Supporting Information

Mechanistic Insight toward the Roles of Anions and Cations in the Degradation of Poly (ethylene terephthalate) Catalyzed by Ionic Liquids

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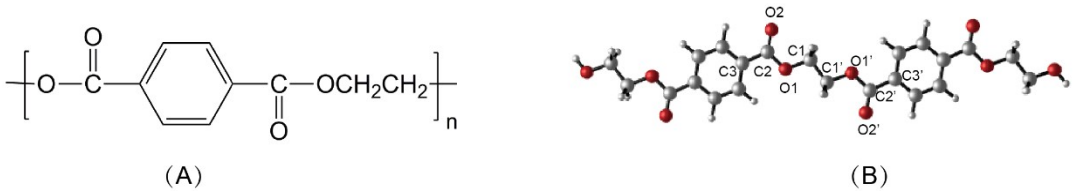

Fig. S1 (A) Molecular formula of PET and (B) the structure of dimer.

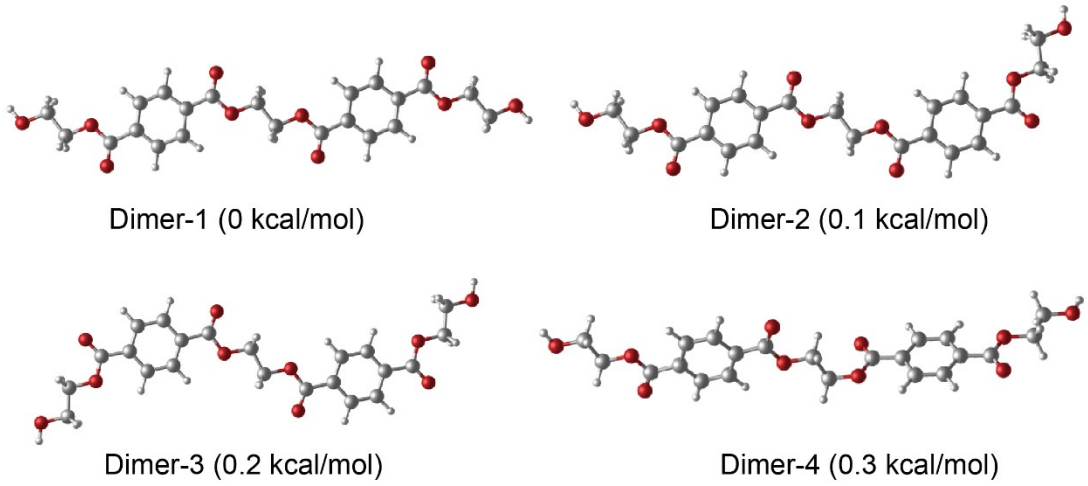

Fig. S2 Conformational isomers of Dimer model compound and the relative energies to Dimer-1 are labeled in parentheses.

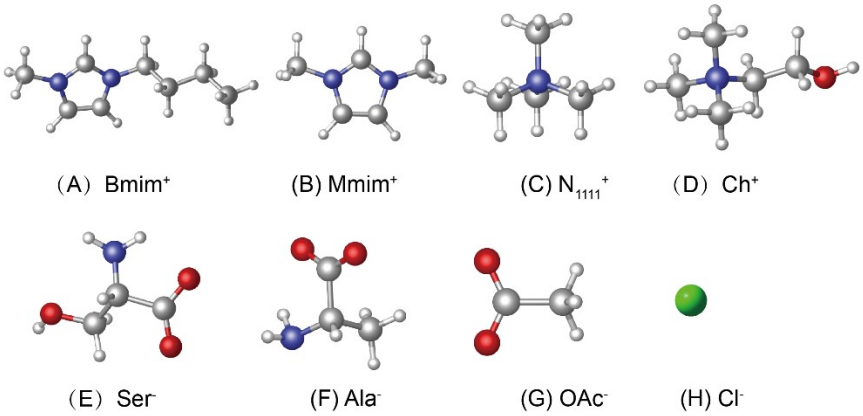

Fig. S3 The structures of (A-D) cations and (E-H) anions optimized at M06-2X-D3/6-311+G** level.

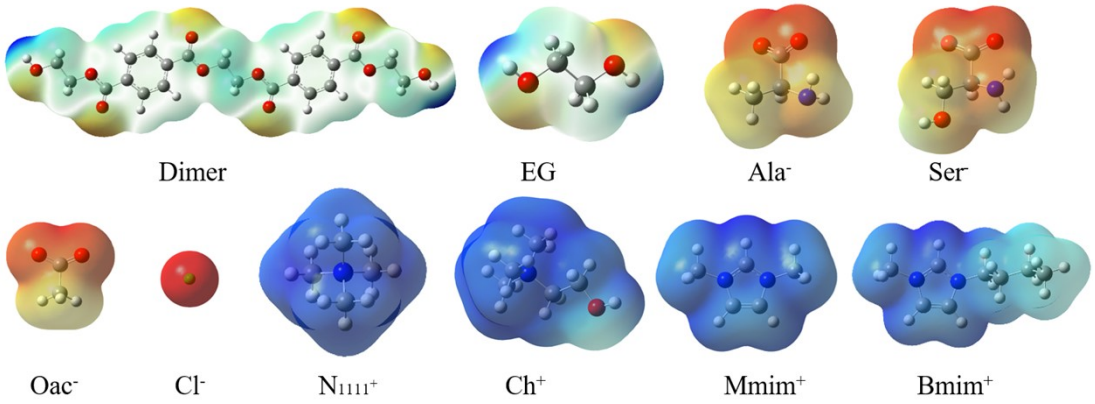

Fig. S4 The electrostatic potential surface of Dimer, EG anions, and cations.

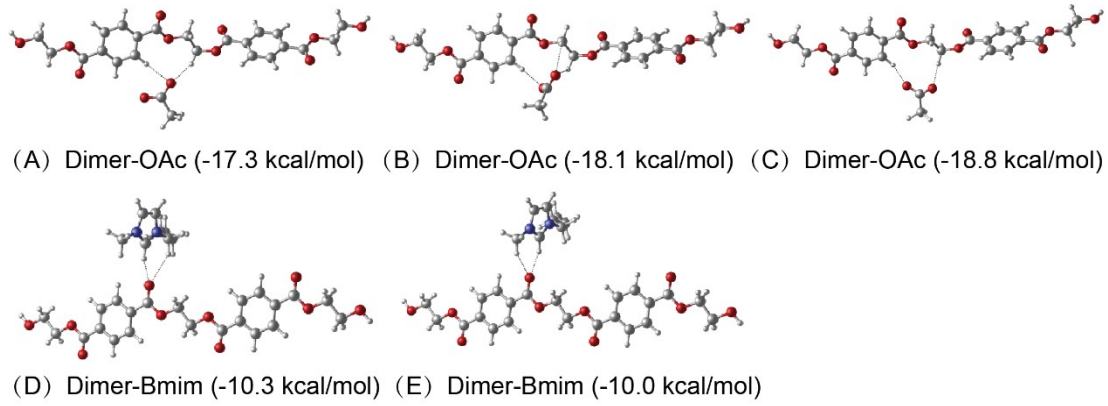

Fig. S5 The optimized configurations of Dimer-OAc and Dimer-Bmim and interaction energies. The hydrogen bonds are indicated by dashed lines. (*RSC Adv., 2018, 8, 8209–8219*)

Table S1 The optimized bond length and Mulliken atomic charge of dimer at M06-2X-D3/ 6-311+G** level.

Bond	**Length (Å)**	**Bond**	**Length (Å)**	**Atom**	**Charge (a.u.)**	**Atom**	**Charge (a.u.)**
C3-C2	1.49242	C3-C2	1.49242	C3	0.381	C3’	0.381
C2-O2	1.20134	C2-O2	1.20134	C2	-0.041	C2’	-0.041
C2-O1	1.34378	C2-O1	1.34378	O2	-0.257	O2’	-0.257
O1-C1	1.42832	O1-C1	1.42833	O1	-0.053	O1’	-0.053
C1-C1’	1.51213			C1	0.022	C1’	0.022

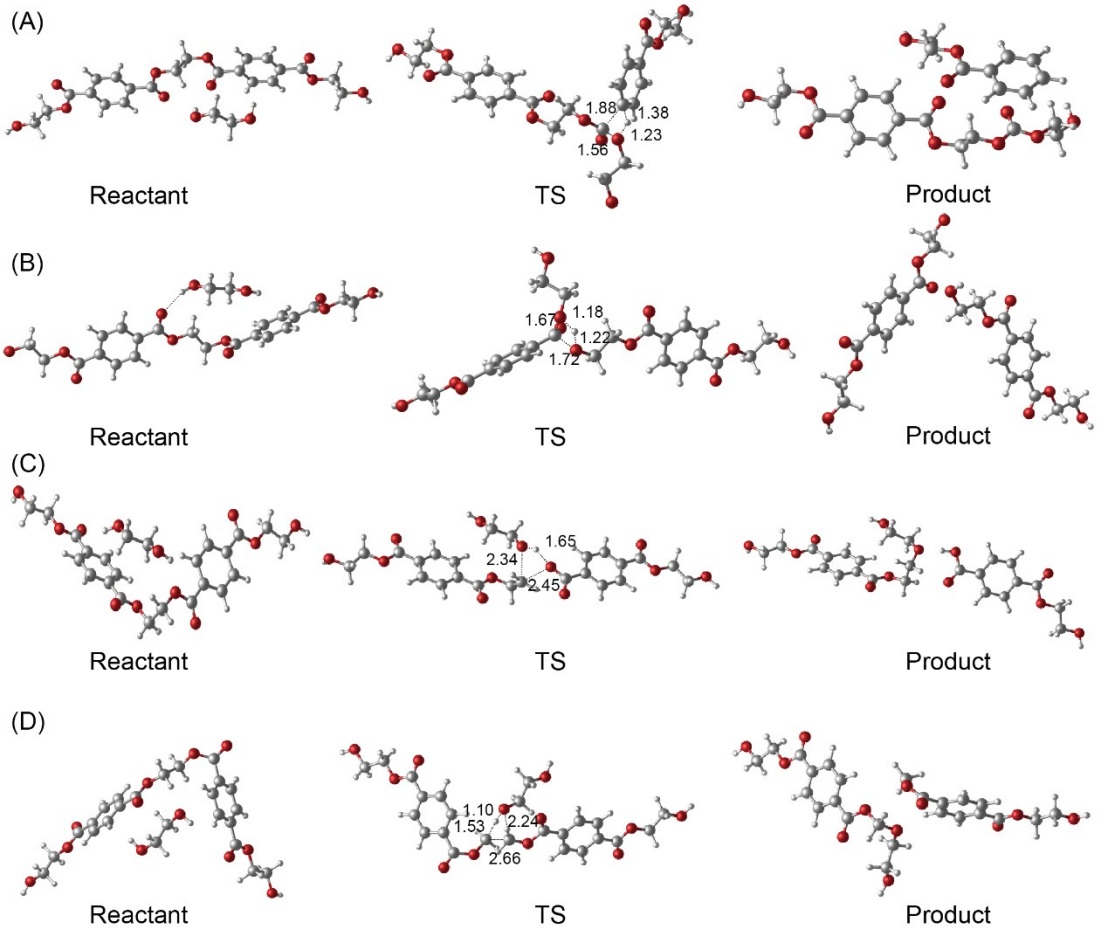

Fig. S6 Optimized reactant, TS, and product structures for the glycolysis of PET with EG corresponding to Scheme 1 (A) path1, (B) path2, (C) path3, (D) path4. Distances are in angstroms.

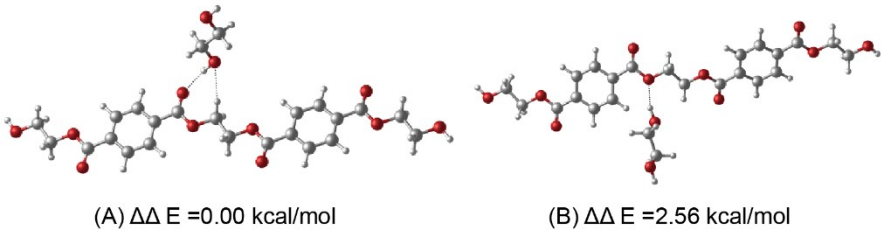

Fig. S7 The optimized structure between dimer and EG and relative energies (A) EG attacks the carbonyl oxygen of dimer (B) EG attacks the ester group oxygen of dimer.

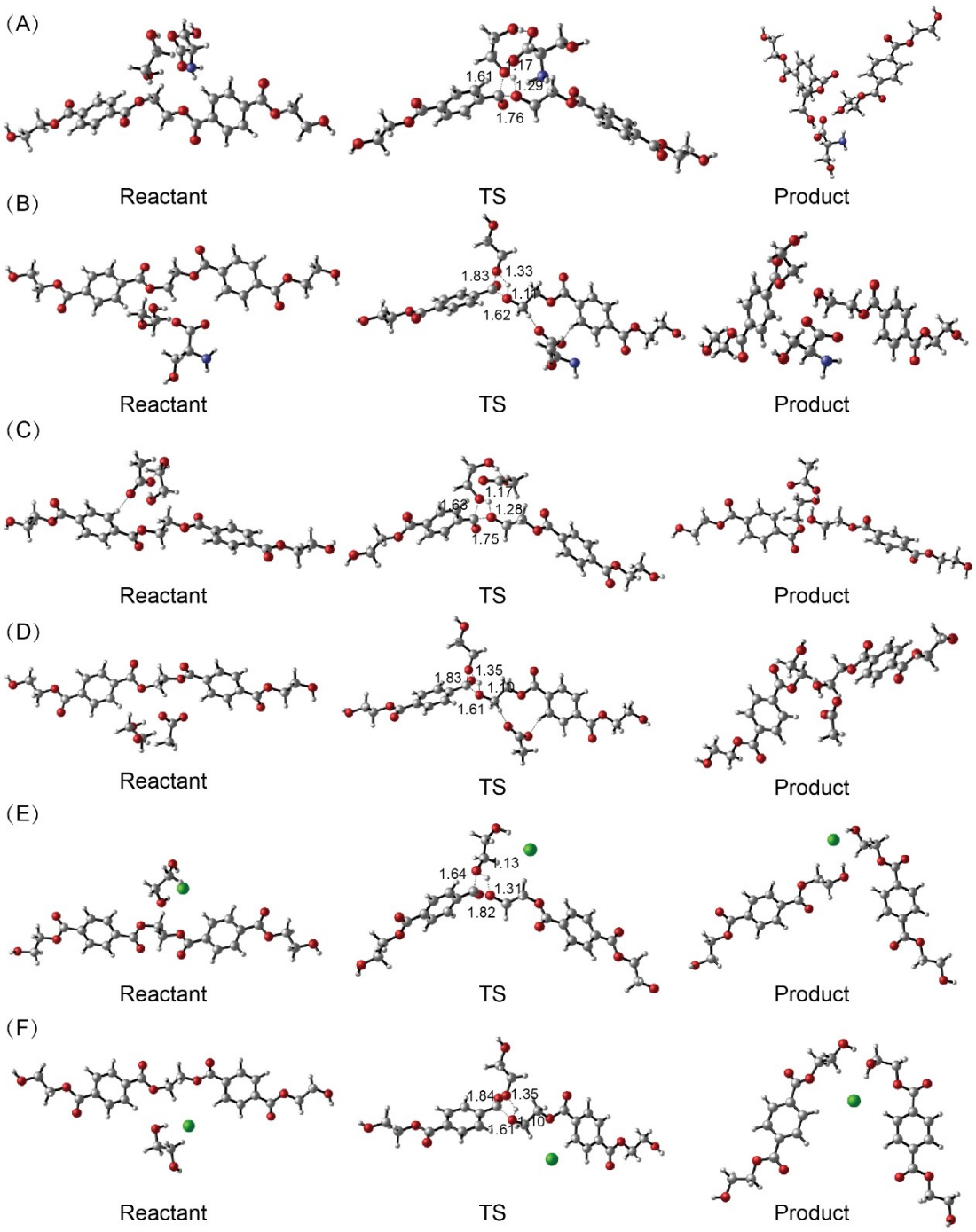

Fig. S8 Optimized reactant, TS, and product structures for the glycolysis of PET to BHET catalyzed by different anions at different sites (A) 1-Ser, (B) 2-Ser, (C) 1-OAc, (D) 2-OAc, (E) 1-Cl, and (F) 2-Cl. Distances are in angstroms.

Table S2 The calculated relative energies (kcal/mol) for the glycolysis of PET to BHET catalyzed by different anions at different sites at M06-2X-D3/6-311+G** level (Ea-activation energy, Er-reaction energy).

Entry	Catalysts	In vacuo		Ethylene glycol	
		Ea	Er	Ea	Er
(A)	Ser^-	53.9	5.9	52.9	6.4
(B)		62.6	-0.2	54.8	-2.2
(C)	OAc^-	54.3	6.8	52.3	5.8
(D)		64.2	-3.4	55.3	-5.4
(E)	Cl^-	52.1	-3.6	51.7	-2.0
(F)		62.7	-8.5	52.0	-7.2

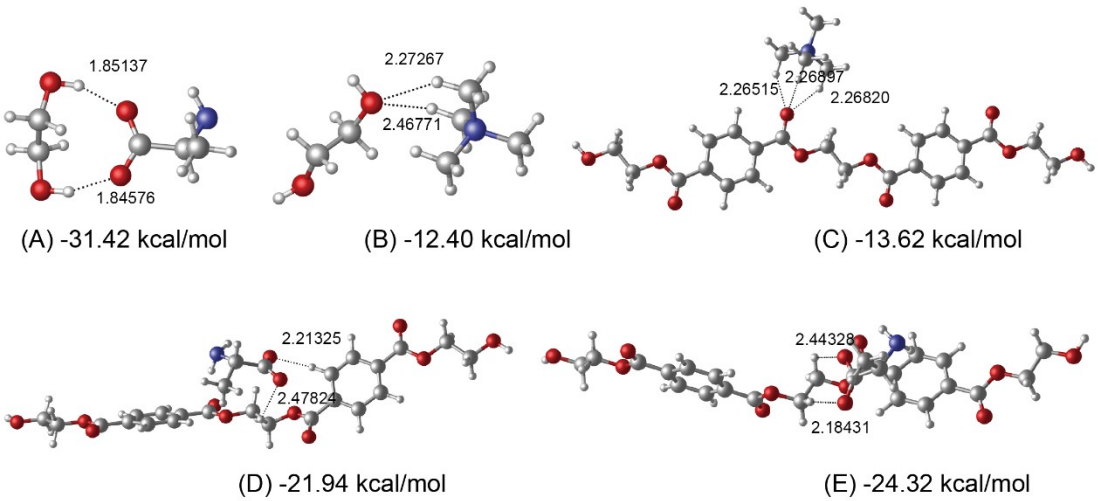

Fig. S9 The optimized interaction conformers and energies corrected by BSSE (A) Ala^--EG (B) N_{1111}^+-EG (C) Dimer-N_{1111}^+ (D-E) Dimer-Ala^- at M06-2X-D3/6-311+G** level.

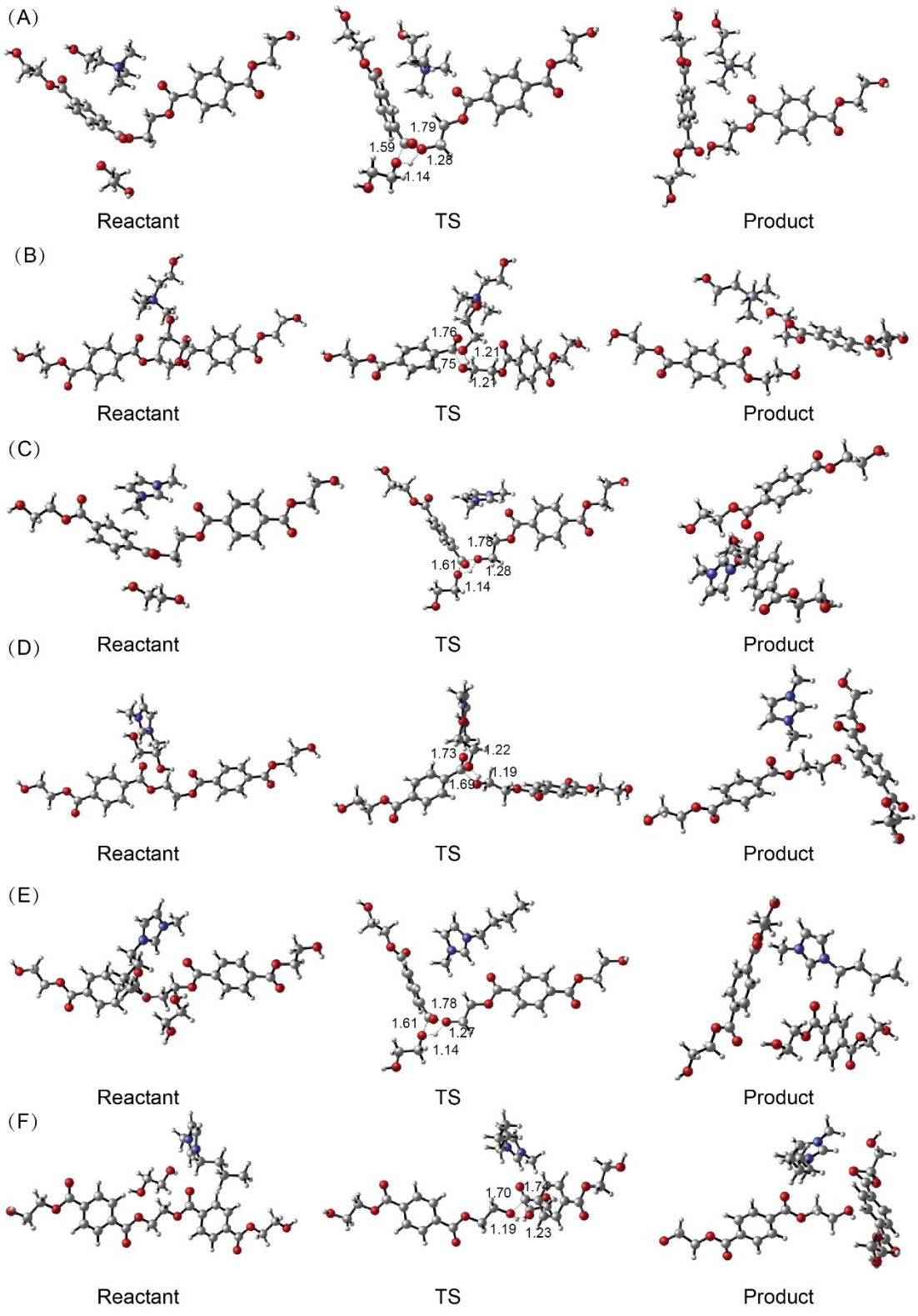

Fig. S10 Optimized reactant, TS, and product structures for the glycolysis of PET to BHET catalyzed by different anions at different sites (A) 1-Ch, (B) 2-Ch, (C) 1-Mmim, (D) 2-Mmim, (E) 1-Bmim, and (F) 2-Bmim. Distances are in angstroms.

Table S3 The calculated relative energies (kcal/mol) for the glycolysis of PET to BHET catalyzed by different cations at different sites at M06-2X-D3/6-311+G** level (Ea-activation energy, Er-reaction energy).

Entry	Catalysts	In vacuo		Ethylene glycol	
		Ea	Er	Ea	Er
(A)	Ch^+	40.3	-16.3	42.0	-12.9
(B)		49.2	2.6	48.4	-3.5
(C)	$Mmin^+$	42.2	-10.7	44.8	-11.6
(D)		45.6	-0.4	45.8	-0.5
(E)	$Bmim^+$	46.5	-2.1	46.3	-2.2
(F)		47.2	-8.9	46.7	-5.8

Experiments

Materials

PET pellets (2.0× 2.5× 2.7 mm) were purchased from Jingdong Commercial *Co.*, Jiangsu Province, China. The pellets were ground into 40-60 mesh by a small grinding miller (ZN-02). BmimCl, ChCl, $N_{1111}Cl$, EG, and the other reagents were purchased from Sinopharm Chemical Reagent Beijing *Co.*, China. All reagents were used as purchased without further purification.

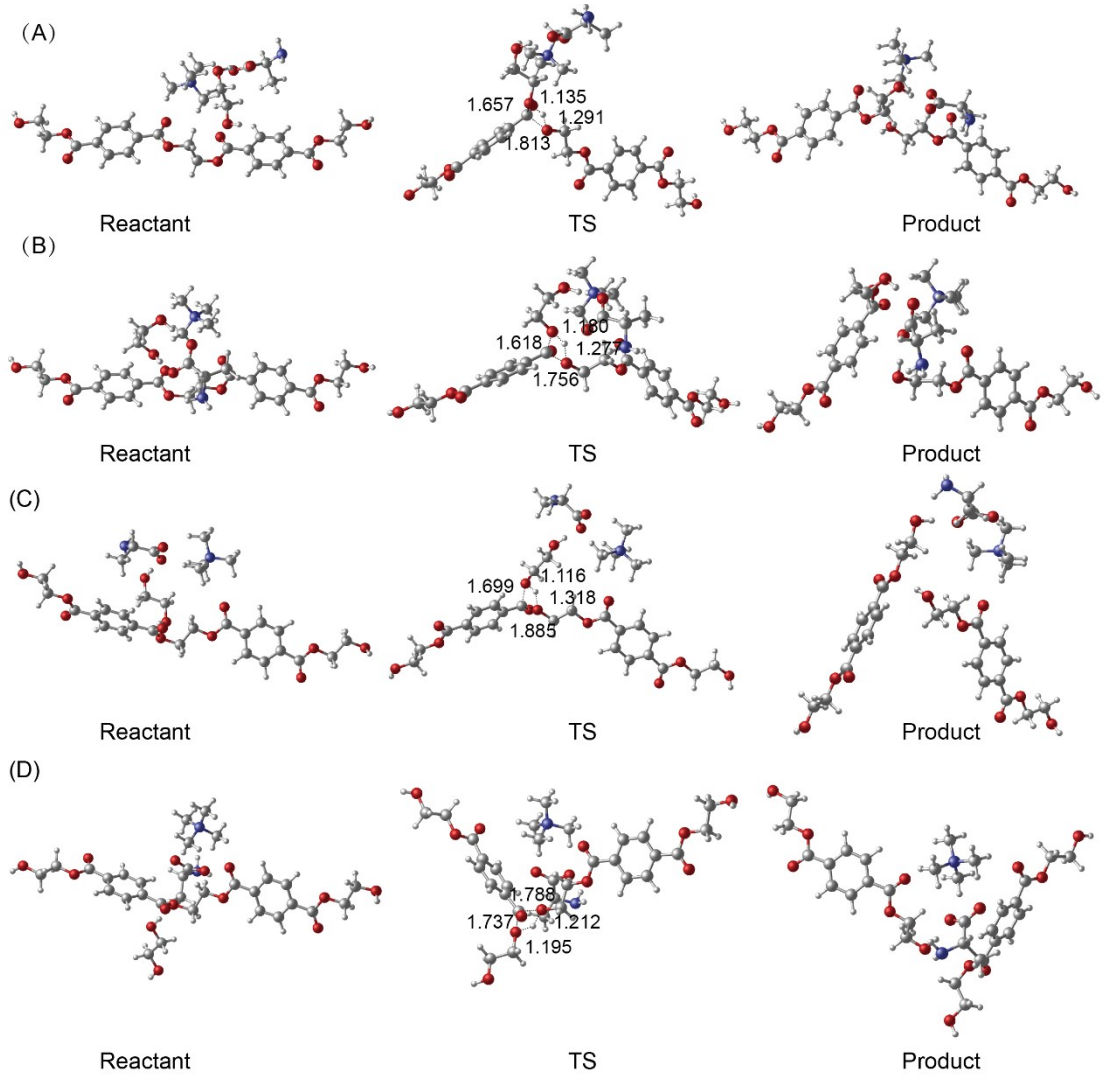

Fig. S11 Optimized reactant, TS, and product structures for the glycolysis of PET to BHET catalyzed by N_{1111}Ala (A-D) at different sites. Distances are in angstroms.

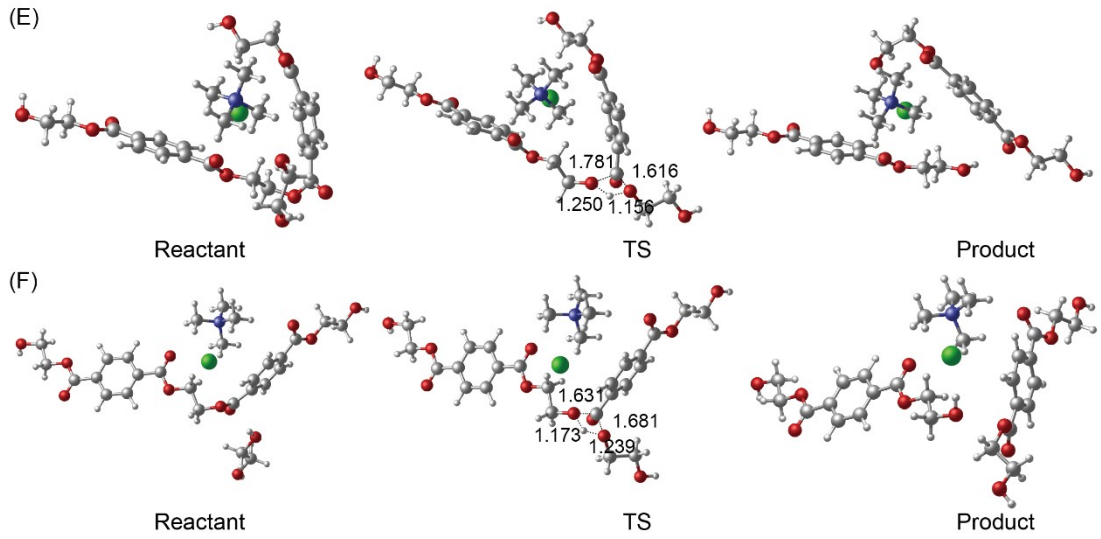

Fig. S12 Optimized reactant, TS, and product structures for the glycolysis of PET to BHET catalyzed by $N_{1111}Cl$ (E-F) at different sites. Distances are in angstroms.

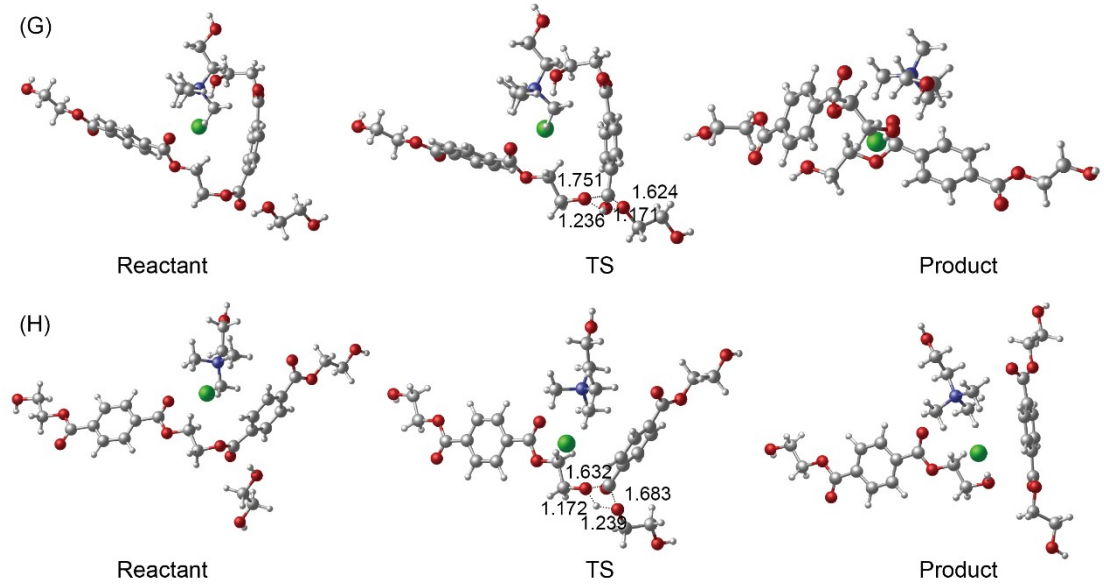

Fig. S13 Optimized reactant, TS, and product structures for the glycolysis of PET to BHET catalyzed by ChCl (G-H) at different sites. Distances are in angstroms.

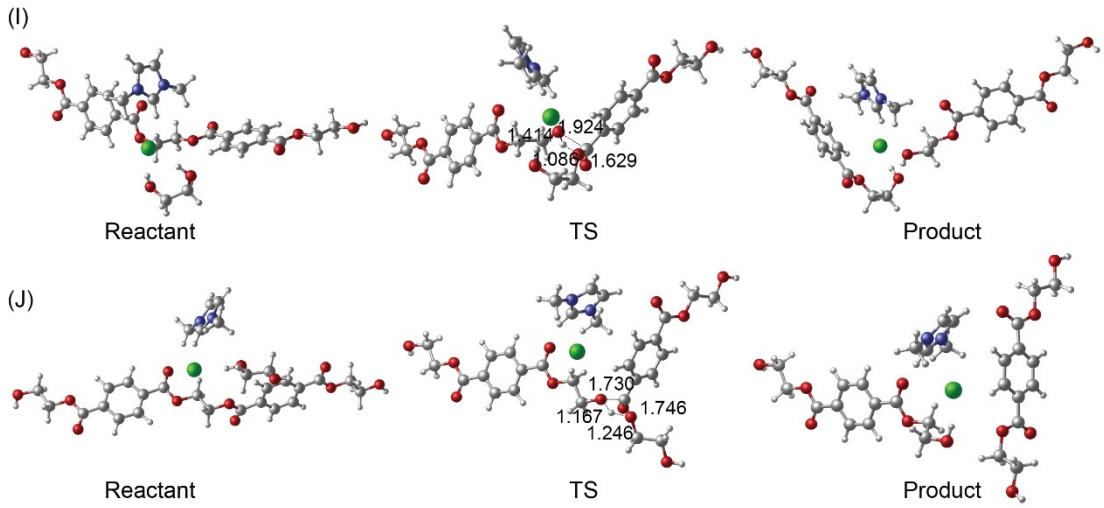

Fig. S14 Optimized reactant, TS, and product structures for the glycolysis of PET to BHET catalyzed by MmimCl (I-J) at different sites. Distances are in angstroms.

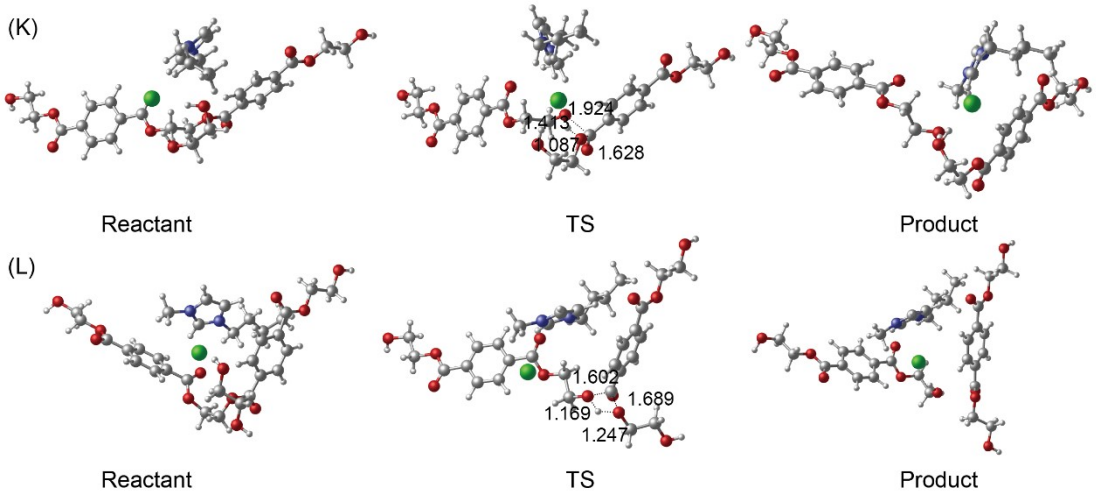

Fig. S15 Optimized reactant, TS, and product structures for the glycolysis of PET to BHET catalyzed by BmimCl (K-L) at different sites. Distances are in angstroms.

Table S4 The calculated relative energies (kcal/mol) for the glycolysis of PET to BHET catalyzed by different ILs at different sites at M06-2X-D3/6-311+G** level (Ea-activation energy, Er-reaction energy).

Entry	Catalysts	In vacuo		Ethylene glycol	
		Ea	Er	Ea	Er
(A)	N_{1111}Ala	52.5	0.6	52.2	-0.1
(B)		53.6	5.2	52.8	6.0
(C)		50.0	-0.3	51.8	0.7
(D)		41.5	-15.3	42.8	-8.8
(E)	N_{1111}Cl	42.4	-14.9	44.6	-7.3
(F)		47.2	-18.1	46.9	-14.5
(G)	ChCl	43.4	-14.6	44.9	-7.5
(H)		54.9	-7.0	53.5	-6.3
(I)	MminCl	43.9	-9.8	47.4	-5.9
(J)		49.8	-6.4	47.6	-4.1
(K)	BmimCl	48.1	-5.0	49.9	-4.3
(L)		57.2	-4.4	53.8	-1.5

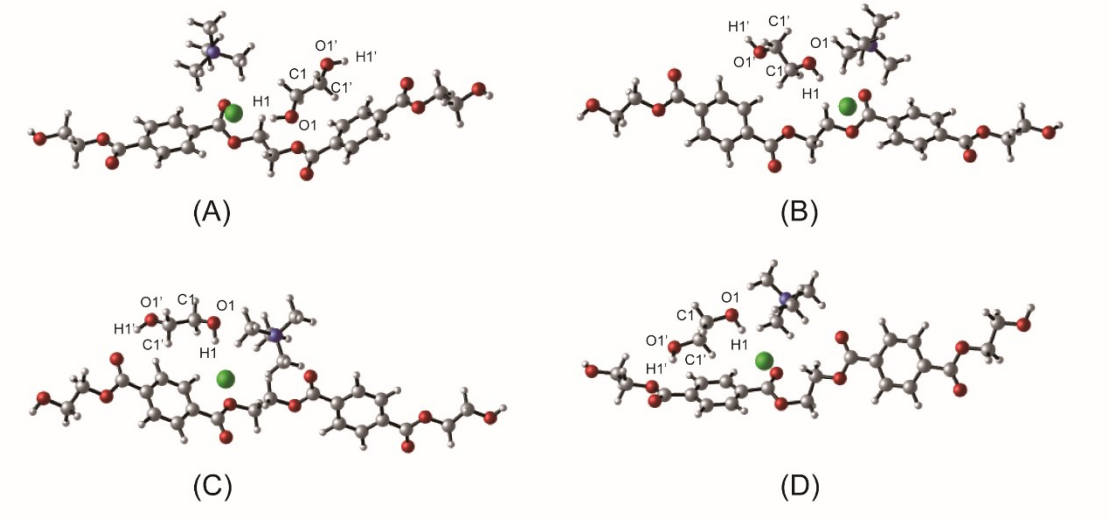

Fig. S16 Optimized the structures of PET, N_{1111}Cl, and EG complexes at different sites.

Table S5 Changes in bond length for EG in PET, $N_{1111}Cl$, and EG system. Distances are in angstroms.

Bond	EG	A	B	C	D
O1-H1	0.95857	0.97524	0.97676	0.97789	0.98688
O1-C1	1.41714	1.40661	1.40949	1.41414	1.41540
C1-C1’	1.51335	1.51676	1.51488	1.52006	1.52330
C1’-O1’	1.41714	1.42310	1.41948	1.41486	1.41887
O1’-H1’	0.95857	0.95931	0.95937	0.96477	0.96283

The interaction of ILs and EG makes the electronegativity of oxygen of hydroxyl in EG stronger. The Mulliken atomic charges of EG-$N_{1111}Cl$ at different sites corresponding to Fig. S16 are summarized in Table S6. The interaction of anion, cation, and EG make the electronegativity of oxygen of hydroxyl in EG stronger than that of before interaction (from -0.335 to about -0.200 a.u.), which make the oxygen in EG prefer to attacking the carbon of the ester group in PET and finally results in degradation of PET.

Table S6 The calculated Mulliken atomic charges for EG in PET, $N_{1111}Cl$, and EG system. (unit in a.u.)

Atom	EG	A	B	C	D
H1	0.259	0.307	0.250	0.145	0.137
O1	-0.335	-0.202	-0.228	-0.187	-0.252
C1	-0.257	-0.045	-0.518	-0.157	-0.515
C1’	-0.257	-0.625	-0.260	-0.512	-0.122
O1’	-0.335	-0.242	-0.273	-0.324	-0.154
H1’	0.259	0.247	0.264	0.310	0.228