Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Electronic Supporting Information (ESI)

## Development of the ReaxFF$_{CBN}$ Reactive Force Field for the Improved Design of Liquid CBN Hydrogen Storage Materials

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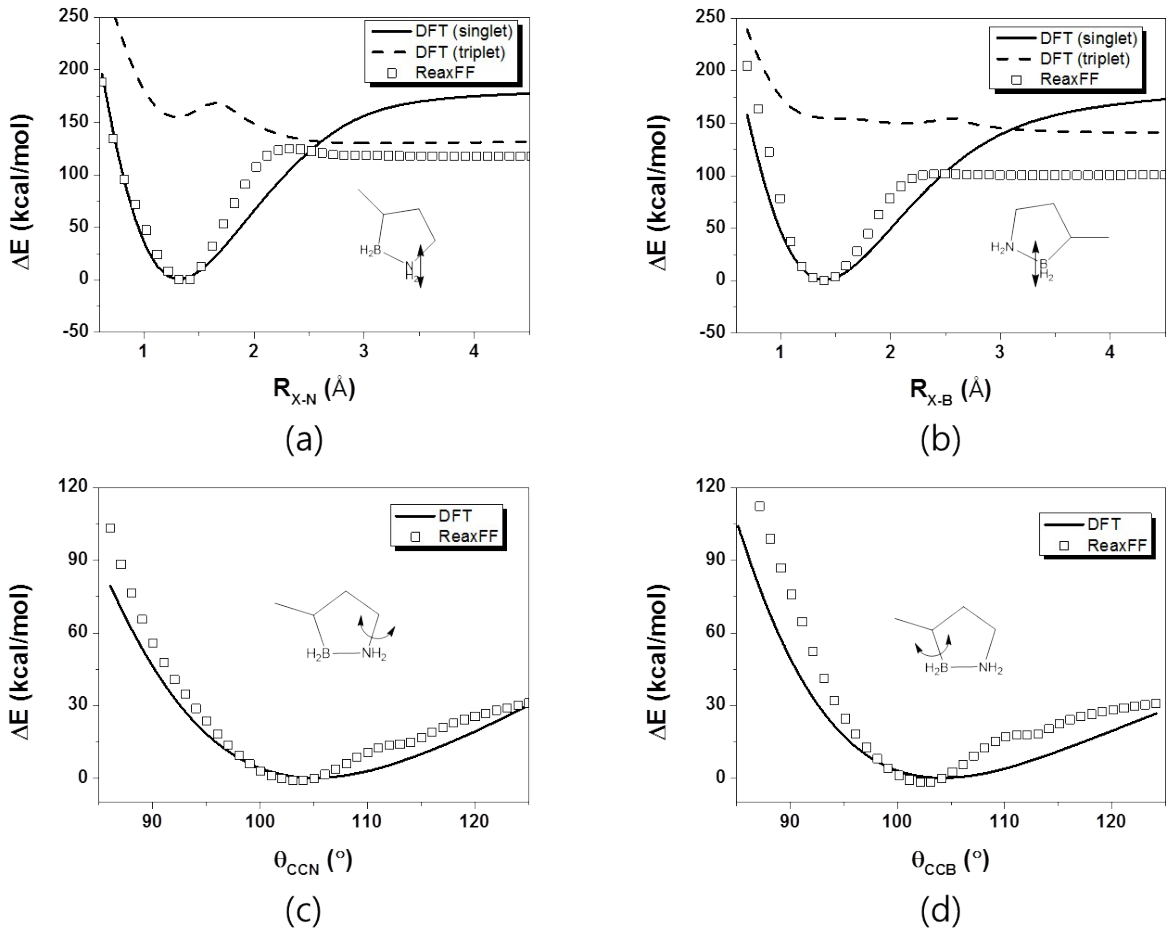


**Figure S1.** Comparison of the QM and developed $ReaxFF_{CBN}$ for CBN-B (3-methyl-1,2-BN-cyclopentane). Here, (a) and (b) show the bond dissociation curves of CBN-B as functions of movement of $NH_2$ and $BH_2$ moieties, respectively. And (c) and (d) show the valence angle bending curves of $NH_2$ and $BH_2$ in CBN-B, respectively.

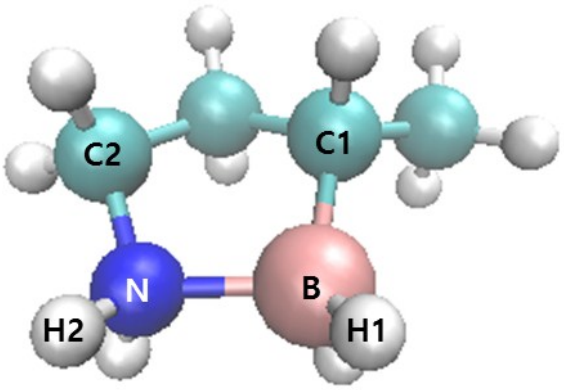


**Figure S2.** A molecular structure of CBN-B.

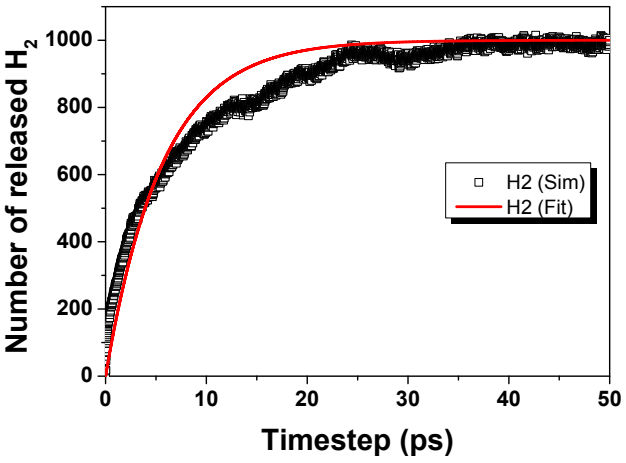


**Figure S3.** Dehydrogenation reaction rate from ReaxFF-MD simulation at 3000 K.

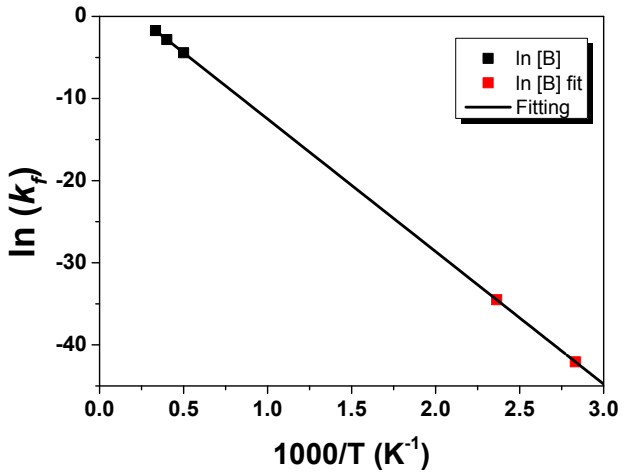


**Figure S4.** Arrhenius plot of dehydrogenation reaction rate constants. Here, a solid line shows the extrapolation to 353 and 423 K with a fitting equation $y = -16142\,x + 3.6451$.

**Table S1** Comparison of QM and ReaxFF for optimized structures of the CBN-B molecule.

| Method | $R_{B\text{-}N}$ (Å) | $R_{C1\text{-}B}$ (Å) | $R_{C2\text{-}N}$ (Å) | $R_{B\text{-}H1}$ (Å) | $R_{N\text{-}H2}$ (Å) | $\theta_{C1BN}$ (degree) | $\theta_{C2NB}$ (degree) |
|---|---|---|---|---|---|---|---|
| QM | 1.69 | 1.63 | 1.51 | 1.21 | 1.02 | 100.2 | 107.4 |
| ReaxFF | 1.64 | 1.60 | 1.63 | 1.21 | 0.99 | 104.6 | 105.8 |

**Table S2** Atomic charges of the CBN-B molecule obtained from QM and ReaxFF.

| Method | B | N | C1 | C2 | H1 | H2 |
|---|---|---|---|---|---|---|
| QM | 0.123 | -0.387 | -0.286 | -0.102 | -0.105 | 0.249 |
| ReaxFF | 0.155 | -0.409 | -0.124 | -0.175 | -0.035 | 0.181 |

**Table S3** The intramolecular B-N distances of the CBN type materials shown in Table 1 using ReaxFF-MD simulations, where the distances were obtained from radial distribution functions in the temperature ranges of 300 ~ 500 K. And the values in parentheses are from the DFT calculation.

| Material | CBN-A | CBN-B | CBN-C | CBN-D | CBN-E | CBN-F | CBN-G |
|---|---|---|---|---|---|---|---|
| $R_{B\text{-}N}$ (Å) | 1.615 (1.701) | 1.625 (1.694) | 1.615 (1.704) | 1.595 (1.690) | 1.545 (1.629) | 1.605 (1.662) | 1.625 (1.656) |

**Table S4.** Calculated densities for the CBN type materials shown in Table 1 using ReaxFF NPT MD simulations. Values in parentheses are the experimental values.

| Material | CBN-A | CBN-B | CBN-C | CBN-D | CBN-E | CBN-F | CBN-G |
|---|---|---|---|---|---|---|---|
| Density ($g/cm^3$) | 0.870 (0.920) | 0.896 (0.890) | 0.910 (0.890) | 0.886 (0.890) | 0.784 (-) | 0.893 (1.000) | 0.684 (-) |

**Table S5** The developed $ReaxFF_{CBN}$ for the CBN system

```
Reactive MD-force field: C/H/B/N force field Dec 2015
 39       ! Number of general parameters
   50.0000 !Overcoordination parameter
    9.5469 !Overcoordination parameter
   26.5405 !Valency angle conjugation parameter
    1.7224 !Triple bond stabilisation parameter
    6.8702 !Triple bond stabilisation parameter
   60.4850 !C2-correction
    1.0588 !Undercoordination parameter
    4.6000 !Triple bond stabilisation parameter
   12.1176 !Undercoordination parameter
   13.3056 !Undercoordination parameter
  -70.5044 !Triple bond stabilization energy
    0.0000 !Lower Taper-radius
   10.0000 !Upper Taper-radius
    2.8793 !Not used
   33.8667 !Valency undercoordination
    6.0891 !Valency angle/lone pair parameter
    1.0563 !Valency angle
    2.0384 !Valency angle parameter
    6.1431 !Not used
    6.9290 !Double bond/angle parameter
    0.3989 !Double bond/angle parameter: overcoord
    3.9954 !Double bond/angle parameter: overcoord
   -2.4837 !Not used
    5.7796 !Torsion/BO parameter
   10.0000 !Torsion overcoordination
    1.9487 !Torsion overcoordination
   -1.2327 !Conjugation 0 (not used)
    2.1645 !Conjugation
    1.5591 !vdWaals shielding
    0.0010 !Cutoff for bond order (*100)
    2.1365 !Valency angle conjugation parameter
    0.6991 !Overcoordination parameter
   50.0000 !Overcoordination parameter
    1.8512 !Valency/lone pair parameter
    0.5000 !Not used
   20.0000 !Not used
    5.0000 !Molecular energy (not used)
    0.0000 !Molecular energy (not used)
    2.6962 !Valency angle conjugation parameter
  4    ! Nr of atoms; ro,s;val;a.m;Rvdw;Evdw;gammaEEM;ro,p;val(e)
            alfa;gammavdW;val(angle);pvoun5;n.u.;chiEEM;etaEEM;n.u.
            ro,pp;plp2;HeatInc;pboc4;pboc3;pboc5;n.u.;n.u.
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```
           povun2;pval3(ang);n.u.;val(boc);pval5(ang);n.u.;n.u.;n.u.
 C    1.3825   4.0000  12.0000   1.9133   0.1853   0.9000   1.1359   4.0000
      9.7602   2.1346   4.0000  33.2433  79.5548   8.0066   6.8000   0.0000
      1.2104   0.0000 199.0303   8.6991  34.7289  13.3894   0.8563   0.0000
     -2.8983   2.5000   1.0564   4.0000   2.9663   1.4000   0.1000  10.0000
 H    0.6867   1.0000   1.0080   1.3525   0.0616   0.7492  -0.1000   1.0000
      9.3858   5.0013   1.0000   0.0000 121.1250   6.5362   7.0327   1.0000
     -0.1000   0.0000  59.5599   6.1752   4.8714   0.0009   1.0698   0.0000
    -15.7683   2.1504   1.0338   1.0000   2.8793   0.6000   0.1000  10.0000
 B    1.3484   3.0000  10.8110   1.8276   0.0500   0.9088   1.0000   3.0000
     12.4662   2.6721   3.0000   7.2404  80.0000   6.8775   6.7020   0.0000
     -1.3000   0.0000  -2.3700   4.0943   6.8208   1.0943   0.0000   0.0000
     -3.6082   1.8000   1.0564   3.0000   2.8413   1.4000   0.1000  12.0000
 N    1.5520   3.0000  14.0000   1.7695   0.1375   1.0000   1.2641   5.0000
     10.0677   7.6886   4.0000  27.4217 100.0000   8.1308   7.0000   2.0000
      1.0972  29.9200  -2.3700   2.5862   2.7645   2.6432   0.9745   0.0000
     -6.4340   2.6491   1.0183   4.0000   2.8793   1.4000   0.1000  10.0000
 10      ! Nr of bonds; Edis1;Edis2;Edis3;pbe1;pbo5;13corr;pbo6;povu
                         pbe2;pbo3;pbo4;n.u.;pbo1;pbo2;ovcorr;n.u.
  1  1 156.5953 100.0397  80.0000  -0.8157  -0.4591   1.0000  37.7369
0.4235
         0.4527  -0.1000   9.2605   1.0000  -0.0750   6.8316   1.0000
0.0000
  1  2 164.4970   0.0000   0.0000  -0.4426   0.0000   1.0000   6.0000
0.6668
         6.2320   1.0000   0.0000   1.0000  -0.0476   5.5015   0.0000
0.0000
  2  2 165.7021   0.0000   0.0000  -0.8238   0.0000   1.0000   6.0000
0.3597
         6.5603   1.0000   0.0000   1.0000  -0.0113   5.6991   0.0000
0.0000
  1  3 182.8256 134.3150   0.0000  -0.7467  -0.3388   1.0000  30.7152
0.2751
         0.5734  -0.2121  11.6795   1.0000  -0.1374   5.9223   1.0000
0.0000
  2  3 177.4103   0.0000   0.0000  -0.4601  -0.3000   1.0000  25.0000
0.4971
         9.2806   0.0000   0.0000   1.0000  -0.0722   5.1245   1.0000
0.0000
  3  3 109.1015   0.0000   0.0000   1.0000  -0.2500   1.0000  25.0000
0.1000
         0.8313  -0.2000  15.0000   1.0000  -0.0691   5.0065   1.0000
0.0000
  1  4 187.3038 101.8119 118.7455  -0.9626  -0.2187   1.0000   8.3529
0.4161
         0.4543  -0.4591  21.7699   1.0000  -0.1244   6.2791   1.0000
0.0000
```

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  2  4 231.8918   0.0000   0.0000  -0.7398   0.0000   1.0000   6.0000
0.4224
         9.1469   1.0000   0.0000   1.0000  -0.0491   5.7202   0.0000
0.0000
  3  4 143.9715  94.2037   0.0000   0.2868  -0.2500   1.0000  25.0000
0.1083
         0.5585  -0.2935  10.2737   1.0000  -0.1650   6.5248   1.0000
0.0000
  4  4 104.5870  85.8215 151.8152  -0.9395  -0.2820   1.0000  12.0357
1.0000
         0.3279  -0.4426   8.2367   1.0000  -0.1884   5.6414   1.0000
0.0000
  6    ! Nr of off-diagonal terms;a1;a2;Dij;RvdW;alp;ros;rop;ropp
  1  2   0.0415   1.6927  10.3459   1.0426  -1.0000  -1.0000
  1  3   0.1329   1.8035  11.0558   1.3418   0.9000  -1.0000
  2  3   0.0526   1.5010  11.2019   1.1648  -1.0000  -1.0000
  1  4   0.1115   1.7854  10.2359   1.3643   1.2674   0.9778
  2  4   0.0367   1.6470  10.5106   0.9496  -1.0000  -1.0000
  3  4   0.0564   1.7000  10.7561   1.4037   1.2073  -1.0000
 36    ! Nr of angles;a1;a2;a3;Tho;pva1;pva2;pcoa1;pva7;ppen1;pva4
  1  1  1  67.2326  22.0695   1.6286   0.0000   1.7959  15.4141   1.8089
  1  1  2  69.6421   9.2578   3.6521   0.0000   0.0058   0.0000   1.0400
  2  1  2  75.4958  14.5436   2.7438   0.0000   0.0127   0.0000   1.0400
  1  2  2   0.0000   0.0000   6.0000   0.0000   0.0000   0.0000   1.0400
  1  2  1   0.0000   3.4110   7.7350   0.0000   0.0000   0.0000   1.0400
  2  2  2   0.0000  27.9213   5.8635   0.0000   0.0000   0.0000   1.0400
  2  3  2  62.5987  14.6089   2.3811   0.0000   3.0000   0.0000   3.0000
  2  3  3  55.0000  32.2012   4.7029   0.0000   3.0000   0.0000   1.0400
  2  2  3   0.0000   5.0019   1.0000   0.0000   0.0000   0.0000   1.5000
  3  2  3   0.0000   5.0000   1.0000   0.0000   1.0000   0.0000   1.0400
  1  1  3  55.2354   4.8896   1.1332   0.0000   1.5533   0.0000   0.9657
  1  3  1  30.4469   2.9502   1.9735   0.0000   2.3791   0.0000   1.1179
  3  1  3  51.2292  14.2777   0.8300   0.0000   1.7820   0.0000   0.8913
  2  1  3  68.7093   3.5601   3.5152   0.0000  -0.1213   0.0000   1.3713
  1  3  2  71.1954  22.6026   3.1828   0.0000   0.0130   0.0000   1.1667
  1  3  3  27.0691  11.9197   0.9805   0.0000   1.0377   0.0000   1.1300
  3  3  3  70.0000  35.0000   3.0000   0.0000   1.5000   0.0000   1.0100
  2  1  4  43.8591   5.2941   0.5853   0.0000   0.7547   0.0000   0.6289
  1  4  2  92.3431  14.6346   1.5505   0.0000   0.9201   0.0000   0.6889
  2  4  4  72.7618  24.2550   2.3034   0.0000   0.1000   0.0000   1.0400
  2  4  2  85.5836  27.9831   4.0538   0.0000   0.7544   0.0000   1.2487
  4  2  4   0.0000   5.0000   2.0000   0.0000   0.0000   0.0000   1.0400
  2  2  4   0.0000  10.0019   1.0000   0.0000   0.0000   0.0000   1.0400
  2  4  3  55.0000   2.5000   0.1000   0.0000   0.1000   0.0000   2.2627
  2  3  4  55.0000   2.5000   0.1000   0.0000   0.1000   0.0000   2.2627
  4  3  4  72.3075  38.0571   4.2562   0.0000   1.1083   0.0000   1.3861
  3  4  3  50.0000  30.8700   0.8444   0.0000   3.0000   0.0000   1.0576
```

```
 3  2  4   0.0000   9.6980   1.0000   0.0000   1.0000   0.0000   1.0400
 4  4  4  70.0000  35.0000   3.0000   0.0000   1.5000   0.0000   1.0100
 1  4  1  62.2681   7.7197   0.0207   0.0000   1.5838   0.0000   1.0430
 4  1  4 110.1539  12.1105   2.4783   0.0000   1.5624   0.0000   0.9905
 1  1  4  50.2255  12.7546   0.9761   0.0000   1.5333   0.0000   1.0500
 1  4  4  60.1844  10.6877   0.3922   0.0000   1.1860   0.0000   1.0500
 1  3  4  45.0029  18.6356   0.9204   0.0000   1.1613   0.0000   1.1158
 1  4  3  44.0283  -0.3928  -0.3598   0.0000   1.0159   0.0000   0.9794
 3  1  4  54.1678  16.3254   0.5841   0.0000   1.0956   0.0000   1.1026
35    ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;ptor1;pcot1;n.u.
 1  1  1  1  -0.2500  11.5822   0.1899  -4.7057  -2.2047   0.0000   3.6702
 1  1  1  2   0.0000  49.1001   0.2713  -8.5284  -1.5309   0.0000   0.0000
 2  1  1  2   0.0000  34.0265   0.3804  -6.3917  -0.9965   0.0000   0.0000
 0  1  2  0   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
 0  2  2  0   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000   0.0000
 0  2  4  0   0.0000   0.1000   0.0200  -2.5415   0.0000   0.0000   0.0000
 0  4  4  0  -2.0000  24.4048  -0.1617  -3.3327  -2.0000   0.0000   0.0000
 0  3  4  0  -2.0000  19.3351   0.3228  -5.4735   0.0000   0.0000   0.0000
 0  3  3  0   0.2500  50.0000   0.3000  -7.5000   0.0000   0.0000   0.0000
 2  3  4  2  -0.1007  23.8639   0.3443  -3.0822  -5.8276   0.0000   0.0000
 1  1  1  3  -0.1100  34.6047  -0.0128  -5.9379  -1.9886   0.0000   0.0000
 3  1  1  3  -0.2500  34.7453   0.0288  -6.3507  -1.6000   0.0000   0.0000
 1  1  3  1  -0.2500  34.7453   0.0288  -6.3507  -1.6000   0.0000   0.0000
 1  1  3  2   0.0000  49.1001   0.2713  -8.5284  -1.5309   0.0000   0.0000
 2  1  3  1   0.0000  49.1001   0.2713  -8.5284  -1.5309   0.0000   0.0000
 2  1  3  2  -0.1491  23.9139   0.3015  -3.2203  -5.7735   0.0000   0.0000
 1  1  3  3  -0.5888  34.6343  -0.3716  -6.4877  -1.5764   0.0000   0.0000
 2  1  1  3   0.0000  50.0000   0.3000  -4.0000  -2.0000   0.0000   0.0000
 2  1  3  3  -0.2500  34.7453   0.0288  -6.3507  -1.6000   0.0000   0.0000
 3  1  3  1  -0.3461  34.1343  -1.0446 -10.9658  -1.8018   0.0000   0.0000
 1  3  3  3  -0.7796  35.3481   0.5161  -5.2825  -1.5504   0.0000   0.0000
 2  1  4  2   0.0134  34.0609  -0.0630  -6.0516  -1.2887   0.0000   0.0000
 1  1  1  4  -0.0888  34.8553   0.0670  -6.3632  -1.5765   0.0000   0.0000
 1  1  4  4  -0.6800  34.7750  -0.0114  -6.4101  -1.0960   0.0000   0.0000
 1  4  4  4  -0.2928  34.9471  -0.0729  -6.4675  -1.4813   0.0000   0.0000
 4  1  4  1  -0.2001  36.9660   0.0938  -6.7107  -1.3023   0.0000   0.0000
 1  4  4  1  -0.2000  34.7042  -0.3758  -6.6607  -1.7959   0.0000   0.0000
 4  1  1  4  -0.2039  34.9911  -0.2512  -6.0767  -1.2376   0.0000   0.0000
 1  1  4  1  -0.2259  34.8211   0.3488  -6.3307  -1.7320   0.0000   0.0000
 1  1  3  4  -1.1345  36.8371  -0.5533  -6.6298  -1.6621   0.0000   0.0000
 1  1  4  3  -0.7527  33.5523  -0.5207  -7.1302  -2.4036   0.0000   0.0000
 4  1  3  1  -0.4700  34.5453  -0.0112  -6.5507  -1.7000   0.0000   0.0000
 3  1  4  1  -0.1150  34.8425   0.1065  -6.4788  -1.7339   0.0000   0.0000
 1  3  4  1  -0.9249  33.8546   0.6616  -7.2472  -0.9719   0.0000   0.0000
 3  1  1  4  -0.1305  34.7103  -0.4508  -6.8580  -1.7917   0.0000   0.0000
 1    ! Nr of hydrogen bonds;at1;at2;at3;r(hb);p(hb1);p(hb2);p(hb3)
 4  2  4   2.0000  -2.5002   3.0000  15.0000
```