

# Electronic Supplementary Information

## Enhanced tunability afforded by aqueous biphasic systems formed by fluorinated ionic liquids and carbohydrates

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## 1. Experimental data

**Table S1.** Binodal weight fraction data for [C<sub>2</sub>C<sub>1</sub>py][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>] (1) + monosaccharide (2) + H<sub>2</sub>O (3).

| Glucose                   |                           | Galactose                 |                           | Fructose                  |                           |
|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 100 <i>w</i> <sub>1</sub> | 100 <i>w</i> <sub>2</sub> | 100 <i>w</i> <sub>1</sub> | 100 <i>w</i> <sub>2</sub> | 100 <i>w</i> <sub>1</sub> | 100 <i>w</i> <sub>2</sub> |
| 13.8195                   | 0.1606                    | 2.0060                    | 0.5598                    | 2.7241                    | 0.5905                    |
| 7.9024                    | 0.2860                    | 1.8149                    | 0.5965                    | 2.3143                    | 0.6416                    |
| 3.9789                    | 0.3545                    | 1.6399                    | 0.6390                    | 2.0899                    | 0.6701                    |
| 3.4303                    | 0.4140                    | 1.4836                    | 0.6832                    | 1.9679                    | 0.7080                    |
| 3.0170                    | 0.4604                    | 1.3387                    | 0.7310                    | 1.8844                    | 0.7205                    |
| 2.6679                    | 0.5077                    | 1.2522                    | 0.7585                    | 1.7646                    | 0.7759                    |
| 2.3864                    | 0.5551                    | 1.0924                    | 0.8192                    | 1.6001                    | 0.8409                    |
| 2.1185                    | 0.6139                    | 1.0179                    | 0.8511                    | 1.4732                    | 0.8791                    |
| 1.9208                    | 0.6620                    | 0.9544                    | 0.8786                    | 1.3708                    | 0.9081                    |
| 1.7473                    | 0.7102                    | 0.9002                    | 0.9037                    | 1.2862                    | 0.9211                    |
| 1.6107                    | 0.7476                    | 0.8383                    | 0.9364                    | 1.2354                    | 0.9551                    |
| 1.5161                    | 0.7696                    | 0.7573                    | 0.9805                    | 1.1541                    | 0.9926                    |
| 1.4124                    | 0.8056                    | 0.6975                    | 1.0237                    | 1.0847                    | 1.0188                    |
| 1.3141                    | 0.8444                    | 0.6443                    | 1.0545                    | 1.0310                    | 1.0477                    |
| 1.2497                    | 0.8623                    | 0.5944                    | 1.0885                    | 0.9883                    | 1.0608                    |
| 1.1783                    | 0.8905                    | 0.5371                    | 1.1364                    | 0.9645                    | 1.0654                    |
| 1.1085                    | 0.9213                    | 0.4849                    | 1.1727                    | 0.9357                    | 1.1030                    |
| 1.0504                    | 0.9536                    | 0.4592                    | 1.2057                    | 0.8927                    | 1.1311                    |
| 1.0091                    | 0.9662                    | 0.4373                    | 1.2424                    | 0.8525                    | 1.1482                    |
| 0.9573                    | 0.9942                    | 0.3693                    | 1.3153                    | 0.8056                    | 1.2021                    |
| 0.9076                    | 1.0239                    | 0.2886                    | 1.4251                    | 0.7667                    | 1.2120                    |
| 0.8844                    | 1.0287                    | 0.2667                    | 1.5571                    | 0.7676                    | 1.2060                    |
| 0.8396                    | 1.0589                    | 0.1617                    | 2.0250                    | 0.7376                    | 1.2326                    |
| 0.8170                    | 1.0659                    |                           |                           | 0.6990                    | 1.2750                    |
| 0.7801                    | 1.0929                    |                           |                           | 0.6689                    | 1.2819                    |
| 0.7490                    | 1.1129                    |                           |                           | 0.6478                    | 1.2955                    |
| 0.7257                    | 1.1238                    |                           |                           | 0.6394                    | 1.3179                    |
| 0.6965                    | 1.1442                    |                           |                           | 0.6197                    | 1.3423                    |
| 0.6656                    | 1.1710                    |                           |                           | 0.5876                    | 1.3687                    |
| 0.6432                    | 1.1876                    |                           |                           | 0.5584                    | 1.3861                    |
| 0.6421                    | 1.1858                    |                           |                           | 0.5314                    | 1.4265                    |
| 0.6217                    | 1.2024                    |                           |                           | 0.5188                    | 1.4500                    |
| 0.6042                    | 1.2141                    |                           |                           | 0.5064                    | 1.4448                    |
| 0.5297                    | 1.2819                    |                           |                           | 0.4195                    | 1.5703                    |
| 0.4022                    | 1.4272                    |                           |                           |                           |                           |
| 0.3130                    | 1.5866                    |                           |                           |                           |                           |
| 0.1891                    | 2.7327                    |                           |                           |                           |                           |

**Table S2.** Binodal weight fraction data for  $[C_2C_1py][C_4F_9SO_3]$  (1) + monosaccharide (2) +  $H_2O$  (3).

| Arabinose |           | Mannose   |           |
|-----------|-----------|-----------|-----------|
| 100 $w_1$ | 100 $w_2$ | 100 $w_1$ | 100 $w_2$ |
| 5.3213    | 0.4689    | 1.5248    | 0.8037    |
| 3.5129    | 0.6454    | 1.2824    | 0.8845    |
| 3.0337    | 0.7324    | 1.1079    | 0.9350    |
| 2.7047    | 0.8120    | 0.9467    | 1.0121    |
| 2.3394    | 0.9156    | 0.8551    | 1.0711    |
| 1.9780    | 1.0424    | 0.7634    | 1.1218    |
| 1.6069    | 1.2039    | 0.6701    | 1.1991    |
|           |           | 0.5906    | 1.2371    |
|           |           | 0.5434    | 1.2655    |
|           |           | 0.5041    | 1.2987    |
|           |           | 0.4636    | 1.3429    |
|           |           | 0.4363    | 1.3624    |
|           |           | 0.4118    | 1.4009    |
|           |           | 0.3839    | 1.4347    |
|           |           | 0.3549    | 1.4769    |
|           |           | 0.3269    | 1.4977    |
|           |           | 0.2856    | 1.5630    |
|           |           | 0.2627    | 1.6111    |
|           |           | 0.2403    | 1.6378    |
|           |           | 0.2254    | 1.6712    |
|           |           | 0.2015    | 1.7398    |
|           |           | 0.1792    | 1.8172    |
|           |           | 0.1588    | 1.8689    |
|           |           | 0.1246    | 2.0379    |

**Table S3.** Binodal weight fraction data for [C<sub>2</sub>C<sub>1</sub>py][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>] (1) + disaccharide (2) + H<sub>2</sub>O (3).

| Sucrose   |           | Maltose   |           |
|-----------|-----------|-----------|-----------|
| 100 $w_1$ | 100 $w_2$ | 100 $w_1$ | 100 $w_2$ |
| 11.6500   | 0.1774    | 14.9766   | 0.0823    |
| 3.6823    | 0.2591    | 2.7314    | 0.2243    |
| 2.8357    | 0.3057    | 2.4874    | 0.2377    |
| 2.5012    | 0.3257    | 2.3362    | 0.2516    |
| 2.2483    | 0.3711    | 2.1728    | 0.2691    |
| 2.0357    | 0.3940    | 1.9676    | 0.2978    |
| 1.8109    | 0.4359    | 1.8499    | 0.3106    |
| 1.6938    | 0.4517    | 1.7493    | 0.3259    |
| 1.5963    | 0.4756    | 1.6639    | 0.3403    |
| 1.5157    | 0.4928    | 1.5736    | 0.3500    |
| 1.3827    | 0.5332    | 1.4960    | 0.3605    |
| 1.2929    | 0.5461    | 1.3881    | 0.3851    |
| 1.2395    | 0.5587    | 1.2990    | 0.4032    |
| 1.1410    | 0.5903    | 1.2446    | 0.4124    |
| 1.0836    | 0.5977    | 1.1919    | 0.4191    |
| 1.0327    | 0.6223    | 1.1272    | 0.4353    |
| 0.9793    | 0.6234    | 1.0923    | 0.4425    |
| 0.9484    | 0.6356    | 1.0328    | 0.4612    |
| 0.8935    | 0.6608    | 0.9572    | 0.4773    |
| 0.8923    | 0.6601    | 0.9124    | 0.4900    |
| 0.8373    | 0.6874    | 0.8722    | 0.5028    |
| 0.8033    | 0.6980    | 0.8338    | 0.5174    |
| 0.7998    | 0.6894    | 0.8105    | 0.5212    |
| 0.7709    | 0.7107    | 0.7789    | 0.5317    |
| 0.7574    | 0.7192    | 0.7518    | 0.5415    |
| 0.7447    | 0.7140    | 0.7223    | 0.5537    |
| 0.7264    | 0.7237    | 0.7035    | 0.5560    |
| 0.7028    | 0.7442    | 0.6829    | 0.5645    |
| 0.6724    | 0.7557    | 0.6607    | 0.5742    |
| 0.6609    | 0.7656    | 0.6399    | 0.5831    |
| 0.6557    | 0.7635    | 0.6202    | 0.5936    |
| 0.6278    | 0.7773    | 0.6079    | 0.5956    |
| 0.6092    | 0.7961    | 0.5922    | 0.6032    |
| 0.5912    | 0.7983    | 0.5740    | 0.6118    |
| 0.5733    | 0.8185    | 0.5421    | 0.6263    |
| 0.5536    | 0.8289    | 0.5270    | 0.6368    |
| 0.5262    | 0.8357    | 0.5129    | 0.6417    |
| 0.4819    | 0.8747    | 0.4942    | 0.6519    |
| 0.4490    | 0.9016    | 0.4712    | 0.6677    |
| 0.4253    | 0.9373    | 0.4757    | 0.6626    |
| 0.3889    | 0.9650    | 0.4521    | 0.6788    |
| 0.3563    | 0.9955    | 0.4378    | 0.6863    |
| 0.3197    | 1.0366    | 0.4218    | 0.6948    |
| 0.2826    | 1.0837    | 0.3751    | 0.7344    |
| 0.1077    | 3.4617    | 0.3328    | 0.7733    |
|           |           | 0.2888    | 0.8078    |

**Table S4.** Binodal weight fraction data for [C<sub>2</sub>C<sub>1</sub>py][C<sub>4</sub>F<sub>9</sub>SO<sub>3</sub>] (1) + polyols (2) + H<sub>2</sub>O (3).

| Sorbitol           |                    | Xylitol            |                    | Maltitol           |                    |
|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| 100 w <sub>1</sub> | 100 w <sub>2</sub> | 100 w <sub>1</sub> | 100 w <sub>2</sub> | 100 w <sub>1</sub> | 100 w <sub>2</sub> |
| 25.5674            | 0.1526             | 3.2144             | 0.4493             | 1.6627             | 0.3255             |
| 4.3647             | 0.2572             | 2.8015             | 0.4894             | 1.3869             | 0.3563             |
| 3.4525             | 0.3358             | 2.2748             | 0.5829             | 1.2438             | 0.3762             |
| 2.5907             | 0.4186             | 2.1217             | 0.6200             | 1.1030             | 0.3986             |
| 2.2624             | 0.4577             | 1.9618             | 0.6778             | 1.0093             | 0.4284             |
| 2.0249             | 0.5010             | 1.7958             | 0.7067             | 0.9114             | 0.4556             |
| 1.8410             | 0.5214             | 1.6393             | 0.7330             | 0.8069             | 0.4784             |
| 1.6780             | 0.5571             | 1.5574             | 0.7678             | 0.7329             | 0.5082             |
| 1.5258             | 0.5878             | 1.4424             | 0.7953             | 0.6690             | 0.5244             |
| 1.4212             | 0.6059             | 1.3756             | 0.8257             | 0.6125             | 0.5413             |
| 1.3251             | 0.6282             | 1.3068             | 0.8374             | 0.5679             | 0.5665             |
| 1.2359             | 0.6672             | 1.2584             | 0.8637             | 0.5044             | 0.6409             |
| 1.1661             | 0.6843             | 1.2050             | 0.8803             | 0.4805             | 0.6504             |
| 1.1006             | 0.7021             | 1.1591             | 0.9110             | 0.4441             | 0.6600             |
| 0.9685             | 0.7475             | 1.1045             | 0.9406             | 0.4088             | 0.6763             |
| 0.9262             | 0.7509             | 1.0445             | 0.9557             | 0.3838             | 0.6903             |
| 0.9030             | 0.7603             | 1.0117             | 0.9507             | 0.3657             | 0.7010             |
| 0.8727             | 0.7894             | 0.9800             | 0.9677             | 0.3476             | 0.7154             |
| 0.8295             | 0.7895             | 0.9500             | 0.9824             | 0.3304             | 0.7259             |
| 0.8062             | 0.8051             | 0.9217             | 1.0070             | 0.3166             | 0.7316             |
| 0.7822             | 0.8083             | 0.8931             | 1.0312             | 0.2997             | 0.7503             |
| 0.7625             | 0.8204             | 0.8596             | 1.0340             | 0.2862             | 0.7568             |
| 0.7440             | 0.8431             | 0.8368             | 1.0550             | 0.2723             | 0.7705             |
| 0.7196             | 0.8448             | 0.8172             | 1.0716             | 0.2561             | 0.7883             |
| 0.6860             | 0.8748             | 0.7889             | 1.0789             | 0.2394             | 0.7937             |
| 0.6608             | 0.8828             | 0.7696             | 1.0979             | 0.2225             | 0.8019             |
| 0.6388             | 0.8871             | 0.7490             | 1.1128             | 0.2060             | 0.8251             |
| 0.6177             | 0.8995             | 0.7236             | 1.1170             | 0.1903             | 0.8816             |
| 0.5945             | 0.9219             | 0.7058             | 1.1316             | 0.1697             | 0.9102             |
| 0.5780             | 0.9192             | 0.6890             | 1.1473             | 0.1535             | 0.9435             |
| 0.5572             | 0.9401             | 0.6738             | 1.1614             | 0.1342             | 1.0105             |
| 0.5389             | 0.9532             | 0.6537             | 1.1688             |                    |                    |
| 0.5206             | 0.9737             | 0.6297             | 1.1960             |                    |                    |
| 0.5024             | 0.9959             | 0.6035             | 1.2239             |                    |                    |
| 0.4586             | 1.0201             | 0.5427             | 1.2786             |                    |                    |
| 0.4381             | 1.0443             | 0.5195             | 1.3018             |                    |                    |
| 0.4232             | 1.0562             | 0.4944             | 1.3256             |                    |                    |
| 0.4070             | 1.0599             | 0.4703             | 1.3443             |                    |                    |
| 0.3927             | 1.0744             | 0.4495             | 1.3802             |                    |                    |
| 0.3589             | 1.1211             | 0.4277             | 1.3965             |                    |                    |
| 0.3370             | 1.1567             | 0.4075             | 1.4344             |                    |                    |
| 0.3148             | 1.1852             |                    |                    |                    |                    |
| 0.2682             | 1.2554             |                    |                    |                    |                    |
| 0.2474             | 1.2893             |                    |                    |                    |                    |
| 0.2267             | 1.3104             |                    |                    |                    |                    |
| 0.2100             | 1.3432             |                    |                    |                    |                    |
| 0.1952             | 1.3732             |                    |                    |                    |                    |

Table S5. Binodal weight fraction data for  $[C_2C_1Im][C_4F_9SO_3]$  (1) + disaccharide (2) +  $H_2O$  (3).

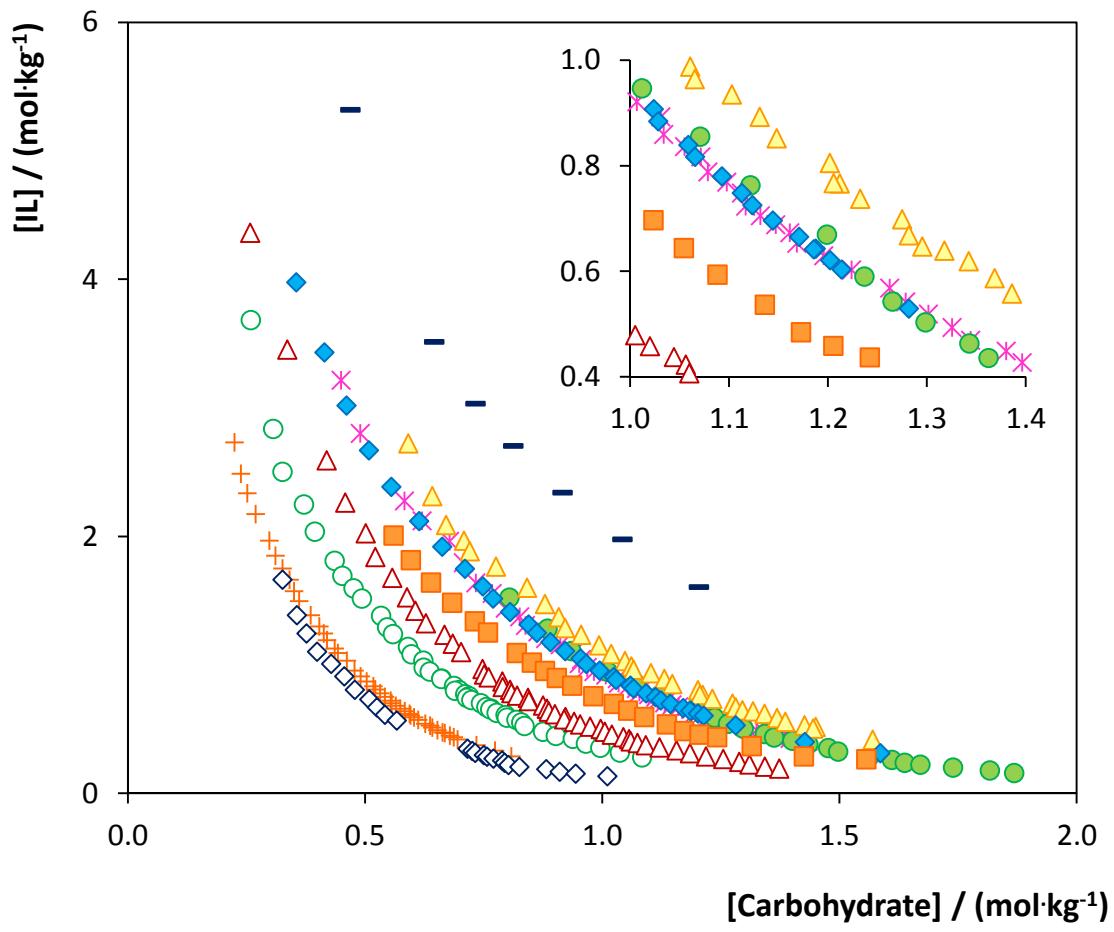
| Maltose   |           |
|-----------|-----------|
| $100 w_1$ | $100 w_2$ |
| 78.9560   | 2.7736    |
| 68.5987   | 4.9861    |
| 62.4715   | 6.8247    |
| 56.2474   | 8.9464    |
| 49.2490   | 11.7382   |
| 43.6179   | 14.0140   |
| 39.1680   | 15.8738   |
| 35.3856   | 17.3774   |
| 31.8022   | 18.9034   |
| 28.2091   | 20.5664   |
| 25.5545   | 21.7155   |
| 23.0762   | 22.8943   |
| 19.7297   | 24.7350   |
| 16.9589   | 26.0657   |
| 14.8521   | 27.2839   |
| 11.7211   | 29.1675   |

**Table S6.** Experimental data for TLs and TLLs of the ABS composed of  $[C_2C_1py][C_4F_9SO_3]$  + D-(+)-Maltose + H<sub>2</sub>O for initial mixture compositions ( $[IL]_M$  and  $[CH]_M$ ), and pH of the respective phases (the subscripts IL and CH refer to IL-rich and CH-rich phases, respectively).

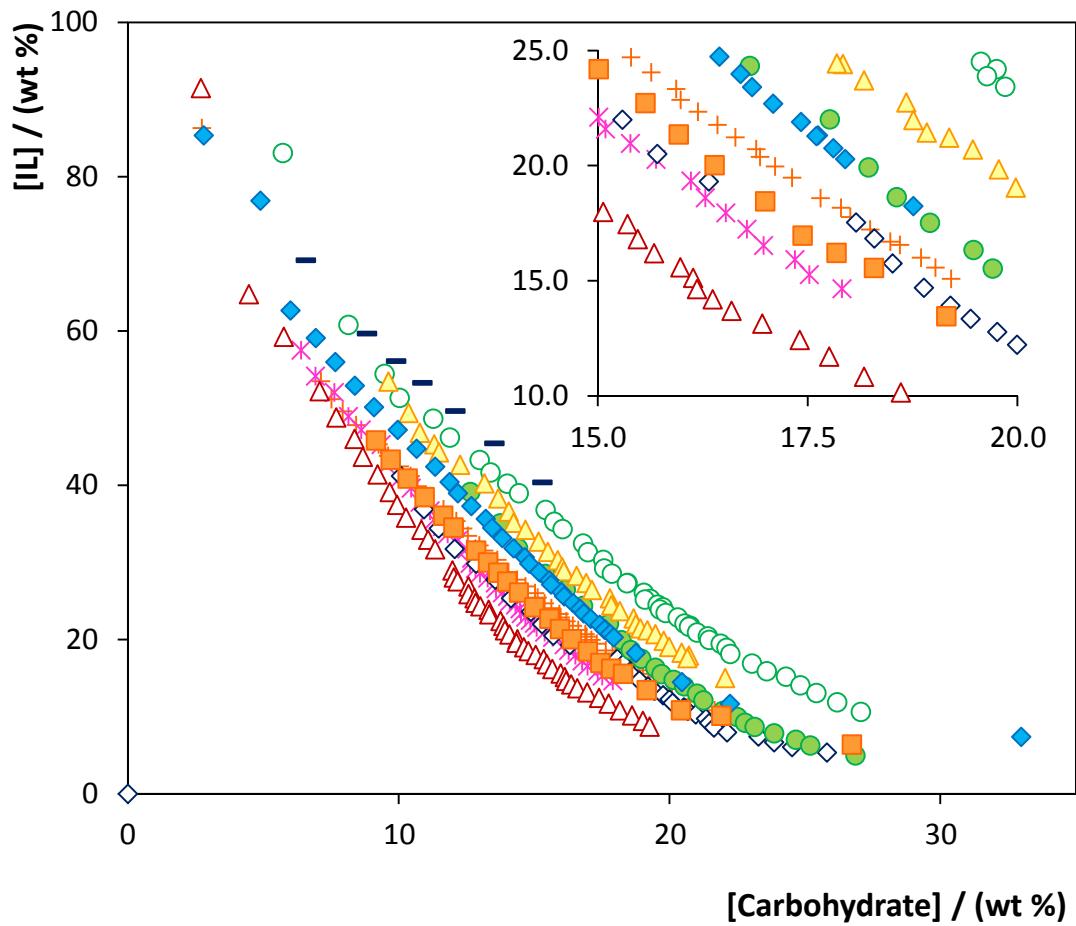
| Weight fraction composition / wt % |             |           |          |          |             |             |           |       |  |
|------------------------------------|-------------|-----------|----------|----------|-------------|-------------|-----------|-------|--|
| $[IL]_{IL}$                        | $[CH]_{IL}$ | $pH_{IL}$ | $[IL]_M$ | $[CH]_M$ | $[IL]_{CH}$ | $[CH]_{CH}$ | $pH_{CH}$ | TLL   |  |
| 87.16                              | 2.60        | 4.75      | 39.94    | 18.27    | 1.44        | 31.05       | 5.49      | 90.32 |  |
| 68.56                              | 4.71        | 4.84      | 39.73    | 14.10    | 5.67        | 25.20       | 5.40      | 66.14 |  |

**Table S7.** Correlation parameters used to describe the experimental binodal data by Eq. 1.<sup>25</sup>

| IL                       | Carbohydrate    | $A \pm \sigma$ | $B \pm \sigma$ | $10^5(C \pm \sigma)$ | $R^2$  |
|--------------------------|-----------------|----------------|----------------|----------------------|--------|
| $[C_2C_1py][C_4F_9SO_3]$ | D-(+)-glucose   | 159.5 ± 6.9    | -0.359 ± 0.018 | 8.98 ± 0.79          | 0.9918 |
| $[C_2C_1py][C_4F_9SO_3]$ | D-(+)-galactose | 269.1 ± 37.8   | -0.563 ± 0.046 | 6.85 ± 1.03          | 0.9955 |
| $[C_2C_1py][C_4F_9SO_3]$ | D-(+)-fructose  | 185.7 ± 14.3   | -0.388 ± 0.025 | 6.67 ± 0.48          | 0.9978 |
| $[C_2C_1py][C_4F_9SO_3]$ | D-(+)-mannose   | 355.3 ± 26.2   | -0.559 ± 0.029 | 2.91 ± 1.05          | 0.9992 |
| $[C_2C_1py][C_4F_9SO_3]$ | D-(+)-arabinose | 154.0 ± 5.3    | -0.310 ± 0.013 | 3.44 ± 5.70          | 0.9995 |
| $[C_2C_1py][C_4F_9SO_3]$ | D-(+)-maltose   | 170.9 ± 2.2    | -0.417 ± 0.005 | 2.21 ± 0.21          | 0.9990 |
| $[C_2C_1py][C_4F_9SO_3]$ | Sucrose         | 238.6 ± 13.3   | -0.456 ± 0.019 | 3.53 ± 0.38          | 0.9927 |
| $[C_2C_1py][C_4F_9SO_3]$ | Maltitol        | 273.9 ± 39.8   | -0.581 ± 0.046 | 10.0 ± 0.75          | 0.9960 |
| $[C_2C_1py][C_4F_9SO_3]$ | D-Sorbitol      | 200.2 ± 5.6    | -0.490 ± 0.012 | 14.4 ± 0.70          | 0.9963 |
| $[C_2C_1py][C_4F_9SO_3]$ | Xylitol         | 154.1 ± 6.7    | -0.373 ± 0.016 | 14.4 ± 0.60          | 0.9982 |
| $[C_2C_1im][C_4F_9SO_3]$ | D-(+)-maltose   | 115.9 ± 0.5    | -0.231 ± 0.002 | 4.19 ± 0.04          | 0.9999 |



**Figure S1.** Ternary phase diagrams for ABS composed of  $[C_2C_1py][C_4F_9SO_3]$  + carbohydrate + water at 298 K and atmospheric pressure: ( $\diamond$ ) maltitol; ( $+$ ) maltose; ( $\circ$ ) sucrose; ( $\triangle$ ) sorbitol; ( $\blacksquare$ ) galactose; ( $\blacklozenge$ ) glucose; ( $*$ ) xylitol; ( $\bullet$ ) mannose; ( $\blacktriangle$ ) fructose; (—) arabinose.



**Figure S2.** Ternary phase diagrams for ABS composed of  $[C_2C_1py][C_4F_9SO_3]$  + carbohydrate + water at 298 K and atmospheric pressure: ( $\diamond$ ) maltitol; ( $\square$ ) maltose; ( $\circ$ ) sucrose; ( $\triangle$ ) sorbitol; ( $\blacksquare$ ) galactose; ( $\blacklozenge$ ) glucose; ( $*$ ) xylitol; ( $\bullet$ ) mannose; ( $\blacktriangleright$ ) fructose; ( $-$ ) arabinose.