

Supplementary Information

Urea as an efficient and reusable catalyst for the glycolysis of poly(ethylene terephthalate) wastes and the role of hydrogen bond in this process

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Supporting information

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S1 Experimental Section

NMR of ionic liquids: [N₂₂₂₂][Ala]: ¹H NMR (600 MHz, DMSO, 25 °C, TMS): δ=0.94(d, 3H; CH₃CN), 1.11 (t, 12H; CH₃C), 2.75 (q, 1H; CH), 3.20 ppm (q, 8H; CH₂N); ¹³C NMR (150 MHz, DMSO, 25 °C): δ=7.65, 23.57, 51.91, 52.40, 178.24 ppm.

[N₂₂₂₂][Ser]: ¹H NMR (600 MHz, DMSO, 25 °C, TMS): δ=1.12 (t, 12H; CH₃C), 2.82(s, 1H), 3.17 (q, 8H; CH₂N), 3.24 (dd, 1H; CH); ¹³C NMR (150 MHz, DMSO, 25 °C): δ=7.61, 51.89, 55.55, 65.95, 176.50 ppm.

[N₂₂₂₂][Asp]: ¹H NMR (600 MHz, DMSO, 25 °C, TMS): δ=1.11 (s, 12H; CH₃C), 2.01 (dd, 1H), 2.26 (dd, H), 3.17 ppm (d, 8H; CH₂N); ¹³C NMR (150 MHz, DMSO, 25 °C): δ=7.62, 38.70, 51.90, 52.49, 172.73, 174.44 ppm.

[N₂₂₂₂][Lys]: ¹H NMR (600 MHz, DMSO, 25 °C, TMS): δ=1.11 (t, 12H; CH₃C), 1.16 (m, 2H), 1.21 (m, 2H), 1.63 (m, 2H), 2.41 (t, 2H, CH₂NH₂), 2.64 (dd, 1H, CHN), 3.20 ppm (q, 8H; CH₂N); ¹³C NMR (150 MHz, DMSO, 25 °C): δ=7.65, 24.14, 34.44, 37.04, 42.48, 51.92, 57.01, 177.78 ppm.

[N₁₁₁₁][Ala]: ¹H NMR (600 MHz, DMSO, 25 °C, TMS): δ=0.95(d, 3H; CH₃C), 2.77(q, 1H), 3.10(s, 12H; CH₃N); ¹³C NMR (150 MHz, DMSO, 25 °C): δ=23.39, 52.20, 54.77, 178.61 ppm.

[N₁₁₁₁][Asp]: ¹H NMR (600 MHz, DMSO, 25 °C, TMS): δ= 1.99 (dd, 1H), 2.27 (dd, 1H), 3.08 (s, 12H; CH₃N), 3.13 (m, 1H; CHN); ¹³C NMR (150 MHz, DMSO, 25 °C): δ=52.86, 54.87, 173.39, 174.83 ppm.

S2 The study on the role of hydrogen bond formed between [Ala]⁻ and EG

The optimized structures of the anion and the cation of catalyst were showed in Fig. S1.

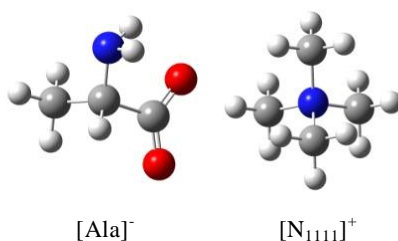


Fig. S1 Optimized structures of reactants by B3LYP/6-311+G(d,p). O atoms (red), N atoms (blue), H atoms (light gray), C atoms (dark gray).

There are possible positions in which anion locates around cation, and different initial configurations were optimized at B3LYP/6-311+G(d,p) level. Two conformers with almost same energy were finally obtained and shown in Fig. S2.

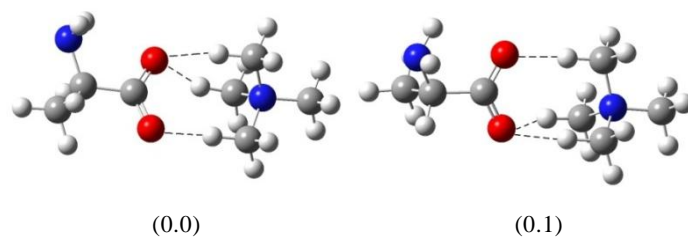


Fig. S2 Optimized structures of ion-pair by B3LYP/6-311+G(d,p) with relative energy (kcal/mol). O atoms (red), N atoms (blue), H atoms (light gray), C atoms (dark gray). The dashed lines note the H-bonds formed in the ion pairs.

Fig.3s shows that there are different energy minimum structures for the coordinating EG with anion via hydrogen bonds by calculations. The interaction of EG with anion will lead to the formation of several kinds of structure A-E. The hydrogen bonds will form between oxygen and hydrogen in most case, while hydrogen bond between nitrogen and hydrogen is also found in structure A. The structure B is more stable and are the main existing modes due to its lower energy than A, C-F.

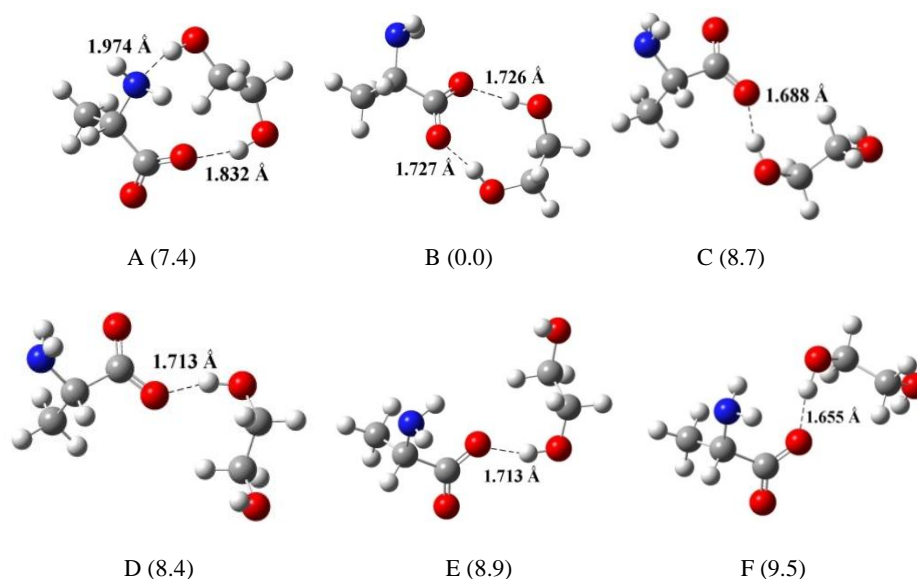


Fig. S3 Optimized structures of EG and [Ala]⁻ with relative energy (kcal/mol). O atoms (red), N atoms (blue), H atoms (light gray), C atoms (dark gray). The dashed lines note the H-bonds formed in the ion pairs.

The interaction forms of A, B and C will be considered in the calculations for interactions of anion, cation and EG. Several typical stable structures were obtained and shown in Fig. S4. In these structures, I is more stable and are the main existing modes due to its lower energy than G, H and J.

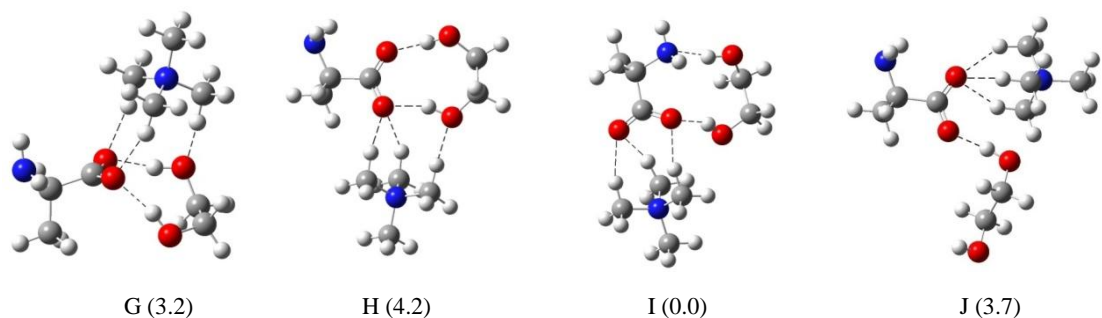
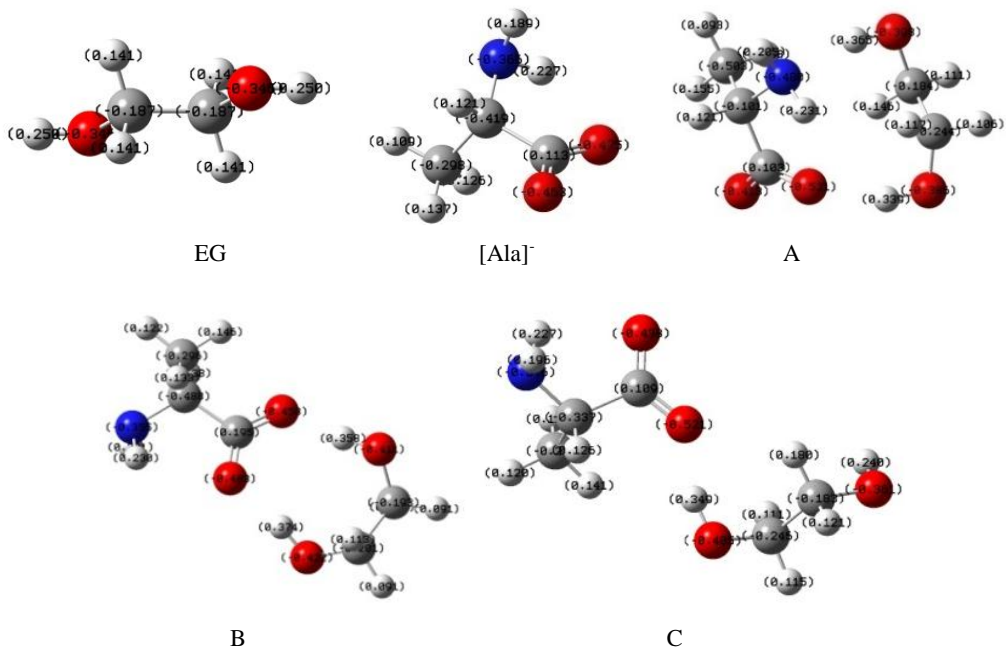


Fig. S4 Optimized structures of anion, cation and EG by B3LYP/6-311+G(d,p) with relative energy (kcal/mol). O atoms (red), N atoms (blue), H atoms (light gray), C atoms (dark gray). The dashed lines note the H-bonds formed in the ion pairs.

Table S1 The changes of bond length for EG when it interacts with [Ala]⁻

Bond	EG	A	B	C	D	E	F	G	H	I	J
O1-H5	0.963	0.982	0.990	0.994	0.996	0.996	0.997	0.990	0.983	0.979	0.996
O1-C2	1.426	1.417	1.411	1.410	1.405	1.405	1.410	1.425	1.410	1.424	1.418
C2-C3	1.516	1.542	1.533	1.531	1.531	1.531	1.531	1.527	1.526	1.528	1.530
C3-O4	1.426	1.425	1.410	1.441	1.441	1.441	1.440	1.412	1.426	1.414	1.430
O4-H10	0.963	0.983	0.991	0.963	0.963	0.963	0.963	0.978	0.989	0.982	0.962

The interaction of EG and anion make the O-H bond length of hydroxyl in EG longer (see Table S1) and electronegativity of the oxygen of hydroxyl in EG stronger (see Fig. S5) than that of before interaction, which make the hydrogen in EG lost more easily, the oxygen in EG prefer to attacking the carbon of the ester group in PET and finally results in degradation of PET.



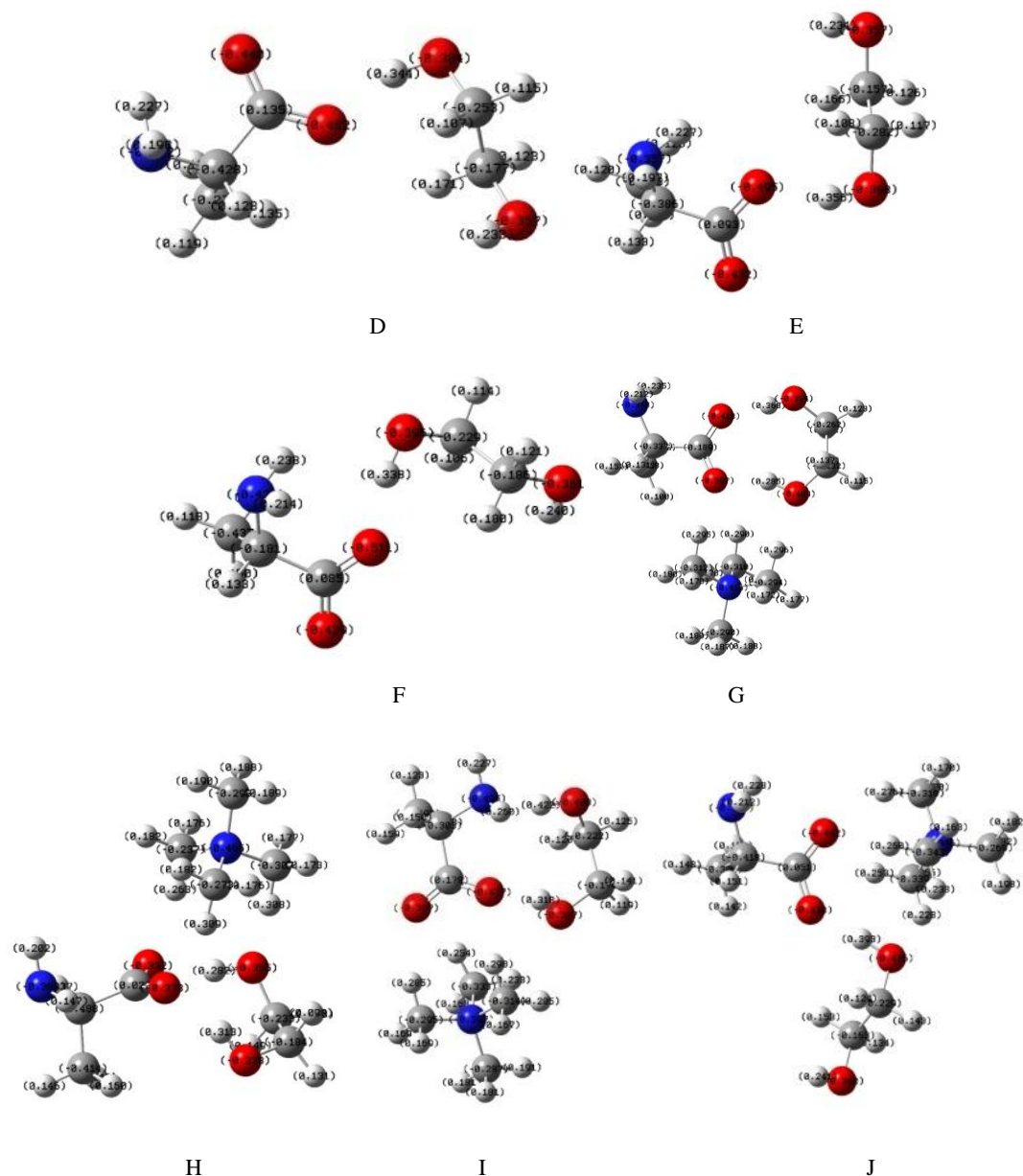


Fig. S5 The calculated mulliken atomic charges. O atoms (red), N atoms (blue), H atoms (light gray), C atoms (dark gray).

S3 The interaction between $[N_{1111}]^+$ and PET

The interaction between PET and cation will probably lead to the formation of hydrogen bonds between oxygen of C=O group and hydrogen of cation (Fig. S6).

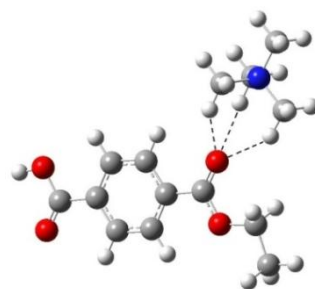


Fig. S6 The interaction between $[N_{1111}]^+$ and PET. O atoms (red), N atoms (blue), H atoms (light gray), C atoms (dark gray). The dashed lines note the H-bonds formed in the ion pairs.