Electronic Supplementary Material (ESI) for CrystEngComm.

X-ray diffraction and computational studies of the pressure-dependent diphenylanthracene-tetrachloroethane solvation

ELECTRONIC SUPPLEMENTARY INFORMATION

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Contents

Experimental

Raman spectra

A single crystal of DPA grown from 1,1,2,2-tetrachloroethane was loaded in the DAC using a 4:1 MeOH/EtOH solution as pressure transmitting medium. Raman spectra were collected at 0.03 GPa intervals up to 3.0 GPa using a Horiba Jobin Yvon HR800 UV Micro-Raman spectrometer equipped with an air-cooled 325 mW 785 nm diode laser. This particular laser was chosen in order to minimise the otherwise considerable fluorescence signal from the sample. Raman spectra were collected in the 150-1800 cm-1 range with a spectral resolution of ca. 2.2 cm−1 using a grating of 600 grooves/mm and a Peltier-cooled CCD detector (Andor, 1024 × 256 pixels). No phase transition was observed up to 3.0 GPa.

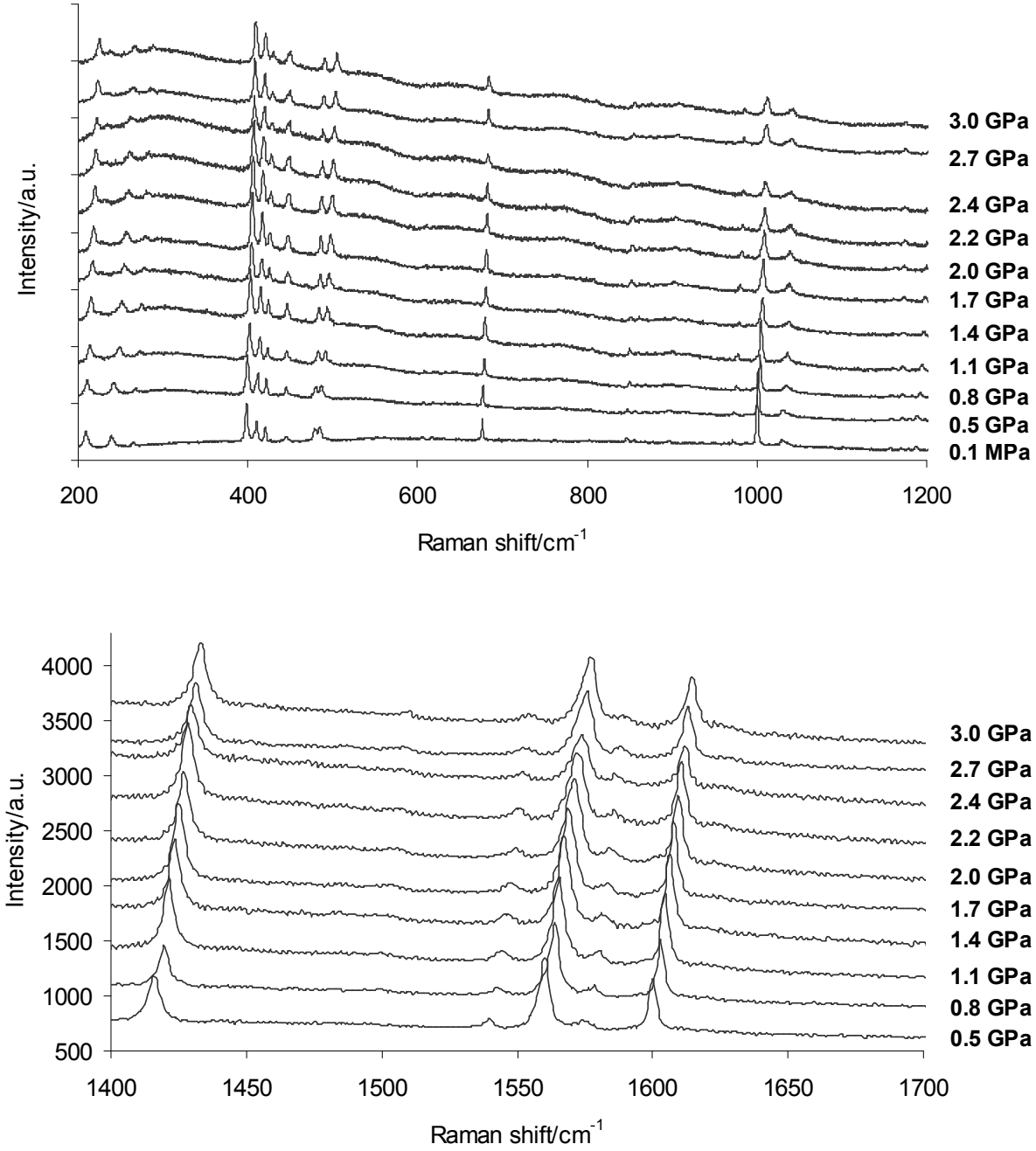


Fig. S1. Selected wavenumber regions of Raman spectra of DPA at ambient temperature contained in a DAC and compressed to 3.0 GPa using a 4:1 MeOH/EtOH solution as pressure transmitting medium. The region around the first-order peak of diamond at *ca.* 1330 cm^{-1} is not shown.

GRADE-restraints

Please refer to grade-XXX_dpa.dfix and grade-XXX_solvent.dfix files

CheckCIF reports

Please note that responses to CheckCIF alerts are embedded in the respective CIF files under _refine_special_details.

checkCIF/PLATON report (basic structural check)

No syntax errors found. CIF dictionary

Please wait while processing .... Interpreting this report

Datablock: diphenylanthracene_TTCE_solvate_0p5_GPa

Bond precision: C-C = 0.0136 A Wavelength=0.71073

Cell: a=8.7874(3) b=12.0308(7) c=13.8215(8)
alpha=90 beta=104.964(3) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1411.65(13)	1411.65(13)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C26 H18, 2(C2 H2 Cl4)	C26 H18, 2(C2 H2 Cl4)
Sum formula	C30 H22 Cl8	C30 H22 Cl8
Mr	666.08	666.07
Dx,g cm-3	1.567	1.567
Z	2	2
Mu (mm-1)	0.819	0.819
F000	676.0	676.0
F000'	678.54	
h,k,lmax	7,10,11	7,9,11
Nref	862	650
Tmin,Tmax	0.921,0.937	0.745,0.862
Tmin'	0.921	

Correction method= # Reported T Limits: Tmin=0.745
Tmax=0.862 AbsCorr = MULTI-SCAN

Data completeness= 0.754 Theta(max)= 17.284

R(reflections)= 0.0515(504) wR2(reflections)= 0.1314(650)

S = 1.062 Npar= 172

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

REFNR01 ALERT 3 A Ratio of reflections to parameters is < 6 for a centrosymmetric structure
sine(theta)/lambda 0.4180
Proportion of unique data used 1.0000
Ratio reflections to parameters 3.7791

THETM01 ALERT 3 A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4180

PLAT029 ALERT 3 A _diffrn_measured_fraction_theta_full Low ..... 0.754 Note

PLAT088 ALERT 3 A Poor Data / Parameter Ratio ..... 5.01 Note

Alert level B

PLAT340 ALERT 3 B Low Bond Precision on C-C Bonds ..... 0.01362 Ang.

Alert level C

PLAT244 ALERT 4 C Low 'Solvent' Ueq as Compared to Neighbors of C1CL Check

Alert level G

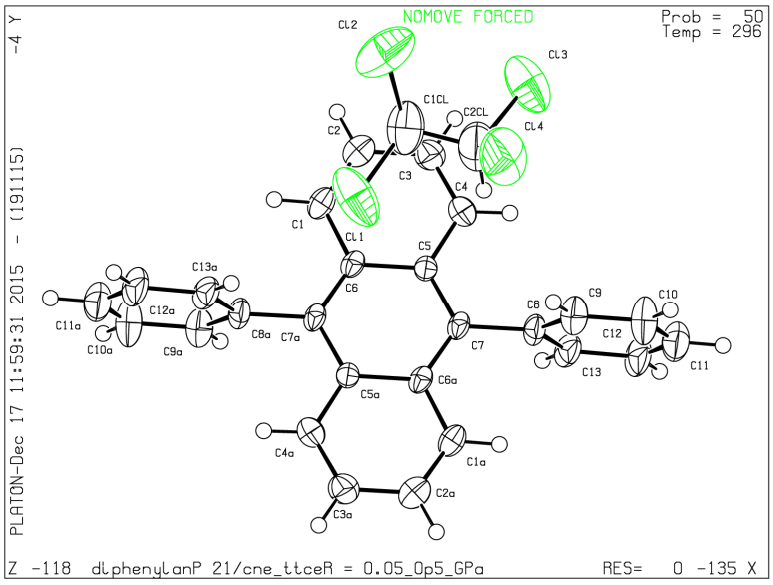
PLAT002 ALERT 2 G	Number of Distance or Angle Restraints on AtSite	19 Note
PLAT003 ALERT 2 G	Number of Uiso or Uij Restrained non-H Atoms ...	19 Report
PLAT083 ALERT 2 G	SHELXL Second Parameter in WGHT Unusually Large	6.55 Why ?
PLAT720 ALERT 4 G	Number of Unusual/Non-Standard Labels	4 Note
PLAT860 ALERT 3 G	Number of Least-Squares Restraints	172 Note

4 **ALERT level A** = Most likely a serious problem - resolve or explain
1 **ALERT level B** = A potentially serious problem, consider carefully
1 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
5 **ALERT level G** = General information/check it is not something unexpected

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
3 ALERT type 2 Indicator that the structure model may be wrong or deficient
6 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

PLATON version of 19/11/2015; check.def file version of 17/11/2015

Datablock diphenylanthracene_TTCE_solvate_0p5_GPa - ellipsoid plot



Datablock: diphenylanthracene_0p5_GPa

Bond precision: C-C = 0.0031 A Wavelength=0.71073

Cell: a=10.4702(9) b=13.3923(10) c=12.0158(11)
alpha=90 beta=89.931(8) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1684.9(2)	1684.9(2)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C26 H18	C26 H18
Sum formula	C26 H18	C26 H18
Mr	330.40	330.40
Dx,g cm-3	1.303	1.303
Z	4	4
Mu (mm-1)	0.074	0.074
F000	696.0	696.0
F000'	696.26	
h,k,lmax	12,16,14	11,15,12
Nref	1553	937
Tmin,Tmax	0.987,0.994	0.794,0.884
Tmin'	0.985	

Correction method= # Reported T Limits: Tmin=0.794
Tmax=0.884 AbsCorr = MULTI-SCAN

Data completeness= 0.603 Theta(max)= 25.337

R(reflections)= 0.0365(765) wR2(reflections)= 0.0954(937)

S = 1.101 Npar= 119

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT029 ALERT 3 A _diffrn_measured_fraction_theta_full Low ..... 0.607 Note

Alert level C

PLAT157 ALERT 4 C Non-standard Monoclinic Beta Angle less 90 Deg 89.93 Degree

Alert level G

PLAT002 ALERT 2 G Number of Distance or Angle Restraints on AtSite 13 Note
PLAT003 ALERT 2 G Number of Uiso or Uij Restrained non-H Atoms ... 13 Report
PLAT158 ALERT 4 G The Input Unitcell is NOT Standard/Reduced ..... Please Check
PLAT860 ALERT 3 G Number of Least-Squares Restraints ..... 128 Note
PLAT952 ALERT 5 G Calculated (ThMax) and CIF-Reported Lmax Differ 2 Units

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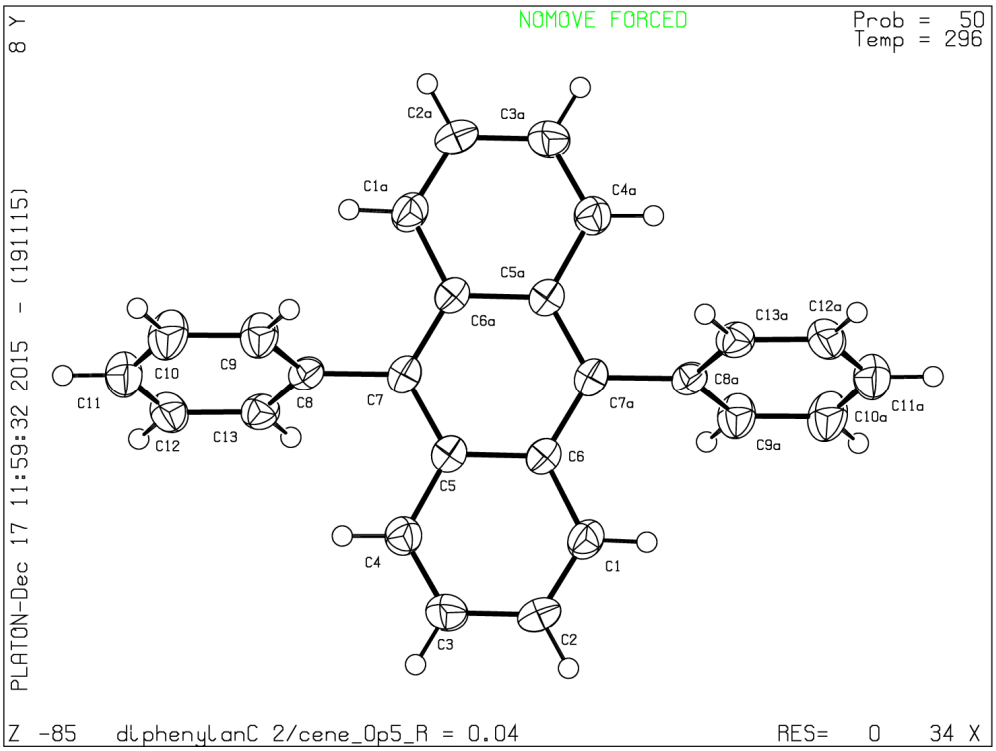
2 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

Datablock diphenylanthracene_0p5_GPa - ellipsoid plot



Datablock: diphenylanthracene_3_GPa

Bond precision: C-C = 0.0089 A Wavelength=0.71073

Cell: a=10.041(2) b=13.150(2) c=11.378(2)
alpha=90 beta=88.483(17) gamma=90

Temperature: 296 K

	Calculated	Reported
Volume	1501.8(5)	1501.8(5)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C26 H18	C26 H18
Sum formula	C26 H18	C26 H18
Mr	330.40	330.40
Dx,g cm-3	1.461	1.461
Z	4	4
Mu (mm-1)	0.083	0.083
F000	696.0	696.0
F000'	696.26	
h,k,lmax	9,12,10	8,12,10
Nref	687	422
Tmin,Tmax	0.985,0.993	0.525,0.884
Tmin'	0.984	

Correction method= # Reported T Limits: Tmin=0.525 Tmax=0.884 AbsCorr = MULTI-SCAN

Data completeness= 0.614 Theta(max)= 19.779

R(reflections)= 0.0528(308) wR2(reflections)= 0.1475(422)

S = 1.058 Npar= 119

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

REFNR01 ALERT 3 A Ratio of reflections to parameters is < 6 for a centrosymmetric structure
sine(theta)/lambda 0.4761
Proportion of unique data used 1.0000
Ratio reflections to parameters 3.5462
THETM01 ALERT 3 A The value of sine(theta_max)/wavelength is less than 0.550
Calculated sin(theta_max)/wavelength = 0.4761
PLAT029 ALERT 3 A _diffrn_measured_fraction_theta_full Low ..... 0.614 Note
PLAT088 ALERT 3 A Poor Data / Parameter Ratio ..... 5.77 Note

Alert level C

PLAT031 ALERT 4 C Refined Extinction Parameter within Range ..... 2.750 Sigma
PLAT157 ALERT 4 C Non-standard Monoclinic Beta Angle less 90 Deg 88.48 Degree
PLAT340 ALERT 3 C Low Bond Precision on C-C Bonds ..... 0.00887 Ang.

Alert level G

PLAT002 ALERT 2 G Number of Distance or Angle Restraints on AtSite 13 Note
PLAT003 ALERT 2 G Number of Uiso or Uij Restrained non-H Atoms ... 13 Report
PLAT072 ALERT 2 G SHELXL First Parameter in WGHT Unusually Large 0.11 Report
PLAT158 ALERT 4 G The Input Unitcell is NOT Standard/Reduced ..... Please Check
PLAT432 ALERT 2 G Short Inter X...Y Contact C12 .. C12 .. 3.16 Ang.
PLAT860 ALERT 3 G Number of Least-Squares Restraints ..... 128 Note

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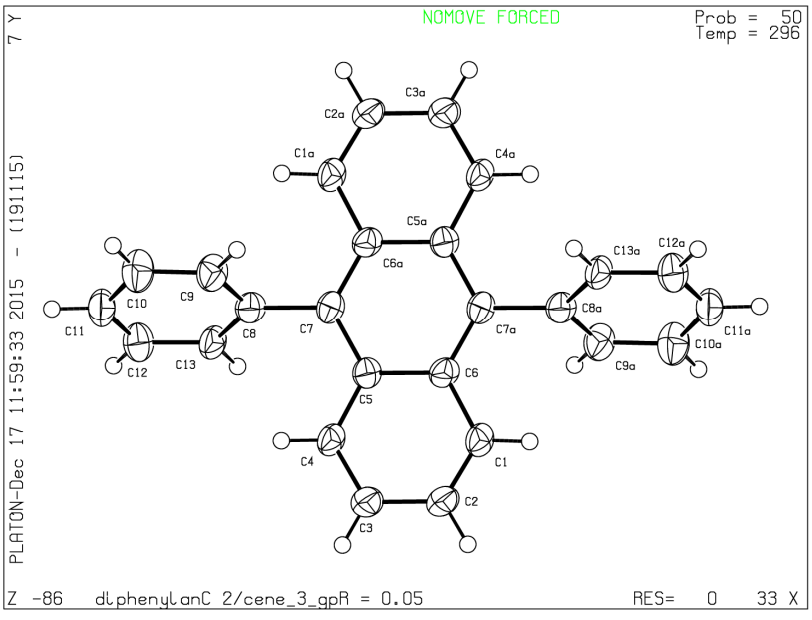
Datablock diphenylanthracene_3_GPa - ellipsoid plot



Structural and energetic features

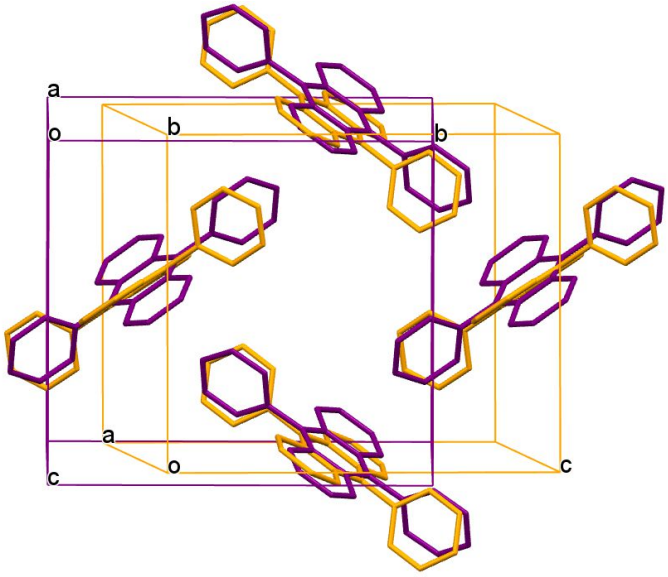


Fig. S2. Overlay of (100) molecular layers in DPA (purple) and DPA-S (orange). H-atoms and solvent molecules have been omitted for clarity. The arrangement of the molecules in the (100) plane of DPA-S is similarly present in the first (100) layer of the structure of DPA. DPA and DPA-S have in fact almost identical *b* and *c* axes, but a different orientation of the cell (the axes are swapped in the two structures, see Table 1 in the main manuscript). The widening of the β angle in DPA-S (formerly γ= 90° in DPA) together with the length reduction of the *a*-axis prevent the formation of the second layer of DPA molecules, which is replaced by solvent molecules.

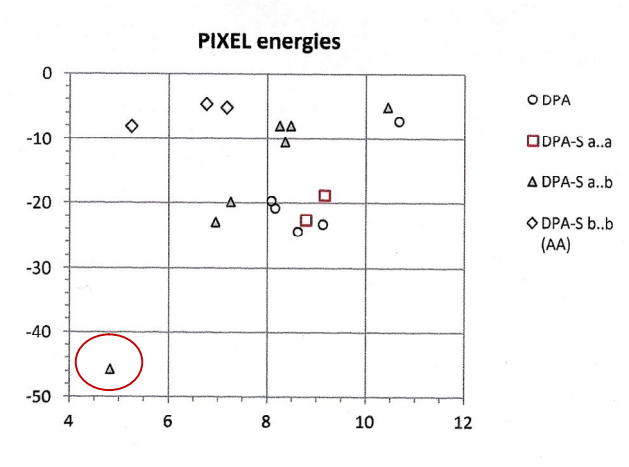


Fig. S3 Molecule-molecule pair energies in kJ mol^{-1} as a function of distance between centres of mass in Å. Circles: DPA-DPA in the unsolvated crystal; red squares, *id.* in the solvate; triangles DPA-solvent interactions; diamonds, solvent-solvent interactions. The red circle highlights the dominating solute-solvent interaction.

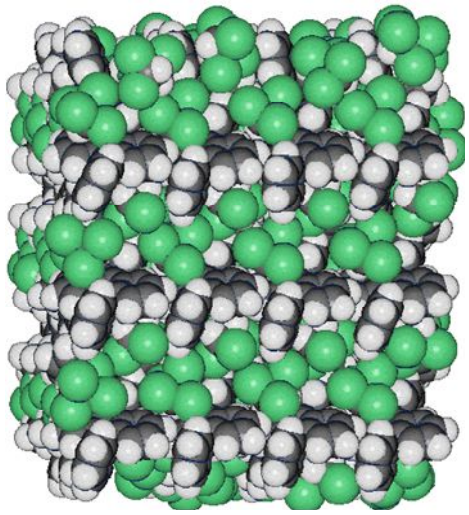


Fig. S4 The final frame of a Monte Carlo simulation without periodic boundary conditions, *i.e.* with surfaces exposed, at room pressure. No solvent molecule is seen detaching from the crystal slab.