

## Supporting information

### Cooperative CO<sub>2</sub> Absorption by Amino Acid based Ionic Liquids with Balanced Dual Sites

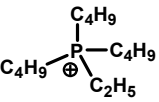
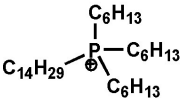
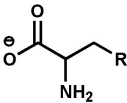
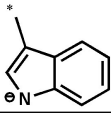
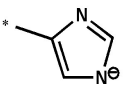
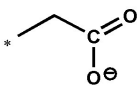
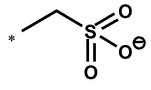
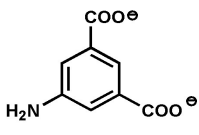
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**Content:**

|                                                        |           |
|--------------------------------------------------------|-----------|
| <b>1. Supporting table.....</b>                        | <b>S1</b> |
| <b>2. Supporting Figures .....</b>                     | <b>S3</b> |
| <b>3. NMR and IR data of amine acid-based ILs.....</b> | <b>S5</b> |
| <b>4. References.....</b>                              | <b>S7</b> |

## 1. Supporting table

**Table S1.** Structures, names and abbreviations of ILs discussed in this work.

| Structure                                                                           | Ion name                        | Abbreviation          |
|-------------------------------------------------------------------------------------|---------------------------------|-----------------------|
|    | Tributyl(ethyl)phosphonium      | [P <sub>4442</sub> ]  |
|    | Trihexyl(tetradecyl)phosphonium | [P <sub>66614</sub> ] |
|    | Dual sites ion                  | [AA-R]                |
|    | Tryptophan                      | Ind                   |
|   | Histidine                       | Im                    |
|  | Glutamate                       | Ac                    |
|  | DL-homocysteic Acid             | Su                    |
|  | 5-Aminoisophthalic Acid         | [Am-iPA]              |

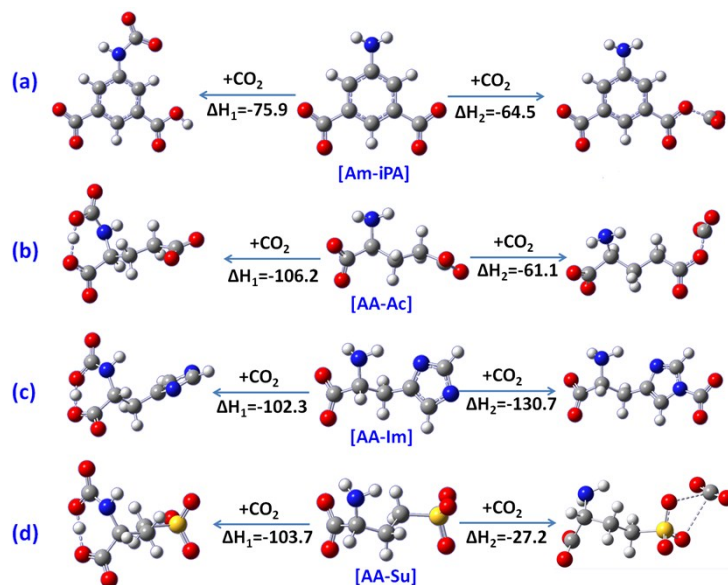
**Table S2.** The H<sub>2</sub>O content in ILs detected by Karl Fisher detector and the ILs' content calculated from NMR spectra.

| IL                                          | 1 <sup>st</sup> detection (wt.%) | 2 <sup>nd</sup> detection (wt.%) | H <sub>2</sub> O content (wt.%) | IL content (%) |
|---------------------------------------------|----------------------------------|----------------------------------|---------------------------------|----------------|
| [P <sub>66614</sub> ] <sub>2</sub> [AA-Im]  | -0.007                           | -0.005                           | <0.03                           | 97.1           |
| [P <sub>66614</sub> ] <sub>2</sub> [AA-su]  | -0.002                           | -0.005                           | <0.03                           | 97.4           |
| [P <sub>66614</sub> ] <sub>2</sub> [AA-Ac]  | 0.403                            | 0.403                            | 0.40                            | 97.5           |
| [P <sub>66614</sub> ] <sub>2</sub> [AA-Ind] | -0.004                           | -                                | <0.03                           | >99            |
| [P <sub>66614</sub> ] <sub>2</sub> [Am-iPA] | 0.252                            | -                                | 0.25                            | 97.8           |

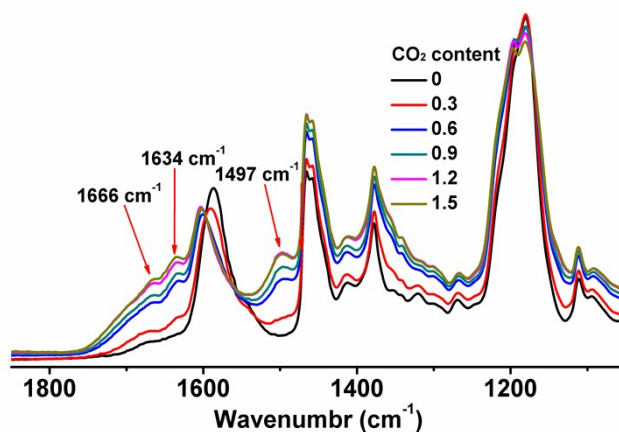
**Table S3.** Comparison of CO<sub>2</sub> absorption properties of some typical ILs with dual sites.

| Absorbent                                                                                                                                                                                                                                                                         | T (°C) | CO <sub>2</sub> capacity <sup>a</sup> (mol/mol IL) | reference |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|----------------------------------------------------|-----------|
| [P <sub>66614</sub> ] <sub>2</sub> [Am-iPA]                                                                                                                                                                                                                                       | 30     | 2.38                                               | This work |
| [P <sub>66614</sub> ] <sub>2</sub> [Asp]                                                                                                                                                                                                                                          | 30     | 1.96                                               | 1         |
| [P <sub>4442</sub> ] <sub>2</sub> [IDA]                                                                                                                                                                                                                                           | 40     | 1.69                                               | 2         |
| [P <sub>4442</sub> ][Suc]                                                                                                                                                                                                                                                         | 20     | 1.87                                               | 3         |
| [P <sub>4442</sub> ][Cy-Suc]                                                                                                                                                                                                                                                      | 20     | 2.21                                               | 4         |
| [P <sub>66614</sub> ][2-Op]                                                                                                                                                                                                                                                       | 20     | 1.58                                               | 5         |
| [P <sub>66614</sub> ][4-CHO-Im]                                                                                                                                                                                                                                                   | 30     | 1.24                                               | 6         |
| [P <sub>66614</sub> ][2-Op]                                                                                                                                                                                                                                                       | 20     | 1.69                                               | 7         |
| [TBP][Arg]                                                                                                                                                                                                                                                                        | 30     | 1.52 (4.79) <sup>b</sup>                           | 8         |
| [TBP][Lys]                                                                                                                                                                                                                                                                        | 30     | 1.59 (5.02) <sup>b</sup>                           | 8         |
| 1-(2-hydroxyethyl)-2,3-dimethylimidazolium phenoxide                                                                                                                                                                                                                              | 25     | 1.58                                               | 9         |
| [P <sub>66614</sub> ][PhO]                                                                                                                                                                                                                                                        | 22     | 0.68 <sup>c</sup>                                  | 10        |
| [N <sub>66614</sub> ][Lys]                                                                                                                                                                                                                                                        | 22     | 2.1                                                | 11        |
| [NH <sub>2</sub> -pmim][Im]                                                                                                                                                                                                                                                       | 40     | ~0.75                                              | 12        |
| <sup>a</sup> CO <sub>2</sub> capacity was obtained under 1 bar CO <sub>2</sub> pressure. <sup>b</sup> the CO <sub>2</sub> capacity in brackets is belonged to 3% IL aqueous solution. <sup>c</sup> CO <sub>2</sub> capacity was obtained under 1.38 bar CO <sub>2</sub> pressure. |        |                                                    |           |

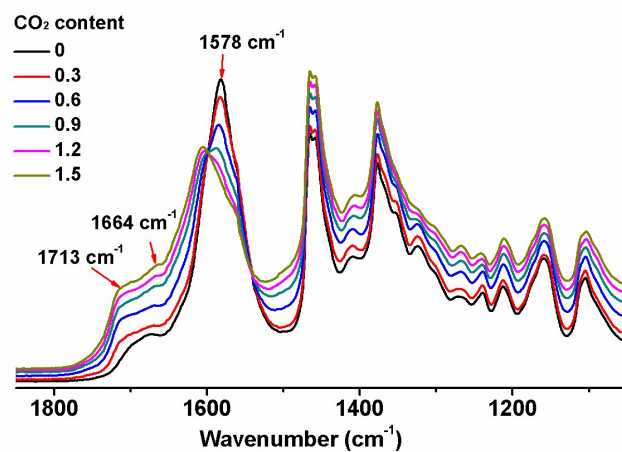
## 2. Supporting Figures



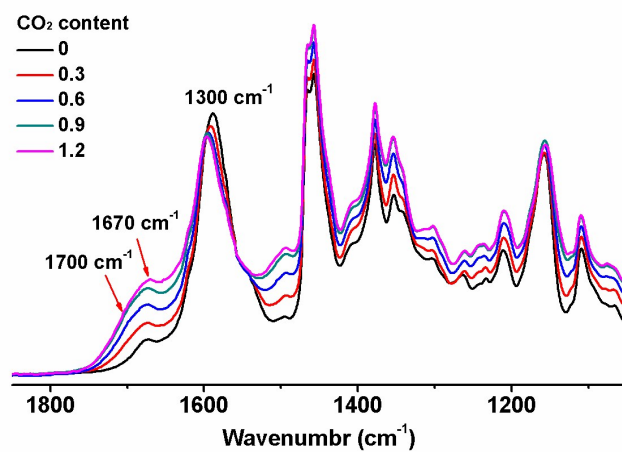
**Figure S1.** Reaction enthalpies of CO<sub>2</sub> with one site of [AA-anion] calculated by Gaussian program at B3LYP-31++G(d,p) level.  $\Delta H$ , kJ/mol; gray, C atom; white, H atom; red, O atom; blue, N atom; yellow, S atom.



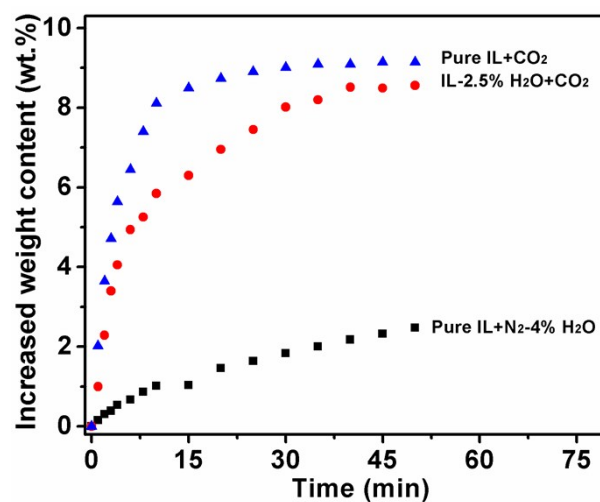
**Figure S2.** Partial IR spectra of [P<sub>66614</sub>]<sub>2</sub>[AA-Su] varied with CO<sub>2</sub> content.



**Figure S3.** Partial IR spectra of  $[P_{66614}]_2[AA-Im]$  varied with  $CO_2$  content.



**Figure S4.** Partial IR spectra of  $[P_{66614}]_2[AA-Ind]$  varied with  $CO_2$  content.



**Figure S5.**  $CO_2$  and moisture absorption with  $[P_{66614}]_2[Am-iPA]$  and its  $H_2O$  containing complex.

### 3. NMR and IR data of amine acid-based ILs

**[P<sub>66614</sub>]<sub>2</sub>[AA-Ac]:** <sup>1</sup>H NMR (DMSO, ppm): 0.851 (t, 6H, CH<sub>3</sub>), 0.882 (t, 18H, CH<sub>3</sub>), 1.237 (m, 36H, CH<sub>2</sub>), 1.378 (m, 16H, CH<sub>2</sub>), 1.448 (m, 16H, CH<sub>2</sub>), 1.557 (m, 4H, CH<sub>2</sub>), 1.728 (m, 4H, CH<sub>2</sub>), 2.181 (m, 16H, CH<sub>2</sub>), 2.582 (m, 1H, CH); <sup>13</sup>C NMR(DMSO, ppm): 14.231, 17.313, 17.699, 20.647, 21.834, 22.105, 28.181, 28.749, 29.046, 29.106, 29.743, 29.863, 30.453, 31.323, 33.516, 36.826, 57.014, 176.128, 177.002.

**[P<sub>66614</sub>]<sub>2</sub>[AA-Ac]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.857 (t, 6H, CH<sub>3</sub>), 0.877 (t, 18H, CH<sub>3</sub>), 1.243 (m, 32H, CH<sub>2</sub>), 1.285(m, 28H, CH<sub>2</sub>), 1.379 (m, 16H, CH<sub>2</sub>), 1.460 (m, 16H, CH<sub>2</sub>), 1.567 (m, 4H, CH<sub>2</sub>), 1.680 (m, 2H, CH<sub>2</sub>), 1.979 (m, 1H, CH), 2.091(m, 2H, CH<sub>2</sub>), 2.193(m, 16H, CH<sub>2</sub>); <sup>13</sup>C NMR(DMSO, ppm): 13.559, 17.345, 17.730, 20.661, 21.802, 22.087, 28.225, 28.776, 29.073, 29.711, 29.832, 30.402, 31.337, 37.021, 42.803, 51.717, 157.539, 159.935, 174.052, 176.380.

**[P<sub>66614</sub>]<sub>2</sub>[AA-Im]:** <sup>1</sup>H NMR (DMSO, ppm): 0.858 (t, 6H, CH<sub>3</sub>), 0.879 (t, 18H, CH<sub>3</sub>), 1.243 (m, 32H, CH<sub>2</sub>), 1.285(m, 28H, CH<sub>2</sub>), 1.378 (m, 16H, CH<sub>2</sub>), 1.456 (m, 16H, CH<sub>2</sub>), 1.566 (m, 4H, CH<sub>2</sub>), 2.191 (m, 12H, CH<sub>2</sub>), 2.389 (m, 2H, CH<sub>2</sub>), 2.798 (m, 2H, NH<sub>2</sub>), 2.931 (t, 2H, CH<sub>2</sub>), 6.574 (s, 1H, Im), 7.374 (s, 1H, Im); 13.469, 13.726, 17.218, 17.594, 20.539, 21.180, 21.872, 20.047, 27.099, 27.575, 28.094, 29.044, 29.660, 29.780, 30.371, 30.804, 31.261, 33.383, 56.657, 120.951, 133.69, 134.577, 176.65.

**[P<sub>66614</sub>]<sub>2</sub>[AA-Im]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.859 (t, 6H, CH<sub>3</sub>), 0.879 (t, 18H, CH<sub>3</sub>), 1.244 (m, 32H, CH<sub>2</sub>), 1.286(m, 28H, CH<sub>2</sub>), 1.379 (m, 16H, CH<sub>2</sub>), 1.457 (m, 16H, CH<sub>2</sub>), 1.567 (m, 4H, CH<sub>2</sub>), 2.174 (m, 12H, CH<sub>2</sub>), 2.676 (m, 1H, CH<sub>2</sub>), 2.866 (m, 2H, NH<sub>2</sub>), 3.539 (t, 2H, CH<sub>2</sub>), 6.654 (s, 1H, Im), 7.419 (s, 1H, Im); <sup>13</sup>C NMR (DMSO, ppm): 13.860, 13.924, 17.344, 17.720, 20.651, 21.283, 21.893, 22.002, 22.180, 27.160, 27.622, 28.211, 28.761, 28.822, 29.078, 29.117, 29.772, 29.892, 29.996, 30.116, 30.207, 30.312, 30.492, 30.915, 31.394, 56.027, 121.379, 131.739, 133.828, 157.44, 174.701.

**[P<sub>66614</sub>]<sub>2</sub>[AA-Ind]:** <sup>1</sup>H NMR (DMSO, ppm): 0.858 (t, 6H, CH<sub>3</sub>), 0.878 (t, 18H, CH<sub>3</sub>), 1.244 (m, 32H, CH<sub>2</sub>), 1.289 (m, 28H, CH<sub>2</sub>), 1.376 (m, 16H, CH<sub>2</sub>), 1.453 (m, 16H, CH<sub>2</sub>), 1.566 (m, 4H, CH<sub>2</sub>), 2.182(m, 12H, CH<sub>2</sub>), 2.483 (m, 1H, CH), 3.060 (m, 2H, CH<sub>2</sub>), 6.921(t, 1H, Ph), 7.014(t, 1H, Ph), 7.099(s, 1H, Im), 7.297(d, 1H, Ph), 7.508(d, 1H, Ph); <sup>13</sup>C NMR (DMSO, ppm): 13.455, 13.871, 17.282, 17.659, 21.600, 21.264, 21.858, 21.960, 22.138, 27.138, 27.612, 28.153, 28.806, 29.017, 29.060, 29.738, 29.585, 29.952, 30.151, 30.455, 30.865, 31.342, 32.802, 57.170, 117.258, 113.252,

117.609, 118.492, 120.273, 123.095, 127.834, 136.397, 176.783.

**[P<sub>66614</sub>]<sub>2</sub>[AA-Ind]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.860 (t, 6H, CH<sub>3</sub>), 0.880 (t, 18H, CH<sub>3</sub>), 1.245 (m, 32H, CH<sub>2</sub>), 1.286(m, 28H, CH<sub>2</sub>), 1.378 (m, 16H, CH<sub>2</sub>), 1.454 (m, 16H, CH<sub>2</sub>), 1.567 (m, 4H, CH<sub>2</sub>), 2.177(m, 12H, CH<sub>2</sub>), 2.897 (m, 1H, CH), 3.122 (m, 2H, CH<sub>2</sub>), 6.933(t, 1H, Ph), 7.030(t, 1H, Ph), 7.107 (s, 1H, Im), 7.308 (d, 1H, Ph), 7.494(d,1H, Ph); <sup>13</sup>C NMR (DMSO, ppm): 13.451, 13.878, 13.947, 17.321, 17.697, 20.608, 20.643, 21.198, 21.290, 21.903, 22.014, 22.194, 27.128, 27.614, 28.22, 28.770, 28.833, 29.128, 29.165, 29.185, 29.769, 29.889, 29.992, 30.112, 30.212, 30.317, 30.501, 30.924, 31.405, 31.317, 56.936, 111.350, 117.748, 118.380, 121.274, 123.606, 127.902, 136.157, 165.622, 174.403.

**[P<sub>66614</sub>]<sub>2</sub>[AA-Su]:** <sup>1</sup>H NMR (DMSO, ppm): 0.850 (t, 6H, CH<sub>3</sub>), 0.872 (t, 18H, CH<sub>3</sub>), 1.236 (m, 32H, CH<sub>2</sub>), 1.281 (m, 28H, CH<sub>2</sub>), 1.378 (m, 16H, CH<sub>2</sub>), 1.462 (m, 16H, CH<sub>2</sub>), 1.557 (m, 4H, CH<sub>2</sub>), 1.829 (m, 1H, CH), 2.417 (m, 2H, CH<sub>2</sub>), 2.703 (t, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (DMSO, ppm): 13.705, 17.289, 17.665, 20.599, 21.811, 22.080, 28.186, 28.740, 29.036, 29.080, 29.718, 29.839, 29.970, 30.090, 30.148, 30.253, 30.433, 31.309, 32.233, 49.614, 55.911, 176.331.

**[P<sub>66614</sub>]<sub>2</sub>[AA-Su]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.840 (t, 6H, CH<sub>3</sub>), 0.862 (t, 18H, CH<sub>3</sub>), 1.226 (m, 32H, CH<sub>2</sub>), 1.275 (m, 28H, CH<sub>2</sub>), 1.378 (m, 16H, CH<sub>2</sub>), 1.460 (m, 16H, CH<sub>2</sub>), 1.558 (m, 4H, CH<sub>2</sub>), 1.811 (m, 1H, CH), 1.950 (m, 2H, CH<sub>2</sub>), 2.484 (t, 2H, CH<sub>2</sub>); <sup>13</sup>C NMR (DMSO, ppm): 13.731, 17.386, 17.762, 20.677, 21.267, 21.875, 21.989, 22.163, 27.124, 27.637, 28.277, 28.839, 29.133, 29.185, 29.758, 29.878, 30.015, 30.134, 30.235, 30.342, 30.502, 30.931, 31.403, 48.653, 55.368, 60.622, 157.454, 158.358, 174.219.

**[P<sub>66614</sub>]<sub>2</sub>[Am-iPA]:** <sup>1</sup>H NMR (DMSO, ppm): 0.860 (t, 6H, CH<sub>3</sub>), 0.878 (t, 18H, CH<sub>3</sub>), 1.247 (m, 32H, CH<sub>2</sub>), 1.283 (m, 28H, CH<sub>2</sub>), 1.374 (m, 16H, CH<sub>2</sub>), 1.454(m, 16H, CH<sub>2</sub>), 2.193 (m,16H, CH<sub>2</sub>), 4.390 (s, 2H, NH<sub>2</sub>), 6.997 (s, 2H, Ph), 7.528 (s 1H, Ph); <sup>13</sup>C NMR (DMSO, ppm): 14.261, 17.851, 18.228, 21.146, 22.332, 22.608, 28.708, 29.557, 29.602, 30.225, 30.346, 30.463, 30.582, 30.967, 56.237, 116.211, 122.194, 141.672, 145.995, 170.326.

**[P<sub>66614</sub>]<sub>2</sub>[Am-iPA]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.857 (t, 6H, CH<sub>3</sub>), 0.869 (t, 18H, CH<sub>3</sub>), 1.244 (m, 32H, CH<sub>2</sub>), 1.279 (m, 28H, CH<sub>2</sub>), 1.368 (m, 16H, CH<sub>2</sub>), 1.458(m, 16H, CH<sub>2</sub>), 2.188 (m, 16H, CH<sub>2</sub>), 7.092 (s, 2H, Ph), 7.604 (s 1H, Ph); <sup>13</sup>C NMR(DMSO, ppm): 14.213, 17.900, 18.276, 21.174, 22.338, 22.628, 28.739, 29.298, 29.642, 30.230, 30.350, 30.473, 30.599, 30.982, 56.278, 116.382, 119.946, 139.760, 146.761, 156.544, 157.669, 170.883.

#### 4. References

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