A Robust Ionic Liquid as Reaction Medium and Efficient Organocatalyst for Carbon Dioxide Fixation

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S1. Experimental details for the synthesis of ionic liquid 1-Br3:

The intermediate of 3-bromopropylmethylpyrrolidinium bromide was prepared in quantitative yield according to a literature method (A. P. Gray, D. C. Schlieper, E. E. Spinner, C. J. Cavallito, J. Am. Chem. Soc. 1955, 77, 3648-3649). 1H NMR (400 MHz D2O): δ 2.14-2.25 (m, 4H), 2.30-2.41 (m, 2H), 3.08 (s, 3H), 3.51-3.62 (m, 8H).

Synthesis of ionic liquid 1-Br3: A mixed solution of 2,2'-dipyridylamine (1.71 g, 10 mmol) in dichloromethane (4 ml), 3-bromopropylmethylpyrrolidinium bromide (7.2 g, 25 mmol), and N,N-diisopropylethylamine (8 ml) was heated to 130 °C for 10 h. The reaction mixture was allowed to cool down to room temperature and then added with 20 ml of acetone. The organic solvent was decanted to obtain an oily mixture. The mixture was then washed with chloroform for several times to remove unreacted starting materials. A pale yellow hygroscopic solid of ionic liquid 1-Br3 with 90% yield (6.0 g) was obtained after drying under vacuum. 1H NMR (400 MHz D2O): δ 2.25 (s, 8H), 2.40-2.62 (m, 4H), 3.09 (s, 6H), 3.43-3.80 (m, 12H), 4.58 (t, 4H, J= 8Hz), 7.02 (t, 2H, J= 8Hz), 7.46 (d, 2H, J= 8Hz), 7.911 (t, 2H, J= 8Hz), 8.14 (d, 2H, J= 8Hz); 13C NMR (400 MHz, D2O): δ 21.25, 23.42, 48.13, 50.53, 61.03, 64.64, 114.48, 116.49, 140.98, 143.22, 156.31; ESI-MS m/z: 141.5, [M -3Br3]+, 251.6, 252.6 [M -2Br -]2+; Anal. Calcd for C26H42N5Br3·H2O: C, 47.00; H, 6.37; N, 10.54. Found: C, 47.05; H, 6.40; N, 10.56.
**S2. Procedures for the synthesis of tetrabromozincate complex [1]₂[ZnBr₄]₃:**

Ionic liquid 1-Br (0.682 g, 1 mmol) and dihydrated zinc bromide (0.522 g, 2 mmol) in ethanol solution (20 ml) were refluxed for 1 hour. The mixture was cooled in ice-water and precipitates were formed. The precipitate was collected by filtration and washed with cold ethanol and then acetone. After drying under vacuum, a quantitative yield of the tetrabromozincate complex was isolated. The single crystals suitable for X-ray analysis was obtained by slow evaporation of an ethanol-water solution of the complex under room temperature and atmosphere conditions.

**S3. X-ray crystal structure of [1]₂[ZnBr₄]₃:**

The crystal data can be obtained from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). (Deposition number: CCDC 653539)

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**Figure S1.** X-ray crystal structure of [1]₂[ZnBr₄]₃: ORTEP representation (30% probability chosen for the ellipsoids).

**Figure S2.** X-ray crystal structure of [1]₂[ZnBr₄]₃: Molecular packing
Figure S3. ESI mass spectrum of ionic liquid 1-Br₃. (Solvent: H₂O)
Figure S4. $^1$H (top) and $^{13}$C (bottom) NMR spectra of ionic liquid 1-Br$_3$ (Solvent: D$_2$O)
Figure S5. $^1$H (top) and $^{13}$C (bottom) NMR spectra of the crude cyclic carbonate product collected in the 8th cycle (Solvent: CDCl$_3$)