Supporting Information to the manuscript “Glass-Like Behavior of Intercalated Organic Solvent in Graphite Oxide Detected by Spin-Probe EPR”

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Figure S1. CW EPR spectra for TEMPO in the B-GO (A) and B-GO - acetonitrile (B) samples at different temperatures. The GO native signal was clipped. Spectra are shifted upward for clarity.

Figure S2. CW EPR spectra for TEMPO in the B-GO with acetonitrile at 324 K (A) and 341 K (B), red curves, and simulated spectra for the probes in solid-like and liquid-like acetonitrile (blue and pink curves, correspondently), and the sum spectrum (black dashed curve). The GO native signal was clipped.
In neutron scattering experiments, the temperature of the dynamical transition ($T_d$) is defined as the temperature at which the atoms mean square displacement (msd) deviates from a linear dependence.

The same enhancement of dynamical librations can be determined from the $\Delta B$ splitting in CW EPR spectra as follows:

(i) Since msd is linear on the angular amplitude of dynamical motion, the averaged $\alpha_d^2$ was calculated from the $\Delta B$ as:

$$\Delta B = 2 A_{zz} = 2(A_{zz} - (A_{zz} - A_{yy}) < \alpha_d^2 >),$$

(ii) Then, the low-temperature and high-temperature diapasons were determined as ranges in which the averaged square of angular amplitude of the dynamical motion ($\alpha_d^2$) is linear;

(iii) Then, the $\alpha_d^2$ was fitted by linear dependence in both temperature ranges;

(iv) The $T_d$ was defined as the temperature at which the fitted lines crossover;

(v) The uncertainty in $T_d$ estimation was determined by varying both the low- and high-temperature diapasons within 5-15 K;

The $T_d$ evaluation for sample without and with acetonitrile sample is given in Figure S3.

Figure S3. The averaged square of angular amplitude of dynamical motion ($\alpha_d^2$) for TEMPO in the B-GO without (A) and with acetonitrile (B) at low-temperature range (blue circles) and high-temperature range (red circles). The data in the intermediate range are shown by grey circles. Linear fits in both temperature ranges are shown by dashed lines, the intersect of these lines defines the $T_d$, shown by arrows.
SI 2. ED EPR spectra

In some measurements, the $B_0$ field gradient was insufficient to suppress the free induction decay from the native GO, which manifested as small oscillations to the right of the narrow GO line (marked in Figure S4 by the arrow). These oscillations were observed only for a few measurements and had no significant effect on further data analysis.

![Figure S4. ED EPR spectra for TEMPO in B-GO at different temperatures and $\tau$ delays. Dashed curves show the ED EPR spectra at $\tau=120$ ns, the GO native signal was clipped.](image)

S4
Figure S5. ED EPR spectra for TEMPO in B-GO - acetonitrile sample at different temperatures and τ delays, the GO native signal was clipped. Dashed curves show the ED EPR spectra at τ=120 ns.
Figure S6. ED EPR spectra for TEMPO in B-GO without and with acetonitrile at 75 K, \( \tau=120 \text{ ns} \), the GO native signal was not clipped.

In addition, the non-zero relaxation rate in both samples under study at the absence of molecular motions - 75 and 100 K (Figures S4, S5) should be noted. Relaxation in the frozen state is caused by dipole-dipole interaction due to instantaneous diffusion mechanism, and comes to 22-30 and 15-27 kHz for vacuumed B-GO and B-GO with acetonitrile, correspondently. The difference is due to slightly different nitroxide concentrations in the samples, and difference in the GO inter-plane distance, which increases when graphite oxide is swelled by acetonitrile. The received values are close to the estimated values of the echo decay rate of 32 kHz for a case of uniform distribution of spin probes on the surface of B-GO planes. Therefore, we can conclude that the spin probes are isolated molecules on the B-GO surface or inside intercalated acetonitrile.
SI 3. Longitudinal relaxation times for nitroxides in B-GO samples

Longitudinal relaxation time $T_1$ was measured by the inversion-recovery (IR) pulse sequence $2t_{\text{pulse}} - T - t_{\text{pulse}} - \tau - 2t_{\text{pulse}} - \tau - \text{echo}$, with $t_{\text{pulse}} = 16$ ns, the time delay $\tau$ was fixed at 120 ns and the time delay $T$ was scanned from 500 ns. The measurements were performed at the low-field EPR line for the nitroxide. The microwave power was adjusted to maximize electron spin echo signal intensity.

The IR decays were normalized to be varied from -1 to 1, and fitted by the stretched exponential (SE) function $\text{SE}(T) = 1 - 2 \times \exp(-T/T_1)\beta$, where $T_1$ is the longitudinal relaxation time, and $\beta$ is the stretching parameter were extracted as fit parameters.

The IR decays and their fitting are given in Figure S7 and show that the stretching parameter $\beta$ is almost the same in both samples. The $T_1$ time differs in the vacuumed sample and sample containing acetonitrile. It can be explained by a change in the local environment of the spin probe in B-GO with acetonitrile, which alters the coupling to the matrix and varies the longitudinal relaxation time. However, for both samples at all tested temperatures, the $T_1$ time is much longer than the $\tau$ delay in the detection sequence, indicating that the longitudinal relaxation mechanism is not responsible for the observed ED EPR line shape evolving in Figures S3 and S4.

![Figure S7. Inversion-recovery decays for nitroxides in B-GO, and B-GO - acetonitrile samples at different temperatures (grey circles) and its exponential fits (red curves). Fit parameters are given in corresponding plots.](image-url)