SUPPORTING INFORMATION

Mechanistic Insight into the Superoxide Induced Ring Opening in Propylene Carbonate Based Electrolytes using *in situ* Surface-Enhanced Infrared Spectroscopy

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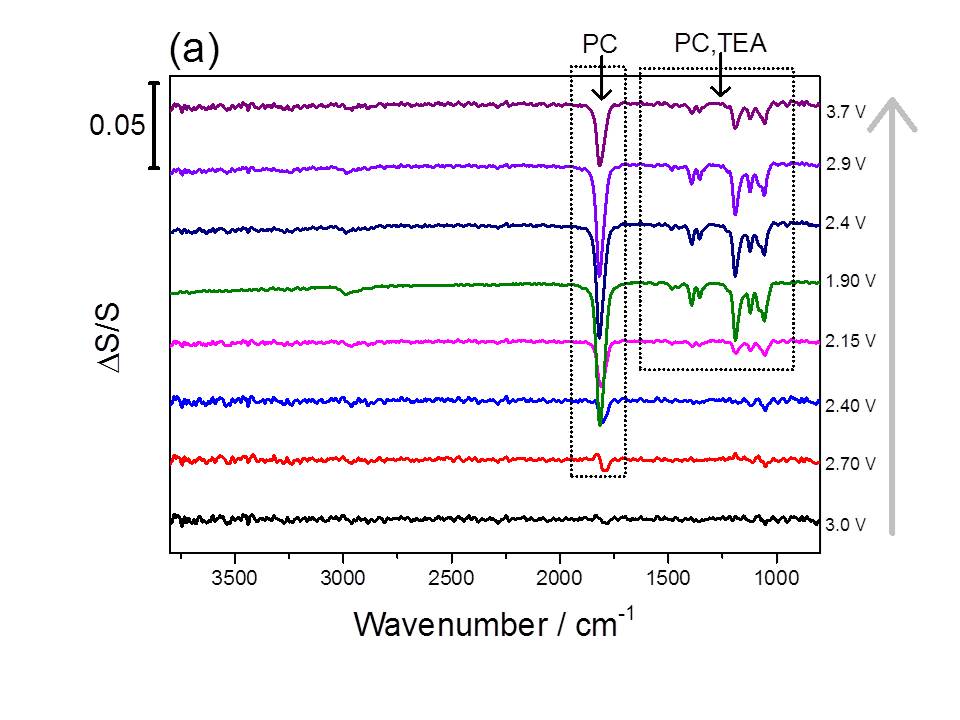
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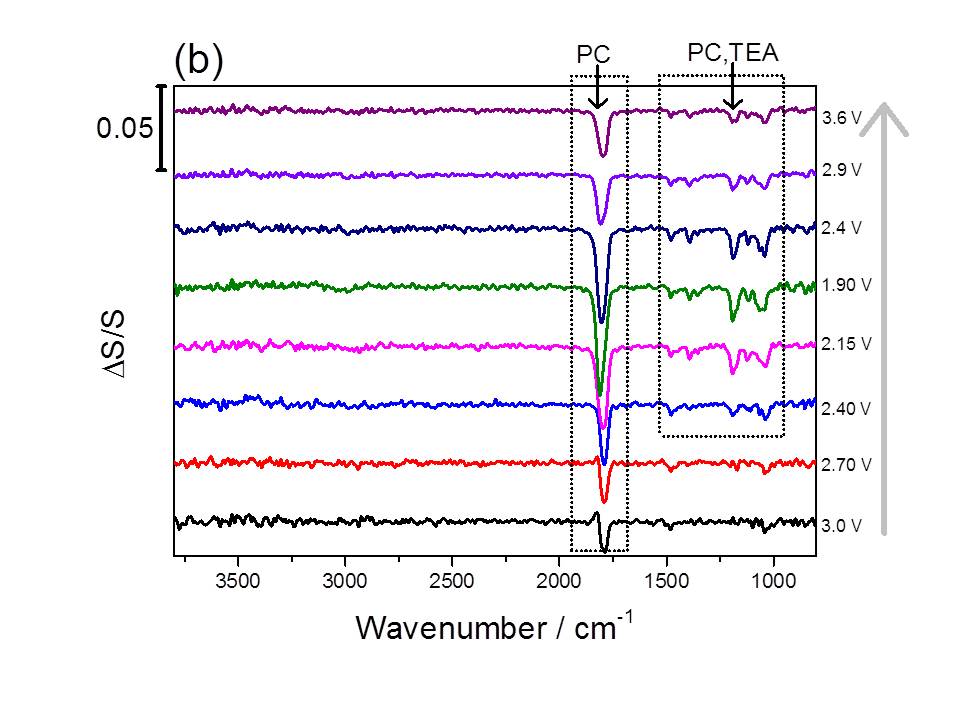
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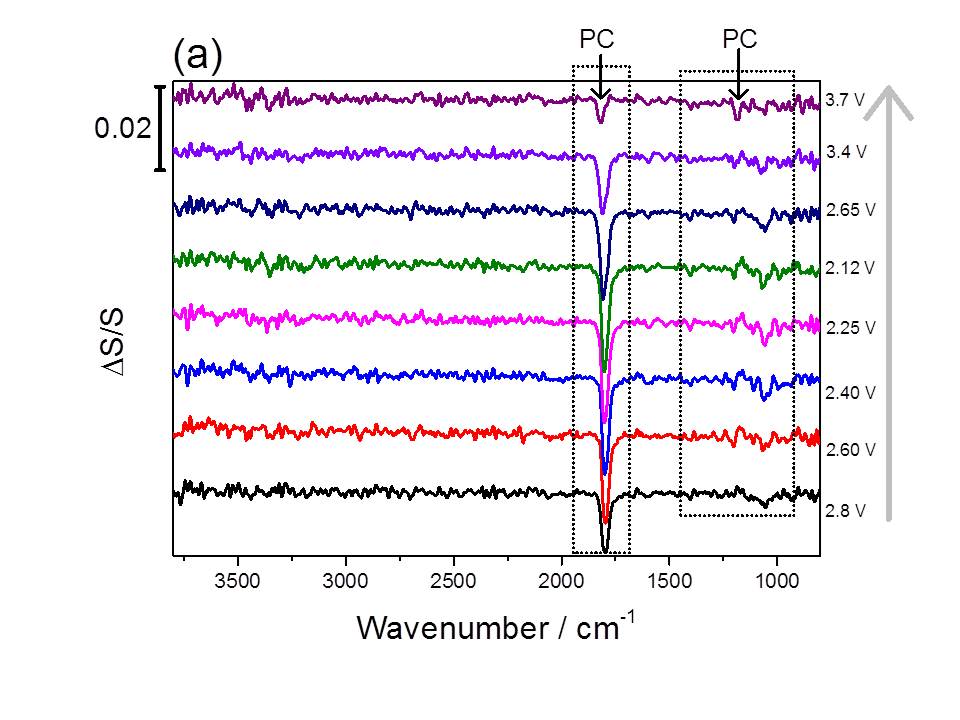
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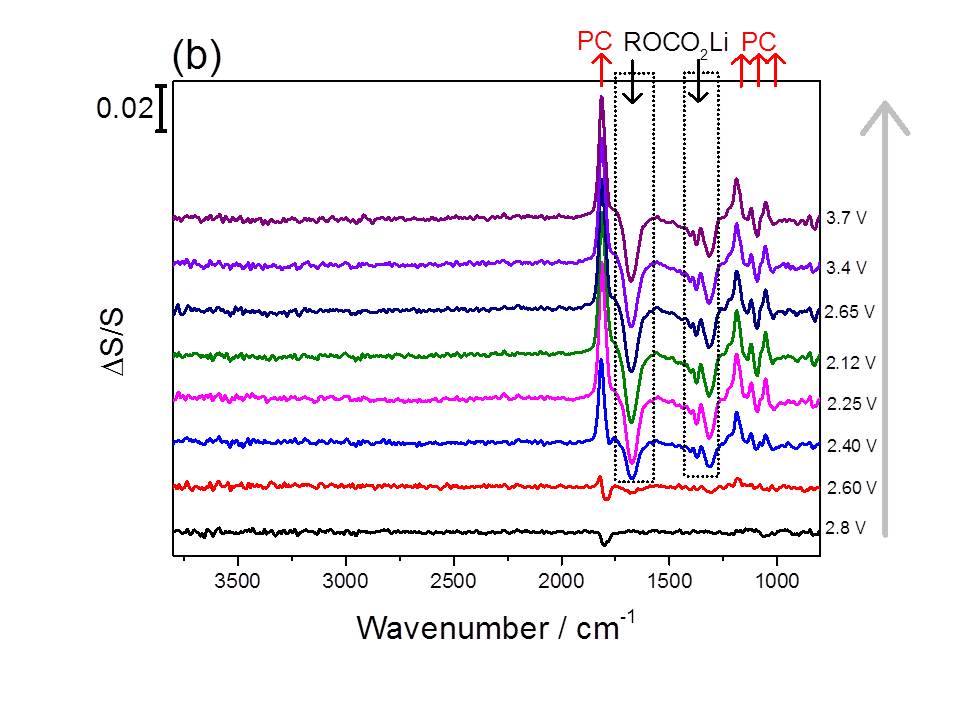
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**Supplementary figure S1: Expanded view of the SEIRA spectra shown in Figure 3, extending to higher wavenumbers.**

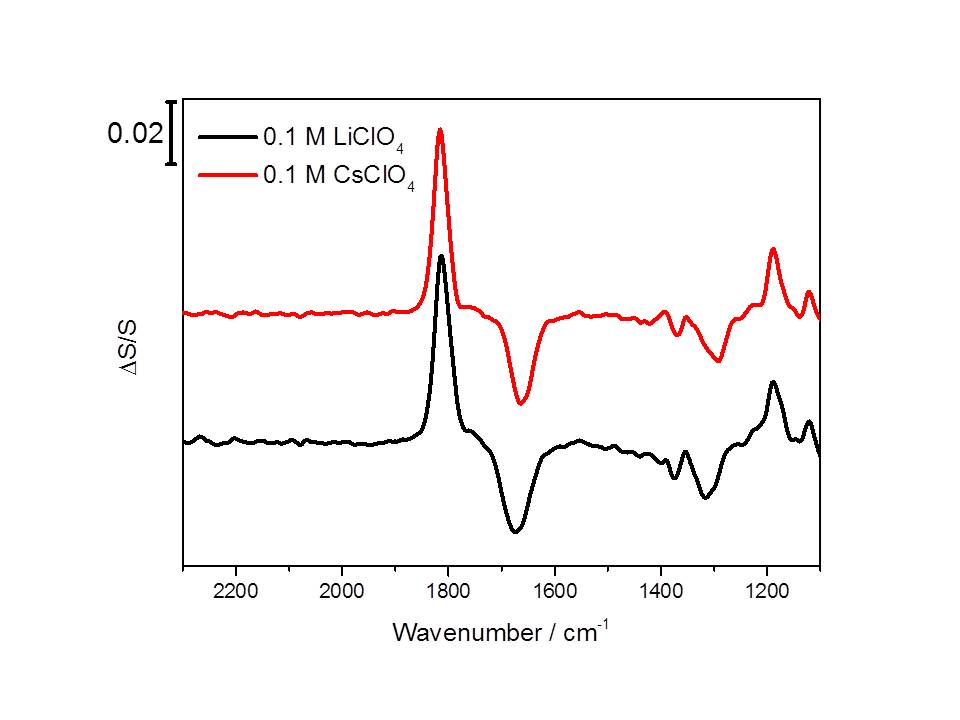
**(a) Deoxygenated 0.1 M TEAClO4/PC (b) oxygen saturated 0.1 M TEAClO4/PC.**

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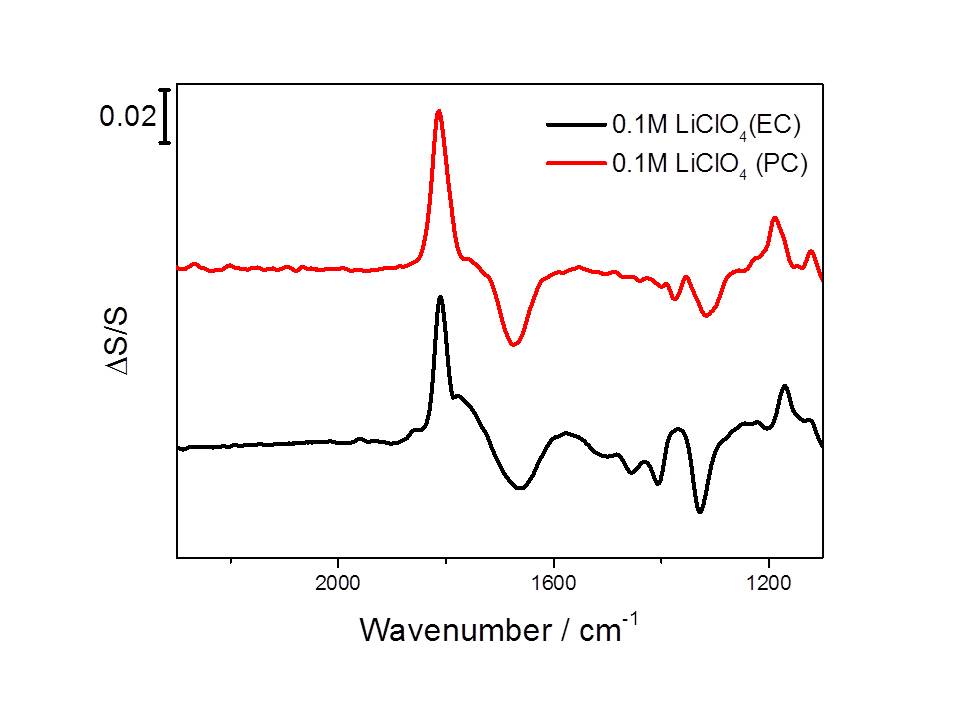


**Supplementary figure S2: Expanded view of the SEIRA spectra shown in Figure 5, extending to higher wavenumbers**

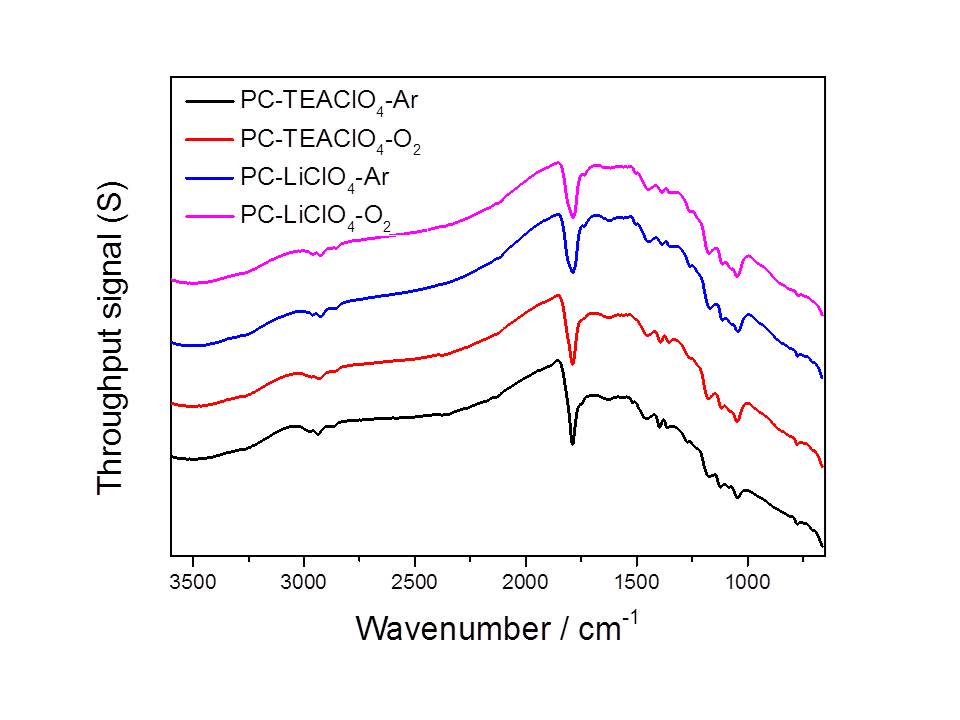
**(a) Deoxygenated 0.1 M LiClO4/PC (b) oxygen saturated 0.1 M LiClO4/PC.**



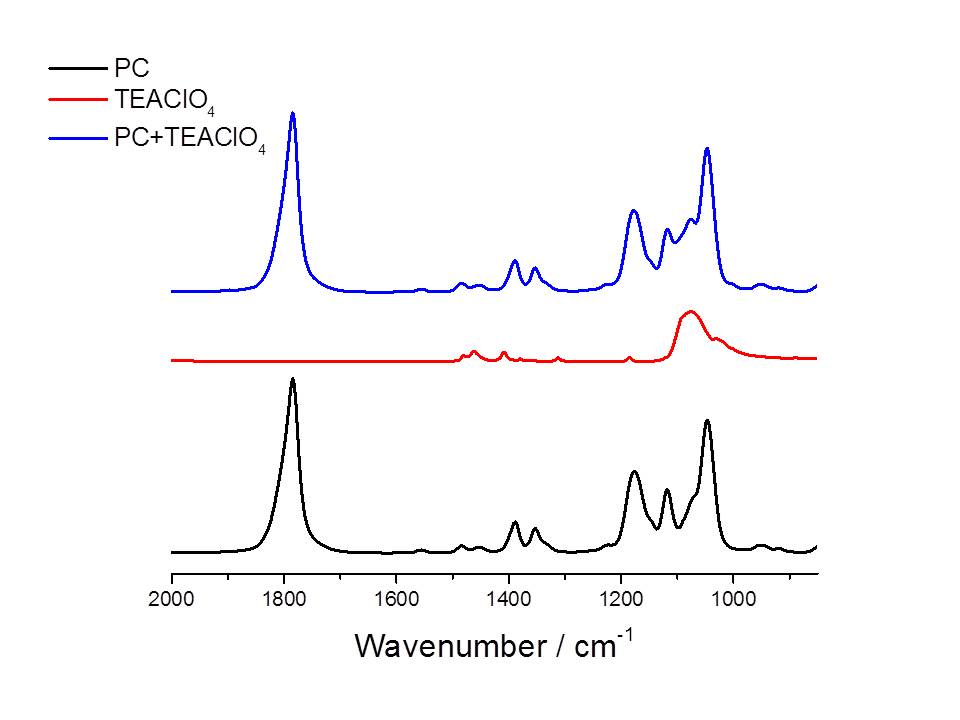
Supplementary figure S3: SEIRA spectra corresponding to PC ring opening in 0.1 M LiClO4, PC as well as 0.1M CsClO4, PC



Supplementary figure S4: SEIRA spectra recorded for Au thin film electrode in oxygenated 0.1 M LiClO4/PC compare to 0.1 M LiClO4/EC. The downward peak around 1670 cm-1 corresponds to the ring opened species were observed in both cases. SEIRA of EC/LiClO4 was carried out at 40oC (above the melting point of EC).



Supplementary figure S5: The original spectra at open circuit potential of PC-TEAClO4 and of PC-LiClO4 systems.



Supplementary figure S6: Standard ATR spectra of PC, TEAClO4 and PC+ 1M TEAClO4.

**Supplementary Table S1: Band assignment for solvents, salts, model reaction products and main SEIRA bands from graphs presented in the paper.**

|  |  |  |
| --- | --- | --- |
|  | **Band Positions** | **Assignments** |
| Propylene Carbonate | 1787 | C═O) |
| 1556  1484  1452  1389  1353 | CH2) + C  C  CH2), −CH2)  Ring,CH2) |
| 1118 | s(CH2−CH−CH3) |
| 1176, 1075  1046 | s(C−O−C) +as(O−C−O), s(C−O) s(C−CH3) |
| Tetraethylammonium Perchlorate | 1482,  1463,  1408,  1380,  1312 | CH2)  C  as(C  sC  CH2) |
| 1185 | C-C-N |
| 1077 | ClO4) |
| Lithium Propyl  Dicarbonate | 1660 | C═O) |
| 1506  1454  1380  1314 | s(C−CH3)  C  sC  CH2) |
| Lithium Triethoxy Dicarbonate | 1680 | C═O) |
| 1478, 1424, 1342 | CH2) + C  CH2), −CH2) |
| Reaction product in PC-LiClO4 at 2.12 V | 1676 | C═O) |
| 1401, 1375, 1315 | CH2) + −CH2), CH2) |
| Dimethyl sulfoxide | 2994, 2912  1437, 1406, 1309 | asCsC  aCa’CsC |
| Reaction product in DMSO-LiClO4 at 2 V | 1443, 1306, 1290 | aCsCC |

\* stretching, twisting, scissoring, bending,s= symmetric stretching, as= asymmetric stretching, =wagging

The band assignments were on the basis of [1]-[8]

|  |  |
| --- | --- |
| (a) | (b) |
| (c) |

Supplementary figure S7: (a) Cyclic Voltammogram for the reduction of oxygen in 0.1 M LiClO4/ dimethyl sulfoxide at 0.1 V/s scan rate. (b) Standard ATR spectrum of DMSO. (c) *In situ* SEIRA spectra obtained on a Au thin film electrode formed on a silicon prism, at representative potentials.

Unlike oxygenated PC/LiClO4 or EC/LiClO4 electrolytes, no new downward band can be seen in oxygenated DMSO/LiClO4, suggesting superior stability of DMSO solvent in Li-O2 environment.

Table S2

Coordinates of reactants, transition states and products for data shown in Figure 7

PC Li Reactants

6 1.752037000 -0.011479000 0.232270000

8 1.139614000 0.931867000 -0.499134000

6 -0.336000000 0.630212000 -0.579472000

6 -0.433231000 -0.703850000 0.164674000

8 0.979478000 -0.954890000 0.623905000

1 -0.847984000 1.433514000 -0.057640000

1 -0.569461000 0.566822000 -1.637137000

1 -1.007687000 -0.582568000 1.078056000

8 2.950380000 0.132884000 0.448111000

6 -0.856013000 -1.891374000 -0.659608000

1 -0.230859000 -1.990477000 -1.551052000

1 -1.893555000 -1.733567000 -0.952825000

1 -0.781628000 -2.807319000 -0.072882000

8 -2.726374000 0.358210000 -0.204253000

8 -2.669468000 1.132259000 0.846213000

3 2.873562000 1.795759000 -0.404875000

PC Li TS

6 1.737424000 -0.001267000 0.224636000

8 1.156435000 0.910876000 -0.540707000

6 -0.440844000 0.645503000 -0.522633000

6 -0.451790000 -0.692784000 0.206096000

8 0.941812000 -0.902514000 0.691778000

1 -0.795679000 1.496941000 0.043737000

1 -0.662415000 0.633250000 -1.581192000

1 -1.053651000 -0.612426000 1.106767000

8 2.947619000 0.085204000 0.428988000

6 -0.817780000 -1.878125000 -0.653174000

1 -0.170840000 -1.934166000 -1.532915000

1 -1.853376000 -1.757217000 -0.970414000

1 -0.718288000 -2.803260000 -0.085054000

8 -2.616506000 0.419266000 -0.313547000

8 -2.784296000 1.024530000 0.822953000

3 2.924403000 1.671747000 -0.551118000

PC Li Products

6 1.724814000 0.075019000 0.132467000

8 1.527510000 0.421587000 -1.070024000

6 -1.144426000 0.720387000 -0.292960000

6 -0.582051000 -0.572119000 0.299168000

8 0.709801000 -0.369333000 0.888054000

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1 -0.802537000 0.899275000 -1.308584000

1 -1.202776000 -0.810269000 1.164944000

8 2.851176000 0.139701000 0.674800000

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1 0.024574000 -1.506436000 -1.550570000

1 -1.621101000 -1.905156000 -1.016563000

1 -0.230678000 -2.636169000 -0.197989000

8 -2.580025000 0.593962000 -0.400310000

8 -3.161813000 0.635876000 0.759972000

3 3.351750000 0.776332000 -0.978570000

PC TEA Reactants

6 -1.766539000 0.953668000 0.747404000

8 -2.817120000 0.377064000 1.311009000

6 -3.635865000 -0.237869000 0.304810000

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1 4.085546000 0.435518000 -0.330673000

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1 1.117777000 0.729552000 -3.158908000

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