Supporting information

Mechanistic Insights into Mixed-Solvent-Induced Swelling of Amine-Cured Epoxy Networks: A Combined MD and DFT Study

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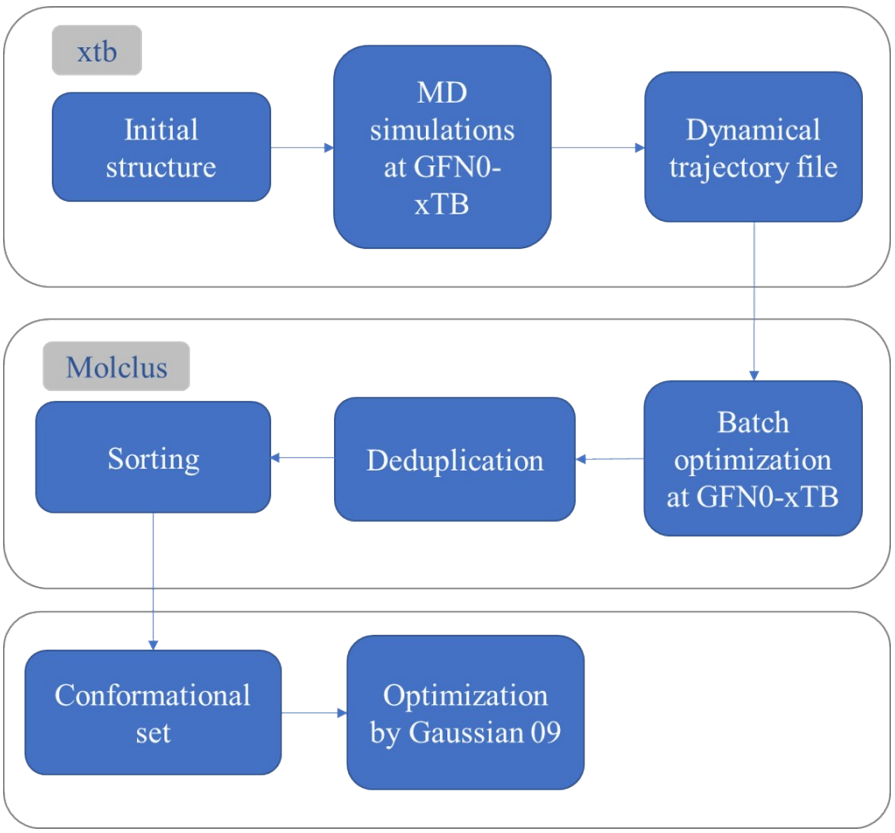


Figure S1 Flowchart of conformational search.

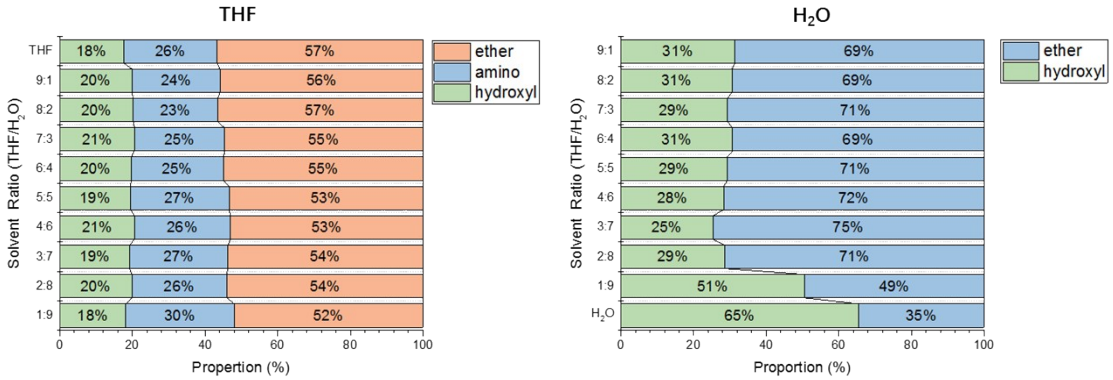


Figure S2 THF and H_2O occupancies in the first solvation shell of ether, amino, and hydroxyl groups, obtained by RDF analysis.

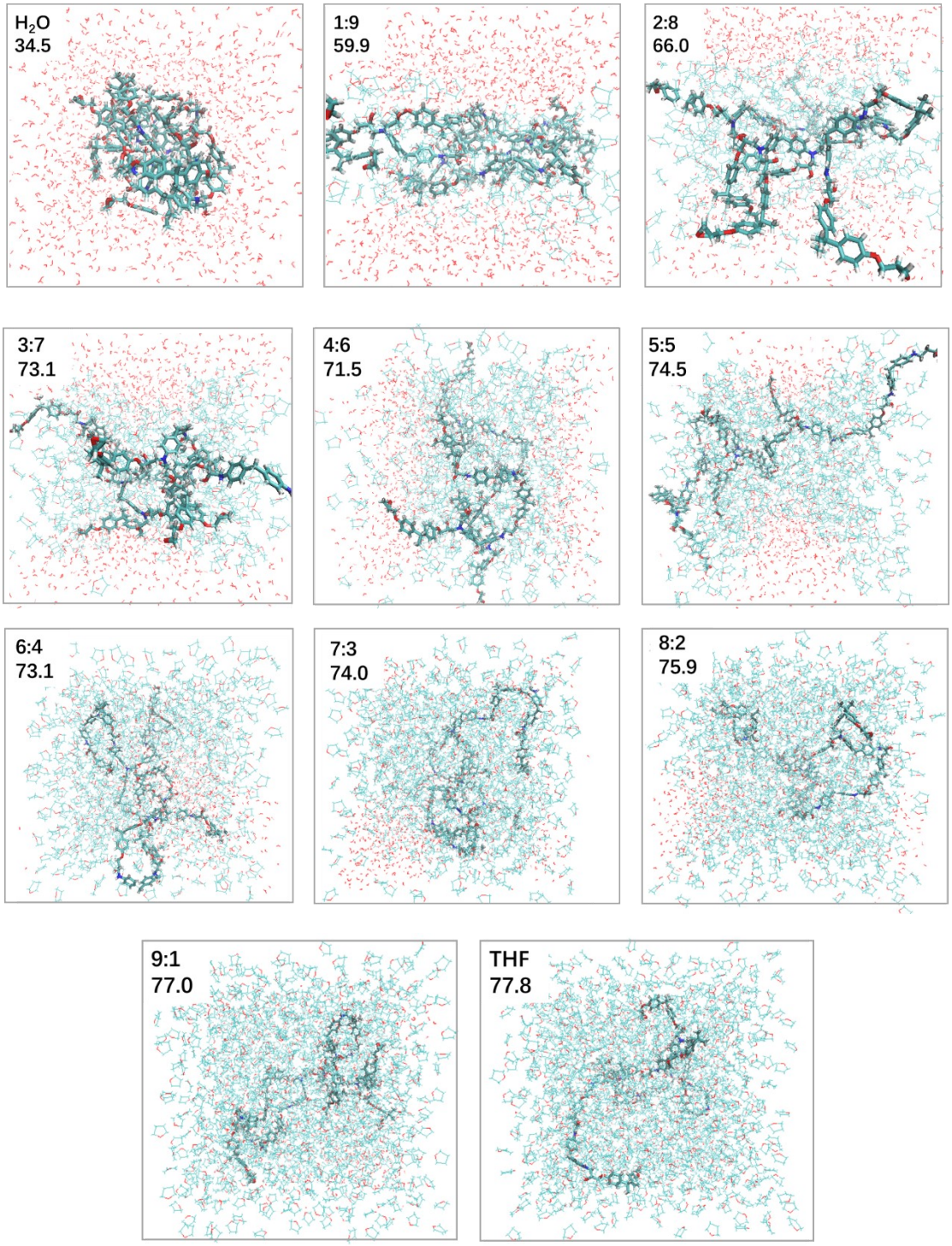


Figure S3 Final simulated configurations of the DGEBA-DDM in the THF/H_2O mixture and the value of averaged SASA (nm^2).

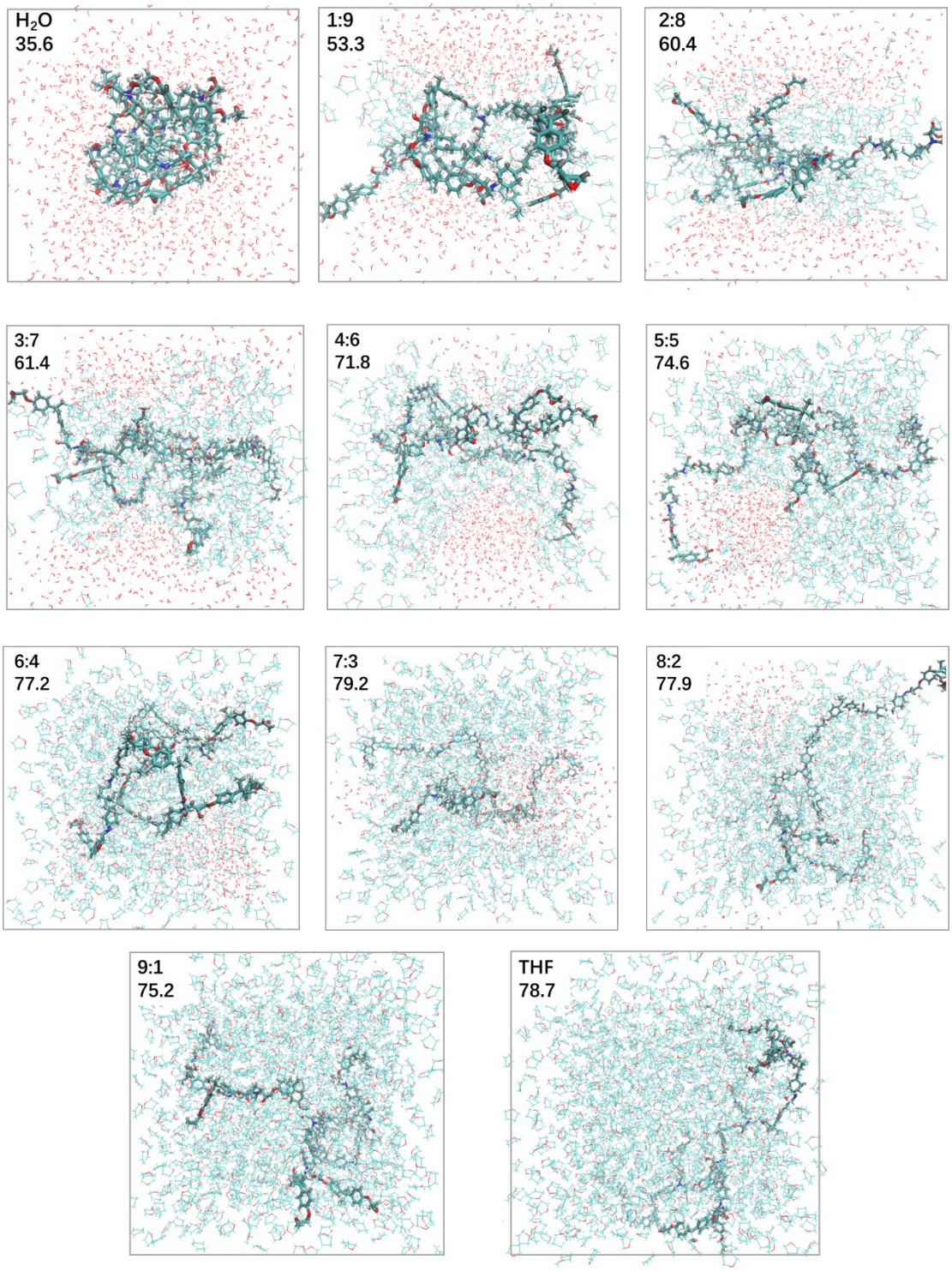


Figure S4 Final simulated configurations of the DGEBA-PACM in the THF/H_2O mixture and the value of averaged SASA (nm^2).

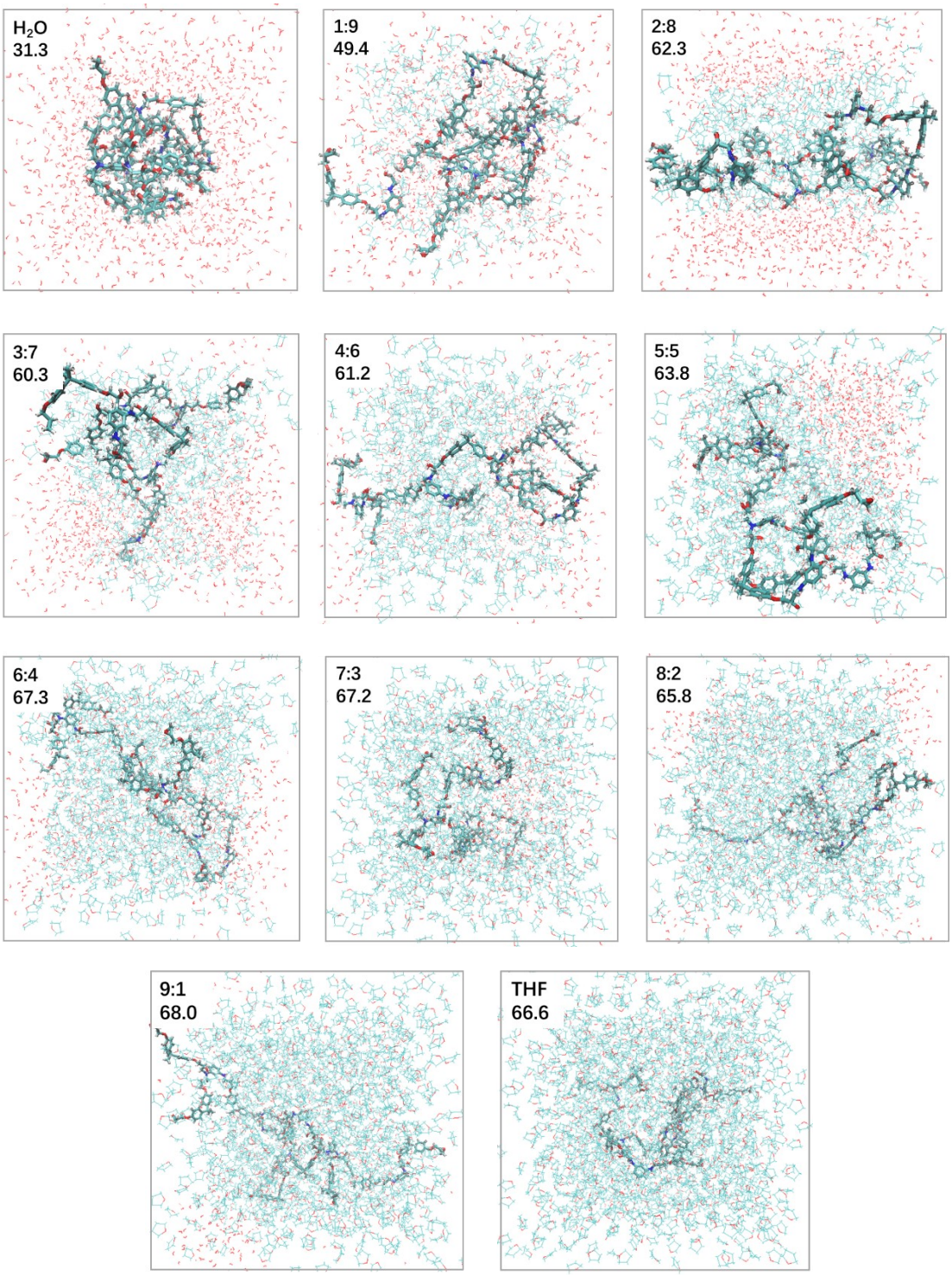


Figure S5 Final simulated configurations of the DGEBA-MPDA in the THF/H_2O mixture and the value of averaged SASA (nm^2).

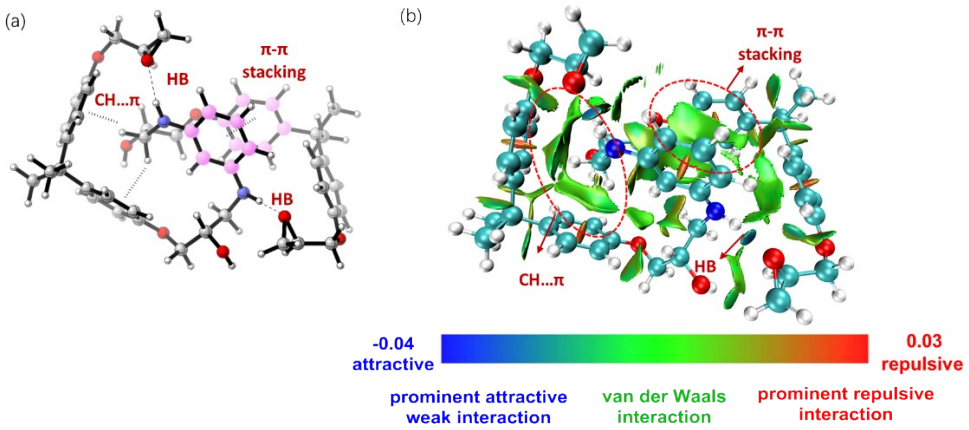


Figure S6 (a) Optimized geometry of a cross-linked cluster (2 DGEBA / 1 MPDA). (b) Visualizing non-covalent interactions analysis by RDG.

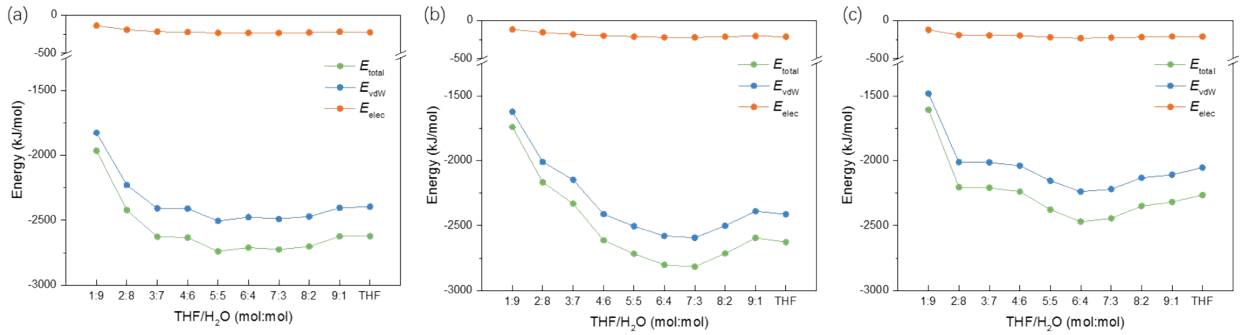


Figure S7 Weak interactions between THF and polymers: (a) DGEBA-DDM; (b) DGEBA-PACM; (c) DGEBA-MPDA.

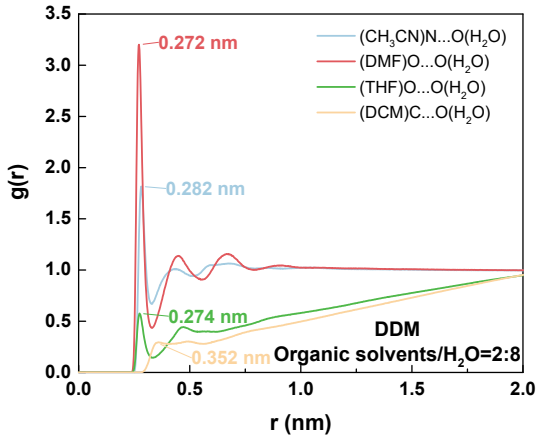
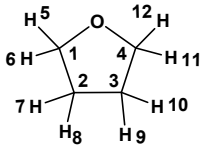
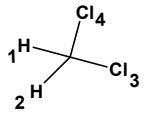
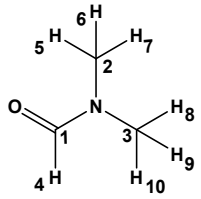
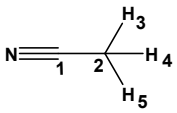


Figure S8 Radial distribution function (RDF) curves for selected atoms in different organic solvents and H_2O.

Table S1 Atomic charge, total dispersion energy and the corresponding contribution to dispersion energy obtained at B3LYP/def2-TZVP level of theory.

Organic solvent	Atomic Number	Charge	Atomic contribution to dispersion energy	Total dispersion energy
 THF	O	-0.491	-0.941	-9.689
	C1	-0.075	-1.161	
	C2	-0.423	-1.209	
	C3	-0.423	-1.209	
	C4	-0.075	-1.161	
	H5	0.149	-0.521	
	H6	0.187	-0.452	
	H7	0.204	-0.513	
	H8	0.203	-0.519	
	H9	0.203	-0.519	
	H10	0.204	-0.513	
	H11	0.187	-0.452	
	H12	0.149	-0.521	
 DCM	C	-0.379	-0.833	-4.130
	H1	0.217	-0.452	
	H2	0.217	-0.452	
	Cl3	-0.027	-1.197	
	Cl4	-0.027	-1.197	
 DMF	O	-0.610	-0.729	-8.599
	N	-0.399	-1.233	
	C1	0.507	-1.241	
	C2	-0.412	-1.086	
	C3	-0.390	-1.062	
	H4	0.100	-0.464	
	H5	0.240	-0.480	
	H6	0.190	-0.464	
	H7	0.190	-0.464	
	H8	0.189	-0.459	
	H9	0.189	-0.459	
	H10	0.206	-0.457	
 CH_3CN	N	-0.323	-0.584	-2.995
	C1	0.278	-0.779	
	C2	-0.701	-0.644	
	H3	0.249	-0.329	
	H4	0.249	-0.329	
	H5	0.249	-0.329	

To decouple the competitive interactions between water and organic solvents that ultimately

govern solvent–polymer affinity and swelling behavior, a simplified solvent model containing one organic solvent molecule and 1000 water molecules was constructed. Molecular dynamics simulations were performed for 1 ns under NVT conditions. Weak interactions between organic solvent and water were shown in Table S2. The visualization of averaged RDG (aRDG) and their stability (analyzed by thermal fluctuation index) during 1ns at 298K were shown in Figure S9.

Table S2 Comparison of dipole moments (μ, Debye), calculated molecular vdW volumes (V, Å^3), total dispersion energy (E_{disp}, kcal/mol), obtained by multiwfn 3.8 (dev) software, for the investigated organic solvents. Electrostatic interaction energy (E_{elec}), Van der Waals interaction energy (E_{vdW}) and total H_2O–organic solvent interaction energies (E_{total}, kJ/mol) were obtained by GROMACS 2018.8 package.

Organic solvent	[a]E_{elec}	[b]E_{vdW}	E_{total}	μ	[c]E_{disp}	V
CH_3CN	-46.0	-23.7	-69.7	3.92	-3.0	66
DMF	-58.9	-37.8	-96.7	3.82	-8.6	107
THF	-26.4	-40.8	-67.1	1.75	-9.7	107
DCM	-14.2	-30.0	-44.2	1.60	-4.1	85

[a] Electrostatic interaction energy between H_2O–organic solvent;

[b] Van der Waals interaction energy between H_2O–organic solvent;

[c] Total dispersion energy.

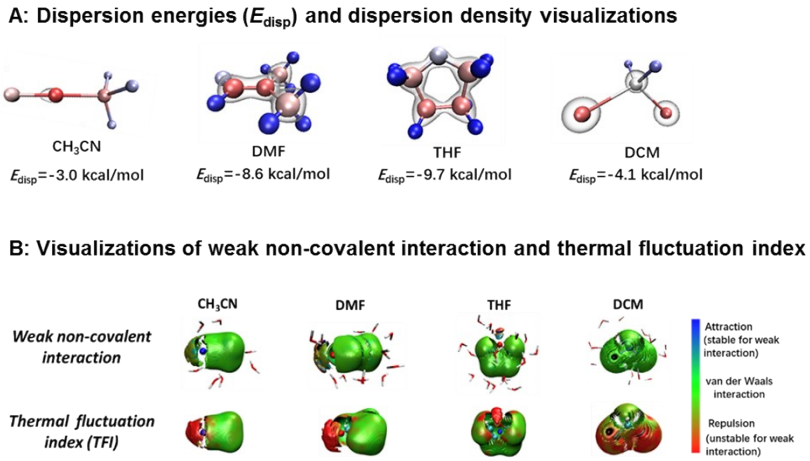


Figure S9 Dispersion energies (E_{disp}) and dispersion density visualizations highlighting atomic contributions to dispersion interactions in CH_3CN, DMF, THF, and DCM, obtained by Multiwfn 3.8 (dev) software analysis (isovalue surface = -0.05). Visualizations of aRDG analysis and thermal fluctuation index between organic solvents as well as water.

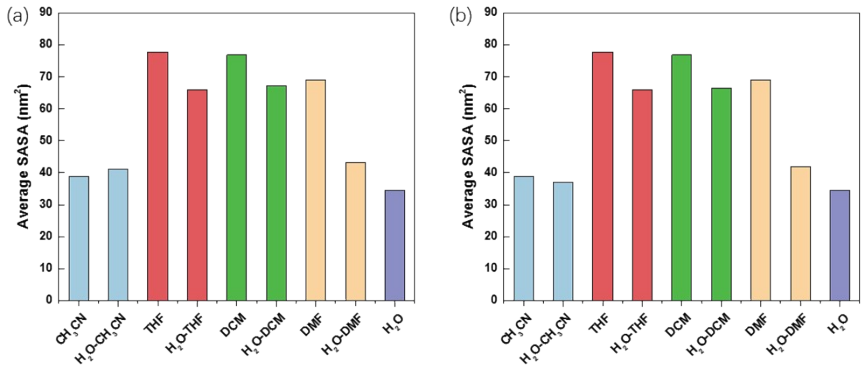


Figure S10 Comparison of the solvent-accessible surface area (SASA) of the DGEBA–DDM polymer in different pure and mixed solvents: (a) mixed solvents with molar ratio of 2:8; (b) mixed solvents with volume ratio of 1:1.

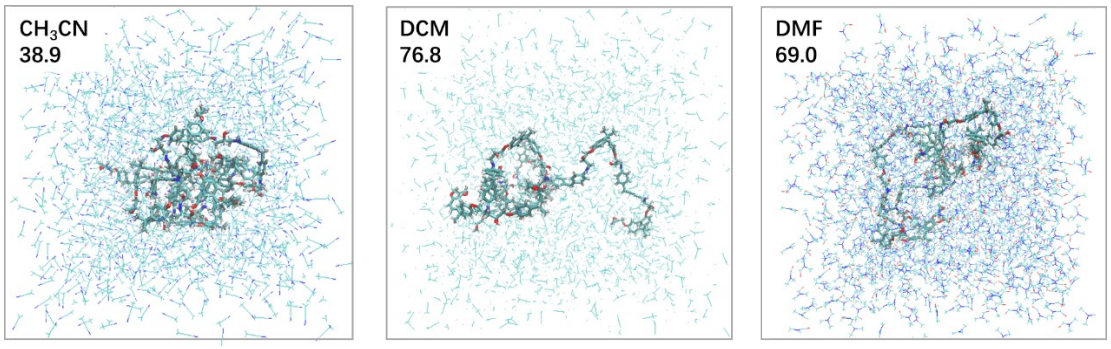


Figure S11 Final simulated configurations of the DGEBA-DDM in pure organic solvents and the value of averaged SASA (nm^2).

Table S3 Electronic energies (E_e), enthalpies (H) and Gibbs free energies (G) for all stationary points (in Hartree), obtained at the B3LYP-D3(BJ)/6-31G* theoretical level.

Structures	[a]*ZPE*	E_e	[b]H_{corr}	*H*	[c]G_{corr}	*G*
THF	0.11745	-232.34747	0.12335	-232.34157	0.08872	-232.37620
H_2O	0.02117	-76.38836	0.02495	-76.38458	0.00351	-76.40602
DDMa	0.66019	-1728.36019	0.69783	-1728.32255	0.58867	-1728.43171
DDMa-2THF-8H_2O	1.10960	-2804.40326	1.17800	-2804.33487	1.00410	-2804.50876
2DGEBA /1MPDA	0.96697	-2573.28952	1.02112	-2573.23537	0.88152	-2573.37497

[a] Zero-point correction energy;

[b] Thermal correction to enthalpy obtained at the B3LYP-D3(BJ)/6-31G* level of theory;

[c] Thermal correction to Gibbs free energy obtained at the B3LYP-D3(BJ)/6-31G* level of theory.

Cartesian coordinates of all structures.

THF

C	-0.05145200	-0.46012800	1.16808100
O	0.09801800	-1.27427200	0.00058100
C	0.26022900	-0.44509100	-1.15447700
C	-0.10343400	0.97885400	-0.71955600
C	0.32742500	0.96596700	0.75320800
H	-1.09541700	-0.50520300	1.51458700
H	0.58740200	-0.86302800	1.96224100
H	1.30458600	-0.49678600	-1.49902100
H	-0.38098000	-0.82927300	-1.95594400
H	0.39783600	1.74668200	-1.31638300
H	-1.18544600	1.13790400	-0.79721700
H	1.41106400	1.11243000	0.83293900
H	-0.16556000	1.73049400	1.36106000

H_2O

O	-0.01712000	-0.05623400	0.00000000
H	0.95021400	-0.00693300	0.00000000
H	-0.29354900	0.87207200	0.00000000

DDMa

C	-0.04102900	-2.62817600	1.85341100
H	0.27369600	-2.03214500	2.72223400
H	0.10830900	-3.67733300	2.14216100
C	0.85636500	-2.31769400	0.66872700
C	1.92471700	-3.15376500	0.32987600
C	0.66696800	-1.16152000	-0.09927400
C	2.80080800	-2.83370400	-0.70612300
H	2.08189200	-4.07277400	0.89174000
C	1.53454200	-0.82973000	-1.13175300
H	-0.16381000	-0.49939100	0.12513500
C	2.63669000	-1.64472800	-1.43798700
H	3.62499800	-3.49675500	-0.95385700
H	1.38838000	0.09482200	-1.68380700
C	-1.50759500	-2.36545000	1.59567000
C	-2.20282300	-3.08926200	0.62081900
C	-2.21077900	-1.37576200	2.28704200
C	-3.54412400	-2.84614700	0.34616800
H	-1.67912100	-3.85745100	0.05689600
C	-3.55001700	-1.11346500	2.01635400
H	-1.69808300	-0.78179600	3.04022700
C	-4.24398300	-1.84061800	1.03753800
H	-4.04566600	-3.44806300	-0.40425600
H	-4.06311900	-0.31747800	2.55036600
N	-5.60266500	-1.57766000	0.81316200
H	-5.89939500	-0.73504600	1.29206600
N	3.53234100	-1.30381300	-2.45421800
H	4.46773500	-1.66478100	-2.28779500
H	3.56923100	-0.30528200	-2.62688800
C	-6.18847500	-1.68767700	-0.51271600
H	-5.76522100	-2.55254400	-1.02693300
H	-7.26276200	-1.87974000	-0.41781000
C	-5.99972900	-0.46315600	-1.42393500
H	-6.62387300	0.36580200	-1.05267500
C	-4.55994900	0.05758500	-1.48982400
H	-3.84032900	-0.76902100	-1.52153900
H	-4.43489600	0.66043900	-2.40231000
O	-4.34928600	0.87090200	-0.34258600
C	-3.14138700	1.49247100	-0.19774600
C	-2.06880400	1.36069400	-1.08582500
C	-3.00767800	2.32191800	0.91893900
C	-0.90118800	2.08918900	-0.86134500
H	-2.12856000	0.69939900	-1.94186900
C	-1.83350400	3.04006400	1.12462100
H	-3.84180000	2.40352100	1.60861700
C	-0.75810900	2.95217300	0.23116700
H	-0.07687600	1.98000300	-1.56002300
H	-1.77006000	3.68458000	1.99408900
C	0.51098000	3.81105600	0.35214300
C	0.44286400	4.89020100	-0.75066900
H	0.40476300	4.44744700	-1.75058200
H	-0.46522400	5.48657000	-0.61868900
H	1.30435000	5.56607400	-0.70167900
C	0.59926800	4.54430000	1.70781500
H	-0.22150700	5.25975600	1.82878500
H	0.57591100	3.84876900	2.55203900
H	1.54024800	5.10071700	1.75928100
C	1.75107600	2.91695500	0.21201900
C	1.95184600	1.87597400	1.12639500
C	2.71653800	3.08872100	-0.78766400
C	3.06522300	1.04269900	1.06861300
H	1.20286900	1.68760100	1.89026300
C	3.83040200	2.25642300	-0.87203000
H	2.60996700	3.87818000	-1.52304700
C	4.01052300	1.22726900	0.05505000
H	3.15868800	0.23200200	1.78064800

H	4.57389500	2.39141600	-1.65172300
O	5.12347900	0.45244800	-0.12183500
C	5.27197800	-0.70368600	0.69340800
H	5.48399600	-0.41476400	1.73418900
H	4.36134600	-1.31138200	0.67113100
O	-6.43258100	-0.89380600	-2.71095100
H	-6.51945700	-0.11232200	-3.27835900
C	6.42527200	-1.48700100	0.13512600
C	6.41790500	-2.95543300	0.17034500
O	6.16267400	-2.25133500	-1.05267100
H	7.38214600	-0.96469800	0.11392300
H	5.55675100	-3.47320700	0.59133700
H	7.35982500	-3.50080300	0.20432500

DDMa-2THF-8H_2O

C	5.58230500	-1.52558900	-0.13521400
H	5.98677500	-2.47190300	-0.51663800
H	6.44004300	-0.91924000	0.17936100
C	4.68065200	-1.78892700	1.06106500
C	4.84321900	-1.11309000	2.27398200
C	3.59293300	-2.66492000	0.94857600
C	3.94096200	-1.27089200	3.32621000
H	5.68732100	-0.43637000	2.39805300
C	2.68466900	-2.82983700	1.98643100
H	3.42741100	-3.21064000	0.02562700
C	2.82893300	-2.12093100	3.19403000
H	4.07976100	-0.72499600	4.25534200
H	1.83591200	-3.49510100	1.85793200
C	4.82648000	-0.82019500	-1.24624200
C	4.79412100	0.57229600	-1.34978200
C	4.03721600	-1.54971900	-2.14647400
C	3.97962100	1.22552900	-2.27832000
H	5.41356800	1.17026900	-0.68408800
C	3.21328000	-0.91618300	-3.06508100
H	4.03331400	-2.63362400	-2.10830700
C	3.15326800	0.48642800	-3.14175800
H	3.99988400	2.30942300	-2.33076700
H	2.60340100	-1.51213300	-3.73890700
N	2.32296800	1.07836700	-4.09696700
H	1.61304300	0.44660600	-4.44495400
N	1.91692400	-2.27739900	4.23952000
H	1.69950300	-1.39830900	4.70847100
H	1.06381200	-2.74171000	3.94067700
C	1.86599200	2.44610400	-3.96464400
H	2.72558700	3.12552100	-4.01753400
H	1.23797300	2.66528900	-4.83561600
C	1.06838800	2.74532300	-2.68375400
H	1.70670900	2.55298000	-1.81383800
C	0.64845000	4.21669300	-2.65568300
H	1.50823900	4.84672900	-2.90348400
H	-0.12993500	4.39894000	-3.40651200
O	0.24557800	4.67377500	-1.36493300
C	-0.94135500	4.22043100	-0.83394700
C	-2.04285800	3.80725700	-1.59215800
C	-1.02139300	4.19269100	0.55601500
C	-3.15689400	3.28500900	-0.94775600
H	-2.01272100	3.82295200	-2.67363200
C	-2.15083400	3.67161100	1.18663500
H	-0.17445500	4.54232300	1.13763200
C	-3.22244100	3.16706000	0.44800200
H	-3.97337700	2.90124500	-1.55265500
H	-2.14548300	3.60521400	2.26649000
C	-4.39958300	2.41360000	1.07730000
C	-4.25514800	2.29269500	2.60914900
H	-5.08044200	1.69569500	3.00990300
H	-3.31742100	1.80364900	2.88728000
H	-4.28361600	3.27756300	3.08990800
C	-5.69949100	3.19599800	0.78329100
H	-5.92374800	3.22166000	-0.28735000
H	-6.56014600	2.76030700	1.30167300
H	-5.59018300	4.22782600	1.13175900
C	-4.44169600	0.98715900	0.49279500
C	-3.25762700	0.32665900	0.13625700
C	-5.64209600	0.28231900	0.33363900
C	-3.25939400	-0.97162500	-0.37476200
H	-2.30637300	0.83905800	0.21689200
C	-5.66277900	-1.01977400	-0.16081400
H	-6.58629500	0.74610100	0.59855700
C	-4.47115200	-1.65307500	-0.52026100
H	-2.32642900	-1.42294900	-0.68917100
H	-6.59676600	-1.56037700	-0.27711000
O	-4.59182100	-2.92619200	-1.02709100
C	-3.50307600	-3.82574900	-0.87164700
H	-2.83383300	-3.52380000	-0.06299300
H	-3.93560400	-4.79937900	-0.60901800
O	-0.06287500	1.87433800	-2.62971800
H	-0.19135900	1.60245600	-1.68153900
C	-2.69826000	-4.01471400	-2.13349000

C	-3.21789100	-3.66837400	-3.45830000	H	1.41852000	-3.83976800	-2.47839100
O	-2.22828200	-2.82406200	-2.81547400	H	1.20404700	-4.23768300	-0.99346400
H	-1.93726400	-4.78780400	-2.04601400	O	-0.46568300	-3.94441000	-0.00672500
H	-4.20128600	-3.21209400	-3.52986900	H	-0.33016800	-3.04012100	-0.36816600
H	-2.85655900	-4.19583200	-4.33875900	H	-0.41295600	-3.80346800	0.96308800
O	0.06941400	0.90286900	-0.11997400	O	0.32399200	-3.41230200	-3.89093900
H	0.86708400	1.42478400	0.11965400	H	-0.55170700	-3.29870800	-3.46712300
H	0.38685400	-0.01253800	-0.34801900	H	0.52409200	-2.49496000	-4.14572200
O	-0.30254700	-0.65377600	-3.53188200	O	-0.19505500	1.68926800	2.61386600
H	-1.24421600	-0.88718300	-3.46642800	H	-0.44432500	1.21892600	1.79252600
H	-0.23180300	0.31212500	-3.30769900	H	0.49628900	2.28780800	2.26981200
O	1.10206000	0.54815000	4.75627700				
H	0.59289100	0.87323000	3.97601900	**2 DGEBA / 1 MPDA**			
H	0.68257300	0.98029700	5.51402600	C	2.04417300	-0.28179900	-2.06834300
O	0.50064700	-1.55564500	-1.05962100	C	1.55058800	0.37807900	-0.92674300
H	0.24489000	-1.31926200	-1.98430500	C	1.20085800	-1.12617200	-2.78259300
H	1.27966000	-2.16216300	-1.16763300	C	0.21613100	0.18344000	-0.54531900
C	2.90235100	1.42349700	1.72632300	C	-0.11940700	-1.34193000	-2.39878900
O	2.03504900	2.36658100	1.04702100	H	1.58383900	-1.63248300	-3.66595400
C	2.84135100	3.53666400	0.84121300	C	-0.62814300	-0.68141700	-1.26333700
C	3.59299200	3.71543900	2.17053500	H	-0.17497700	0.70621700	0.31452400
C	3.64942600	2.27593500	2.75949700	H	-0.77032300	-1.99532500	-2.97267800
H	2.27528500	0.64676400	2.15812400	N	-1.94263800	-0.88639500	-0.90051600
H	3.57067500	0.96921400	0.99053700	H	-2.51073500	-1.39977700	-1.56012200
H	3.53729400	3.34284000	0.01297200	C	-2.59319900	-0.33638000	0.25934100
H	2.17418600	4.35210100	0.55888500	H	-2.17662900	0.65160700	0.48350700
H	4.58515800	4.14829500	2.01450700	H	-3.64136700	-0.17332200	0.01885600
H	3.04027800	4.38594900	2.83550900	C	-2.55253800	-1.17979400	1.55008700
H	4.67244400	1.91984500	2.89957500	H	-3.06789700	-2.13205700	1.37848900
H	3.13842500	2.21699000	3.72401600	C	-1.15003700	-1.47096400	2.08030500
C	-0.72660900	-1.56307800	2.30915300	H	-0.57034900	-0.54032800	2.10545700
O	-0.65376500	-2.98066800	2.60333100	H	-1.22542600	-1.85310700	3.10738600
C	-1.88943000	-3.41197000	3.22107700	O	-0.52880800	-2.43309800	1.23976500
C	-2.80095200	-2.17954800	3.27347000	C	0.83241600	-2.53305500	1.25114400
C	-1.79674900	-1.01967000	3.24536200	C	1.67199400	-1.85563100	2.14261700
H	0.26716000	-1.14719500	2.47030300	C	1.39632400	-3.37597700	0.29127200
H	-1.00439900	-1.42775300	1.25997600	C	3.05123100	-2.01844300	2.04612800
H	-2.30760200	-4.23304800	2.62861400	H	1.26645800	-1.19719800	2.90146300
H	-1.64865700	-3.79131200	4.22076700	C	2.77588000	-3.54533100	0.22847400
H	-3.44086600	-2.13241500	2.38565000	H	0.73781300	-3.87062600	-0.41439900
H	-3.44456600	-2.17786100	4.15773700	C	3.63616500	-2.87265400	1.10486500
H	-2.23916300	-0.09274900	2.87756000	H	3.68734100	-1.44863100	2.71735400
H	-1.36321700	-0.83045000	4.23342200	H	3.17737800	-4.20710000	-0.53091200
O	1.86256600	-3.83593400	-1.59795400	C	5.16771000	-3.00240700	1.05926700

C	5.66847000	-3.49647100	2.43182400	C	-2.85417500	2.83094800	2.26026100
H	6.75772600	-3.61854100	2.43367200	C	-3.53177000	3.10981200	-0.40807100
H	5.39981100	-2.81367100	3.24271800	H	-1.48323800	3.65184600	-0.74202500
H	5.21712300	-4.46829800	2.65496100	C	-4.15561300	2.58583800	1.83226100
C	5.63764800	-4.03220700	0.01051100	H	-2.58290500	2.74482400	3.30821400
H	6.73088500	-4.09066300	0.02118200	C	-4.53128100	2.70838600	0.48300600
H	5.23940700	-5.02865500	0.23315200	H	-3.75365700	3.21681300	-1.46304900
H	5.33186100	-3.75891200	-1.00315900	H	-4.88592600	2.28743800	2.57580900
C	5.74692100	-1.62960100	0.68340500	C	-5.95602000	2.33320900	0.01376800
C	6.63980800	-0.91088900	1.48660800	C	-7.01148500	2.85561900	1.01497600
C	5.35225200	-1.04210000	-0.52314500	H	-6.89349800	2.45536100	2.02354300
C	7.10079500	0.35012600	1.11046100	H	-6.95193400	3.94690000	1.08481300
H	6.97960200	-1.32219800	2.43091000	H	-8.01468000	2.58342200	0.67102700
C	5.82070600	0.20333500	-0.93027000	C	-6.29228700	2.99892700	-1.33444300
H	4.62512100	-1.54879900	-1.14969400	H	-7.30648100	2.72339800	-1.64039100
C	6.68569900	0.91734800	-0.09583100	H	-6.24580800	4.08830300	-1.23563600
H	7.77854300	0.91115800	1.74637200	H	-5.61781500	2.71324900	-2.14409200
H	5.47492300	0.61752700	-1.86720900	C	-6.01326400	0.79363800	-0.08999800
O	7.17387300	2.17767200	-0.36354500	C	-5.80164300	0.11852000	-1.29700400
C	6.71027400	2.87211300	-1.51191500	C	-6.15238100	0.00080300	1.06098200
H	7.32317200	3.77856700	-1.54083200	C	-5.68615200	-1.27386200	-1.36448200
H	6.89031700	2.30229600	-2.43438700	H	-5.68327600	0.67245200	-2.22072800
O	-3.27845900	-0.50371500	2.57694200	C	-6.04245200	-1.38120700	1.01747400
H	-3.15845800	0.44960400	2.43212400	H	-6.30521600	0.46137000	2.02950200
C	5.24659400	3.24981100	-1.43336500	C	-5.78079900	-2.02812800	-0.19368400
C	4.52319000	3.83082500	-2.57414800	H	-5.46889400	-1.74043500	-2.31671400
O	4.32058700	2.46186300	-2.19830900	H	-6.10553000	-1.97287000	1.92398700
H	4.89698700	3.49146600	-0.42894900	O	-5.63008200	-3.39094400	-0.10951400
H	5.04210600	3.96712100	-3.52296000	C	-5.08067500	-4.10730300	-1.20723300
H	3.67275100	4.48152600	-2.38724400	H	-5.13819600	-5.15436100	-0.89476700
H	3.06879500	-0.11659400	-2.38294200	H	-5.68301700	-3.98459800	-2.11811800
N	2.41823000	1.19091800	-0.19288700	O	2.12761500	4.24755500	-0.47281000
H	3.16450600	1.56770900	-0.76771400	H	2.72169000	4.55657100	0.23145100
C	1.90484100	2.13962900	0.76846900	C	-3.64284100	-3.74123300	-1.49791300
H	1.23245800	1.63261200	1.46605000	C	-2.95621100	-4.22636000	-2.70164900
H	2.74792800	2.50762800	1.37218300	O	-3.41086000	-2.86735100	-2.62413100
C	1.19195800	3.34584700	0.13588500	H	-3.03337000	-3.50236700	-0.62596800
H	0.57345100	2.98221700	-0.68784600	H	-3.49263100	-4.84371800	-3.42201400
C	0.34509500	4.15643600	1.12532100	H	-1.87539400	-4.35613500	-2.68161600
H	1.00368300	4.58251700	1.89313800				
H	-0.14494000	4.98574000	0.60181600				
O	-0.61042700	3.38743200	1.85450400				
C	-1.86678700	3.21174700	1.34129100				
C	-2.21851900	3.36460300	-0.00021500				