

## **Enhanced CO<sub>2</sub> capture by reducing cation-anion interactions in hydroxyl-pyridine anion-based ionic liquids**

Xiao-Yan Luo,<sup>a</sup> Xiao-Yan Chen,<sup>a</sup> Rong-Xing Qiu,<sup>a</sup> Bao-You Pei,<sup>a</sup> Yi Wei,<sup>a</sup> Min Hu,<sup>a</sup> Jin-Qing Lin,<sup>\*a</sup> Jing-Yang Zhang<sup>a</sup> and Geng-Geng Luo<sup>\*a,b</sup>

<sup>a</sup> Key Laboratory of Environmental Friendly Function Materials Ministry of Education, Ministry of Education, College of Materials Science and Engineering, Huaqiao University, Xiamen 361021, P.R. China;

<sup>b</sup> State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou 350002, P.R. China

*E-mail:* linlab@hqu.edu.cn;

[ggluo@hqu.edu.cn](mailto:ggluo@hqu.edu.cn)

### **Electronic supplementary information (ESI)**

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**(1) NMR and IR spectra data of ILs used in this work** (py C<sub>n</sub> represents the H on the n<sup>th</sup> position of the hydroxyl pyridium anion, im C<sub>n</sub> represents the H on the n<sup>th</sup> position of the imidazolium cation)

**N<sub>4442</sub>Br:** <sup>1</sup>H NMR(DMSO, ppm): 0.79 (t, 9H, CH<sub>3</sub>), 1.02 (t, 3H, CH<sub>3</sub>), 1.20 (m, 6H, CH<sub>2</sub>), 1.49 (m, 6H, CH<sub>2</sub>), 3.03 (m, 6H, CH<sub>2</sub>), 3.15 (q, 2H, CH<sub>2</sub>).

**[N<sub>4442</sub>][2-Op]:** <sup>1</sup>H NMR (DMSO, ppm): 0.78 (m, 9H, CH<sub>3</sub>), 1.05 (m, 3H, CH<sub>3</sub>), 1.18 (m, 6H, CH<sub>2</sub>), 1.44 (m, 6H, CH<sub>2</sub>), 2.95 (m, 6H, CH<sub>2</sub>), 3.06 (m, 2H, CH<sub>2</sub>), 6.27 (m, 1H, py C4), 6.35 (m, 1H, py C5), 7.33 (m, 1H, py C3), 7.61 (m, 1H, py C6); <sup>13</sup>C NMR (DMSO, ppm): 6.6, 12.8, 19.1, 23.0, 53.4, 57.4, 110.3, 114.5, 139.9, 145.1, 170.0; FT-IR (cm<sup>-1</sup>): 2960, 2873, 1580 (s, ν<sub>C-O</sub>), 1531, 1353 and 1140 (w, ν<sub>C-N</sub>), 1280 (s, ν<sub>C-O</sub>), 978, 778, 730.

**[N<sub>4442</sub>][2-Op]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.73 (m, 9H, CH<sub>3</sub>), 1.00 (m, 3H, CH<sub>3</sub>), 1.19~1.39 (m, 12H, CH<sub>2</sub>), 1.88~2.06 (m, 8H, CH<sub>2</sub>), 6.38 (m, 2H, py C4 and C5), 7.33 (m, 1H, py C3), 7.50 (m, 1H, Py C6); <sup>13</sup>C NMR (DMSO, ppm): 4.6, 11.4, 11.9, 12.6, 16.9, 17.3, 22.5, 22.3, 109.0, 118.8, 143.8, 160.4, 164.4, 172.6; FT-IR (cm<sup>-1</sup>): 2961, 2874, 1671 (m, ν<sub>C=O</sub>), 1647 (s, ν<sub>C=O</sub>), 1599 (s, ν<sub>C-O</sub>), 1542, 1374 (s, ν<sub>C-O</sub>), 1338 and 1152 (w, ν<sub>C-N</sub>), 1237, 981, 778, 730.

**[P<sub>4442</sub>][2-Op]:** <sup>1</sup>H NMR (DMSO, ppm): 0.90 (t, 9H, CH<sub>3</sub>), 1.10 (m, 3H, CH<sub>3</sub>), 1.34~1.50 (m, 12H, CH<sub>2</sub>), 2.20~2.36 (m, 8H, CH<sub>2</sub>), 5.75 (m, 2H, py C4 and C5), 6.88 (m, 1H, py C3), 7.58 (m, 1H, py C6); <sup>13</sup>C NMR (DMSO, ppm): 5.9, 11.6, 12.0, 13.7, 17.3, 17.7, 23.5, 23.8, 23.9, 103.9, 114.0, 135.8, 148.5, 173.3; FT-IR (cm<sup>-1</sup>): 2958, 2931, 2874, 1584 (s, ν<sub>C-O</sub>), 1526, 1355 and 1136 (w, ν<sub>C-N</sub>), 1284, 972, 774, 728.

**[P<sub>4442</sub>][2-Op]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.91 (m, 9H, CH<sub>3</sub>), 1.12 (m, 3H, CH<sub>3</sub>), 1.30~1.54 (m, 6H, CH<sub>2</sub>), 2.22 (m, 8H, CH<sub>2</sub>), 6.15 (m, 1H, py C4), 6.28 (m, 1H, py C5), 7.40 (m, 1H, Py C3), 7.46 (m, 1H, Py C6); <sup>13</sup>C NMR (DMSO, ppm): 5.8, 11.6, 12.0, 13.7, 17.2, 17.6, 23.1, 23.8, 23.9, 105.3, 120.0, 136.8, 141.2, 159.9, 177.6; FT-IR (cm<sup>-1</sup>): 2958, 2931, 2874, 1668 (m, ν<sub>C=O</sub>), 1647 (s, ν<sub>C=O</sub>), 1600 (s, ν<sub>C-O</sub>), 1540, 1371 and 1238 (s, ν<sub>C-O</sub>), 1149 (m, ν<sub>C-N</sub>), 974, 771, 728.

**[P<sub>8884</sub>][2-Op]:** <sup>1</sup>H NMR (DMSO, ppm): 0.87 (m, 12H, CH<sub>3</sub>), 1.20~1.50 (m, 40H, CH<sub>2</sub>), 2.18 (m, 8H, CH<sub>2</sub>), 5.74 (m, 2H, py C4 and py C5), 6.89 (m, 1H, py C3), 7.54 (m, 1H, py C6);

$^{13}\text{C}$  NMR (DMSO, ppm): 13.7, 14.4, 17.7, 18.1, 21.0, 22.5, 23.2, 23.9, 28.6, 28.8, 30.4, 30.6, 31.7, 103.6, 114.6, 136.2, 147.5, 172.2; FT-IR ( $\text{cm}^{-1}$ ): 3045, 2957, 2873, 2923, 1649 (w,  $\nu_{\text{C=N}}$ ), 1585 (s,  $\nu_{\text{C-O}}$ ), 1526, 1491, 1466, 1377 (w,  $\delta_{\text{-CH}_3}$ ), 1353 and 1135 (m,  $\nu_{\text{C-N}}$ ), 1283, 972, 837, 766, 728.

**[P<sub>8884</sub>][2-Op]-CO<sub>2</sub>**:  $^1\text{H}$  NMR (DMSO, ppm): 0.89 (m, 12H, CH<sub>3</sub>), 1.18~1.52 (m, 40H, CH<sub>2</sub>), 2.20 (m, 8H, CH<sub>2</sub>), 6.13 (m, 1H, py C4), 6.27 (m, 1H, py C5), 7.37 (m, 1H, py C3), 7.47 (m, 1H, py C6);  $^{13}\text{C}$  NMR (DMSO, ppm): 13.7, 14.4, 17.7, 18.1, 21.0, 22.5, 23.2, 23.8, 28.6, 28.8, 30.5, 30.6, 31.7, 106.2, 119.8, 137.3, 140.9, 158.8, 163.8, 172.2; FT-IR ( $\text{cm}^{-1}$ ): 3045, 2957, 2873, 2925, 1669 (m,  $\nu_{\text{C=O}}$ ), 1649 (s,  $\nu_{\text{C=O}}$ ), 1629 (s,  $\nu_{\text{C-O}}$ ), 1604, 1542, 1466, 1375 and 1240 (s,  $\nu_{\text{C-O}}$ ), 1148 (m,  $\nu_{\text{C-N}}$ ), 1006, 986, 837, 767, 728, 687.

**[P<sub>4442</sub>OH][2-Op]**:  $^1\text{H}$  NMR (DMSO, ppm): 0.89 (t, 9H, CH<sub>3</sub>), 1.45 (m, 14H, CH<sub>3</sub>), 1.63 (m, 4H, CH<sub>2</sub>), 2.27 (m, 2H, CH<sub>2</sub>), 6.14 (m, 1H, py C4), 6.41 (m, 1H, py C5), 7.31 (m, 1H, py C3), 7.50 (m, 1H, py C4);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, ppm): 13.6, 23.6, 24.2, 24.3, 106.2, 107.2, 119.6, 140.1, 140.6, 162.7; FT-IR ( $\text{cm}^{-1}$ ): 3018, 2957, 2872, 2931, 1647 (w,  $\nu_{\text{C=N}}$ ), 1583 (s,  $\nu_{\text{C-O}}$ ), 1537, 1482, 1462, 1424, 1378 (w,  $\delta_{\text{-CH}_3}$ ), 1347 and 1155 (m,  $\nu_{\text{C-N}}$ ), 1284, 1093, 1006, 900, 770, 729.

**[P<sub>4442</sub>OH][2-Op]-CO<sub>2</sub>**:  $^1\text{H}$  NMR (DMSO, ppm): 0.89 (t, 9H, CH<sub>3</sub>), 1.42 (m, 14H, CH<sub>3</sub>), 1.65 (m, 4H, CH<sub>2</sub>), 2.26 (m, 2H, CH<sub>2</sub>), 6.18 (m, 1H, py C4), 6.47 (m, 1H, py C5), 7.37 (m, 1H, py C3), 7.46 (m, 1H, py C4);  $^{13}\text{C}$  NMR (DMSO, ppm): 13.6, 23.7, 24.2, 24.3, 106.3, 107.4, 119.8, 140.8, 141.0, 160.4, 162.7; FT-IR ( $\text{cm}^{-1}$ ): 3018, 2957, 2872, 2931, 1649 (s,  $\nu_{\text{C=O}}$ ), 1605 (s,  $\nu_{\text{C-O}}$ ), 1592, 1540, 1464, 1462, 1438, 1377 (s,  $\nu_{\text{C-O}}$ ), 1345 and 1148 (m,  $\nu_{\text{C-N}}$ ), 1278, 1232, 1093, 1002, 986, 968, 903, 768, 728.

**[C<sub>4</sub>mlm][2-Op]**:  $^1\text{H}$  NMR (CDCl<sub>3</sub>, ppm): 0.73 (t, 3H, CH<sub>3</sub>), 1.14 (m, 2H, CH<sub>2</sub>), 1.54 (m, 2H, CH<sub>2</sub>), 3.70 (s, 3H, CH<sub>3</sub>), 3.94 (t, 2H, CH<sub>2</sub>), 5.94 (m, 1H, py C4), 6.14 (m, 1H, py C5), 7.08 (m, 1H, im C5), 7.23 (m, 1H, im C2), 7.42 (m, 1H, py C3), 7.47 (m, 1H, py C6);  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, ppm): 13.4, 19.4, 31.5, 35.5, 43.3, 106.1, 118.9, 121.0, 123.0, 139.3, 143.0, 147.1, 160.1; FT-IR ( $\text{cm}^{-1}$ ): 2958, 2933, 2869, 1663, 1648 (w,  $\nu_{\text{C=N}}$ ), 1588, 1532, 1351 and 1142 (m,  $\nu_{\text{C-N}}$ ), 1282, 975, 780, 731.

**[C<sub>4</sub>mlm][2-Op]-CO<sub>2</sub>**:  $^1\text{H}$  NMR (CDCl<sub>3</sub>, ppm): 0.81 (m, 3H, CH<sub>3</sub>), 1.20 (m, 2H, CH<sub>2</sub>), 1.61

(m, 2H, CH<sub>2</sub>), 3.79 (s, 3H, CH<sub>3</sub>), 4.02 (t, 2H, CH<sub>2</sub>), 6.11 (m, 1H, py C4), 6.37 (m, 1H, py C5), 7.30 (m, 1H, im C5), 7.32 (m, 1H, im C2), 7.47 (m, 1H, py C3), 7.49 (m, 1H, py C6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 13.4, 19.5, 31.6, 35.2, 48.2, 105.9, 119.6, 121.0, 123.0, 136.4, 141.0, 143.4, 160.5, 164.9; FT-IR (cm<sup>-1</sup>): 3142, 3072, 3017, 2959, 2874, 2934, 1670 (m, ν<sub>C=O</sub>), 1646 (s, ν<sub>C=O</sub>), 1599 (s, ν<sub>C-O</sub>), 1570, 1464, 1435, 1378 (s, ν<sub>C-O</sub>), 1336 and 1149 (m, ν<sub>C-N</sub>), 1240, 1170, 1095, 981, 835, 773, 730, 689.

**[Me-C<sub>4</sub>mlm][2-Op]:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.89 (t, 3H, CH<sub>3</sub>), 1.26 (m, 2H, CH<sub>2</sub>), 1.66 (m, 2H, CH<sub>2</sub>), 2.58 (s, 3H, CH<sub>3</sub>), 3.77 (s, 3H, CH<sub>3</sub>), 4.12 (t, 2H, CH<sub>2</sub>), 5.86~5.96 (m, 2H, im C<sub>4</sub> and C<sub>5</sub>), 7.04 (m, 1H, py C4), 7.64 (m, 1H, py C5), 7.77 (m, 2H, py C3 and C6); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 9.6, 13.8, 19.4, 31.7, 35.0, 47.7, 104.5, 115.0, 121.5, 137.4, 144.5, 145.5, 170.4; FT-IR (cm<sup>-1</sup>): 3135, 2960, 2934, 2873, 1648 (w, ν<sub>C=N</sub>), 1587 (s, ν<sub>C-O</sub>), 1536, 1423, 1350 and 1142 (m, ν<sub>C-N</sub>), 1288, 979, 778, 732.

**[Me-C<sub>4</sub>mlm][2-Op]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.90 (t, 3H, CH<sub>3</sub>), 1.28 (m, 2H, CH<sub>2</sub>), 1.68 (m, 2H, CH<sub>2</sub>), 2.59 (s, 3H, CH<sub>3</sub>), 3.76 (s, 3H, CH<sub>3</sub>), 4.12 (t, 2H, CH<sub>2</sub>), 5.98 (m, 2H, im C<sub>4</sub>), 6.06 (m, 2H, im C<sub>5</sub>), 7.17 (m, 1H, py C4), 7.57 (m, 1H, py C5), 7.70 (m, 2H, py C3 and C6); <sup>13</sup>C NMR (DMSO, ppm): 9.6, 13.4, 19.5, 31.6, 35.2, 48.2, 106.0, 119.6, 121.0, 136.4, 140.9, 143.4, 160.4, 164.8; FT-IR (cm<sup>-1</sup>): 3070, 2957, 2932, 2872, 1670 (m, ν<sub>C=O</sub>), 1648 (s, ν<sub>C=O</sub>), 1602 (s, ν<sub>C-O</sub>), 1587, 1550, 1376 (s, ν<sub>C-O</sub>), 1330 and 1148 (m, ν<sub>C-N</sub>), 972, 772, 729.

**[Me-C<sub>6</sub>mlm][2-Op]:** <sup>1</sup>H NMR (DMSO, ppm): 0.87 (t, 3H, CH<sub>3</sub>), 1.27 (m, 2H, CH<sub>2</sub>), 1.69 (m, 2H, CH<sub>2</sub>), 2.58 (s, 3H, CH<sub>3</sub>), 3.75 (s, 3H, CH<sub>3</sub>), 4.10 (t, 2H, CH<sub>2</sub>), 5.80 (m, 2H, im C<sub>4</sub> and C<sub>5</sub>), 7.57 (m, 1H, py C4), 7.71 (m, 1H, py C5), 7.73 (m, 2H, py C3 and C6); <sup>13</sup>C NMR (DMSO, ppm): 9.5, 14.2, 22.1, 28.1, 29.3, 35.1, 47.9, 55.3, 104.3, 114.4, 121.4, 122.8, 136.3, 144.6, 147.7, 172.5; FT-IR (cm<sup>-1</sup>): 3131, 2957, 2866, 2930, 1646 (w, ν<sub>C=N</sub>), 1587 (s, ν<sub>C-O</sub>), 1532, 1470, 1428, 1353 and 1140 (m, ν<sub>C-N</sub>), 1284, 1242, 977, 851, 778, 729.0.

**[Me-C<sub>6</sub>mlm][2-Op]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.83 (t, 3H, CH<sub>3</sub>), 1.24 (m, 2H, CH<sub>2</sub>), 1.68 (m, 2H, CH<sub>2</sub>), 2.55 (s, 3H, CH<sub>3</sub>), 4.10 (m, 5H, CH<sub>2</sub> and CH<sub>3</sub>), 6.20 (m, 1H, im C<sub>4</sub>), 6.31 (m, 1H, im C<sub>5</sub>), 7.43 (m, 2H, py C4 and py C5), 7.61 (m, 2H, py C3 and C6); <sup>13</sup>C NMR (DMSO, ppm): 9.4, 14.1, 22.0, 28.1, 35.0, 47.9, 106.0, 119.9, 121.3, 122.8, 136.6, 141.7, 144.5, 159.3, 163.8; FT-IR (cm<sup>-1</sup>): 3069, 2956, 2866, 2932, 1669 (m, ν<sub>C=O</sub>), 1644 (s, ν<sub>C=O</sub>), 1601

(s,  $\nu_{C-O}$ ), 1540, 1465, 1435, 1420, 1370 (s,  $\nu_{C-O}$ ), 1340 and 1148 (m,  $\nu_{C-N}$ ), 1285, 1240, 1095, 977, 837, 772, 728.

**[Me-C<sub>8</sub>mIm][2-Op]:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.83 (t, 3H, CH<sub>3</sub>), 1.23 (m, 2H, CH<sub>2</sub>), 1.69 (m, 2H, CH<sub>2</sub>), 3.70 (s, 3H, CH<sub>3</sub>), 4.14 (t, 2H, CH<sub>2</sub>), 6.13 (m, 2H, im C<sub>4</sub>), 6.40 (m, 1H, im C<sub>5</sub>), 7.42 (m, 1H, py C<sub>4</sub>), 7.48 (m, 1H, py C<sub>5</sub>), 7.73 (m, 2H, py C<sub>3</sub> and C<sub>6</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 14.0, 22.5, 26.3, 29.9, 31.6, 49.8, 105.9, 121.0, 123.3, 139.3, 140.6, 143.5, 147.3; FT-IR (cm<sup>-1</sup>): 3136, 2956, 2855, 2924, 1648 (w,  $\nu_{C=N}$ ), 1589 (s,  $\nu_{C-O}$ ), 1533, 1469, 1429, 1353 and 1139 (m,  $\nu_{C-N}$ ), 1283, 1243, 979, 851, 777, 729, 668.

**[Me-C<sub>8</sub>mIm][2-Op]+CO<sub>2</sub>:** <sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm): 0.84 (t, 3H, CH<sub>3</sub>), 1.23 (m, 2H, CH<sub>2</sub>), 1.69 (m, 2H, CH<sub>2</sub>), 3.68 (s, 3H, CH<sub>3</sub>), 4.07 (t, 2H, CH<sub>2</sub>), 6.17 (m, 2H, im C<sub>4</sub>), 6.45 (d, 1H, im C<sub>5</sub>), 7.42 (m, 1H, py C<sub>4</sub>), 7.48 (m, 1H, py C<sub>5</sub>), 7.73 (m, 2H, py C<sub>3</sub> and C<sub>6</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, ppm): 14.0, 22.5, 25.3, 29.0, 29.7, 31.6, 35.3, 105.9, 119.9, 120.9, 123.1, 139.8, 141.1, 143.5, 160.3, 164.7; FT-IR (cm<sup>-1</sup>): 3070, 2954, 2869, 2855, 1673 (m,  $\nu_{C=O}$ ), 1647 (s,  $\nu_{C=O}$ ), 1602 (s,  $\nu_{C-O}$ ), 1540, 1466, 1437, 1375 (s,  $\nu_{C-O}$ ), 1329, 1147 (m,  $\nu_{C-N}$ ), 1283, 1238, 1221, 1095, 980, 834, 770, 726, 666.

**[Me-Pyr][2-Op]:** <sup>1</sup>H NMR (DMSO, ppm): 0.92 (t, 3H, CH<sub>3</sub>), 1.30 (m, 2H, CH<sub>2</sub>), 1.66 (m, 2H, CH<sub>2</sub>), 3.00 (s, 3H, CH<sub>3</sub>), 3.33 (m, 2H, CH<sub>2</sub>), 3.48 (m, 4H, CH), 5.73 (m, 2H, py C<sub>4</sub> and C<sub>5</sub>), 6.98 (m, 1H, py C<sub>6</sub>), 7.57 (m, 1H, py C<sub>3</sub>); <sup>13</sup>C NMR (DMSO, ppm): 14.0, 19.8, 21.5, 25.4, 47.7, 63.2, 63.7, 103.8, 114.0, 135.9, 148.6, 173.2; FT-IR (cm<sup>-1</sup>): 2961, 2875, 1653 (w,  $\nu_{C=N}$ ), 1591 (s,  $\nu_{C-O}$ ), 1534, 1496, 1429, 1352 and 1143 (m,  $\nu_{C-N}$ ), 1283, 980, 930, 781, 732.

**[Me-Pyr][2-Op]-CO<sub>2</sub>:** <sup>1</sup>H NMR (DMSO, ppm): 0.92 (t, 3H, CH<sub>3</sub>), 1.30 (m, 2H, CH<sub>2</sub>), 1.66 (m, 2H, CH<sub>2</sub>), 2.99 (s, 3H, CH<sub>3</sub>), 3.32 (m, 2H, CH<sub>2</sub>), 3.48 (m, 4H, CH), 6.00 (m, 2H, py C<sub>4</sub> and C<sub>5</sub>), 7.18 (m, 1H, py C<sub>6</sub>), 7.61 (m, 1H, py C<sub>3</sub>); <sup>13</sup>C NMR (DMSO, ppm): 14.0, 19.8, 21.5, 25.4, 47.7, 63.2, 63.7, 105.0, 116.9, 138.6, 142.7, 158.8, 168.1; FT-IR (cm<sup>-1</sup>): 2961, 2939, 2873, 1644 (m,  $\nu_{C=O}$ ), 1600 (s,  $\nu_{C=O}$ ), 1540, 1465, 1378 (s,  $\nu_{C-O}$ ), 1338 and 1153 (m,  $\nu_{C-N}$ ), 1241, 1096, 985, 928, 835, 777, 731.

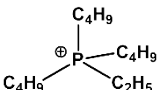
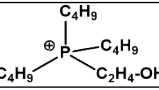
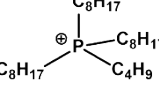
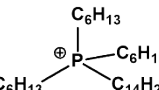
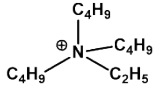
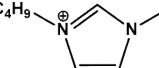
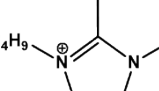
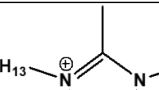
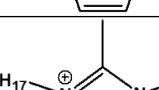
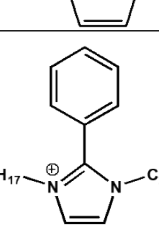
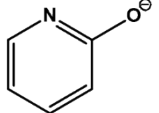
**[Ph-C<sub>8</sub>eIm][2-Op]:** <sup>1</sup>H NMR (DMSO, ppm): 0.83 (t, 3H, CH<sub>3</sub>), 1.06~1.31 (m, 13H, CH<sub>3</sub> and CH<sub>2</sub>), 1.62 (m, 2H, CH<sub>2</sub>), 3.96 (m, 4H, CH<sub>2</sub>), 5.75 (m, 1H, im C<sub>4</sub>), 5.76 (m, 1H, im C<sub>5</sub>), 6.90 (m, 1H, py C<sub>4</sub>), 7.57 (m, 1H, py C<sub>5</sub>), 7.74 (m, 5H, CH), 8.11 (m, 2H, py C<sub>3</sub> and py C<sub>6</sub>); <sup>13</sup>C

NMR (DMSO, ppm): 14.4, 15.4, 22.4, 25.8, 28.6, 28.7, 29.4, 31.6, 44.0, 48.4, 103.8, 114.5, 122.0, 122.3, 122.8, 130.0, 130.9, 132.8, 136.1, 143.9, 147.8, 172.5; FT-IR ( $\text{cm}^{-1}$ ): 3054, 2954, 2869, 2923, 2855, 1646 (w,  $\nu_{\text{C=N}}$ ), 1587 (s,  $\nu_{\text{C-O}}$ ), 1530, 1505, 1483, 1467, 1433, 1377 (w,  $\delta_{\text{-CH}_3}$ ), 1354 and 1138 (m,  $\nu_{\text{C-N}}$ ), 1285, 1218, 975, 848, 775, 726, 701.

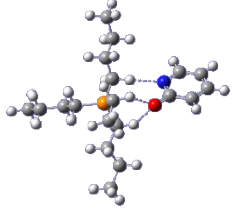
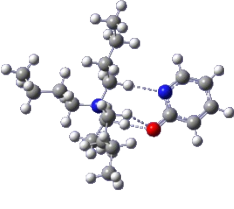
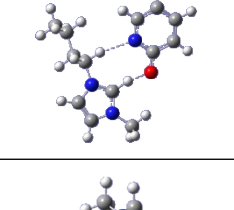
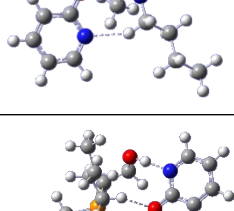
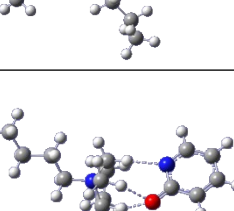
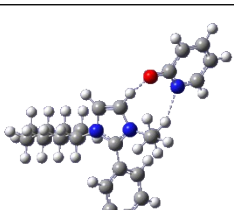

**[Ph-C<sub>8</sub>eim][2-Op]-CO<sub>2</sub>**: <sup>1</sup>H NMR (DMSO, ppm): 0.83 (t, 3H, CH<sub>3</sub>), 1.06~1.31 (m, 13H, CH<sub>2</sub>), 1.62 (m, 2H, CH<sub>2</sub>), 3.96 (m, 4H, CH<sub>2</sub>), 6.14 (m, 1H, Im C4), 6.28 (m, 1H, Im C5), 7.38 (m, 1H, py C<sub>4</sub>), 7.44 (m, 1H, py C5), 7.74 (m, 5H, CH), 8.07 (m, 2H, py C3 and py C6); <sup>13</sup>C NMR (DMSO, ppm): 14.3, 15.4, 22.4, 25.7, 28.5, 28.7, 29.4, 31.6, 44.0, 48.4, 105.2, 120.0, 122.0, 122.3, 122.8, 130.0, 130.9, 132.8, 136.9, 141.1, 144, 158.172.5; FT-IR ( $\text{cm}^{-1}$ ): 3124, 3070, 2955, 2870, 2926, 2855, 1675 (m,  $\nu_{\text{C=O}}$ ), 1645 (s,  $\nu_{\text{C=O}}$ ), 1602 (s,  $\nu_{\text{C-O}}$ ), 1580, 1541, 1505, 1465, 1438, 1377 (s,  $\nu_{\text{C-O}}$ ), 1347 and 1150 (m,  $\nu_{\text{C-N}}$ ), 1241, 1217, 1096, 987, 835, 774, 723, 698.

## (2) Supporting Tables (S1-S3):

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

Structure	Ion name	Abbreviation
	Tributyl(ethyl)phosphonium	[P <sub>4442</sub> ]
	Tributyl(ethoxyl)phosphonium	[P <sub>4442</sub> OH]
	Trioctyl(buthyl)phosphonium	[P <sub>8884</sub> ]
	Trihetyl(tetradecyl)phosphonium	[P <sub>66614</sub> ]
	Tributyl(ethyl)ammonium	[N <sub>4442</sub> ]
	N-butyl-methylimidazolium	[C <sub>4</sub> mim]
	1N-Methyl-3N-butyl-2-methylimidazolium	[Me-C <sub>4</sub> mim]
	1N-methyl-3N-hetyl-methylimidazolium	[Me-C <sub>6</sub> mim]
	1N-methyl-3N-octyl-2-methylimidazolium	[Me-C <sub>8</sub> mim]
	1N-ethyl-3N-octyl-2-phenylimidazolium	[Ph-C <sub>8</sub> eim]
	2-hydroxypyridium	[2-Op]

**Table S2.** Optimized structures of [2-Op] paired with various cation and the corresponding interaction energy.

Abbreviations of IL	Optimized structure	Hydrogen bond length (Å)	Interaction energy (kJ/mol)
[P <sub>4442</sub> ][2-Op]		d (N...H), 2.133 d (O...H), 2.053 d (O...H), 2.059	-322.3
[N <sub>4442</sub> ][2-Op]		d (N...H), 2.159 d (O...H), 2.097 d (O...H), 1.986	-344.9
[Bmim][2-Op]		d (N...H), 2.283 d (O...H), 1.535	-366.8
[Me-C <sub>4</sub> mim][2-Op]		d (N...H), 2.311 d (O...H), 2.423	-364.0
[P <sub>4442</sub> OH][2-Op]		d (N...H), 1.629 d (O...H), 2.021 d (O...H), 2.115	-394.6
[Bmpr][2-Op]		d (N...H), 2.116 d (O...H), 1.984 d (O...H), 1.967	-370.4
[Ph-C <sub>8</sub> eim][2-OP]		d (N...H), 2.183 d (O...H), 1.729	-317.5



**Table S3.** Comparison of the vibration absorption of pyridine ring skeleton and the CO<sub>2</sub> capacity between pure ILs and their Tg mixtures.

IL	CO <sub>2</sub> capacity <sup>a</sup>		u <sub>py</sub> (cm <sup>-1</sup> )		Effect of Tg	
	pure IL	IL-Tg mixture <sup>b</sup>	pure IL	IL-Tg mixture	Increase of CO <sub>2</sub> capacity <sup>c</sup>	Increase of u <sub>py</sub> (cm <sup>-1</sup> )
[P <sub>4442</sub> ][2-Op]	1.40	1.39	1434	1434	-0.01	0
[N <sub>4442</sub> ][2-Op]	1.24	1.28	1433	1434	0.04	1
[Bmim][2-Op]	1.02	1.16	1427	1431	0.14	4
[Me-C <sub>4</sub> mim][2-Op]	1.06	1.52	1423	1434	0.46	11
[P <sub>4442</sub> OH][2-Op]	0.94	0.59	1424	1423	-0.35	-1
[Bmpr][2-Op]	1.17	1.28	1427	1431	0.11	4

<sup>a</sup> mol/mol IL, CO<sub>2</sub> capture was operated under 30 °C and 1atm CO<sub>2</sub> pressure; <sup>b</sup> the mixture was obtained by the ratio of 1:1 (weight) of IL and TG solvent. <sup>c</sup> mol/mol IL

**Table S4.** Comparison of CO<sub>2</sub> capture by ionic liquids varied with cation.

Entry	Ionic liquid	Capacity (mol/mol)	conditions	Reference
1	[Ph-C <sub>8</sub> eim][2-OP]	1.69	30°C, 1atm	This work
2	[Ph-C <sub>8</sub> eim][2-OP]	1.83	20°C, 1atm	This work
3	[P <sub>66614</sub> ][2-OP]	1.58	20°C, 1atm	<i>Angew. Chem. Int. Ed.</i> 2014, <b>53</b> , 7053 –7057.
4	[P <sub>4444</sub> ][2-OP]	1.20	20°C, 1atm	<i>Phys. Chem. Chem. Phys.</i> , 2017, <b>19</b> , 1134-1142.
5	[N <sub>4444</sub> ][2-OP]	0.70	20°C, 1atm	
6	[P <sub>66614</sub> ][3-OP]	1.49	20°C, 1atm	<i>Angew. Chem. Int. Ed.</i> 2014, <b>53</b> , 7053-7057.
7	[P <sub>4444</sub> ][3-OP]	1.05	20°C, 1atm	<i>Phys. Chem. Chem. Phys.</i> , 2017, <b>19</b> , 1134-1142.
8	[N <sub>4444</sub> ][3-OP]	0.50	20°C, 1atm	
9	[P <sub>2224</sub> ][2-CNPyrr]	0.80	22°C, 0.15bar	<i>J. Phys. Chem. B</i> 2015, <b>119</b> , 11807-11814.
10	[P <sub>2228</sub> ][2-CNPyrr]	0.80	22°C, 0.15bar	
11	[P <sub>22212</sub> ][2-CNPyrr]	0.73	22°C, 0.15bar	
12	[P <sub>44412</sub> ][2-CNPyrr]	0.72	22°C, 0.15bar	
13	[P <sub>44418</sub> ][2-CNPyrr]	0.64	22°C, 0.15bar	
14	[P <sub>66614</sub> ][2-CNPyrr]	0.62	22°C, 0.15bar	

(3) Supporting Figures (S1-S3):

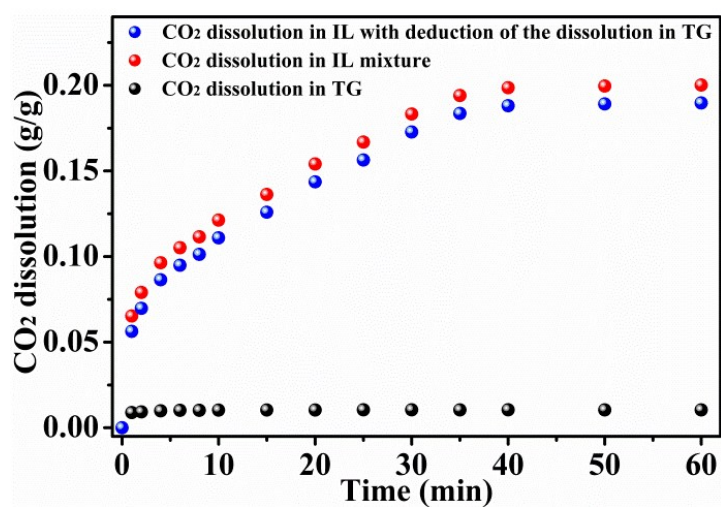


Fig. S1 Comparison of CO<sub>2</sub> capture by IL [P<sub>4442</sub>][2-Op], TG and their mixture with weight ratio as 1:1 .

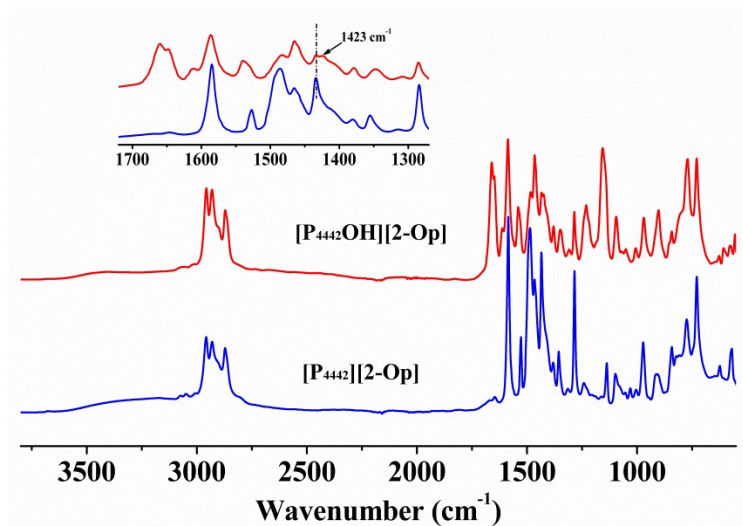
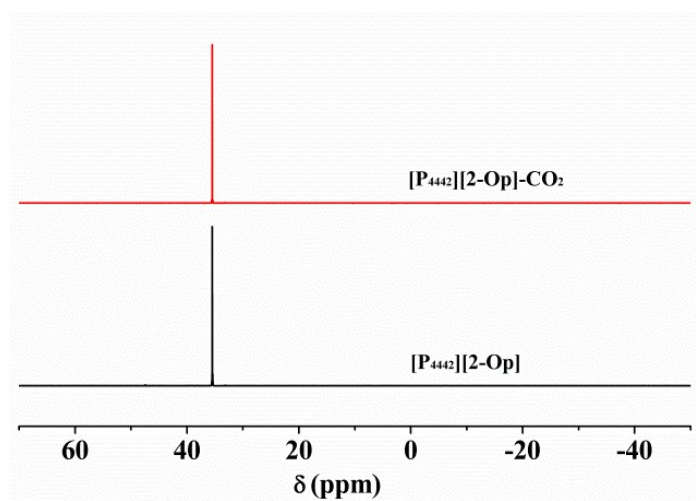
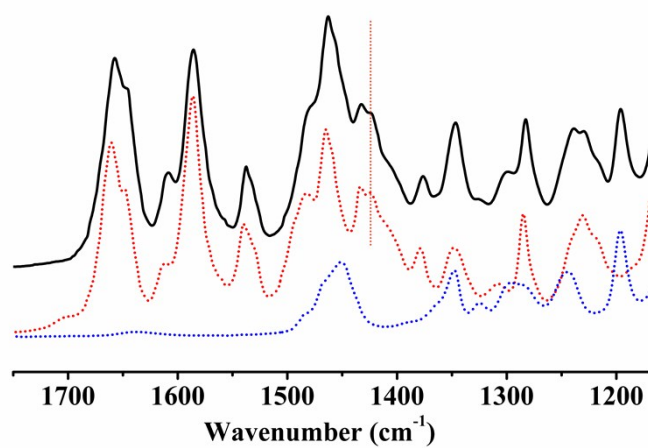


Fig. S2 Comparison of IR spectra of [P<sub>4442</sub>OH][2-Op] and [P<sub>4442</sub>][2-Op].



**Fig. S3**  $^{31}\text{P}$  NMR spectra of  $[\text{P}_{4442}][2\text{-Op}]$  and  $[\text{P}_{4442}][2\text{-Op}]\text{-CO}_2$  complex.



**Fig. S4** Comparison of IR spectra with  $[\text{P}_{4442}][2\text{-Op}]$  (red dot), Tg solvent (the blue dot), and their mixture (black line).