Supporting Information

Delamination of graphite oxide in a liquid upon cooling

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1. X-ray diffraction data for H-GO in acetonitrile.

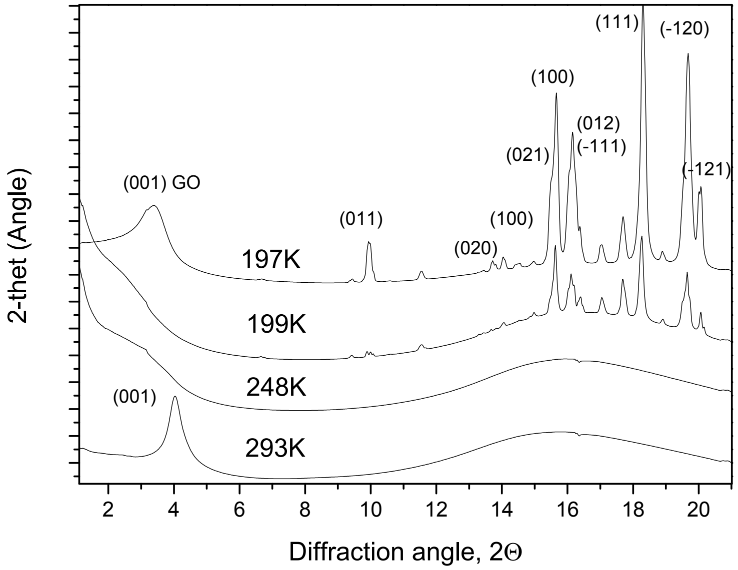


Figure 1S. Selected diffraction patterns recorded from HGO/acetonitrile sample during cooling run. Graphite oxide shows only (001) reflection in the give angle range. The broad peak centered approximately around 16 degrees is due to liquid acetonitrile. When acetonitrile freezes, this broad peak is replaced by sharp peaks from solid acetonitrile, the freezing is completed at 197K. Strongest peaks of solid acetonitrile (α-phase[1]) are indexed on 197K pattern. Note that acetonitrile solidified with relatively large crystal size which results in appearance of spots on 2D images, not diffraction rings.

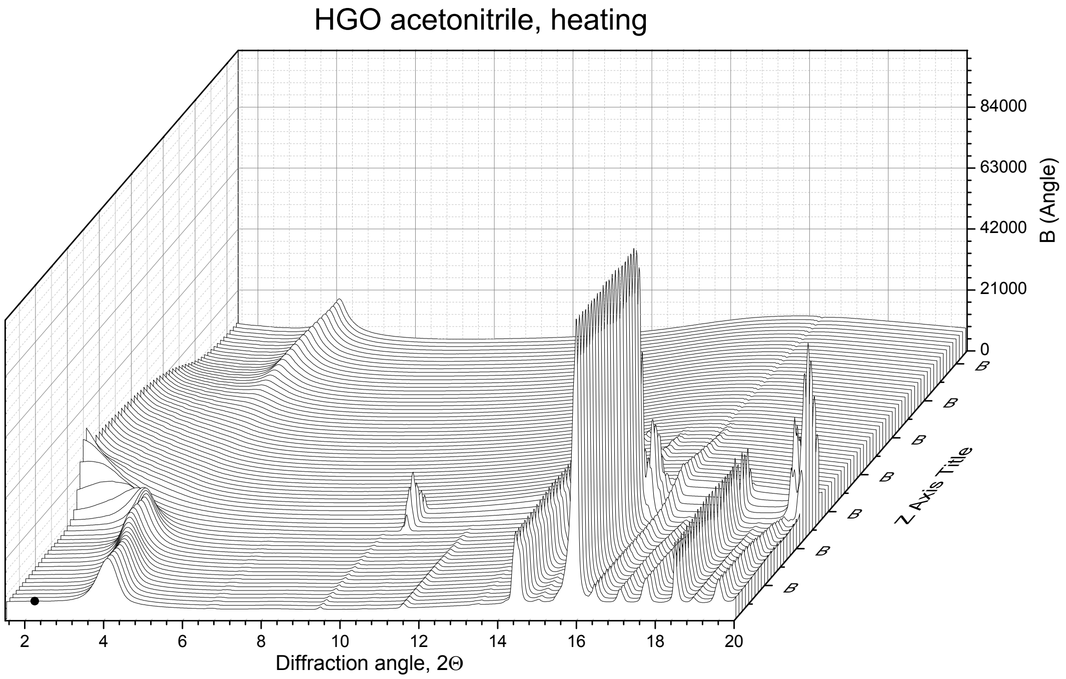


Figure 2S Integrated XRD patterns recorded from GO/acetonitrile sample upon heating from 170K to 290K. Solid acetonitrile (β-phase) undergoes phase transition into α-phase at around 200K. Complete melting of acetonitrile was observed at 221K which can be detected by disappearance of sharp peaks from solid acetonitrile which are replaced by broad diffraction peak of liquid acetonitrile. Note that delamination starts above 200K when bulk acetonitrile is still in solid state.

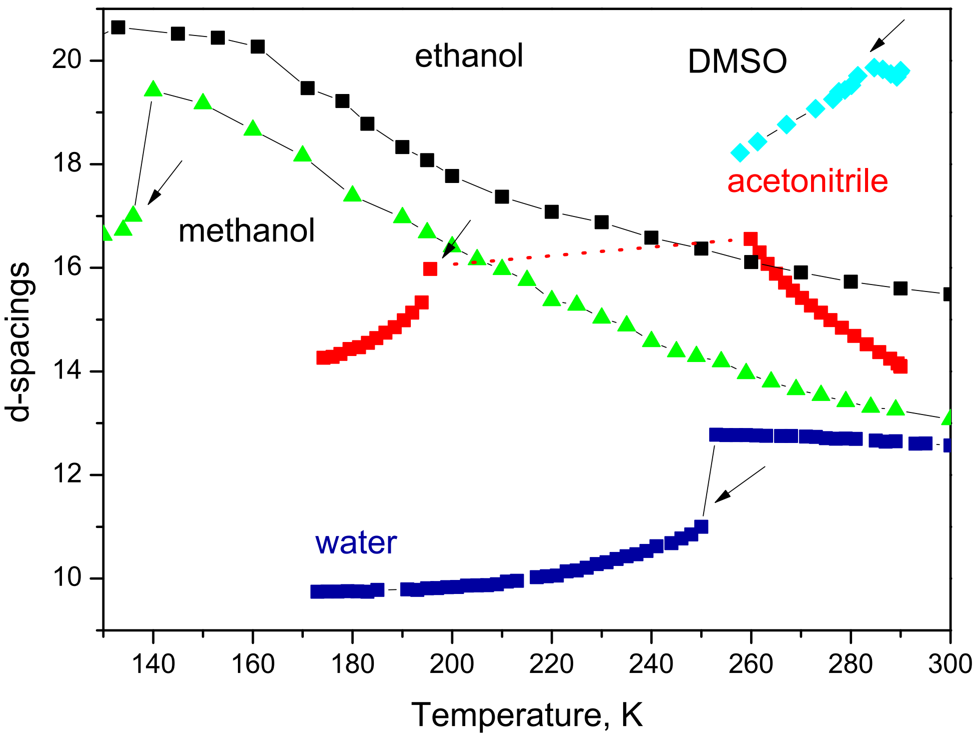


Figure 3S. Temperature dependence of d(001) recorded upon cooling H-GO in several solvents: methanol, ethanol,[2] water,[3] dimethyl sulfoxide (DMSO) as compared with acetonitrile. Temperature points of solvent freezing detected by appearance of diffraction peaks from solid solvents are shown by arrows. Formation of gel-like phase characterized by disappearance of (001) reflection is observed only for HGO/acetonitrile system. Note that inter-layer distance of GO expands even stronger in alcohols but anyway the packing of layers and (001) reflection preserves.[2]

2. X-ray diffraction data for Brodie Graphite oxide immersed in excess of acetonitrile under cooling – heating cycle.

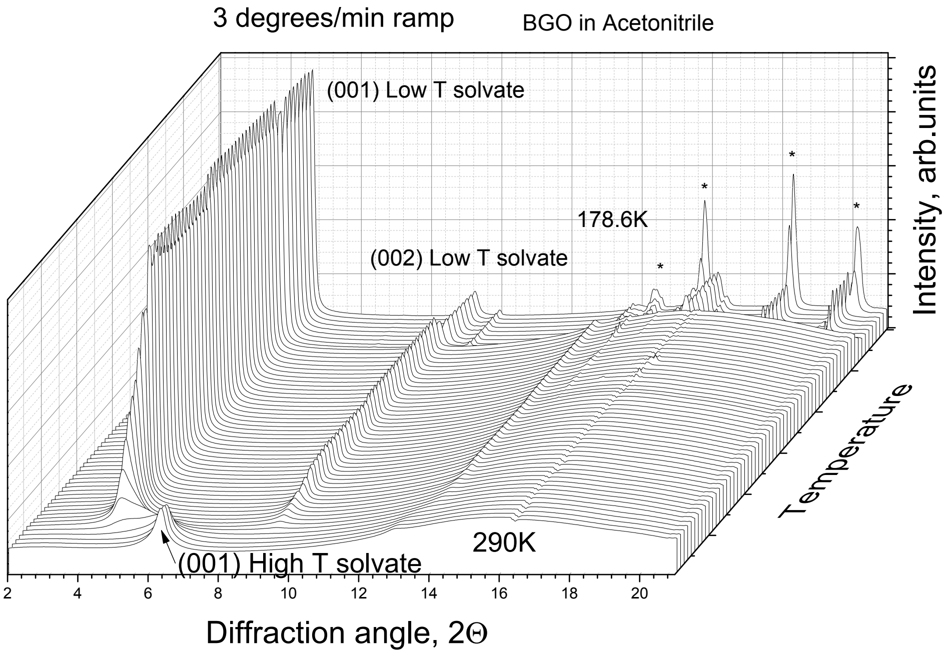


Figure 4S. XRD patterns recorded from BGO/acetonitrile sample upon cooling with 3degree/min ramp. Peaks of High T solvates are replaced by peaks from Low T solvate. Acetonitrile freezing (strongest peaks from solid acetonitrile are marked by stars) do not result in significant changes of BGO structure.

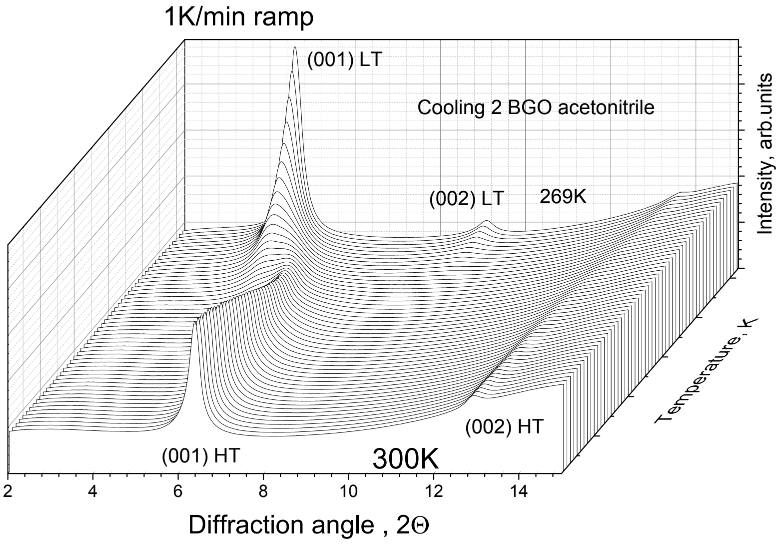


Figure 5S. Second cooling cycle recorded with lower ramp of 1degree/min in the temperature region of phase transition. Peaks from Low Temperature (LT) solvate phase and High Temperature (HT) solvate are indexed.

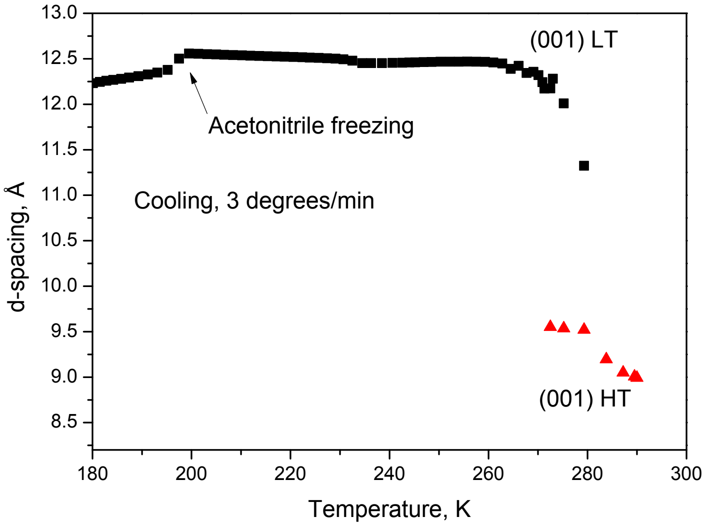


Figure 6S. B-GO (001) peak position as a function of temperature (cooling) for patterns shown in Figure 2S. The phase transition corresponding to insertion of acetonitrile layer results in lattice expansion by ~3.5Å. peaks from both LT and HT solvates are observed in transitional temperature region 279-272K.

3. Details of SFM measurements.

For spin casting, a droplet of GO suspension (3 mg/ml) in acetonitrile (Riedel-de Haen, Chromosolv grade) was deposited onto the surface of mica for 30 seconds and then spun off. For drop casting, a droplet of GO suspension in acetonitrile was dried on the mica surface. Acetonitrile droplet required at least 3 minutes to dry. For cold deposition, the surface temperature of mica was stabilized at the desired value under the flow of nitrogen gas bubbling through liquid nitrogen. The temperature was controlled by the flow rate of nitrogen and measured by a resistance temperature sensor PT100 located just above the surface. The temperature sensor calibration was verified on 1) mixture of crashed water ice with liquid water and 2) boiling water to be within 0.2% of the standard values. The water source was Protegra CS Systems CEDI Technology R > 10 MΩ·cm. The provided temperature error bar covers the drift of the temperature during the GO deposition. GO flakes larger than roughly 20 micrometers were detected in an optical microscope and imaged with SFM.

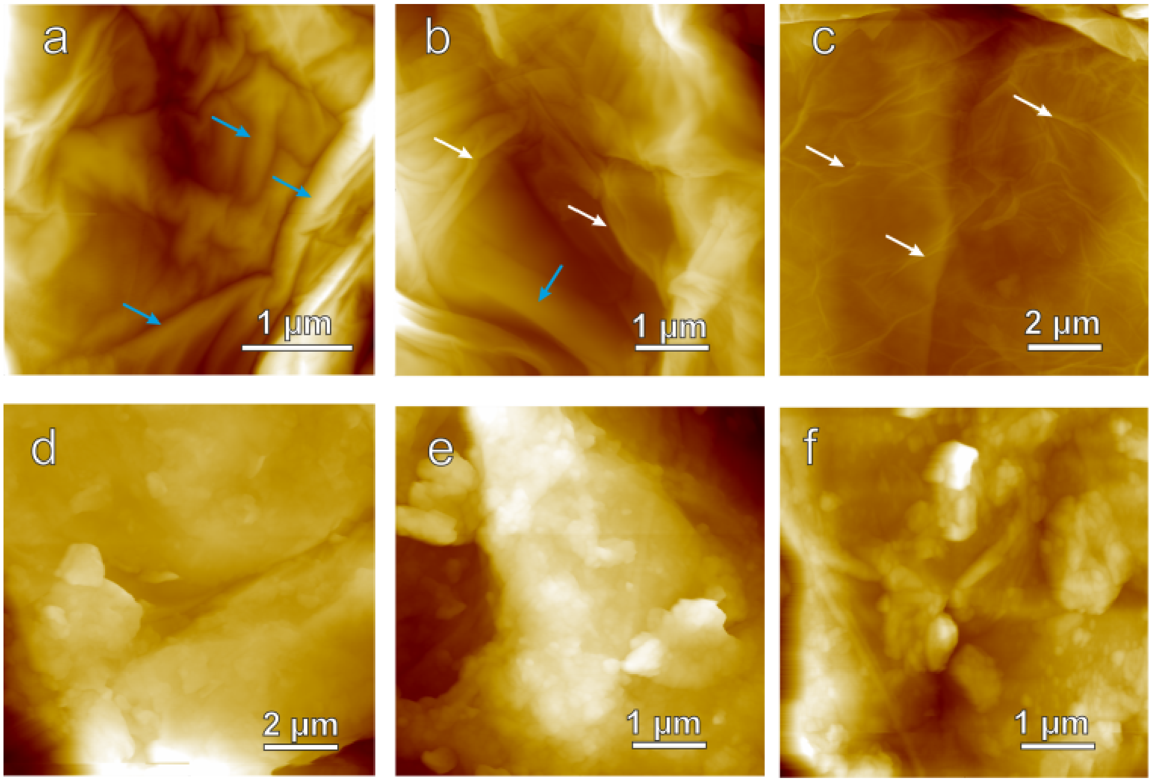


Figure 7S SMF topography images of H-GO flakes deposited onto a solid substrate at 240K±2 K (a,b,c) and at room temperature (297±2 K) (d,e,f). The figure provided here with larger size is identical to Figure 4 in the main text of paper.

4. Schematic model of suggested conformational transition.

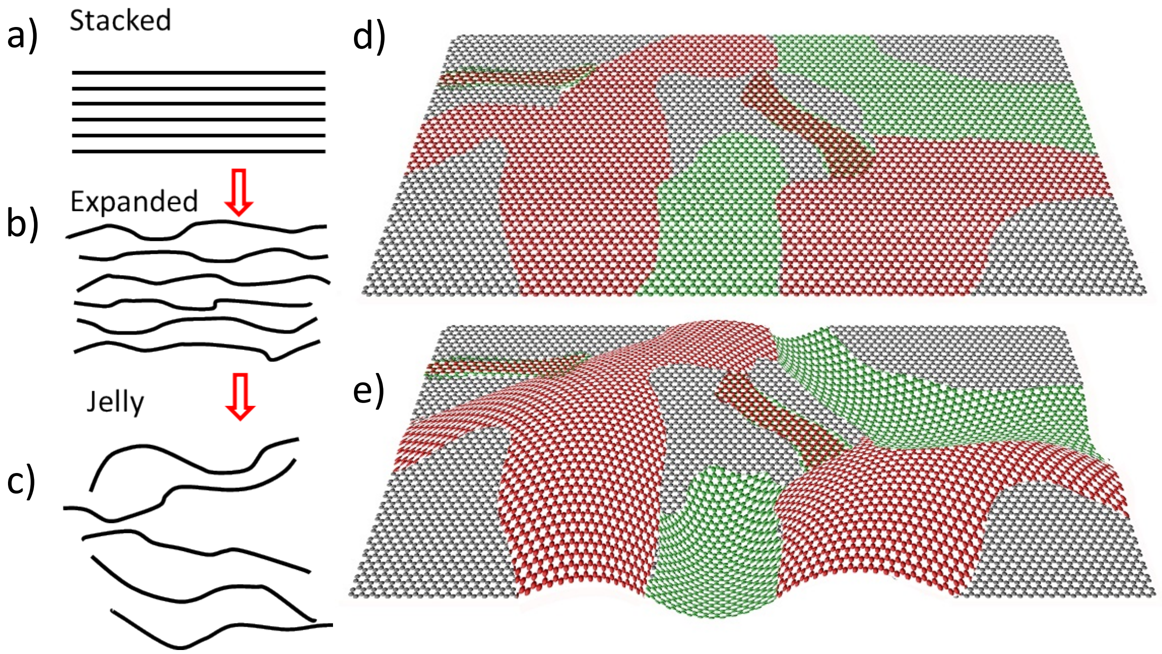


Figure 8S. Schematic sequence of GO multilayer packing along c - direction at a) ambient temperature (approximately parallel), b) slight buckling of layers results in averaged increase of inter-layer distance, c) increased curvature of sheets results in loss of crystalline packing and formation of jelly phase. d) Schematic image of inhomogeneously oxidized graphene sheet: red areas represent oxidized top surface of graphene, green areas – oxidized bottom surface and color free areas- not oxidized areas, e) the same graphene sheet at low temperature with curvature induced by interaction of GO with acetonitrile.

5. Details of isopiestic and DSC experiments.

Materials.

H-GO (C/O = 2.84, M≈18) was purchased from ACS Material. B-GO (C/O = 2.63) was prepared according to the procedure described in ref.1. Detailed characterization of these materials was given elsewhere. Samples of H-GO and B-GO were additionally dried in the desiccators with P_2O_5 for 3-7 days. Typically 10-15 wt% of the initial samples were removed by drying.

Methods.

Isopiestic measurements (IM) were performed in dried desiccators. Equilibration of GO with CH3CN (AN) vapor persisted until mass of GO saturated with AN became constant (5-10 days).

DSC-30 TA from Mettler was used to capture the heating/cooling traces from 173 to 323K. The quantitative measurements rely on heating traces with the scanning rate 5K/min.

Sorption measurements.

Mass of sorbed AN was determined at T=298 K and T =229K (melting temperature of AN) by IM and DSC, respectively.

In IM the sorption, M(AN,sorbed)/M(GO), is obtained directly as a result of weighting of the sample, saturated with AN.

DSC procedure was as follows. Weighted amounts of AN + GO mixtures were sealed in DSC pans. Several samples with the mass ration of AN to GO from 0.9 to 1.5 were scanned. The typical DSC traces are presented in Fig.1. The endotherm at T= 229K corresponds to melting of bulk AN which was not incorporated into GO. This endotherm was used to determine mass of sorbed AN, M (AN,sorbed). It was calculated as a difference

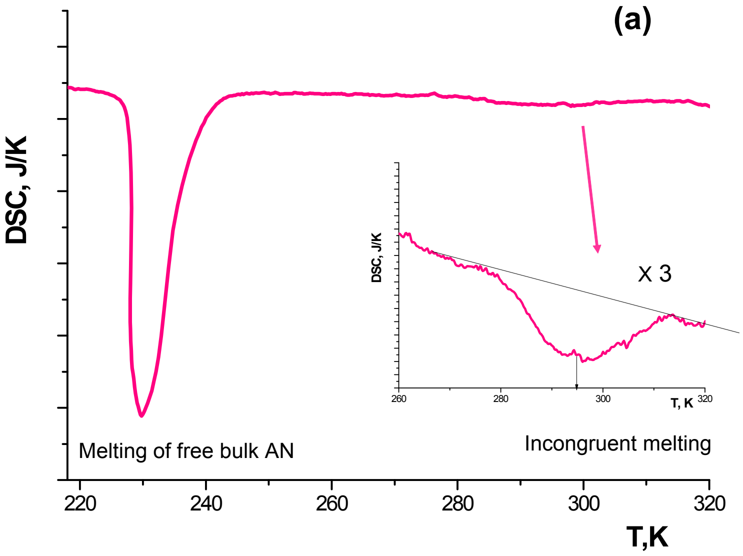
$$M(AN,sorbed) = M(AN,tot) - M(AN,melt)$$

where M (AN,tot), M(AN,melt) are total mass of AN in the sample determined by weighting and mass of free AN calculated from endothermic heat measured at T= 229K , respectively. The sorption, M(AN,sorbed)/M(GO), was the same for the samples with different initial ratio of AN to GO. When this ratio was below or equal to the saturated ratio M(AN,sorbed)/M(GO), the peak at T= 229K disappeared from the trace since all amount of AN in the initial sample was sorbed. The solvent, incorporated into GO did not take part in melting/freezing process.

The results of sorption measurements are given in the Table 1 (see main text).

<u>Additional feature in the DSC trace of B-GO-AN.</u>

The second broad endothermic feature (see inset in Fig. 1a) was attributed to partial de-sorption of AN from B-GO. The temperature of the peak maximum was almost equal to the temperature of abrupt change in the inter-layer distance detected by XRD. No such DSC peak was found for H-GO-AN.



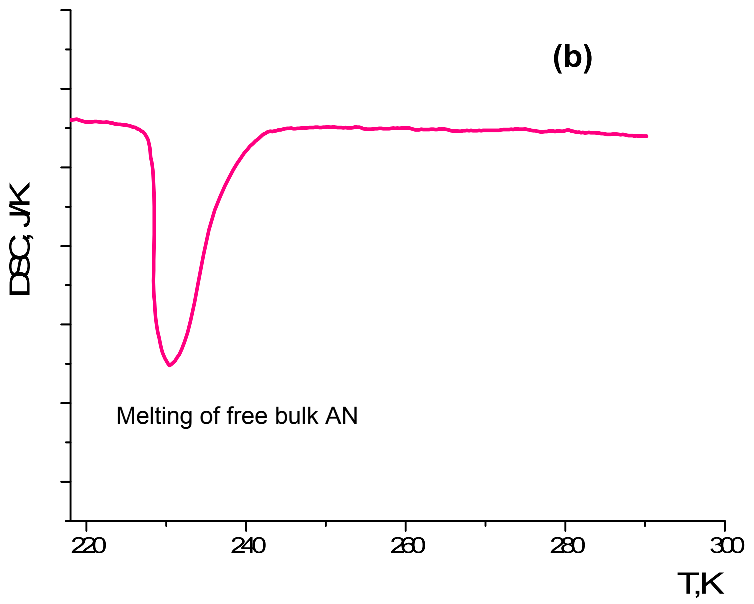


Figure 8S 1. DSC traces in GO-AN systems. (a) B-GO (11.1 mg) – AN (16.6 mg), Inset: endotherm of incongruent melting, the scale is three times more sensitive. (b) B-GO (12.6 mg) – AN (16.0 mg).

Peak of phase transition between two AN solid phases (T=216 K) is not shown.

Temperature dependence of sorbtion from XRD and DSC.

As it is seen from Table 1 (see main text) the sorption of AN by GO is a temperature-dependent value. Let us consider GO saturated with AN as a routine bulk phase, type of solid solution/solid solvate of GO with AN. Both in XRD and DSC experiment this phase is in equilibrium with the liquid AN. The saturated GO in the system H-GO – AN behaves like a sold solution with negative partial enthalpy of mixing (sorption). At temperatures above T_m the sorption goes down gradually with the increase of temperature. B-GO – AN saturated phase demonstrates another type of behavior. It resembles a solid solvate with the fixed composition, which melts incongruently, forming another solid solvate with less amount of AN included. According to the data, presented in Table 1 (see main text), the incongruent melting may be described as

$$\left(B-GO\right)AN_{0.23}=\left(B-GO\right)AN_{0.11}+\ 0.12\,AN \qquad (1)$$

Molar mass of B-GO was calculated according to elemental composition $CO_{0.38}H_{0.12}$.

In Table 1 the characteristics of incongruent melting are compared with those, obtained earlier for the system B-GO – methanol. As it is seen from Table 1 similar results were obtained for both systems.

It is worth noting that with both methanol and acetonitrile the H-GO saturated phase behaves like a solid solution.

Phase reaction	T_{im}	ΔH_{im}, J/g B-GO	ΔH_{av}, kJ/mol	Δd, A
$\left(B-GO\right)AN_{0.23}=\left(B-GO\right)AN_{0.11}+\ 0.12\,AN$	294±3	9±3	1.4	3.5
$\left(B-GO\right)Met_{0.32}=\left(B-GO\right)Met_{0.16}+\ 0.16\,Met$ 1	285	11.5	1.3	3.3

Table S1. Incongruent melting of B-GO solvates with acetonitrile and methanol.[4]

The averaged enthalpy of sorption was calculated according to the formula

$$\Delta H_{av}=\frac{\Delta H_{im}\times M_{B-GO}}{n},$$

were n = 0.16 and 0.12 for methanol and AN, respectively. The calculated ΔH_{av} are ~10 times under the similar values calculated earlier for the solid solvates of fullerenes.[5]

The amount of solvent sorbed.

Roughly half of sorbed AN is de-sorbed from B-GO at T_{im}= 294±3 K according to phase reaction (1). If two layered arrangement of solvent molecules inside B-GO is assumed, the incongruent melting means removing of one layer. This one layer then consists of $6.6*10^{-3}$ moles of AN per gram of B-GO or of $4.7*10^{14}$ molecule of AN per sm^2 of ideal graphene plane.

References.

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3. Talyzin, A. V.; Hausmaninger, T.; You, S. J.; Szabo, T. *Nanoscale* **2014,** 6, (1), 272-281.
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