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Reversible Reaction of CO_2 with Superbasic Ionic Liquid [P_{66614}][benzim] Studied with *In Situ* Photoelectron Spectroscopy

Supporting Information

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X-ray photoelectron spectroscopy (XPS) spectra: survey and region spectra at normal and grazing emission

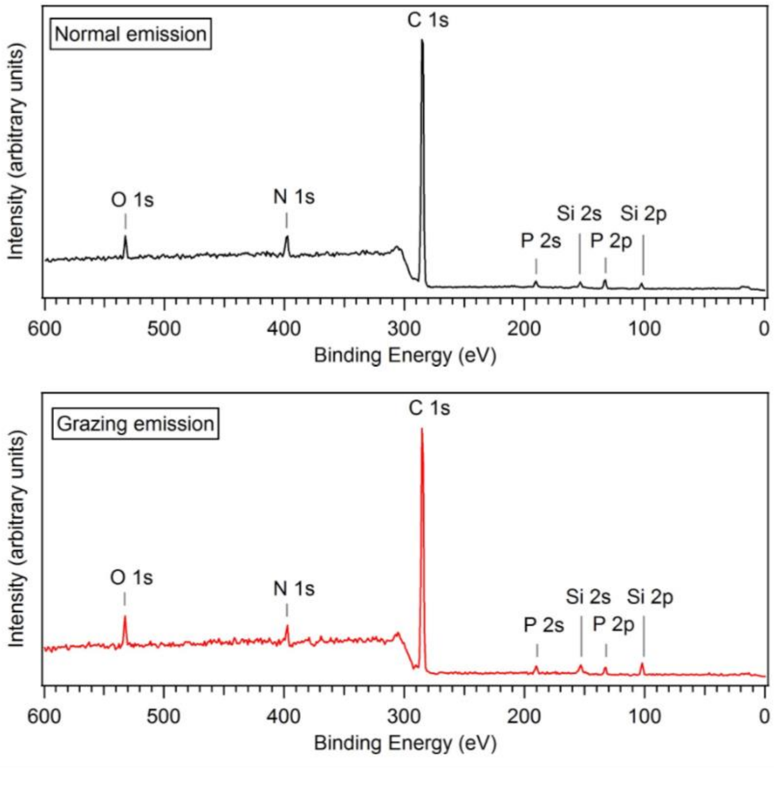

Figure S1. *Survey spectra taken of the IL at normal emission (top, black line) and at a grazing angle of 60° (bottom, red line).*

The XPS spectra for the IL, trihexyltetradecyl-phosphonium benzimidazolide ([P_{66614}][benzim]) in ultra-high vacuum (UHV) conditions (pressure approximately 10^{-9} mbar) are shown below, at both normal emission (NE, in black) and grazing emission (GE, at 60°, in red). All measurements were taken on the same part of the IL.

The survey spectra are annotated with labels of the regions associated with the IL (C 1s, N 1s, and P 2p), as well as the O 1s region. Ta from the sample plate is not visible, indicating the IL layer is thicker than the sampling depth of

XPS (> 100 Å). Also annotated are the Si 2s and Si 2p peaks. These are thought to be due to Si-based contamination from synthesis[1]. This contamination is also likely to contribute to the intensity of the C 1s region.

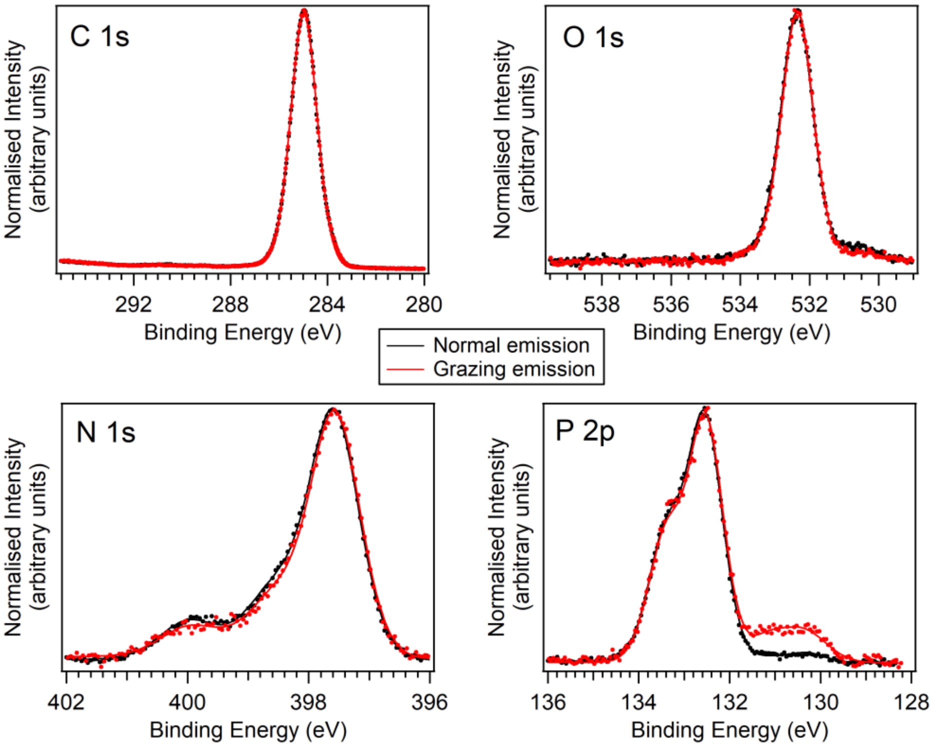

Figure S2. *C 1s (top right), O 1s (top left), N 1s (bottom right), and P 2p (bottom left) regions. Both the normal emission (black line) and grazing emission (red line) spectra are shown. Each region has been normalized to the intensity of the largest peak in the region.*

Figure S2 shows the C 1s, O 1s, N 1s, and P 2p regions taken of the IL in UHV. The C 1s region (Figure S2, top left) does not significantly change shape at GE compared to NE. However, the O 1s, N 1s and P 2p regions do appear to have a slightly different shape at GE.

In the O 1s region, there appears to be one dominating signal at 532.4 eV. This feature is likely to be due, predominantly, to silicon grease. In the survey spectra, the O 1s feature is slightly more intense at GE than at NE, when compared to the N 1s peak in both cases. This is also the case for the Si 2s and Si 2p peaks. These observations corroborate the assignment of Si grease contamination, which is typically found at the surface of the IL rather than in the bulk[1]. While Si contamination at the surface of the IL may affect the rate of gas sorption, it is unlikely to influence the chemical reactions that take place in the IL. Its presence, however, overlaps significantly with peaks associated with hydroxyl groups and with water molecules adsorbed on ILs[2] and makes a definitive deconvolution of the region impossible.

The N 1s region (Figure S2, bottom left) appears to have a more prominent higher binding energy feature at NE than at GE. As stated in the manuscript, the main signal is attributed to imidazolium N, and the higher BE shoulder is composed of two peaks, both linked to carbamate formation (from reaction with CO_2), as well as imidazole formation (from reaction with H_2O) (see the manuscript for more details). It can be seen in Figure S2 that the shoulder at higher binding energy has a slightly greater intensity at NE than at GE. These, too, are attributed to carbamate and imidazole formation due to exposure to atmosphere. It is possible that there is slightly more carbamate in the bulk of the IL due to movement of ionic moieties post-CO_2 reaction into the bulk[3].

Finally, the P 2p region (Figure S2, bottom right) demonstrates the most striking change at GE compared to NE. The main features at 132.5 eV and 133.4 eV are attributed to the P $2p_{3/2}$ and P $2p_{1/2}$ of the P 2p doublet originating from the $[P_{66614}]^+$ cation (these have been fitted in Figure S3). There appears to be a shoulder at the lower BE edge of the region that is much more prevalent at GE than at NE. This is indicative of a P species located nearer to the surface of the IL. The exact nature of the species is not known, but it is speculated that it may be the result of X-ray beam damage. The UHV measurements were taken at the same position on the IL and were not rastered. Figure S3 (shown below) displays the P 2p region during Stages 3 to 7 (please refer to Scheme 1 in the experimental section of the manuscript for more information about the Stages). The measurements taken throughout Stages 3 to 7 were rastered. The shoulder appears to have increased in intensity after the UHV XPS measurements, but does not appear to increase significantly throughout the rest of the experiment. This could indicate that the IL does not suffer any more damage due to prolonged X-ray exposure from the measurements taken.

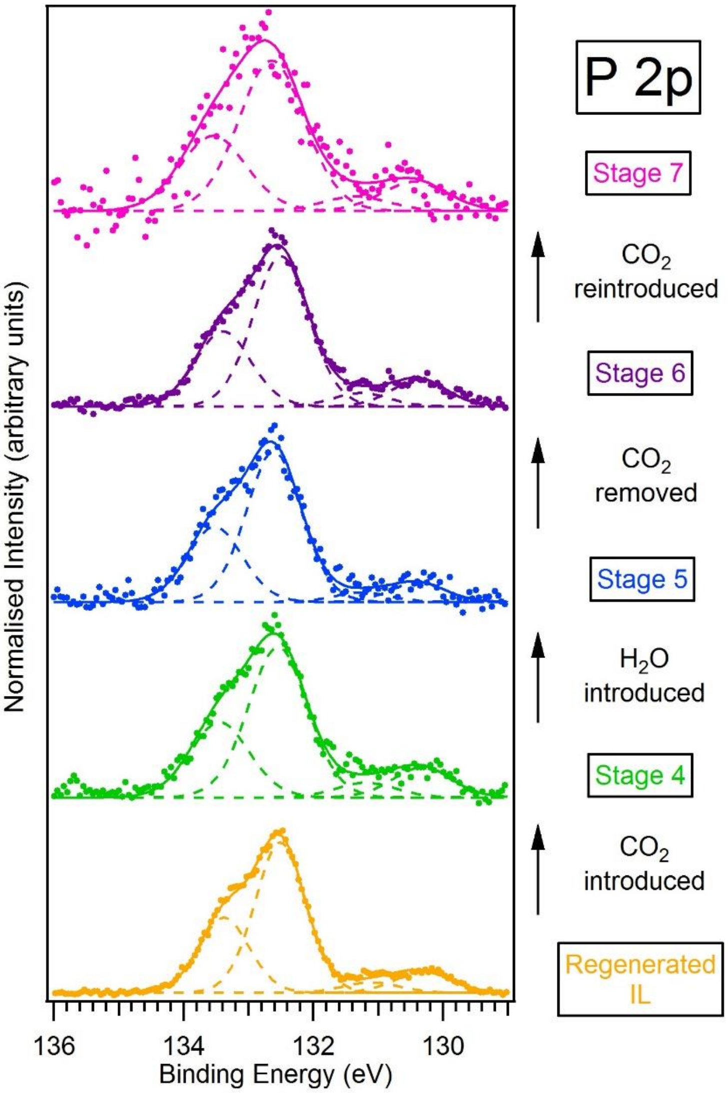

Figure S3. *P 2p spectrum taken of the regenerated IL (Stage 3, amber line), of the IL during exposure to 3 mbar* CO_2 *(Stage 4, green line), during exposure to the first mixed-gas regime (Stage 5, blue line), during exposure to 2 mbar* H_2O *(Stage 6, violet line), and during exposure to the second mixed-gas regime (Stage 7, magenta line).*

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3. T. Lewis, M. Faubel, B. Winter and J. C. Hemminger, *Angewandte Chemie International Edition*, 2011, **50**, 10178-10181.