|--------|--------|----------|----------|
| 6 | 298.15 | 1.505  | -      | 47.9     | -        |
|   | 303.15 | 1.500  | 560.4  | 61.1     | 32.93    |
|   | 308.15 | 1.490  | 383.9  | 89.2     | 29.46    |
|   | 313.15 | 1.490  | 255.7  | 112.6    | 27.71    |
|   | 318.15 | 1.480  | 182.6  | 148.7    | 26.48    |
|   | 323.15 | 1.470  | 132.9  | 199.7    | 25.22    |
| 8 | 298.15 | 1.458  | -      | 43.8     | 33.83    |

| n  | T/K    | $\rho$ | $\eta$ | $\kappa$ | $\gamma$ |
|----|--------|--------|--------|----------|----------|
| 10 | 303.15 | 1.451  | 434.3  | 56.4     | 28.04    |
|    | 308.15 | 1.445  | 290.7  | 81.6     | 25.39    |
|    | 313.15 | 1.439  | 203.1  | 105.5    | 23.61    |
|    | 318.15 | 1.433  | 138.1  | 138.5    | 23.02    |
|    | 323.15 | 1.427  | 103.8  | 183.3    | 22.13    |
|    | 298.15 | 1.426  | -      | 32.0     | 27.48    |
|    | 303.15 | 1.420  | 364.5  | 41.6     | 25.42    |
|    | 308.15 | 1.414  | 250.0  | 58.8     | 24.22    |
|    | 313.15 | 1.409  | 178.7  | 80.5     | 22.29    |
|    | 318.15 | 1.403  | 129.0  | 106.5    | 21.38    |
|    | 323.15 | 1.397  | 97.1   | 145.1    | 20.90    |
|    | 298.15 | 1.384  | -      | 27.4     | 28.86    |
|    | 303.15 | 1.378  | 374.5  | 35.8     | 28.25    |
|    | 308.15 | 1.373  | 268.7  | 54.4     | 26.05    |
|    | 313.15 | 1.367  | 190.8  | 75.7     | 23.73    |
| 12 | 318.15 | 1.361  | 139.0  | 98.4     | 22.39    |
|    | 323.15 | 1.356  | 104.2  | 131.6    | 21.14    |
|    | 298.15 | 1.344  | -      | 23.5     | 39.37    |
|    | 303.15 | 1.339  | 449.8  | 33.1     | 34.15    |
|    | 308.15 | 1.334  | 311.9  | 47.6     | 29.17    |
|    | 313.15 | 1.330  | 217.5  | 66.8     | 26.60    |
| 14 | 318.15 | 1.324  | 157.9  | 94.4     | 24.84    |
|    | 323.15 | 1.318  | 117.5  | 122.6    | 23.72    |

### ESI-MS and IR information

[C<sub>6</sub>mim][Cu(F<sub>6</sub>-acac)<sub>3</sub>]: ESI-MS: [C<sub>6</sub>mim]<sup>+</sup> 167.2; [Cu(F<sub>6</sub>-acac)<sub>3</sub>]<sup>-</sup> 684.0. FT-IR: 3447, 3155, 2938, 2867, 1647, 1552, 1529, 1498, 1463, 1257, 1204, 1149, 1086, 796, 670, 584 cm<sup>-1</sup>.

[C<sub>8</sub>mim][Cu(F<sub>6</sub>-acac)<sub>3</sub>]: ESI-MS: [C<sub>8</sub>mim]<sup>+</sup> 195.2; [Cu(F<sub>6</sub>-acac)<sub>3</sub>]<sup>-</sup> 684.0. FT-IR: 3154, 2934, 2862, 1647, 1552, 1529, 1499, 1464, 1258, 1204, 1150, 1086, 796, 670, 585 cm<sup>-1</sup>.

[C<sub>10</sub>mim][Cu(F<sub>6</sub>-acac)<sub>3</sub>]: ESI-MS: [C<sub>10</sub>mim]<sup>+</sup> 223.1; [Cu(F<sub>6</sub>-acac)<sub>3</sub>]<sup>-</sup> 684.0. FT-IR: 3460, 3155, 2931, 2860, 1647, 1552, 1529, 1499, 1463, 1258, 1204, 1150, 1086, 796, 670, 585 cm<sup>-1</sup>.

[C<sub>12</sub>mim][Cu(F<sub>6</sub>-acac)<sub>3</sub>]: ESI-MS: [C<sub>12</sub>mim]<sup>+</sup> 251.3; [Cu(F<sub>6</sub>-acac)<sub>3</sub>]<sup>-</sup> 684.0. FT-IR: 3455, 3155, 2930, 2858, 1647, 1552, 1529, 1499, 1464, 1257, 1205, 1149, 1086, 796, 670 cm<sup>-1</sup>.

[C<sub>14</sub>mim][Cu(F<sub>6</sub>-acac)<sub>3</sub>]: ESI-MS: [C<sub>14</sub>mim]<sup>+</sup> 279.3; [Cu(F<sub>6</sub>-acac)<sub>3</sub>]<sup>-</sup> 684.0. FT-IR: 3154, 2929, 2857, 1645, 1552, 1530, 1504, 1463, 1256, 1204, 1147, 1086, 796, 670, 585 cm<sup>-1</sup>.