Supplementary material

Novel design of porphyrin based D-s-A systems as molecular rectifiers

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Content

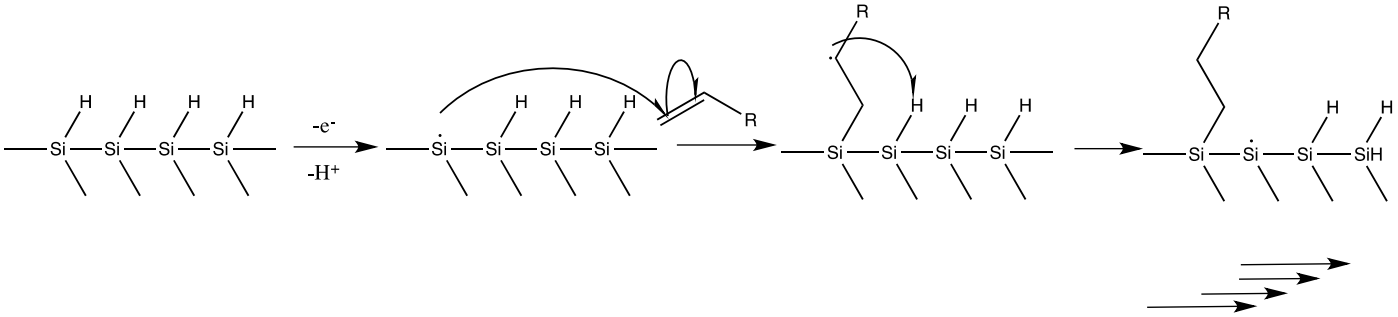

Figure. SL1. Monolayer deposition mechanism

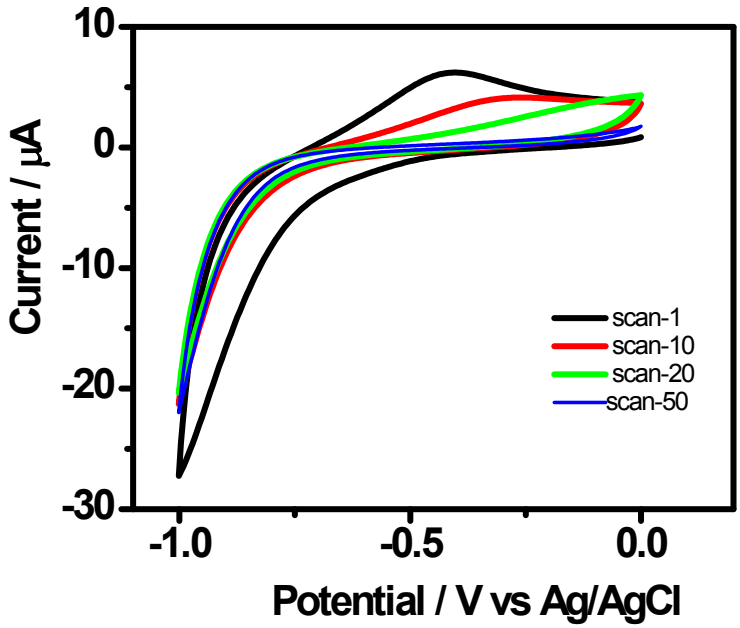

Figure SL-2 Cyclic voltammograms (CVs) of C-11 alkylmonolayers indicating electrografting of the molecules on silicon (n^{++}) wafers.

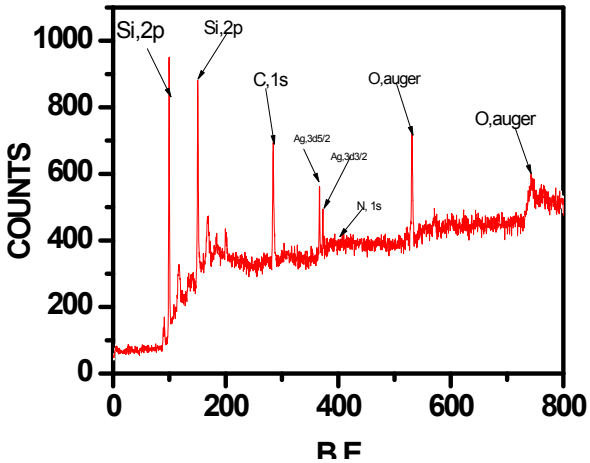

Figure SL3. XPS of monolayers of **6b**

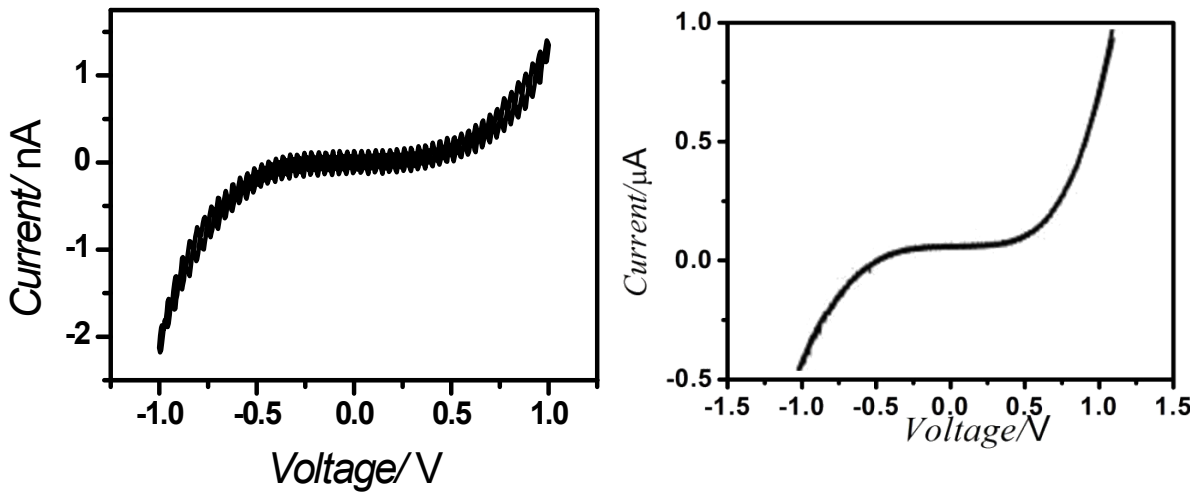

Figure SL-4. Experimental *I-V* characteristics of devices (a) Hg/ undeposited Si(n^{++}). (b) Hg/ C-11alkyl monolayers/Si(n^{++})

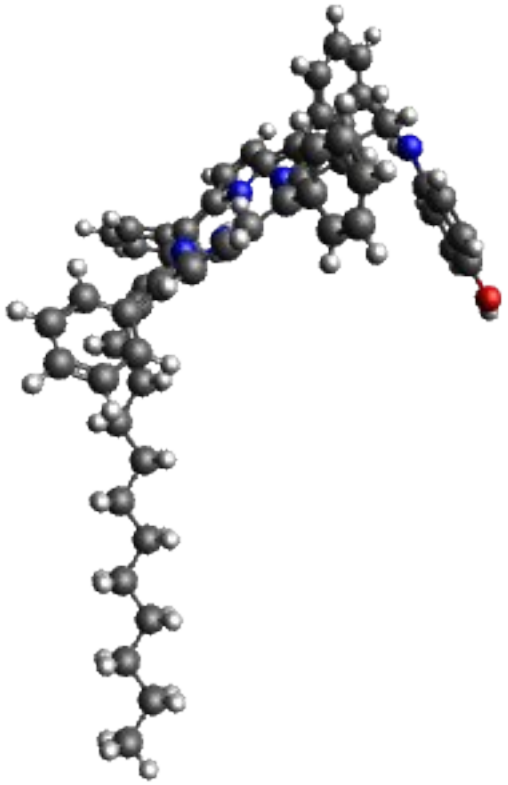

Figure SL-5. The optimized geometry of the **5b**-congener that has alkenyl group at the porphyrin ring.

Input file for p-aminophenol

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 $CONTRL SCFTYP=RHF MPLEVL=0 MAXIT=200 ICHARG=0 MULT=1 COORD=CART
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 $STATPT NSTEP=400 OPTTOL=0.0001 $END
 $SCF DIRSCF=.T. SHIFT=.T. DAMP=.T. DIIS=.T. CONV=1.0d-04 $END
# $DFT DFTTYP=B3LYP METHOD=GRID $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=0 DIFFSP=.F. DIFFS=.F. $END
 $DATA
DMS:/B3LYP/6-31++G(d,p)/acn
C1
C     6.0    0.68659   1.19949  -0.00622
C     6.0   -0.70313   1.21419  -0.00025
C     6.0   -1.41775   0.01743   0.00241
C     6.0   -0.72317  -1.19015  -0.00025
C     6.0    0.67066  -1.20182  -0.00567
C     6.0    1.39935  -0.00785  -0.00668
H     1.0    1.22766   2.14042  -0.01545
H     1.0   -1.24623   2.15171   0.00174
H     1.0   -1.26565  -2.13139   0.00246
H     1.0    1.19419  -2.15250  -0.01428
O     8.0   -2.79223   0.09349   0.00961
H     1.0   -3.16377  -0.79407   0.00208
N     7.0    2.80400  -0.01587  -0.07606
H     1.0    3.24865   0.81309   0.29217
H     1.0    3.23975  -0.85185   0.28685
 $END
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Input file for Tetraphenylporphyrin

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 $STATPT NSTEP=400 OPTTOL=0.0001 $END
 $SCF DIRSCF=.T. SHIFT=.T. DAMP=.T. DIIS=.T. CONV=1.0d-04 $END
# $DFT DFTTYP=B3LYP METHOD=GRID $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=0 DIFFSP=.F. DIFFS=.F. $END
 $DATA
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C     6.0    1.02475   4.17834   0.00310
C     6.0   -0.33925   4.28546  -0.00075
C     6.0   -0.89108   2.96275   0.00492
N     7.0    0.17488   2.09410   0.01669
C     6.0    2.65093   2.23228   0.00537
C     6.0   -2.24943   2.62140  -0.01130
C     6.0   -2.76342   1.31087  -0.01458
C     6.0   -4.19233   1.01588  -0.04271
C     6.0   -4.30382  -0.33217  -0.03901
C     6.0   -2.94265  -0.85747  -0.00601
N     7.0   -2.03185   0.15903   0.00460
C     6.0   -2.64821  -2.23420   0.00120
C     6.0   -1.36061  -2.78745   0.00192
C     6.0   -1.02196  -4.17990   0.02860
C     6.0    0.34220  -4.28694   0.02489
C     6.0    0.89367  -2.96430  -0.00144
N     7.0   -0.17231  -2.09601  -0.01626
C     6.0    2.25222  -2.62303  -0.00513
C     6.0    2.76640  -1.31270  -0.01155
C     6.0    4.19555  -1.01791  -0.00760
C     6.0    4.30741   0.32998   0.00308
C     6.0    2.94599   0.85564  -0.00707
N     7.0    2.03482  -0.16056  -0.01290
C     6.0    3.79699   3.20237   0.01279
C     6.0    4.49924   3.48464  -1.16470
C     6.0    5.55713   4.39272  -1.16135
C     6.0    5.92735   5.03145   0.02099
C     6.0    5.23574   4.75629   1.19942
C     6.0    4.17678   3.84918   1.19417
H     1.0    1.74354   4.98123  -0.00417
H     1.0   -0.92429   5.19067  -0.01141
H     1.0   -4.98563   1.74632  -0.06758
H     1.0   -5.20633  -0.92244  -0.06239
H     1.0   -1.74048  -4.98272   0.05344
H     1.0    0.92736  -5.19184   0.04521
H     1.0    4.98918  -1.74846  -0.00543
H     1.0    5.21041   0.91980   0.01551
H     1.0    4.21117   2.99084  -2.08616
H     1.0    6.08919   4.60296  -2.08255
H     1.0    5.52052   5.24597   2.12407
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C     6.0   -3.22553   3.76302  -0.03116
C     6.0   -3.70809   4.31097   1.16253
C     6.0   -3.66945   4.29802  -1.24581
C     6.0   -4.61749   5.36773   1.14278
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C     6.0   -4.57919   5.35430  -1.26692
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C     6.0   -5.05579   5.89172  -0.07224
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H     1.0   -4.91474   5.75658  -2.21645
H     1.0   -5.76334   6.71318  -0.08801
C     6.0    3.22821  -3.76491   0.00698
C     6.0    3.71848  -4.27045   1.21645
C     6.0    3.66176  -4.34478  -1.19042
C     6.0    4.62483  -5.32976   1.22845
H     1.0    3.38796  -3.82802   2.14972
C     6.0    4.56882  -5.40370  -1.17980
H     1.0    3.28724  -3.96019  -2.13268
C     6.0    5.05256  -5.89900   0.02999
H     1.0    4.99612  -5.70954   2.17395
H     1.0    4.89659  -5.84073  -2.11662
H     1.0    5.75786  -6.72248   0.03888
C     6.0   -3.79438  -3.20367   0.01381
C     6.0   -4.49405  -3.46316   1.19785
C     6.0   -4.18442  -3.86454  -1.15686
C     6.0   -5.55893  -4.36284   1.21193
H     1.0   -4.19923  -2.95647   2.11007
C     6.0   -5.25070  -4.76266  -1.14448
H     1.0   -3.65243  -3.66661  -2.08086
C     6.0   -5.94069  -5.01451   0.04031
H     1.0   -6.08912  -4.55402   2.13842
H     1.0   -5.54343  -5.26267  -2.06120
H     1.0   -6.76994  -5.71300   0.05031
H     1.0   -0.09621  -1.08595  -0.02220
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Input file for **5b**

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 $STATPT NSTEP=400 OPTTOL=0.0001 $END
 $SCF DIRSCF=.T. SHIFT=.T. DAMP=.T. DIIS=.T. CONV=1.0d-04 $END
# $DFT DFTTYP=B3LYP METHOD=GRID $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=0 DIFFSP=.F. DIFFS=.F. $END
 $DATA
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N   7.0   -5.063229   -2.055086    7.139670
C   6.0   -7.380109   -2.389462    7.872034
C   6.0   -3.736519   -2.499647    5.060131
C   6.0   -3.836278   -1.174564    4.666150
C   6.0   -3.292818   -0.659268    3.499900
C   6.0   -3.559769    0.695837    3.383949
C   6.0   -4.294562    1.151793    4.467093
N   7.0   -4.461744   -0.251237    5.336894
C   6.0   -4.410467    2.512766    4.702332
C   6.0   -5.373848    2.984789    5.579891
C   6.0   -5.571425    4.322680    5.883253
C   6.0   -6.852684    4.232088    7.193619
C   6.0   -6.909360    2.862494    7.398601
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C   6.0   -2.496017   -2.998952    3.066434
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C	6.0	-0.849546	2.503292	-2.276581
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C	6.0	-2.716223	1.961823	-0.867598
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C	6.0	1.061998	2.910433	-3.494673
C	6.0	1.619957	3.528388	-4.790220
C	6.0	3.149789	3.355113	-4.825076
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H	1.0	-3.446838	-5.075565	5.610166
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H	1.0	-9.966618	-1.813464	7.874320

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H   1.0   -4.015097    2.018032    1.702125
H   1.0   -2.245602   -0.235832    1.424071
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H   1.0   -2.909832    2.999140   -2.770591
H   1.0   -3.820784    1.973738   -0.670942
H   1.0    1.316062    1.818099   -3.461080
H   1.0    1.517515    3.425076   -2.607816
H   1.0    1.365893    4.620722   -4.823813
H   1.0    1.164439    3.013744   -5.677077
H   1.0    3.403853    2.262779   -4.791482
H   1.0    3.605307    3.869756   -3.938218
H   1.0    3.453684    5.065402   -6.154216
H   1.0    3.252230    3.458424   -7.007480
H   1.0    5.491644    2.707459   -6.121884
H   1.0    5.693098    4.314437   -5.268621
H   1.0    5.541475    5.510082   -7.484618
H   1.0    5.340022    3.903104   -8.337882
H   1.0    7.579435    3.152139   -7.452287
H   1.0    7.780889    4.759117   -6.599023
H   1.0    7.629266    5.954762   -8.815020
H   1.0    7.427813    4.347784   -9.668284
H   1.0    9.667227    3.596819   -8.782689
H   1.0    9.868680    5.203797   -7.929425
H   1.0    9.825649    6.399976  -10.320029
H   1.0   11.039023    5.001130  -11.918723
H   1.0   10.777987    3.458043  -10.766636
$END
```

Input file for **5b**-congener that has alkenyl group at the porphyn ring

```
$SYSTEM TIMLIM=600000.0 MEMORY=51200000 $END
 $CONTRL SCFTYP=RHF MPLEVL=0 MAXIT=200 ICHARG=0 MULT=1 COORD=CART
 RUNTYP=OPTIMIZE DFTTYP=B3LYP QMTTOL=1.0E-06 MPLEVL=0 $END
 $STATPT NSTEP=400 OPTTOL=0.0001 $END
 $SCF DIRSCF=.T. SHIFT=.T. DAMP=.T. DIIS=.T. CONV=1.0d-04 $END
# $DFT DFTTYP=B3LYP METHOD=GRID $END
 $BASIS GBASIS=N31 NGAUSS=6 NDFUNC=1 NPFUNC=0 DIFFSP=.F. DIFFS=.F. $END
 $DATA
DMS:/B3LYP/6-31++G(d,p)/acn

C1
C    6.0    4.18044    0.75782    0.13186
C    6.0    4.37062   -0.52929   -0.10911
C    6.0    2.88782   -0.96559   -0.10602
N    7.0    2.06648    0.07975   -0.01408
C    6.0    2.85024    1.20565    0.10307
C    6.0   -0.60399    4.09150   -0.16199
C    6.0    0.71566    4.11189   -0.28132
C    6.0    1.14754    2.85793    0.02466
N    7.0    0.04313    2.01604    0.08591
C    6.0   -1.05852    2.82602    0.11320
C    6.0    2.51017    2.50571    0.18505
C    6.0   -4.25164   -0.67533    0.27685
C    6.0   -4.35197    0.63540    0.11165
C    6.0   -2.93864    1.21721    0.14846
N    7.0   -2.10903    0.07321    0.07278
C    6.0   -2.86183   -0.99712    0.16886
C    6.0   -2.42589    2.50764    0.27094
C    6.0    0.53445   -4.05015   -0.20454
C    6.0   -0.74720   -4.02924   -0.25763
C    6.0   -1.20993   -2.71851   -0.00896
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C    6.0   -3.22197    3.84866    0.22025
C    6.0    3.51512    3.68556    0.25171
C    6.0    2.98435   -3.78199   -0.11871
C    6.0   -3.41852   -3.69499    0.09399
C    6.0   -4.30827    3.57269   -0.25424
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C    6.0   -4.84033    5.61966   -1.36163
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C    6.0    3.18384    4.98946    0.67929
C    6.0    3.87806    6.11439    0.19949
C    6.0    5.16224    5.94221   -0.26470
C    6.0    5.64224    4.65491   -0.37142
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C	6.0	4.22722	-3.63384	-0.36130
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C	6.0	2.91030	-5.11570	0.33967
C	6.0	-3.12994	-4.98852	0.46901
C	6.0	-3.85562	-6.09225	0.05300
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C	6.0	-5.61839	-4.60006	-0.44697
C	6.0	-4.70859	-3.56879	-0.47292
C	6.0	-5.85665	0.93472	-0.04060
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C	6.0	-7.01624	3.19195	0.40938
C	6.0	-8.31452	3.05909	0.05635
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C	6.0	5.89604	-0.84417	-0.10463
C	6.0	6.24387	-2.27457	0.10949
C	6.0	7.37132	-3.31002	0.12824
C	6.0	6.98138	-4.86874	0.19783
C	6.0	7.89446	-6.06435	0.07695
C	6.0	7.13327	-7.43424	-0.03316
C	6.0	8.23125	-8.44351	-0.15946
C	6.0	7.72778	-9.86091	-0.17926
C	6.0	8.96734	-10.72643	-0.23939
C	6.0	8.58211	-12.18522	-0.22282
C	6.0	9.83239	-13.03318	-0.27004
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H	1.0	-1.09479	5.02107	-0.29649
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H	1.0	-5.10238	-1.30554	0.31308
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H	1.0	-3.82649	7.17658	-0.36308
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H	1.0	5.78544	6.78281	-0.54860
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H	1.0	5.10879	2.70500	-0.84035
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H    1.0   -5.65691    4.86361    1.27340
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H    1.0    6.32285   -0.50506   -1.06314
H    1.0    5.80024   -2.44874   -0.86895
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H    1.0    7.91743   -3.08137    1.02894
H    1.0    7.88534   -3.12178   -0.81048
H    1.0    6.65537   -5.07333   -0.79766
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H    1.0    8.56745   -6.07662    0.92598
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H    1.0    6.52486   -7.59784   -0.93174
H    1.0    6.47069   -7.64175    0.81867
H    1.0    8.91521   -8.29459    0.67947
H    1.0    8.77392   -8.23893   -1.09248
H    1.0    7.08102  -10.04448   -1.04662
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