# Quantum Chemistry Insight Into the Interactions Between Deep Eutectic Solvents and $SO_2$

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**ELECTRONIC SUPPORTING INFORMATION**

**Table S1.** DFT results for optimized initial structures for HBA, HBD and SO2 molecules.

| | Structures | E (eH) |
|---|---|---|
| **HBA** | BmimCl | -883.3831217 |
| | EmimCl | -804.7954558 |
| | ChCl | -788.9625135 |
| **HBD** | Acetamide | -209.1704337 |
| | Citric Acid | -759.9425707 |
| | Ethylene Glycol | -230.2091851 |
| | Fructose | -687.0468922 |
| | Glycerol | -344.7199347 |
| | Lactic Acid | -343.5523307 |
| | Levulinic Acid | -420.9460304 |
| | Malic Acid | -532.0988742 |
| | Phnylacetic Acid | -460.0018162 |
| **Gas** | SO2 | -548.5454487 |

**Table S2.** DFT results for optimized superstructure (sstr) , optimized single structure while the coordinates are fixed at original superstructure and the other structure is considered at ghost orbital, and counterpoise corrected superstructure.

| **Structure** | $E_{sstr}$ **(eH)** | $E\_m^{i}{}_{opt}$ **(eH)** | | $E\_m^{i}{}_{f}$ **(eH)** | | $E\_m^{i^*}{}_{f}$ **(eH)** | | $E_{Bind}$ **(eH)** | $E_{int\_cp}$ **(eH)** |
|---|---|---|---|---|---|---|---|---|---|
| | | **DES** | **$SO_2$** | **DES** | **$SO_2$** | **DES** | **$SO_2$** | | |
| Bmim:Ac+$SO_2$ | -1641.137 | -1092.632 | -548.545 | -1092.628 | -548.544 | -1092.628 | -548.547 | -0.03754 | 0.038 |
| Emim:Ac+$SO_2$ | -1562.536 | -1014.038 | -548.545 | -1014.037 | -548.545 | -1014.037 | -548.547 | -0.02472 | 0.046 |
| Emim:Eg+$SO_2$ | -1583.573 | -1035.067 | -548.545 | -1035.059 | -548.545 | -1035.060 | -548.548 | -0.02282 | 0.036 |
| ChCl:Ca+$SO_2$ | -2097.494 | -1549.022 | -548.545 | -1549.016 | -548.545 | -1549.017 | -548.548 | -0.04379 | 0.070 |
| ChCh:Eg+$SO_2$ | -1567.738 | -1019.233 | -548.545 | -1019.230 | -548.545 | -1019.230 | -548.548 | -0.02081 | 0.037 |
| ChCl:Gy+$SO_2$ | -1682.262 | -1133.765 | -548.545 | -1133.759 | -548.545 | -1133.759 | -548.547 | -0.03417 | 0.045 |
| ChCl:La+$SO_2$ | -1681.095 | -1132.599 | -548.545 | -1132.587 | -548.545 | -1132.587 | -548.548 | -0.03465 | 0.045 |
| ChCl:Lv+$SO_2$ | -1758.483 | -1209.991 | -548.545 | -1209.989 | -548.545 | -1209.990 | -548.547 | -0.02916 | 0.050 |
| ChCl:Ma+$SO_2$ | -1869.631 | -1321.139 | -548.545 | -1321.136 | -548.545 | -1321.137 | -548.548 | -0.02393 | 0.051 |
| ChCl:Pa+$SO_2$ | -1797.538 | -1249.058 | -548.545 | -1249.054 | -548.545 | -1249.055 | -548.547 | -0.02805 | 0.063 |
| ChCl:Fr+$SO_2$ | -2024.583 | -1476.101 | -548.545 | -1476.107 | -548.545 | -1476.107 | -548.548 | -0.02806 | 0.060 |

**Table S3.** DES+$SO_2$(P1-P2-P3-P4) structure interaction energies

| Structure | Energy | Interaction Site |
|---|---|---|
| BmAcSO2_p01 | -1641.148568 | |
| BmAcSO2_p02 | -1641.144505 | |
| BmAcSO2_p03 | -1641.148068 | |
| BmAcSO2_p04 | -1641.13654 | ***H(Bmim/cation-HBA)---O(SO2)*** |
| EmAcSO2_p01 | -1562.558486 | |
| EmAcSO2_p02 | -1562.558489 | |
| EmAcSO2_p03 | -1562.536054 | ***H(Emim/cation-HBA)---O(SO2)*** |
| EmAcSO2_p04 | -1562.549736 | |
| EmEgSO2_p01 | -1583.588249 | |
| EmEgSO2_p02 | -1583.590161 | |
| EmEgSO2_p03 | -1583.588432 | |
| EmEgSO2_p04 | -1583.572911 | ***H(Emim/cation-HBA)---O(SO2)*** |
| ChClCaSO2_p01 | -2097.496827 | |
| ChClCaSO2_p02 | -2097.498376 | |
| ChClCaSO2_p03 | -2097.498917 | |
| ChClCaSO2_p04 | -2097.494318 | ***H(Ch/cation-HBA)---O(SO2)*** |
| ChChEgSO2_p01 | -1567.751228 | |
| ChChEgSO2_p02 | -1567.750135 | |
| ChChEgSO2_p03 | -1567.751219 | |
| ChChEgSO2_p04 | -1567.737960 | ***O(Eg/HBD)---S(SO2)*** |
| ChClGySO2_p01 | -1682.270703 | |
| ChClGySO2_p02 | -1682.270765 | |
| ChClGySO2_p03 | -1682.267707 | |
| ChClGySO2_p04 | -1682.262070 | ***H(Ch/cation-HBA)---O(SO2)*** |

**Table S3. (con't)** DES+$SO_2$(P1-P2-P3-P4) structure interaction energies

| Structure | Energy | Interaction Site |
|---|---|---|
| ChClLaSO2_p01 | -1681.107947 | |
| ChClLaSO2_p02 | -1681.103574 | |
| ChClLaSO2_p03 | -1681.103584 | |
| ChClLaSO2_p04 | -1681.094941 | ***H(Ch/cation-HBA)---O(SO2)*** |
| ChClLvSO2_p01 | -1758.494000 | |
| ChClLvSO2_p02 | -1758.491672 | |
| ChClLvSO2_p03 | -1758.491649 | |
| ChClLvSO2_p04 | -1758.483149 | ***H(Ch/cation-HBA)---O(SO2)*** |
| ChClMaSO2_p01 | -1869.650684 | |
| ChClMaSO2_p02 | -1869.645771 | |
| ChClMaSO2_p03 | -1869.645641 | |
| ChClMaSO2_p04 | -1869.630769 | ***O(Ma/HBD)---S(SO2)*** |
| ChClPaSO2_p01 | -1797.555106 | |
| ChClPaSO2_p02 | -1797.554438 | |
| ChClPaSO2_p03 | -1797.548155 | |
| ChClPaSO2_p04 | -1797.537826 | ***H(Ch/cation-HBA)---O(SO2)*** |
| ChClFrSO2_p01 | -2024.593546 | |
| ChclFrSO2_p02 | -2024.589858 | |
| ChclFrSO2_p03 | -2024.589092 | |
| ChclFrSO2_p04 | -2024.582912 | ***H(Fr/HBD)---O(SO2)*** |

**Table S4.** DFT results on HOMO ($E_{HOMO}$) and LUMO ($E_{LUMO}$) energies; HOMO-LUMO energy gap ($\Delta E_G$).

| **Structure** | **$E_{HOMO}$ / eV** | **$E_{LUMO}$ / eV** | **$\Delta E_G$ / eV** |
|---|---|---|---|
| Bmim:Ac+$SO_2$ | -5.3880 | -3.2998 | 2.088 |
| Emim:Ac+$SO_2$ | -5.4208 | -4.4488 | 0.972 |
| Emim:Eg+$SO_2$ | -5.8618 | -3.4798 | 2.382 |
| ChCl:Ca+$SO_2$ | -6.3718 | -4.6476 | 1.724 |
| ChCh:Eg+$SO_2$ | -5.8618 | -3.4798 | 2.382 |
| ChCl:Gy+$SO_2$ | -6.3437 | -4.5654 | 1.778 |
| ChCl:La+$SO_2$ | -6.5786 | -4.1019 | 2.476 |
| ChCl:Lv+$SO_2$ | -6.0367 | -3.0935 | 2.943 |
| ChCl:Ma+$SO_2$ | -5.6702 | -4.1450 | 1.525 |
| ChCl:Pa+$SO_2$ | -5.9989 | -3.4808 | 2.518 |
| ChCl:Fr+$SO_2$ | -6.0857 | -2.2375 | 3.848 |

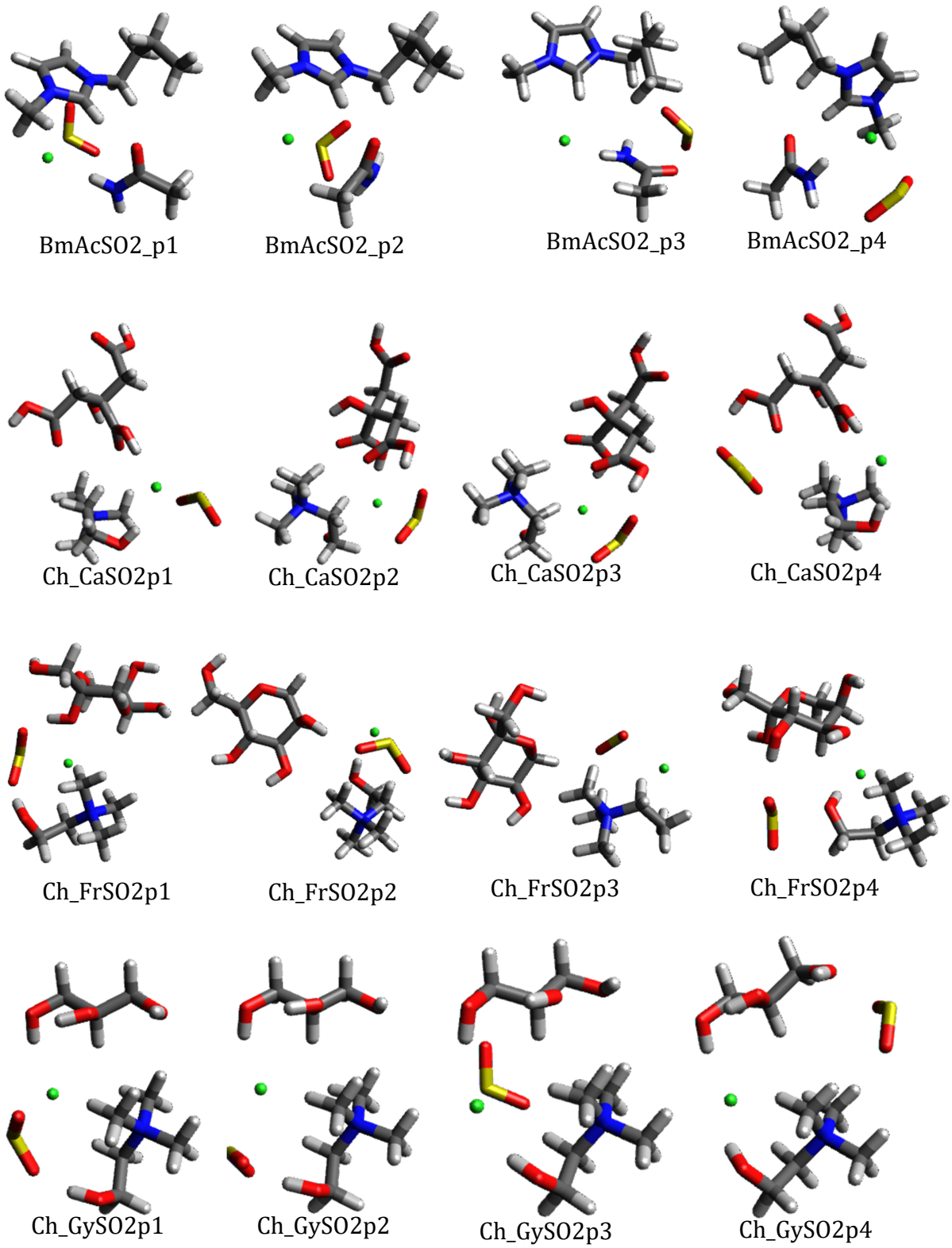


**Figure S1.** Finalized geometry optimizations for each studied DES+SO2 system at different spatial positions of SO2 around DES.

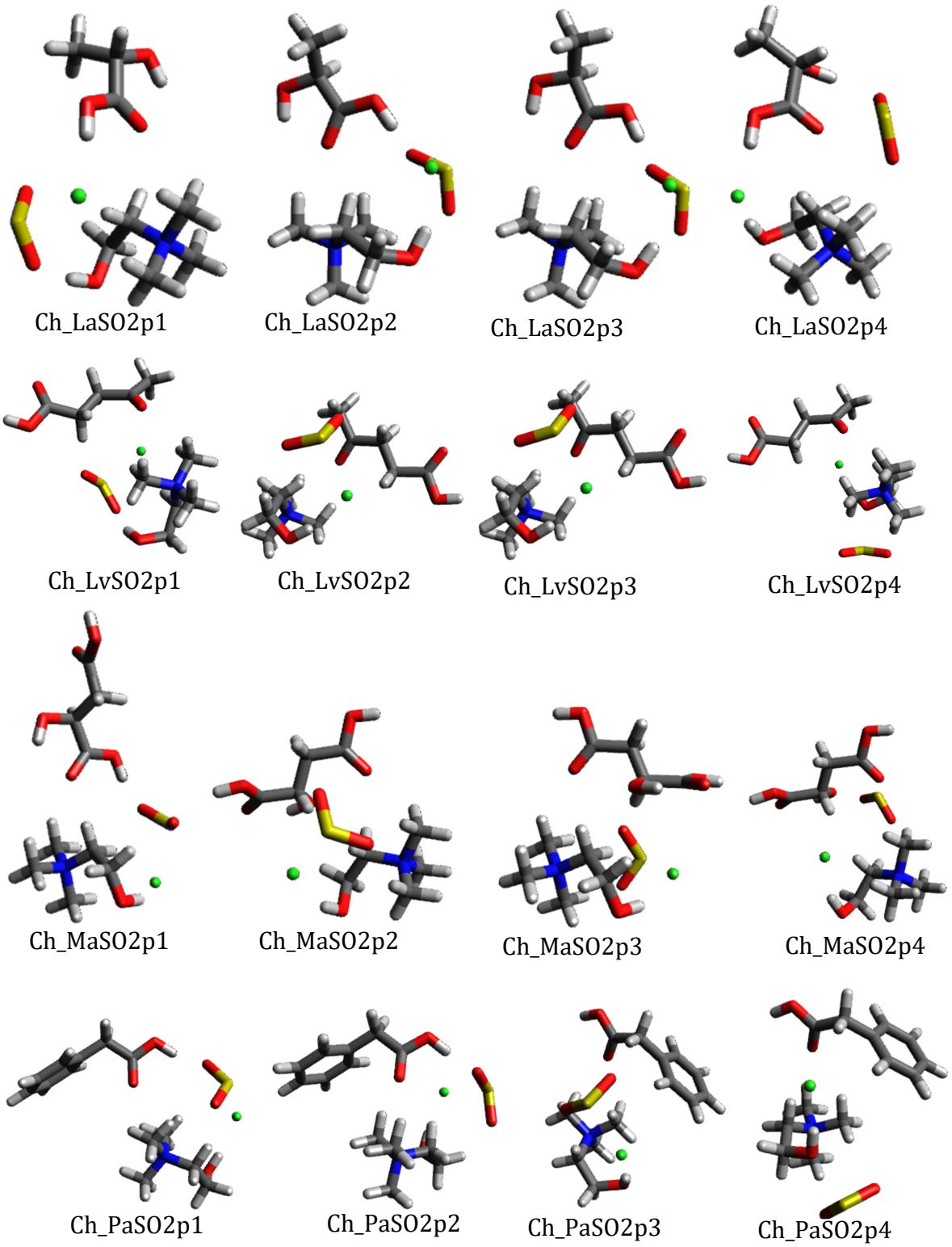


**Figure S1.** (con't)

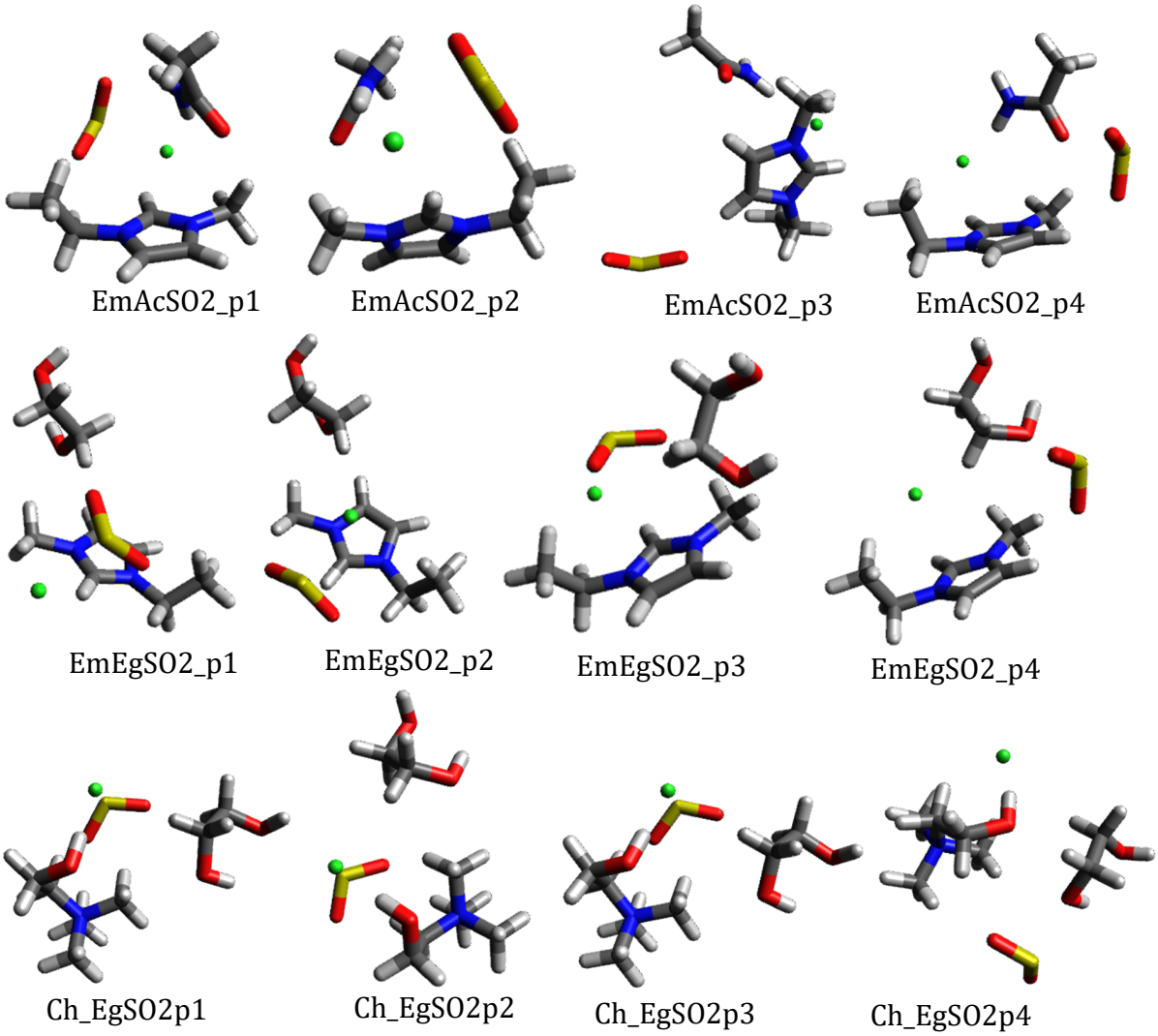


**Figure S1.** (con't)

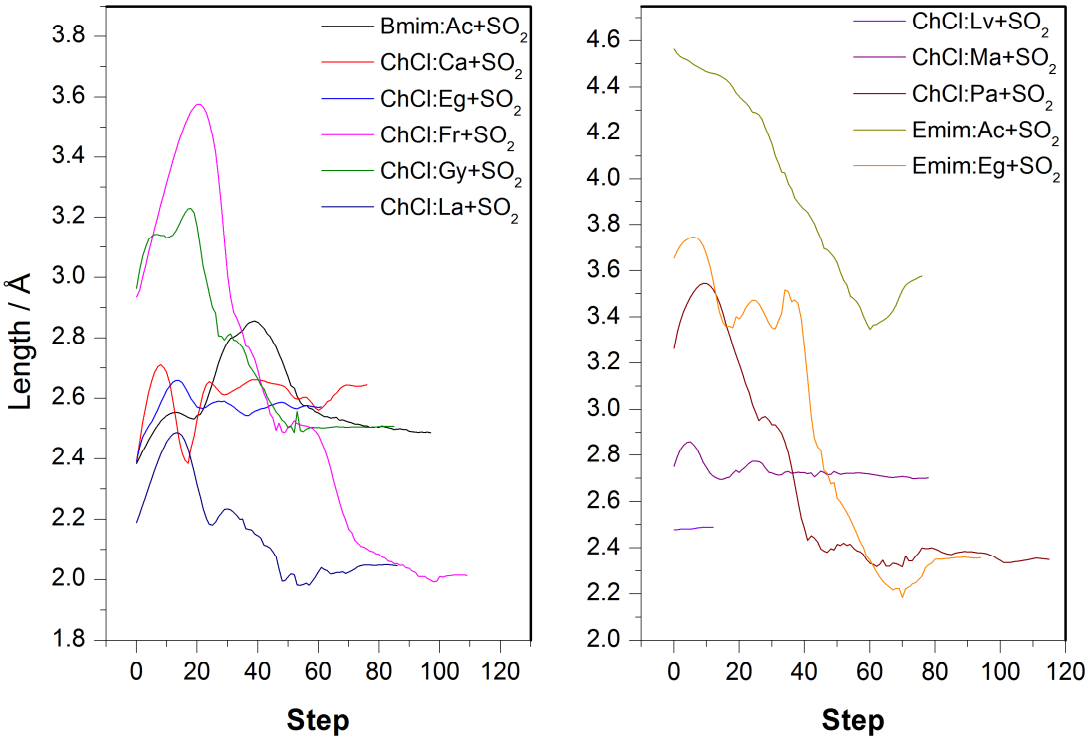


**Figure S2.** Distance evolution between BCP forming sites (DES···$SO_2$) throughout the geometry optimization.

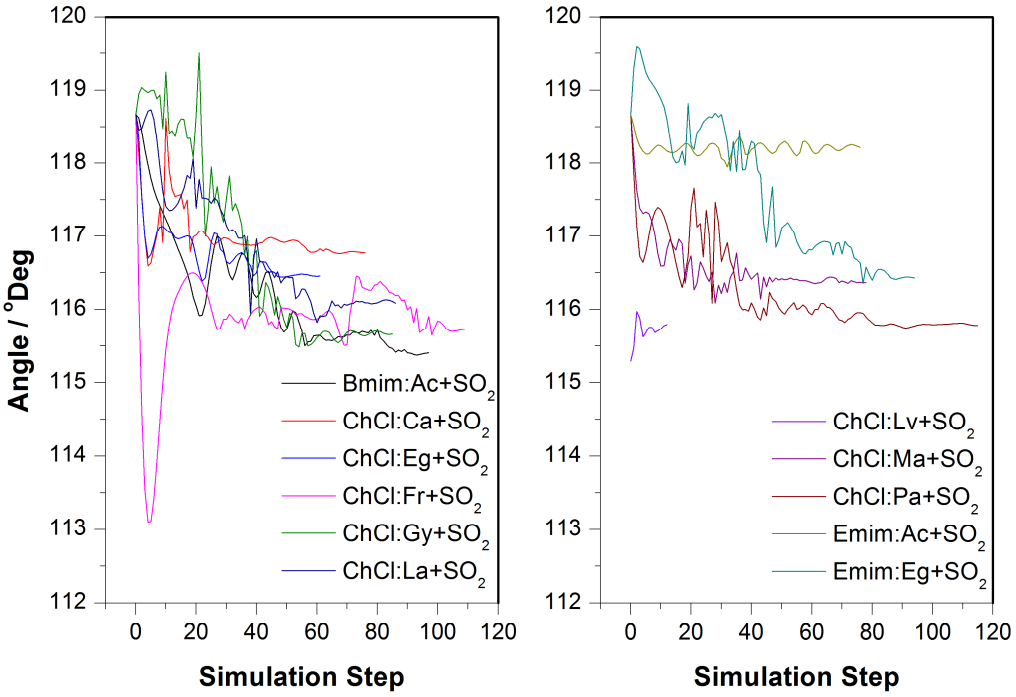


**Figure S3.** $SO_2$ angle evolution for each DES+$SO_2$ case throughout the geometry optimization.