

Supporting Information

Insights into hydrogen bond donors promoted fixation of carbon dioxide with epoxides catalyzed by ionic liquids

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1. Synthesis of task-specific ionic liquids

Synthesis of 1-butylimidazole. The synthesis procedure was carried out according to the literature.¹ NaH (17.6 mmol, 60 wt% in mineral oil) suspended in anhydrous THF (~20 mL) was added to 100 mL round bottom flask. Upon addition of imidazole (16.2 mmol) hydrogen gas was evolved. The reaction mixture was stirred at 40 °C until the gas evolution ceased. Then *n*-butyl bromide (16.2 mmol) was added and the reaction mixture was heated under reflux (70 °C) overnight. After cooling to room temperature, the solid precipitate was filtered off and washed with THF. The filtrate was reduced in volume under reduced pressure. MeOH was added and then washed three times with hexane. Finally the solvent in the MeOH phase was removed via rotary evaporation. The product was dried under vacuum overnight to give yellow-brownish oil. Yield: 89%.

Synthesis of ionic liquid N-(2-hydroxyl-ethyl)-Pyridinium bromide. A mixture of pyridine (14.2 mmol), 2-bromidethanol (11.8 mmol) and toluene (25 mL) was charged into 100 mL round bottom flask and stirred at 70 °C for 12 h. Then the mixture was cooled down to room temperature, and the solvent toluene was dumped. The resultant crude solid was washed repeatedly with ethyl acetate (3×30 mL) and dried at 50 °C for 12 h under vacuum. Yield: 95%. N-(2-hydroxyl-ethyl)-Pyridinium bromide (HEPyBr): ¹H NMR (400 MHz, D₂O): δ = 8.89 (d, *J* = 5.5 Hz, 2H), 8.70–8.58 (m, 1H), 8.13 (t, *J* = 7.1 Hz, 2H), 4.78–4.73 (m, 2H), 4.16–4.06 (m, 2H); FT-IR (cm⁻¹): 3289, 3054, 2876, 1636, 1491, 1177, 1072, 879, 774, 681.

The synthetic procedures for ionic liquids 1-(2-hydroxyl-ethyl)-3-methylimidazolium bromide (HEMimBr) and 1-(2-hydroxyl-ethyl)-3-butylimidazolium bromide (HEBimBr) were similar to that of HEPyBr. The main differences were the corresponding 1-methylimidazole or 1-butylimidazole were used to replace pyridine, respectively.

Synthesis of ionic liquid N-(2-carboxyl-ethyl)-Pyridinium bromide. A mixture of pyridine (14.2 mmol), bromoacetic (12.9 mmol) and toluene (25 mL) was charged into 100 mL round bottom flask and stirred at 70 °C for 12 h. Then the mixture was cooled down to room temperature, and the solvent toluene was dumped. The resultant

crude solid was washed repeatedly with ethyl acetate (3×30 mL) and dried at 50 °C for 12 h under vacuum. Yield: 96%. N-(2-carboxyl-ethyl)-Pyridinium bromide (CEPyBr): ¹H NMR (400 MHz, D₂O): δ = 8.89–8.79 (m, 2H), 8.69–8.60 (m, 1H), 8.19–8.09 (m, 2H), 5.45 (s, 2H); FT-IR (cm⁻¹): 3413, 3059, 2980, 1739, 1636, 1487, 1192, 778, 691.

The synthetic procedures for ionic liquids 1-(2-carboxyl-ethyl)-3-methylimidazolium bromide (CEMimBr) and 1-(2-carboxyl-ethyl)-3-butylimidazolium bromide (CEBimBr) were similar to that of CEPyBr. The main differences were the corresponding 1-methylimidazole or 1-butylimidazole were used to replace pyridine, respectively.

2. The cartesian coordinates of optimized geometries of stable points calculated at M06-2X/6-31G (d, p) level of theory

Fig. 3 A

C	1.131558	3.206686	-0.292687
C	-0.107418	3.477660	0.201079
N	1.238091	1.838490	-0.388617
C	0.105093	1.281351	0.042802
N	-0.723365	2.263992	0.410429
H	1.938592	3.860402	-0.581074
H	-0.596658	4.411994	0.423753
H	-0.069226	0.196520	0.083883
C	2.425806	1.079074	-0.825078
C	3.237030	0.577859	0.362596
H	3.001833	1.744965	-1.473595
H	2.056965	0.220264	-1.391736
C	4.327768	-0.383554	-0.102791
H	2.554469	0.024821	1.016872
H	3.661517	1.422541	0.921291
C	5.100275	-0.968342	1.075163
H	5.013001	0.126277	-0.792760
H	3.836042	-1.194197	-0.652423
H	5.568452	-0.182200	1.676832
H	5.886941	-1.646733	0.736461
H	4.423138	-1.534936	1.720810
C	-2.104350	2.039335	0.838578
C	-3.052169	1.946698	-0.365803
H	-2.388651	2.843122	1.520244
H	-2.125564	1.089362	1.372940
O	-4.264326	1.370671	0.025279

H	-2.549023	1.365173	-1.151278
H	-3.262777	2.945095	-0.763180
H	-4.059980	0.430192	0.159050
C	-2.505795	-2.246307	0.288133
C	-2.442380	-1.698747	-1.070616
O	-2.529125	-0.826776	0.069658
H	-3.339093	-1.712484	-1.687940
H	-1.472504	-1.685858	-1.562222
C	-3.772379	-2.831786	0.844166
H	-1.554013	-2.580979	0.697728
H	-4.646191	-2.415994	0.334029
H	-3.860773	-2.621795	1.913541
H	-3.776298	-3.916776	0.711843
Br	0.927031	-1.918197	-0.289100

Fig. 3 TS_{A-B}

C	3.156778	2.233445	0.791851
C	4.136861	1.383044	0.388358
N	1.955931	1.613881	0.529980
H	3.207585	3.213196	1.238079
N	3.513154	0.261439	-0.111979
H	5.210519	1.476066	0.410475
C	2.189767	0.415621	-0.014742
C	4.216842	-0.914753	-0.651067
H	1.424485	-0.320855	-0.327456
C	0.615130	2.155168	0.824594
C	-0.294666	2.148483	-0.397004
H	0.767488	3.171611	1.195619
H	0.183280	1.563269	1.636396
H	0.109214	2.837940	-1.148714

C	-1.727014	2.528214	-0.019734
H	-0.288515	1.147623	-0.845395
H	-1.716341	3.487845	0.514440
H	-2.142535	1.765984	0.651253
C	-2.636593	2.612588	-1.240511
H	-2.255349	3.325273	-1.980135
H	-3.641218	2.919936	-0.943856
H	-2.744043	1.625915	-1.698431
C	3.262440	-2.048067	-1.003592
H	4.908759	-1.254217	0.123747
H	4.785243	-0.590962	-1.527328
H	2.536154	-1.707130	-1.754691
O	2.630428	-2.505373	0.153818
H	3.869961	-2.835615	-1.470766
H	1.662785	-2.471950	-0.024222
C	-1.433663	-1.327655	-0.761164
H	-1.459921	-0.457784	-1.396517
Br	-3.703527	-0.532412	0.106564
H	-1.863325	-2.250695	-1.122565
C	-0.944345	-2.427574	1.471390
H	-1.888956	-2.195602	1.969932
H	-0.139177	-2.500454	2.208217
H	-1.040601	-3.388803	0.959254
H	-0.517694	-0.362323	0.931307
O	0.259953	-1.640624	-0.573318
C	-0.666700	-1.345702	0.461890

Fig. 3 B

C	2.583514	0.937424	-1.939779
C	2.067547	2.188987	-1.910025

N	1.948954	0.240487	-0.928100
H	3.328994	0.492115	-2.579768
N	1.146321	2.207736	-0.877404
H	2.268962	3.052117	-2.524693
C	1.055437	1.006632	-0.254787
C	0.351365	3.387644	-0.529935
H	0.022570	0.394591	1.017790
C	2.262203	-1.132252	-0.552840
C	3.589232	-1.238548	0.191555
H	2.273885	-1.749955	-1.457697
H	1.442306	-1.475821	0.083455
H	4.396336	-0.846512	-0.441034
C	3.904017	-2.676011	0.599069
H	3.541361	-0.595626	1.078472
H	3.928529	-3.310945	-0.295386
H	3.091012	-3.058565	1.227817
C	5.229739	-2.787493	1.346780
H	6.058949	-2.434332	0.726192
H	5.440676	-3.820404	1.633093
H	5.214508	-2.182067	2.257806
C	0.167405	3.602262	0.975725
H	-0.638283	3.313460	-0.991195
H	0.870185	4.247662	-0.963293
H	1.106699	3.351494	1.488147
O	-0.935902	2.928584	1.510595
H	-0.013818	4.672620	1.124829
H	-0.701531	2.014880	1.757969
C	-1.939238	-1.355540	0.368465
H	-1.049210	-1.562345	-0.226335
Br	-3.452281	-1.627263	-0.838522

H	-2.037549	-2.088638	1.169268
C	-3.080925	0.396099	1.812930
H	-4.024035	0.255671	1.280942
H	-3.006759	1.434356	2.143672
H	-3.066310	-0.255059	2.692448
H	-1.870765	0.763937	0.069388
O	-0.710292	0.175537	1.682057
C	-1.897670	0.065971	0.921792

Fig. 3 C

C	0.598954	3.194609	0.744688
C	1.741480	3.300824	0.024533
N	0.044108	1.974777	0.407329
H	0.148967	3.861704	1.463203
N	1.830661	2.142082	-0.728119
H	2.489500	4.076971	-0.010838
C	0.785945	1.306753	-0.508107
C	2.911870	1.858324	-1.670229
H	0.200586	-0.306564	-0.937538
C	-1.212627	1.448553	0.929051
C	-2.403846	1.848369	0.067503
H	-1.329319	1.806558	1.957742
H	-1.107726	0.360654	0.964343
H	-2.449995	2.942106	-0.014293
C	-3.718034	1.314545	0.633471
H	-2.243283	1.456370	-0.943753
H	-3.898634	1.762825	1.618624
H	-3.627972	0.234532	0.810951
C	-4.900711	1.591913	-0.289889
H	-5.012814	2.666404	-0.464939

H	-5.836556	1.222015	0.136207
H	-4.751834	1.107311	-1.258902
C	3.121441	0.359408	-1.845629
H	3.826995	2.304252	-1.270761
H	2.686500	2.324070	-2.635869
H	2.208667	-0.093531	-2.255309
O	3.532439	-0.264952	-0.656222
H	3.924768	0.215588	-2.574045
H	2.797568	-0.247221	-0.024220
C	0.554220	-2.556330	0.786827
H	1.185022	-3.397681	1.071990
Br	1.178901	-1.049943	1.874919
H	-0.480566	-2.722810	1.085105
C	0.269275	-3.487435	-1.493772
H	0.954260	-4.314843	-1.290695
H	0.299566	-3.255681	-2.560126
H	-0.747407	-3.801041	-1.237073
H	1.684831	-1.962592	-0.929220
O	-0.237558	-1.208263	-1.062289
C	0.642896	-2.237533	-0.702118
C	-2.784406	-1.549390	-0.930808
O	-2.679282	-2.271963	-0.022103
O	-2.983701	-0.837957	-1.828179

Fig. 3 TS_{C-D}

C	-0.700370	3.056411	0.597449
C	0.399069	3.523996	-0.047202
N	-0.758001	1.702551	0.340050
H	-1.426984	3.558760	1.215580
N	0.975695	2.441091	-0.681496

H	0.819956	4.514691	-0.104937
C	0.263010	1.330763	-0.442596
C	2.180407	2.485495	-1.516837
H	0.501192	0.173997	-0.778620
C	-1.762898	0.765593	0.842640
C	-3.119781	0.965937	0.180107
H	-1.821051	0.880709	1.929929
H	-1.365013	-0.234121	0.648847
H	-3.535816	1.940786	0.467199
C	-4.091421	-0.149484	0.561855
H	-2.978138	0.975652	-0.905398
H	-4.217437	-0.171701	1.651646
H	-3.652470	-1.114749	0.280748
C	-5.448185	0.017243	-0.115567
H	-5.913194	0.967493	0.164970
H	-6.133333	-0.787052	0.161904
H	-5.338743	0.006435	-1.203961
C	2.965530	1.177753	-1.443515
H	2.801041	3.302114	-1.140261
H	1.887792	2.703874	-2.548503
H	2.346323	0.344483	-1.800760
O	3.471218	0.955180	-0.151212
H	3.819613	1.279697	-2.120796
H	2.814188	0.480948	0.378553
C	1.160267	-2.349886	0.842970
H	1.856338	-3.036184	1.325045
Br	1.210172	-0.721136	1.954525
H	0.134867	-2.711534	0.913026
C	1.597563	-3.327399	-1.390709
H	2.348254	-4.016279	-0.990595

H	1.852783	-3.092907	-2.426508
H	0.620089	-3.817434	-1.381474
H	2.559767	-1.590575	-0.570594
O	0.648789	-1.131980	-1.184884
C	1.533289	-2.013137	-0.601518
C	-1.447189	-1.612157	-1.504181
O	-1.568765	-2.585354	-0.855992
O	-1.680696	-0.681546	-2.177994

Fig. 3 D

C	-0.081911	-2.627918	-1.214361
C	1.044848	-2.834787	-0.481351
N	-0.934034	-1.867031	-0.442396
H	-0.345212	-2.937712	-2.212337
N	0.854683	-2.195773	0.724294
H	1.965133	-3.346964	-0.706102
C	-0.341868	-1.608632	0.721980
C	1.876163	-2.003842	1.760228
H	-0.700358	-0.973201	1.526202
C	-2.132504	-1.170597	-0.929207
C	-3.173553	-0.951194	0.156457
H	-2.532978	-1.771808	-1.750927
H	-1.782996	-0.209389	-1.320920
H	-3.475350	-1.916162	0.582496
C	-4.388252	-0.216866	-0.408781
H	-2.728232	-0.332384	0.941825
H	-4.819796	-0.789174	-1.240171
H	-4.053791	0.741856	-0.822681
C	-5.450915	0.029067	0.658100
H	-5.811662	-0.915775	1.076151

H	-6.310284	0.564939	0.248142
H	-5.040664	0.623876	1.478825
C	2.870572	-0.932458	1.326977
H	2.373584	-2.965471	1.907989
H	1.368030	-1.686038	2.670877
H	2.345641	0.024133	1.248464
O	3.484026	-1.313236	0.108941
H	3.629491	-0.845041	2.113604
H	3.267190	-0.634226	-0.541058
C	0.452732	2.271832	-1.264545
H	0.777773	2.853564	-2.127023
Br	1.156888	0.463509	-1.554897
H	-0.624032	2.139827	-1.242130
C	0.101602	4.097446	0.381505
H	0.068421	4.813657	-0.445389
H	0.514034	4.598594	1.259452
H	-0.910120	3.754941	0.607371
H	2.001848	3.219813	-0.144196
O	1.091477	2.006283	1.125367
C	0.971498	2.891277	0.034020
C	0.000016	1.199471	1.493710
O	-1.033663	1.260109	0.795180
O	0.257927	0.465362	2.461917

Fig. 3 TS_{D-E}

C	-0.950071	-2.796184	-0.836773
C	0.145732	-3.179385	-0.130892
N	-1.494807	-1.711209	-0.185283
H	-1.374631	-3.180764	-1.749193
N	0.249014	-2.316110	0.937851

H	0.874881	-3.953199	-0.301461
C	-0.740362	-1.426913	0.872854
C	1.392437	-2.218845	1.848544
H	-0.852363	-0.600786	1.566210
C	-2.499436	-0.802840	-0.750349
C	-3.263332	-0.033058	0.315705
H	-3.175993	-1.414965	-1.354308
H	-1.942898	-0.121916	-1.404995
H	-3.722124	-0.734208	1.024211
C	-4.338985	0.846844	-0.319892
H	-2.561496	0.604519	0.863974
H	-5.038144	0.223097	-0.891005
H	-3.863534	1.523814	-1.039629
C	-5.102509	1.657788	0.723007
H	-5.601264	0.999672	1.440993
H	-5.865066	2.287196	0.258213
H	-4.422413	2.306479	1.282257
C	2.552809	-1.505225	1.150837
H	1.673771	-3.236641	2.128123
H	1.073556	-1.656523	2.727984
H	2.280084	-0.455679	0.995898
O	2.884743	-2.144896	-0.055334
H	3.416273	-1.534494	1.824644
H	2.467215	-1.628069	-0.765287
C	0.794923	2.388746	-1.005025
H	1.091176	2.346894	-2.046803
Br	0.872297	-0.055089	-1.727406
H	-0.035947	3.063835	-0.838334
C	2.420353	3.930053	0.024726
H	2.693856	4.323179	-0.957835

H	3.292679	3.987946	0.678368
H	1.624174	4.544156	0.452367
H	2.770336	1.850427	-0.479730
O	1.679637	2.000713	1.229822
C	1.966933	2.471978	-0.070907
C	0.470662	1.357237	1.398267
O	-0.349974	1.461290	0.432939
O	0.322232	0.737168	2.449566

Fig. 3 E

C	0.488050	-3.023701	-0.863387
C	1.633813	-3.016799	-0.132685
N	-0.410657	-2.205297	-0.221426
H	0.240692	-3.523642	-1.784791
N	1.411646	-2.188973	0.944695
H	2.587355	-3.491715	-0.289764
C	0.185105	-1.680132	0.846071
C	2.441893	-1.704969	1.863658
H	-0.248014	-0.922900	1.487633
C	-1.666063	-1.683414	-0.779069
C	-2.838599	-1.810505	0.183457
H	-1.847579	-2.236618	-1.703879
H	-1.458175	-0.639983	-1.042851
H	-3.134281	-2.862453	0.279939
C	-4.013103	-0.956926	-0.288855
H	-2.535377	-1.456202	1.173314
H	-4.312005	-1.262260	-1.299761
H	-3.669692	0.081736	-0.355062
C	-5.205327	-1.051135	0.657760
H	-5.563122	-2.082213	0.742327

H	-6.038183	-0.434122	0.312154
H	-4.926289	-0.709045	1.658841
C	3.162535	-0.504706	1.241022
H	3.140316	-2.528264	2.028017
H	1.962634	-1.449605	2.811905
H	2.443763	0.317081	1.123463
O	3.720992	-0.867041	0.012733
H	3.953061	-0.190568	1.933515
H	3.103388	-0.529423	-0.671780
C	-0.632573	3.133828	-0.900212
H	-0.252724	2.761774	-1.851827
Br	1.124254	0.370898	-1.418397
H	-1.190477	4.066567	-1.020375
C	0.610533	4.599713	0.807751
H	0.920269	5.339548	0.064449
H	1.356604	4.578802	1.604466
H	-0.348653	4.910092	1.231872
H	1.428761	2.879550	-0.264209
O	0.088371	2.272147	1.144448
C	0.487449	3.239739	0.155229
C	-1.009873	1.626980	0.749510
O	-1.523143	2.149652	-0.366211
O	-1.515111	0.714551	1.355520

Fig. 3 F

C	0.953335	-2.226713	1.287245
C	-0.352637	-2.018964	0.972552
N	1.696909	-1.962779	0.155207
H	1.415973	-2.534095	2.210771
N	-0.379338	-1.628503	-0.355046

H	-1.257989	-2.068159	1.558196
C	0.869557	-1.590958	-0.818847
C	-1.558257	-1.191181	-1.102797
H	1.181135	-1.203462	-1.778940
C	3.158844	-1.823404	0.080294
C	3.659461	-0.785943	1.081507
H	3.369265	-1.466159	-0.930072
H	3.611303	-2.807608	0.232210
H	2.978448	0.069743	1.029047
C	5.056416	-0.302269	0.700941
H	3.651133	-1.196079	2.100343
H	4.977640	0.153576	-0.292904
H	5.748277	-1.151781	0.628921
C	5.587261	0.727251	1.692915
H	4.923418	1.596157	1.723659
H	6.582910	1.076032	1.408694
H	5.651647	0.311691	2.704013
C	-2.669518	-2.238152	-1.123517
H	-1.235845	-0.943389	-2.116017
H	-1.941169	-0.292544	-0.617885
H	-2.337004	-3.132797	-1.659378
O	-3.787005	-1.728750	-1.794838
H	-2.898275	-2.529445	-0.087113
Br	2.258563	1.088085	-1.453060
H	-4.017539	-0.867771	-1.400994
C	-0.493317	1.643231	0.388638
C	-1.046611	2.879797	0.944620
C	-1.362030	4.054875	0.066155
H	-1.548305	3.719787	-0.956662
H	-0.514741	4.744366	0.051413

H	-2.241505	4.591827	0.430942
O	-1.887790	1.725679	0.772743
H	0.112225	0.987815	1.010640
H	-0.288708	1.581780	-0.676690
H	-0.845974	3.095525	1.992727
C	-4.814943	0.662988	0.759215
C	-4.387710	-0.618291	1.455440
H	-5.899346	0.651078	0.612094
O	-4.202164	0.800789	-0.510756
H	-4.572903	1.529714	1.389662
H	-4.682299	-1.476657	0.839734
H	-4.909815	-0.696564	2.419830
O	-2.984473	-0.697577	1.628290
H	-3.369517	1.281396	-0.373311
H	-2.622794	0.197292	1.733361

Fig. 3 TS_{F-G}

C	-0.541867	2.390191	1.140745
C	0.765068	2.146106	0.849893
N	-1.281496	2.029357	0.035399
H	-1.005391	2.773317	2.034932
N	0.798384	1.649958	-0.437220
H	1.654393	2.195023	1.456742
C	-0.449860	1.579845	-0.901051
C	1.966587	1.087898	-1.129429
H	-0.763017	1.134466	-1.835900
C	-2.747228	1.942278	-0.044538
C	-3.292515	0.985918	1.011660
H	-2.972482	1.550506	-1.038530
H	-3.158465	2.950839	0.053235

H	-2.658074	0.093476	1.008316
C	-4.723166	0.565709	0.684577
H	-3.241898	1.445461	2.007186
H	-4.705085	0.062534	-0.289089
H	-5.365551	1.450584	0.589575
C	-5.285575	-0.382874	1.738242
H	-4.669581	-1.284851	1.803363
H	-6.304330	-0.690239	1.491668
H	-5.304464	0.086421	2.726987
C	3.253621	1.885293	-0.940522
H	1.718711	1.019730	-2.191374
H	2.123685	0.089931	-0.719248
H	3.176352	2.867000	-1.418459
O	4.299140	1.187919	-1.556725
H	3.428858	2.034736	0.133623
Br	-2.182871	-1.145125	-1.532800
H	4.314759	0.281728	-1.193045
C	0.060959	-1.738812	-0.736407
C	0.077976	-1.479654	0.694742
C	-0.731000	-2.414467	1.564513
H	-0.481366	-3.447568	1.308633
H	-1.798924	-2.255762	1.387192
H	-0.505632	-2.253736	2.621478
O	1.424952	-1.825314	0.515351
H	0.482765	-1.024682	-1.425294
H	-0.011204	-2.767752	-1.062716
H	-0.087195	-0.425133	0.972281
C	4.422129	-1.492433	0.940366
C	4.176653	-0.177360	1.662589
H	5.493481	-1.716985	0.939915

O	3.984589	-1.430108	-0.409222
H	3.898170	-2.304370	1.459457
H	4.757668	0.612206	1.163317
H	4.547904	-0.260771	2.694363
O	2.813314	0.195168	1.651871
H	3.052940	-1.715351	-0.402849
H	2.278588	-0.583733	1.362519

Fig. 3 G

C	-0.471095	1.898074	1.479689
C	0.795059	1.668296	1.034778
N	-1.189866	2.423275	0.426867
H	-0.923244	1.722351	2.442208
N	0.828486	2.065447	-0.283958
H	1.649755	1.227296	1.533459
C	-0.377766	2.507146	-0.628013
C	1.926622	1.818650	-1.237444
H	-0.660979	2.855768	-1.609270
C	-2.643023	2.612877	0.407443
C	-3.344164	1.281371	0.158728
H	-2.874346	3.346021	-0.370234
H	-2.929170	3.045630	1.369958
H	-3.037480	0.891676	-0.820239
C	-4.864755	1.392723	0.215752
H	-2.992368	0.545218	0.891698
H	-5.208003	2.116447	-0.534293
H	-5.165874	1.792055	1.192353
C	-5.535230	0.041240	-0.020454
H	-5.242599	-0.375057	-0.988501
H	-6.623506	0.132065	0.002750

H	-5.232574	-0.680004	0.743869
C	3.309509	1.999466	-0.608086
H	1.790234	2.496310	-2.083595
H	1.813312	0.777408	-1.545055
H	3.499060	3.060494	-0.410284
O	4.276439	1.529926	-1.500051
H	3.337806	1.461078	0.346789
Br	-2.469325	-2.086798	-0.341928
H	4.253100	0.549749	-1.425734
C	-0.723704	-1.280500	-0.765951
C	0.349888	-1.548221	0.292357
C	0.690200	-3.031632	0.406947
H	1.109458	-3.380137	-0.543695
H	-0.182144	-3.641598	0.657954
H	1.449245	-3.161296	1.183340
O	1.434651	-0.782207	-0.075459
H	-0.906662	-0.205559	-0.841897
H	-0.432983	-1.681907	-1.737581
H	-0.077395	-1.215218	1.262818
C	4.404231	-1.635240	0.213884
C	4.387904	-0.642299	1.369664
H	5.442197	-1.884433	-0.034117
O	3.787597	-1.118988	-0.950246
H	3.900686	-2.562335	0.526376
H	4.920516	0.265196	1.035326
H	4.959109	-1.061021	2.209949
O	3.086842	-0.328493	1.810687
H	2.795770	-1.136250	-0.767637
H	2.418841	-0.576685	1.085164

Fig. 3 H

C	0.313402	-2.413255	0.878528
C	-0.898756	-1.977341	0.432284
N	1.147883	-2.508058	-0.214382
H	0.653745	-2.660532	1.871522
N	-0.783905	-1.831646	-0.931211
H	-1.808774	-1.723002	0.965215
C	0.456491	-2.143955	-1.294876
C	-1.789758	-1.224036	-1.816741
H	0.850015	-2.082630	-2.298025
C	2.603762	-2.691552	-0.167864
C	3.303700	-1.339029	-0.064901
H	2.903554	-3.235374	-1.068098
H	2.819728	-3.327966	0.694193
H	3.055840	-0.737934	-0.948547
C	4.819204	-1.463464	0.059905
H	2.900348	-0.789258	0.795519
H	5.213662	-2.037163	-0.788439
H	5.067039	-2.034501	0.963348
C	5.484067	-0.089714	0.111947
H	5.270816	0.478704	-0.797506
H	6.567417	-0.179027	0.219297
H	5.099407	0.495151	0.952294
C	-3.214557	-1.697469	-1.515499
H	-1.512086	-1.456657	-2.847368
H	-1.728136	-0.148717	-1.638801
H	-3.334976	-2.745629	-1.810584
O	-4.106482	-0.917410	-2.252907
H	-3.393381	-1.616445	-0.435328
Br	2.456305	2.123712	-0.600858

H	-4.073723	-0.032988	-1.821210
C	0.763137	1.131943	-0.582259
C	-0.378205	1.862771	0.139570
C	-0.903058	3.018195	-0.711753
H	-1.320154	2.635206	-1.650124
H	-0.107127	3.733302	-0.941084
H	-1.707483	3.535525	-0.182927
O	-1.331448	0.895881	0.403734
H	0.982110	0.205654	-0.053856
H	0.515609	0.936765	-1.629936
H	0.055739	2.293557	1.060656
C	-4.365366	1.418805	0.428171
C	-4.561225	0.124927	1.206115
H	-5.341845	1.799177	0.105210
O	-3.542217	1.228921	-0.695334
H	-3.920184	2.173355	1.097195
H	-5.074102	-0.600089	0.557733
H	-5.206739	0.310125	2.076988
O	-3.332412	-0.442017	1.622760
H	-2.577430	1.119881	-0.306247
H	-2.609566	0.206788	1.491901
C	0.069099	0.032588	2.709774
O	-0.914589	-0.389678	3.162493
O	1.105963	0.403834	2.326977

Fig. 3 TS_{H-I}

C	0.280619	-2.515395	0.537002
C	-0.902933	-1.988280	0.116001
N	1.166206	-2.433089	-0.516499
H	0.572255	-2.924598	1.491161

N	-0.719508	-1.605193	-1.192321
H	-1.842502	-1.821689	0.629574
C	0.534440	-1.871507	-1.547659
C	-1.672033	-0.801125	-1.970704
H	0.980149	-1.638555	-2.502700
C	2.614160	-2.661855	-0.434573
C	3.324066	-1.401643	0.052031
H	2.960744	-2.962199	-1.427341
H	2.770568	-3.505025	0.243311
H	3.122346	-0.581853	-0.647864
C	4.833244	-1.582389	0.186911
H	2.891502	-1.095922	1.014030
H	5.255844	-1.857603	-0.787433
H	5.052043	-2.413654	0.868753
C	5.488397	-0.300006	0.695929
H	5.224654	0.547454	0.056669
H	6.576360	-0.391759	0.723177
H	5.140396	-0.064182	1.705537
C	-3.107622	-1.332532	-1.907827
H	-1.311286	-0.754564	-3.000835
H	-1.650389	0.194330	-1.521636
H	-3.208523	-2.232709	-2.523073
O	-3.963707	-0.350518	-2.410863
H	-3.346760	-1.594719	-0.868563
Br	2.487996	2.212823	-0.616479
H	-3.899612	0.386362	-1.761557
C	0.832459	1.172495	-0.424113
C	-0.241779	1.853020	0.433733
C	-0.850751	3.046111	-0.300721
H	-1.330068	2.722937	-1.231571

H	-0.083835	3.789854	-0.536520
H	-1.623135	3.509026	0.317742
O	-1.163115	0.864214	0.750578
H	1.129813	0.240909	0.054184
H	0.482659	1.000329	-1.445474
H	0.276339	2.233580	1.332112
C	-4.316395	1.234229	0.718115
C	-4.709627	-0.198220	1.044263
H	-5.211404	1.800944	0.430461
O	-3.370805	1.280074	-0.313752
H	-3.907173	1.707939	1.627066
H	-5.151045	-0.662502	0.154218
H	-5.461128	-0.215513	1.847591
O	-3.579616	-0.978893	1.393602
H	-2.431742	1.100999	0.129296
H	-2.974920	-0.439608	1.925292
C	-0.283759	-0.194864	2.576815
O	-1.275148	-0.685846	2.966484
O	0.834414	0.120084	2.437910

Fig. 3 I

C	0.961697	2.459810	1.237259
C	2.072792	1.814300	0.792700
N	0.263405	2.886421	0.128085
H	0.610642	2.652966	2.237671
N	2.037566	1.867249	-0.583495
H	2.853463	1.294434	1.331832
C	0.925196	2.489518	-0.953401
C	2.897814	1.115216	-1.506455
H	0.588645	2.612006	-1.970483

C	-1.087722	3.449662	0.140801
C	-2.124343	2.395923	0.518899
H	-1.280828	3.852565	-0.857314
H	-1.093433	4.287897	0.844169
H	-2.040342	1.551187	-0.174049
C	-3.539175	2.969641	0.528796
H	-1.878013	2.002211	1.513930
H	-3.808468	3.288657	-0.485529
H	-3.570474	3.869561	1.156894
C	-4.552948	1.947757	1.036765
H	-4.520931	1.034877	0.435921
H	-5.569937	2.345506	1.002497
H	-4.335111	1.670954	2.073192
C	4.341760	1.018103	-1.013987
H	2.863536	1.613364	-2.478013
H	2.457435	0.119184	-1.583111
H	4.798202	2.014118	-0.998474
O	5.071621	0.206961	-1.890348
H	4.344217	0.617733	0.006709
Br	-4.215237	-1.489980	-0.913665
H	4.844804	-0.709356	-1.643235
C	-2.331469	-1.970268	-0.709361
C	-1.830061	-1.588605	0.679736
C	-2.439330	-2.437312	1.779588
H	-2.188182	-3.489750	1.619826
H	-3.525923	-2.328419	1.781124
H	-2.044314	-2.133806	2.750875
O	-0.424886	-1.804767	0.716118
H	-1.796609	-1.412571	-1.472931
H	-2.266799	-3.045283	-0.877895

H	-2.041925	-0.526149	0.842322
C	4.295739	-2.576157	0.521312
C	4.711277	-1.510408	1.522831
H	5.140926	-3.249834	0.345671
O	3.907015	-2.030042	-0.725821
H	3.470243	-3.168626	0.938780
H	5.541930	-0.932416	1.092499
H	5.085306	-2.005064	2.430679
O	3.666162	-0.618363	1.857256
H	2.968673	-1.767798	-0.627539
H	2.827238	-0.931479	1.463637
C	0.361994	-0.877815	0.058623
O	1.595481	-1.102737	0.187610
O	-0.188739	0.042790	-0.562081

Fig. 3 TS_{I,J}

C	-0.715832	-2.194526	-1.150725
C	0.562812	-1.815902	-0.878130
N	-1.461025	-1.979884	-0.009310
H	-1.158791	-2.583767	-2.052575
N	0.572097	-1.377367	0.429551
H	1.463402	-1.767324	-1.477054
C	-0.657670	-1.482442	0.930076
C	1.758530	-0.904699	1.150334
H	-0.982049	-1.143013	1.902773
C	-2.917580	-2.121980	0.124132
C	-3.662675	-1.338959	-0.952772
H	-3.170129	-1.720090	1.107419
H	-3.163489	-3.187440	0.097368
H	-3.196181	-0.353075	-1.045485

C	-5.126895	-1.143933	-0.565385
H	-3.586215	-1.850041	-1.920627
H	-5.150017	-0.570903	0.369318
H	-5.596879	-2.115208	-0.365456
C	-5.903732	-0.395574	-1.643620
H	-5.459899	0.588881	-1.819261
H	-6.944983	-0.246284	-1.349736
H	-5.895965	-0.943927	-2.590700
C	2.769296	-2.033872	1.367487
H	1.432929	-0.493489	2.108658
H	2.227295	-0.126545	0.547307
H	2.307172	-2.836357	1.953343
O	3.868989	-1.560500	2.079535
H	3.035765	-2.444351	0.381229
Br	-2.686522	1.085616	1.370469
H	4.287323	-0.841849	1.563154
C	-0.579009	1.954553	0.750392
C	-0.583181	1.491448	-0.703661
C	-1.233828	2.527545	-1.601634
H	-0.697406	3.476356	-1.516646
H	-2.271086	2.670550	-1.286719
H	-1.210231	2.196156	-2.641121
O	0.755169	1.210362	-1.114901
H	-0.102500	1.364887	1.519874
H	-0.927190	2.937294	1.024605
H	-1.102452	0.536215	-0.786729
C	5.379520	0.240245	-0.727833
C	4.702778	-0.959112	-1.372512
H	6.440049	0.014820	-0.574430
O	4.805013	0.554414	0.528592

H	5.309233	1.109924	-1.392541
H	4.844482	-1.836503	-0.727328
H	5.191453	-1.170045	-2.334979
O	3.311047	-0.774579	-1.543428
H	4.111435	1.217649	0.350507
H	3.111861	0.184152	-1.569814
C	1.673208	2.014661	-0.483719
O	2.855851	1.846501	-0.822799
O	1.192603	2.775403	0.393373

Fig. 3 J

C	-0.549157	-2.102694	-1.444098
C	0.707569	-1.735828	-1.076428
N	-1.354018	-1.98526	-0.331408
H	-0.938997	-2.43484	-2.392436
N	0.639946	-1.392430	0.260789
H	1.642445	-1.676808	-1.616162
C	-0.614999	-1.551969	0.689548
C	1.776987	-0.955057	1.074249
H	-1.017845	-1.254525	1.651694
C	-2.817051	-2.143721	-0.30326
C	-3.494074	-1.124074	-1.212943
H	-3.122689	-1.959554	0.728328
H	-3.049323	-3.174368	-0.586762
H	-3.036436	-0.150184	-1.010561
C	-4.983864	-1.017821	-0.898188
H	-3.333218	-1.37952	-2.268848
H	-5.070480	-0.706018	0.148921
H	-5.464929	-1.999155	-0.999989
C	-5.674592	0.003993	-1.795332

H	-5.222476	0.991544	-1.659850
H	-6.737387	0.088023	-1.557084
H	-5.586186	-0.267136	-2.852496
C	2.797502	-2.075820	1.273839
H	1.392571	-0.592938	2.029763
H	2.269955	-0.136691	0.548685
H	2.341081	-2.905201	1.824028
O	3.881532	-1.610780	2.021674
H	3.092686	-2.450656	0.280953
Br	-2.836321	0.546218	1.738598
H	4.233346	-0.807760	1.594057
C	-0.161463	2.424977	0.782691
C	-0.692758	1.858475	-0.531041
C	-1.862506	2.595673	-1.126976
H	-1.634273	3.657810	-1.248088
H	-2.701347	2.466468	-0.436080
H	-2.130765	2.173943	-2.098310
O	0.485276	1.944882	-1.387552
H	-0.551363	1.888043	1.646092
H	-0.342485	3.499955	0.876976
H	-0.928654	0.796063	-0.417694
C	5.419309	0.447767	-0.546950
C	4.916639	-0.813705	-1.228663
H	6.470984	0.317341	-0.273139
O	4.688949	0.728527	0.634253
H	5.355303	1.298462	-1.238187
H	5.027329	-1.662603	-0.544094
H	5.526241	-1.013411	-2.121229
O	3.540903	-0.730965	-1.557769
H	3.960279	1.318785	0.384470

H	3.330648	0.181337	-1.811494
C	1.563777	2.015648	-0.620054
O	2.703989	1.885057	-1.016489
O	1.262824	2.216373	0.661329

3. Reference

- 1 M. Yang, K. Stappert and A. V. Mudring, *J. Mater. Chem. C*, 2014, **2**, 458–473.