

Supplementary Information

High-energy, stable and recycled molecular solar thermal storage material using azo/graphene hybrids by optimizing hydrogen bonds

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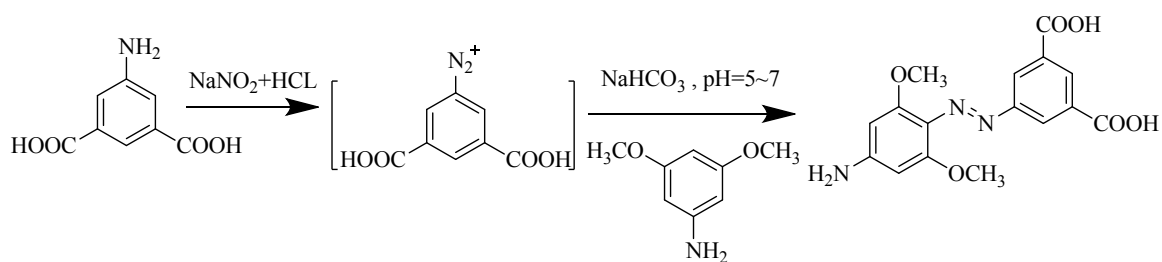


Fig. S1 Synthetic route of AZO by coupling of the diazonium salt.

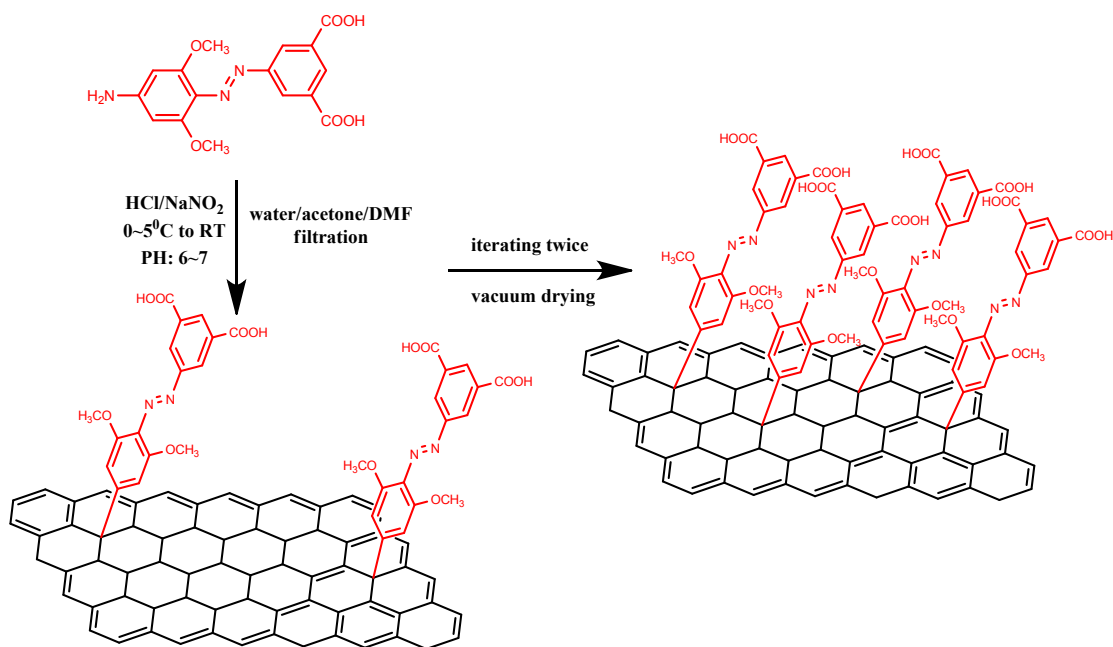


Fig. S2 Preparation of AZO-RGO using a triple iterating aryl radical reaction.

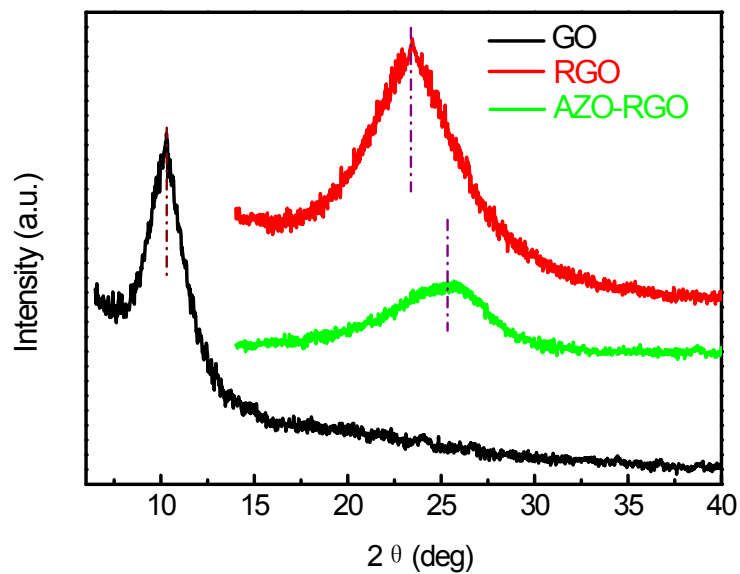


Fig. S3 XRD of GO, RGO and AZO-RGO.

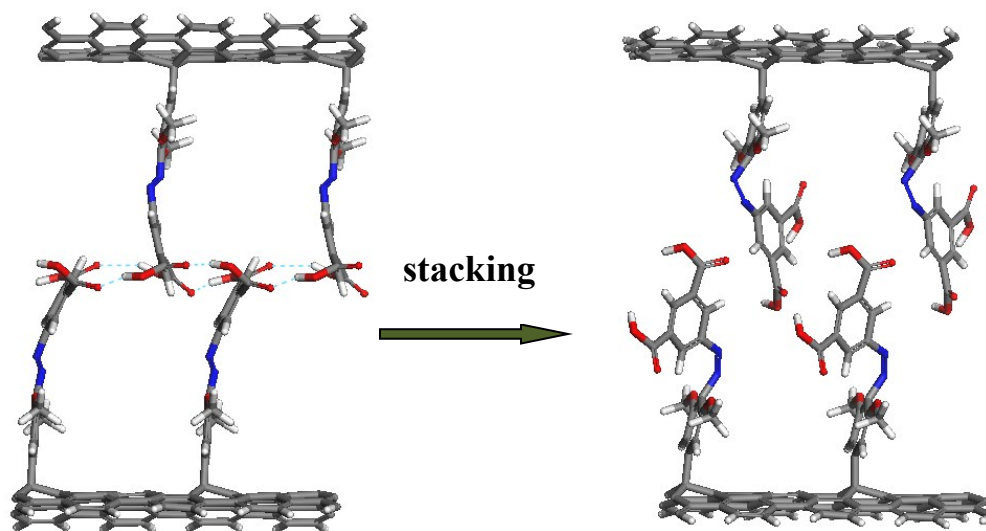


Fig S4. The illustration of inter-planar close interaction for high functionalization density AZO-RGO hybrid in the solid state forms due to the stacking of nearby grapheme nanosheets with a low interlayer space: *E*-rich AZO-RGO(left) and *Z*-rich AZO-RGO(right).

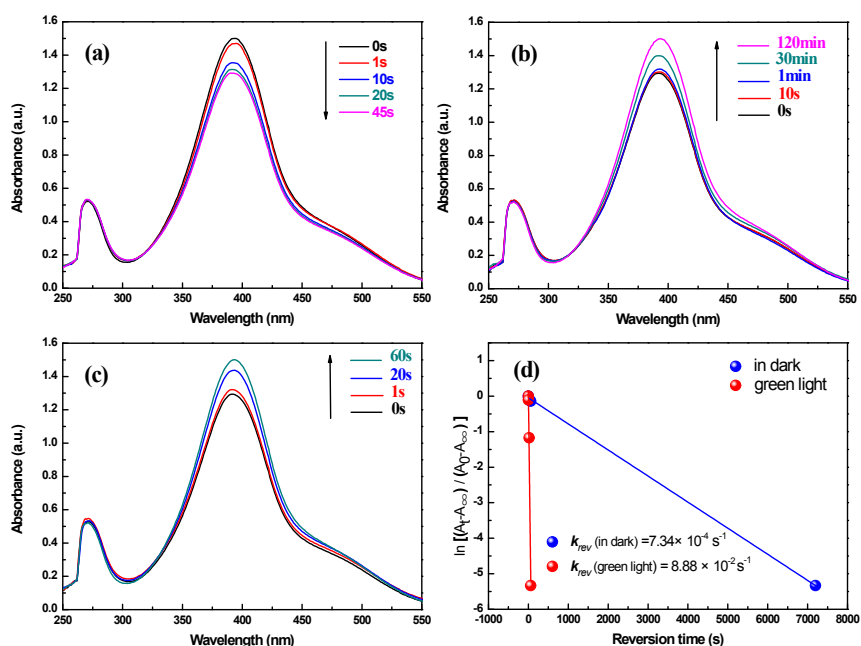


Fig. S5 Time-evolved absorption spectra of AZO with an initial absorbance intensity of 1.5 a.u. at room temperature (25 °C). (a) Irradiated by UV light at 365 nm, (b) reversion in darkness and (c) irradiated by visible light at 520 nm. (d) First plots of *Z*-to-*E* reversion of AZO with different k_{rev} (the inset).

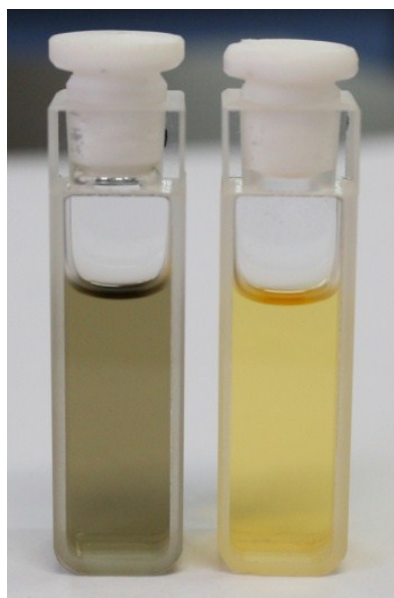


Fig. S6 Photos of AZO-RGO (left) and AZO(right) without any precipitate after 50 and 100 times photo-isomerization respectively.

$$D_g (\%) = \frac{R_g - R}{R_g - R_a} \times 100\% \quad \text{S(1)}$$

Wherein, R_g , R and R_a represent the residual weight percentage (wt%) of RGO, AZO-RGO and AZO, respectively.

$$\ln\left(\frac{A_\infty - A_t}{A_\infty - A_0}\right) = -k_{rev}t \quad \text{S(2)}$$

Wherein, A_0 is the absorption intensity of AZO at a photostationary state between E - and Z -isomers after the irradiation, A_t is the absorption intensity of AZO kept in darkness or irradiated by visible light for a “ t ” time, A_∞ is the absorption intensity of AZO after the complete Z -to- E reversion.

$$\eta = \frac{q}{E_{hv} \Phi t_{irrad}} \quad \text{S(3)}$$

Wherein, q is the heat released by the sample (J, determined by calorimetry), E_{hv} is the energy of photons (J/mol) of 365-nm light, Φ is the photon flux (mol/s), and t_{irrad} is the irradiation time.

Table S1 The enthalpy difference and energy density of AZO and AZO-RGO by DSC and DFT.

	Mn ^(a) g/mol	heat obsd. J/g	energy density Wh/kg	ΔH_{DSC} kJ/mol	ΔH_{DFT} eV
AZO	345	147.6	41	50.9	0.63
AZO-RGO	533	496.8	138	264.8	3.17

(a) Mn of AZO-RGO is the molecular weight of the azobenzene-containing functional group and the average number of RGO carbon atoms associated with each functional group based on the XPS and TGA analysis.

Data S1. The coordinates and of optimized geometries for AZO molecule and AZO-RGO hybrid by DFT.

E- AZO:

C	6.67709	15.03492	11.70054
C	5.97456	14.20448	5.41705
C	6.12352	15.45716	6.03904
C	6.30991	15.54532	7.41802
C	6.41875	17.93063	7.28205
C	6.78967	14.65950	14.48068
C	6.83982	15.95327	13.95219
C	6.79207	16.13260	12.56200
C	6.01784	13.02543	6.18511
C	6.34024	14.36392	8.24052
C	6.19288	13.10328	7.56310
C	6.64449	13.73624	12.24516
C	6.70963	13.54727	13.62624
C	6.01341	10.72577	7.75467
C	6.68995	12.19285	14.27019
C	6.96207	17.18458	14.80217
N	6.60046	15.32704	10.31469
N	6.45623	14.26767	9.60540
N	5.83039	14.12691	4.05018
O	6.98838	11.12784	13.46805
O	6.45922	16.72861	8.05402
O	6.23180	12.00189	8.35764
O	6.43463	12.01151	15.44732
O	6.75557	17.03707	16.14564
O	7.22887	18.28432	14.35435

H	7.23898	11.45068	12.57944
H	6.09456	16.35732	5.42612
H	5.44432	18.04978	6.77952
H	7.22850	17.95392	6.53379
H	6.56162	18.74381	8.00297
H	6.84023	17.14054	12.14673
H	6.83551	14.44483	15.55265
H	6.51217	16.11272	16.34941
H	5.91651	12.06266	5.68573
H	6.53361	12.91347	11.53221
H	6.79518	10.48815	7.01361
H	5.02005	10.67435	7.27776
H	6.06183	10.00144	8.57632
H	5.56496	14.96473	3.54430
H	5.49320	13.25730	3.65085

Z- AZO:

C	6.34547	14.48628	8.67182
C	5.72025	15.39989	7.76135
C	5.53736	15.09349	6.41829
C	6.00250	13.86635	5.91087
C	6.64303	12.95333	6.76792
C	6.80205	13.24876	8.12160
C	8.02335	11.21078	8.47743
C	4.73837	17.55671	7.46803
C	5.14878	12.66164	11.01601
C	4.66112	11.49904	11.62203
C	5.44280	10.81724	12.56885

C	6.70992	11.31556	12.92162
C	7.17490	12.49414	12.33605
C	6.40868	13.17453	11.37313
C	7.60878	10.63270	13.90705
C	3.31624	11.00598	11.17795
N	6.68181	15.04594	9.90592
N	6.86479	14.45786	11.01026
N	5.78737	13.54449	4.58729
O	2.80712	11.29822	10.11327
O	2.64403	10.17982	12.04166
O	8.81697	10.76599	13.92850
O	7.00132	9.81889	14.82974
O	7.46786	12.42898	8.97825
O	5.29061	16.55723	8.32464
H	7.23406	10.54326	8.09558
H	3.79662	17.21401	7.00714
H	5.45182	17.84685	6.67875
H	4.53535	18.41844	8.11407
H	5.02123	15.78500	5.75429
H	7.01441	12.01423	6.35953
H	8.76423	11.40375	7.68494
H	8.51693	10.74042	9.33612
H	8.14447	12.89714	12.63362
H	4.52550	13.16425	10.27544
H	6.03135	9.91955	14.76775
H	5.10859	9.85181	12.96239
H	3.11611	10.14095	12.89603

H 5.55705 14.29581 3.94515

H 6.32289 12.78331 4.18456

E- AZO-RGO:

C 8.278430000 10.851180000 2.407230000

C 1.131390000 10.874700000 2.353150000

C 1.851410000 11.996120000 2.822790000

C 3.296160000 11.955550000 2.892740000

C 4.015060000 10.799050000 2.559580000

C 5.390130000 10.817020000 2.521130000

C 6.110810000 11.976480000 2.884490000

C 7.558140000 11.964220000 2.864520000

C 8.261650000 13.141490000 3.241620000

C 1.153520000 13.126820000 3.257380000

C 1.845780000 14.324480000 3.876450000

C 3.304550000 14.349300000 3.516290000

C 4.001840000 13.134240000 3.265210000

C 5.414640000 13.116930000 3.299900000

C 6.107300000 14.332650000 3.885980000

C 7.564910000 14.350430000 3.521380000

C 8.261560000 15.577790000 3.397040000

C 1.144860000 15.596300000 3.427950000

C 1.855760000 16.788990000 3.163350000

C 3.286230000 16.802820000 3.172160000

C 4.000170000 15.575260000 3.387030000

C 5.405910000 15.594580000 3.411490000

C 6.116590000 16.786190000 3.145010000

C 7.547080000 16.802920000 3.171040000

C	8.242760000	18.001340000	2.921920000
C	1.153820000	18.002510000	2.907970000
C	1.883690000	19.188600000	2.663210000
C	3.251060000	19.190690000	2.669120000
C	3.981760000	18.000020000	2.916540000
C	5.414540000	17.999150000	2.887780000
C	6.145110000	19.183940000	2.638760000
C	7.512000000	19.188380000	2.656520000
C	1.958440000	14.351330000	11.783650000
C	1.772920000	14.214740000	5.443520000
C	1.829750000	15.368380000	6.230220000
C	1.763110000	15.290340000	7.625770000
C	2.226240000	17.627180000	7.843410000
C	2.962860000	13.889680000	14.353770000
C	2.644240000	15.193430000	13.947780000
C	2.096220000	15.419020000	12.679660000
C	1.710710000	12.957840000	6.054830000
C	1.693080000	14.019960000	8.275820000
C	1.676300000	12.859210000	7.444760000
C	2.257430000	13.042880000	12.195800000
C	2.731430000	12.815890000	13.488110000
C	1.797460000	10.473040000	7.356410000
C	3.059930000	11.410180000	13.906790000
C	3.084270000	16.333650000	14.803610000
C	6.178130000	14.844330000	11.779840000
C	6.036290000	14.287500000	5.459690000
C	6.088090000	15.481470000	6.185720000

C	6.024590000	15.483310000	7.582560000
C	6.505130000	17.826660000	7.652250000
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C	6.894230000	15.924940000	13.829260000
C	6.374580000	16.007430000	12.533360000
C	5.980090000	13.066500000	6.139650000
C	5.954200000	14.251980000	8.302160000
C	5.942950000	13.047980000	7.535570000
C	6.418620000	13.583350000	12.351820000
C	6.935740000	13.508730000	13.647090000
C	6.079480000	10.662890000	7.595070000
C	7.413090000	12.207380000	14.204290000
C	7.231450000	17.189300000	14.568740000
N	1.567060000	14.694050000	10.461520000
N	1.856350000	13.775060000	9.629480000
N	5.790740000	15.057980000	10.430970000
N	6.115040000	14.089280000	9.672710000
O	2.118470000	10.709800000	14.522070000
O	1.811760000	16.389240000	8.421530000
O	1.599060000	11.670290000	8.104710000
O	4.158020000	10.897550000	13.670230000
O	2.380270000	17.456850000	14.837050000
O	4.150750000	16.251460000	15.431610000
O	6.732060000	11.094280000	13.977260000
O	6.078380000	16.632270000	8.308700000
O	5.866990000	11.902420000	8.265250000
O	8.485340000	12.168540000	14.826380000

O	6.310500000	17.730810000	15.351120000
O	8.332660000	17.732610000	14.437500000
H	1.364540000	20.124220000	2.467170000
H	3.770410000	20.126520000	2.473550000
H	5.625820000	20.117560000	2.432620000
H	8.031680000	20.123130000	2.455800000
H	1.654400000	10.008560000	1.952490000
H	3.497480000	9.875670000	2.306490000
H	5.914670000	9.911090000	2.225370000
H	7.760800000	9.959240000	2.060490000
H	1.257020000	11.234400000	14.651910000
H	1.894100000	16.343160000	5.751610000
H	1.480830000	18.014850000	7.128160000
H	3.199660000	17.525050000	7.336970000
H	2.317400000	18.323220000	8.685400000
H	1.854370000	16.424390000	12.330280000
H	3.394600000	13.730230000	15.342670000
H	1.433100000	17.392490000	14.498860000
H	1.664300000	12.061280000	5.441310000
H	2.132330000	12.227920000	11.480620000
H	2.757890000	10.492990000	6.814470000
H	0.982130000	10.299480000	6.632820000
H	1.806780000	9.663590000	8.096050000
H	5.768950000	11.222400000	13.700970000
H	6.146800000	16.429760000	5.657320000
H	5.757820000	18.184500000	6.923390000
H	7.469150000	17.679400000	7.138430000

H	6.619600000	18.571340000	8.448980000
H	6.169190000	16.970230000	12.061230000
H	7.638720000	14.598460000	15.373440000
H	5.451560000	17.188330000	15.391470000
H	5.939790000	12.136060000	5.577200000
H	6.257550000	12.690930000	11.744820000
H	7.047530000	10.656750000	7.067100000
H	5.273700000	10.442820000	6.873770000
H	6.082040000	9.900510000	8.383060000

Z- AZO-RGO:

C	2.174790000	14.229460000	8.459920000
C	1.589400000	15.370360000	7.828450000
C	1.262820000	15.375620000	6.473560000
C	1.520660000	14.242980000	5.689870000
C	2.019990000	13.088970000	6.299580000
C	2.360580000	13.071910000	7.656690000
C	3.181700000	10.829280000	7.450870000
C	0.823950000	17.614250000	8.137530000
C	1.542630000	11.909600000	10.779880000
C	1.046990000	10.875440000	11.590580000
C	1.273820000	10.880770000	12.974940000
C	2.054410000	11.894040000	13.549520000
C	2.588710000	12.887740000	12.727980000
C	2.329460000	12.924660000	11.346720000
C	2.516470000	11.816040000	14.969100000
C	0.398600000	9.704640000	10.915450000
C	7.928380000	10.738010000	2.899220000

C	0.788430000	10.767100000	2.828510000
C	1.492400000	11.945490000	3.130500000
C	2.966210000	11.933140000	3.093970000
C	3.673680000	10.827510000	2.623360000
C	5.056510000	10.859080000	2.578700000
C	5.756150000	11.964550000	3.089500000
C	7.224590000	11.911910000	3.165550000
C	7.912070000	13.107110000	3.486230000
C	0.813730000	13.089380000	3.529240000
C	1.501640000	14.303240000	4.123580000
C	2.951860000	14.320610000	3.723680000
C	3.652620000	13.111800000	3.472170000
C	5.074990000	13.092680000	3.531060000
C	5.764400000	14.300360000	4.140230000
C	7.213170000	14.318900000	3.720660000
C	7.915700000	15.539030000	3.590340000
C	0.802640000	15.559570000	3.633480000
C	1.507160000	16.754200000	3.366070000
C	2.951350000	16.772520000	3.386170000
C	3.655510000	15.539780000	3.598810000
C	5.064140000	15.558280000	3.647580000
C	5.768280000	16.753320000	3.375660000
C	7.212230000	16.772720000	3.387290000
C	7.891930000	17.966110000	3.140370000
C	0.820870000	17.963810000	3.106130000
C	1.540920000	19.151930000	2.850480000
C	2.910880000	19.156690000	2.872560000

C	3.630890000	17.965650000	3.141300000
C	5.081690000	17.963080000	3.115160000
C	5.801110000	19.152800000	2.865040000
C	7.171240000	19.158530000	2.882640000
C	6.443850000	14.228250000	8.476350000
C	5.861370000	15.370340000	7.844080000
C	5.536280000	15.376720000	6.488590000
C	5.791280000	14.243690000	5.704060000
C	6.287190000	13.088640000	6.315010000
C	6.627030000	13.070590000	7.672560000
C	7.439330000	10.824950000	7.465830000
C	5.094340000	17.613770000	8.153360000
C	5.804330000	11.910700000	10.794720000
C	5.307050000	10.874740000	11.602070000
C	5.533970000	10.876000000	12.986610000
C	6.316560000	11.885810000	13.564460000
C	6.854150000	12.880000000	12.745630000
C	6.594200000	12.921740000	11.364080000
C	6.771700000	11.803420000	14.986400000
C	4.656580000	9.707750000	10.921970000
N	2.903660000	14.544010000	9.621500000
N	3.044220000	14.016270000	10.749560000
N	7.170330000	14.541860000	9.639730000
N	7.309030000	14.014160000	10.768310000
O	2.983320000	12.010130000	8.247390000
O	1.432860000	16.435610000	8.659210000
O	3.683430000	12.138070000	15.233680000

O	1.722520000	11.349630000	15.913490000
O	0.647570000	9.375770000	9.770720000
O	8.046140000	8.963170000	11.657730000
O	4.899510000	9.388810000	9.772760000
O	3.788930000	8.958520000	11.663420000
O	7.945470000	12.095360000	15.254580000
O	5.961440000	11.366540000	15.930880000
O	7.246810000	12.006680000	8.262630000
O	5.704990000	16.435890000	8.674730000
H	2.218380000	10.438030000	7.089690000
H	8.313410000	17.407010000	7.811200000
H	1.403440000	18.035180000	7.296800000
H	0.809980000	18.329930000	8.967930000
H	0.840670000	16.270210000	6.019930000
H	2.222170000	12.209520000	5.693270000
H	3.844910000	11.044990000	6.598090000
H	3.648570000	10.099020000	8.118460000
H	3.249220000	13.649310000	13.142560000
H	1.354320000	11.860600000	9.712430000
H	0.741620000	11.510110000	15.684610000
H	0.921470000	10.057510000	13.603120000
H	7.814750000	9.446470000	12.476370000
H	1.019200000	20.081790000	2.635390000
H	3.433670000	20.088190000	2.665490000
H	5.278110000	20.083680000	2.657210000
H	7.692700000	20.091960000	2.681570000
H	1.318550000	9.854290000	2.565840000

H	3.155210000	9.942650000	2.259180000
H	5.591140000	10.010970000	2.156370000
H	7.407440000	9.799440000	2.718410000
H	6.473720000	10.436770000	7.107570000
H	4.062140000	17.405030000	7.828090000
H	5.672240000	18.035120000	7.311890000
H	5.080450000	18.329590000	8.983620000
H	5.115610000	16.272530000	6.035380000
H	6.488130000	12.208710000	5.709110000
H	8.100020000	11.037960000	6.610530000
H	7.906260000	10.093350000	8.131940000
H	7.516410000	13.639560000	13.162040000
H	5.615120000	11.865220000	9.727380000
H	4.983900000	11.544560000	15.693940000
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