Supporting Information
New Insights to Solubility of Graphene Oxide in Water and Alcohols

Vadim V. Neklyudov [a], Nail R. Khafizov [a], Igor A. Sedov [b], Ayrat M. Dimiev [a]*

[a] Laboratory for Advanced Carbon Nanomaterials, Kazan Federal University, 18 Kremlevskaya str., 420008, Russian Federation
[b] Department of Physical Chemistry, Kazan Federal University, 18 Kremlevskaya str., 420008, Russian Federation

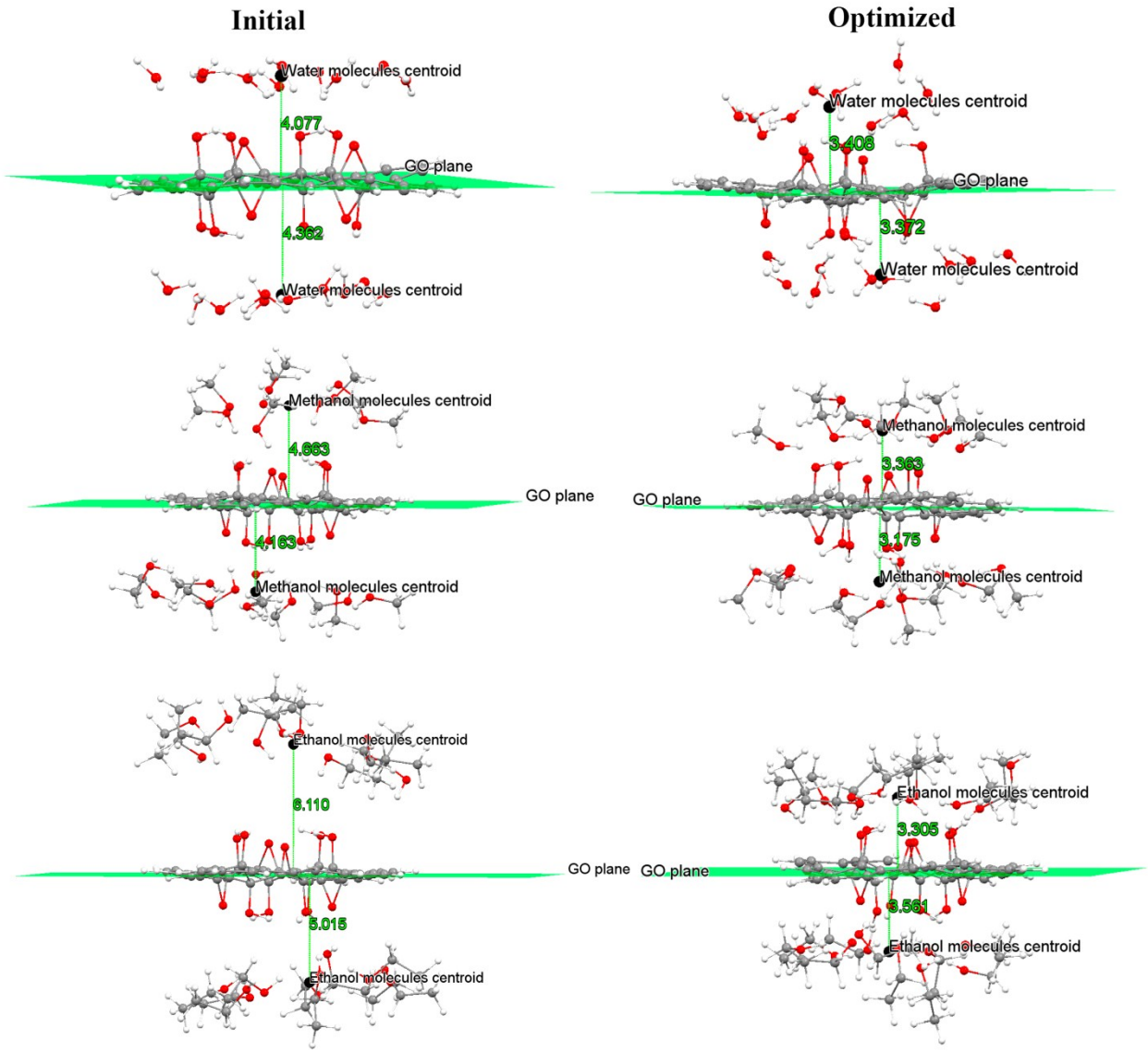

Figure S1. Initial (left) and optimized (right) GO-20H_2O, GO-20MeOH and GO-20EtOH structures. The optimization was performed using the QM method. Only the structures whose optimization led to a configuration with the lowest total energy are shown. "GO plane" is an averaged plane drawn through the carbon atoms belonging to the oxydized area. "Centroid" is a center of mass of the solvent molecules hydroxyl groups oxygens.

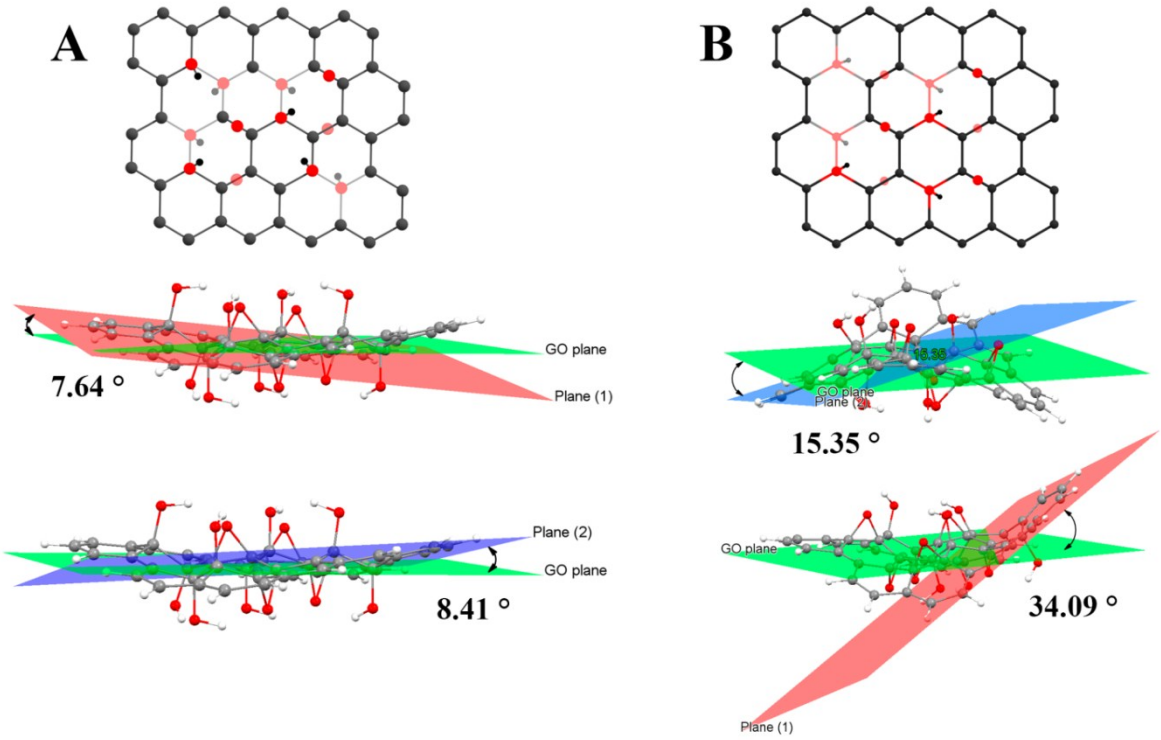

Figure S2. Structure distortion caused by distribution of the functional groups for the structure used in this paper (**A**) and for the structure with hydroxyl and epoxy groups located at neighboring carbon atoms at the same side of the GO flake (**B**).

Note, that slight distortion of the given GO model is observed owing to the finite size of the GO skeleton. The influence of the distribution of the functional groups on the degree of the GO flake distortion from the ideal planar structure is given in Figure S2. It can be concluded from Figure S2 that the distortion is a consequence of the close arrangement of the oxygen-containing groups on one side of the GO sheet.

Table S1. Topological parameters of hydrogen bonds in the GO-H_2O solvate

Bond path between GO functional groups and atom of water molecule	ρ(r), a.u.	$\nabla^2\rho(r)$, a.u.	v(r), a.u.	E, kcal·mol-1
GO-O(81)-H(82) ... O(102)	0.057840	0.152712	-0.059318	18.61
GO-O(54)-H(77) ... O(132)	0.051067	0.138210	-0.049304	15.47
GO-O(57)-H(80) ... O(111)	0.043867	0.127067	-0.039724	12.46
GO-O(85)-H(86) ... O(117)	0.033411	0.108185	-0.027357	8.58
GO-O(55)-H(78) ... O(99)	0.063693	0.148173	-0.065716	20.62
GO-O(53)-H(76) ... O(144)	0.054575	0.140032	-0.053489	16.78
GO-H(78)-O(55) ... H(145)	0.034473	0.115246	-0.029303	9.19

GO-H(82)-O(81) ... H(142)	0.028403	0.101032	-0.022436	7.04
GO-H(76)-O(53) ... H(137)	0.033738	0.114574	-0.028509	8.94
GO-H(76)-O(53) ... H(140)	0.020701	0.071303	-0.014529	4.56
GO-H(78)-O(55) ... H(97)	0.025998	0.090331	-0.019704	6.18
GO-H(84)-O(83) ... H(116)	0.037731	0.128272	-0.033856	10.62
GO-H(80)-O(57) ... H(121)	0.023168	0.082149	-0.017019	5.34
GO-H(86)-O(85) ... H(125)	0.031638	0.108179	-0.025919	8.13
GO-H(79)-O(56) .... H(100)	0.042359	0.135774	-0.039726	12.46
GO-H(86)-O(85) ... H(110)	0.010142	0.034498	-0.006220	1.95
GO-O(51) ... H(110)	0.015835	0.064705	-0.011610	3.64

ρ(r) - electron density in BCPs, $\nabla^2\rho(r)$ - Laplacian of electron density in BCPs, v(r) - potential energy density in BCPs, E - the bond energy calculated according to eq.(1).

Table S2. Topological parameters of hydrogen bonds in the GO-MeOH solvate

Bond path between GO functional groups and atom of methanol molecule	ρ(r), a.u.	$\nabla^2\rho(r)$, a.u.	v(r), a.u.	E, kcal·mol-1
GO-O(54)-H(77) ... O(99)	0.016806	0.058082	-0.011676	3.66
GO-O(55)-H(78) ... O(125)	0.052021	0.142075	-0.050692	15.90
GO-O(57)-H(80) ... O(103)	0.042303	0.134093	-0.039518	12.40
GO-O(53)-H(76) ... O(97)	0.051185	0.147520	-0.050935	15.98
GO-H(76)-O(53) ... H(120)	0.040928	0.135378	-0.038010	11.93
GO-H(78)-O(55) ... H(94)	0.028587	0.104855	-0.023317	7.32
GO-H(77)-O(54) ... H(116)	0.021421	0.078499	-0.015385	4.83
GO-H(84)-O(83) ... H(114)	0.022097	0.081318	-0.016069	5.04
GO-H(80)-O(57) ... H(106)	0.009243	0.030695	-0.005564	1.75
GO-H(80)-O(57) ... H(100)	0.025535	0.092904	-0.019514	6.12
GO-H(86)-O(85) ... H(112)	0.029352	0.104344	-0.023667	7.43
GO-H(86)-O(85) ... H(108)	0.027516	0.096251	-	6.74

			0.021470	
GO-H(82)-O(81) ... H(124)	0.034871	0.119420	-0.030221	9.48

Table S3. Topological parameters of hydrogen bonds in the GO-EtOH solvate

Bond path between GO functional groups and atom of ethanol molecule	ρ(r), a.u.	$\nabla^2\rho(r)$, a.u.	v(r), a.u.	E, kcal·mol-1
GO-O(57)-H(80) ... O(101)	0.009184	0.034239	-0.005740	1.80
GO-O(85)-H(86) ... O(107)	0.054377	0.149557	-0.054774	17.19
GO-O(56)-H(79) ... O(91)	0.010090	0.036923	-0.006801	2.13
GO-O(53)-H(76) ... O(97)	0.015127	0.053129	-0.010017	3.14
GO-O(55)-H(78) ... O(95)	0.043285	0.127249	-0.039455	12.38
GO-H(86)-O(85) ... H(112)	0.024617	0.084172	-0.018019	5.65
GO-H(86)-O(85) ... H(100)	0.025928	0.091128	-0.019729	6.19
GO-H(84)-O(83) ... H(106)	0.026518	0.096613	-0.020722	6.50
GO-H(77)-O(54) ... H(116)	0.026562	0.098652	-0.020971	6.58
GO-H(84)-O(83) ... H(114)	0.011815	0.040381	-0.007344	2.30
GO-H(82)-O(81) ... H(124)	0.028149	0.102045	-0.022608	7.09
GO-H(79)-O(56) ... H(96)	0.033343	0.115629	-0.028455	8.93
GO-H(78)-O(55) ... H(126)	0.023661	0.084544	-0.017401	5.46
GO-H(78)-O(55) ... H(94)	0.014313	0.046806	-0.008800	2.76

Table S4. Structural parameters of hydrogen bonds in the GO-H_2O solvate. The O ... HO angle appears in bold

Bond path between GO functional groups and atom of molecule water	H ... O distance, Å	Angle, °	O ... O distance, Å
GO-**O(81)-H(82) ... O(102)**	1.59352	165.948	2.59907
GO-**O(54)-H(77) ... O(132)**	1.65360	152.398	2.60059
GO-**O(57)-H(80) ... O(111)**	1.71935	159.682	2.68824
GO-**O(85)-H(86) ... O(117)**	1.83032	154.627	2.76642
GO-**O(55)-H(78) ... O(99)**	1.57007	167.945	2.58725
GO-**O(53)-H(76) ... O(144)**	1.63664	153.298	2.58999
GO-H(78)-**O(55) ... H(145)-O(144)**	1.80728	165.249	2.77454
GO-H(82)-**O(81) ... H(142)-O(141)**	1.86721	170.767	2.84802
GO-H(76)-**O(53) ... H(137)-O(135)**	1.80729	170.688	2.78961
GO-H(76)-**O(53) ... H(140)-O(138)**	2.04174	151.582	2.94441
GO-H(78)-**O(55) ... H(97)-O(96)**	1.92377	164.778	2.88750
GO-H(84)-**O(83) ... H(116)-O(114)**	1.74917	170.073	2.73486
GO-H(80)-**O(57) ... H(121)-O(120)**	1.97301	154.829	2.89635
GO-H(86)-**O(85) ... H(125)-O(123)**	1.83951	162.012	2.79813
GO-H(79)-**O(56) .... H(100)-O(99)**	1.72717	158.134	2.67454
GO-H(86)-**O(85) ... H(110)-O(108)**	2.37375	145.506	3.22997
GO-**O(51) ... H(110)-O(108)**	2.13445	127.633	2.84133

Table S5. Structural parameters of hydrogen bonds in GO-MeOH solvate. The O ... HO angle appears in bold

Bond path between GO functional groups and atom of molecule methanol	H ... O distance, Å	Angle, °	O ... O distance, Å
GO-**O(54)-H(77) ... O(99)**	2.15991	130.907	2.91179
GO-**O(55)-H(78) ... O(125)**	1.64594	170.781	2.65168
GO-**O(57)-H(80) ... O(103)**	1.71134	161.334	2.68296
GO-**O(53)-H(76) ... O(97)**	1.64019	162.341	2.62161

GO-H(76)-**O(53) ... H(120)-O(119)**	1.72156	173.656	2.71401
GO-H(78)-**O(55) ... H(94)-O(93)**	1.85974	162.403	2.81722
GO-H(77)-**O(54) ... H(116)-O(115)**	2.00000	174.778	2.97604
GO-H(84)-**O(83) ... H(114)-O(113)**	1.98315	155.158	2.90282
GO-H(80)-**O(57) ... H(106)-O(105)**	2.42825	142.131	3.25590
GO-H(80)-**O(57) ... H(100)-O(99)**	1.91571	175.637	2.89706
GO-H(86)-**O(85) ... H(112)-O(111)**	1.86444	169.598	2.83983
GO-H(86)-**O(85) ... H(108)-O(107)**	1.90465	157.651	2.84059
GO-H(82)-**O(81) ... H(124)-O(123)**	1.78876	167.275	2.76630

Table S6. Structural parameters of hydrogen bonds in GO-EtOH solvate. The O ... HO angle appears in bold

Bond path between GO functional groups and atom of molecule ethanol	H ... O distance, Å	Angle, °	O ... O distance, Å
GO-**O(57)-H(80) ... O(101)**	2.38825	139.857	3.20970
GO-**O(85)-H(86) ... O(107)**	1.62157	154.725	2.58085
GO-**O(56)-H(79) ... O(91)**	2.42412	117.199	3.01819
GO-**O(53)-H(76) ... O(97)**	2.18712	138.376	2.99654
GO-**O(55)-H(78) ... O(95)**	1.72035	160.450	2.69092
GO-H(86)-**O(85) ... H(112)-O(111)**	1.96023	171.639	2.93713
GO-H(86)-**O(85) ... H(100)-O(99)**	1.92069	169.734	2.89846
GO-H(84)-**O(83) ... H(106)-O(105)**	1.90409	163.780	2.86421
GO-H(77)-**O(54) ... H(116)-O(115)**	1.89512	161.045	2.84585
GO-H(84)-**O(83) ... H(114)-O(113)**	2.28427	147.131	3.14960
GO-H(82)-**O(81) ... H(124)-O(123)**	1.88007	160.333	2.82847
GO-H(79)-**O(56) ... H(96)-O(95)**	1.81070	175.479	2.79956
GO-H(78)-**O(55) ... H(126)-O(125)**	1.95766	177.861	2.94278
GO-H(78)-**O(55) ... H(94)-O(93)**	2.21570	154.193	3.12797

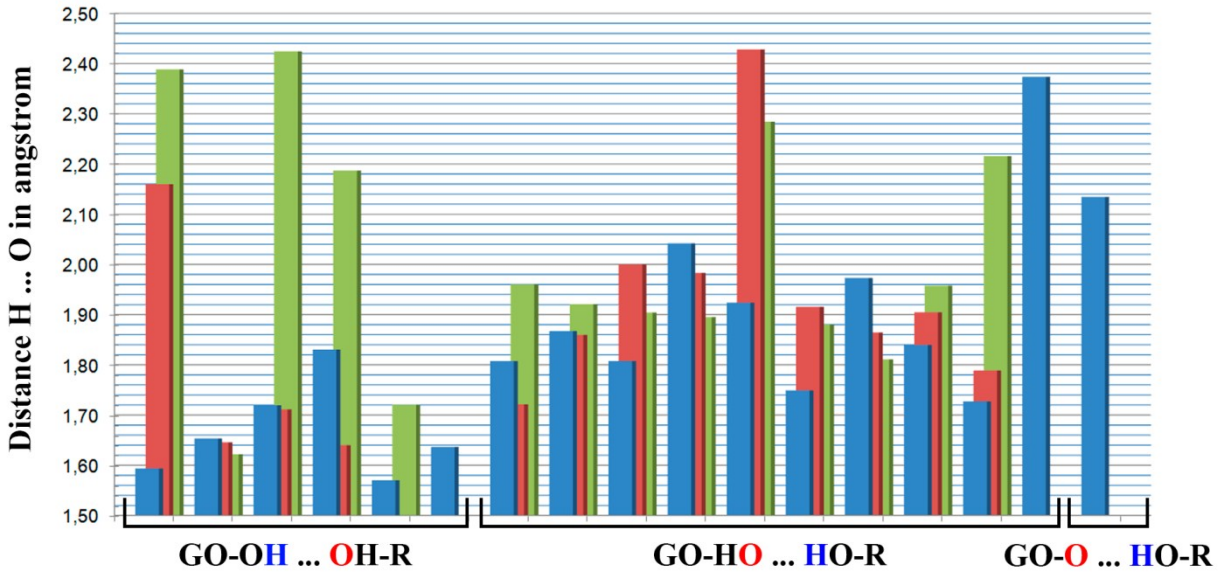

Figure S3. Distribution of the H ... O distances between the atoms of the GO and atoms of the solvent molecules involved in H-bonding. Blue, red and green columns correspond to water, methanol and ethanol molecules, respectively.

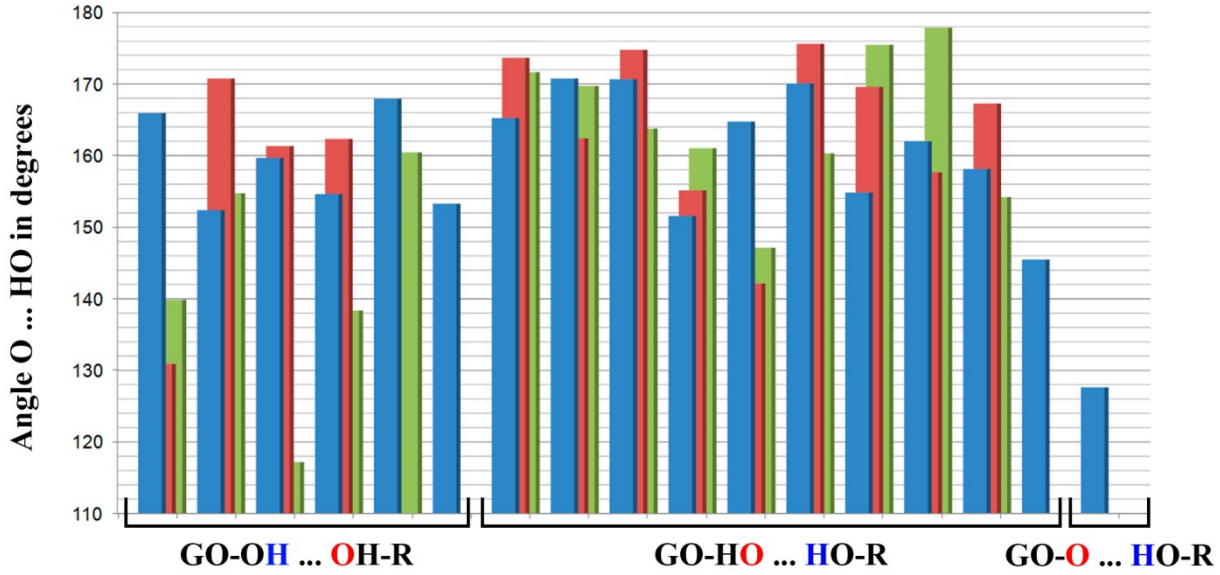

Figure S4. Distribution of the H-bond angles between GO and solvent molecules involved in H-bonding. Blue, red and green columns correspond to water, methanol and ethanol molecules, respectively.

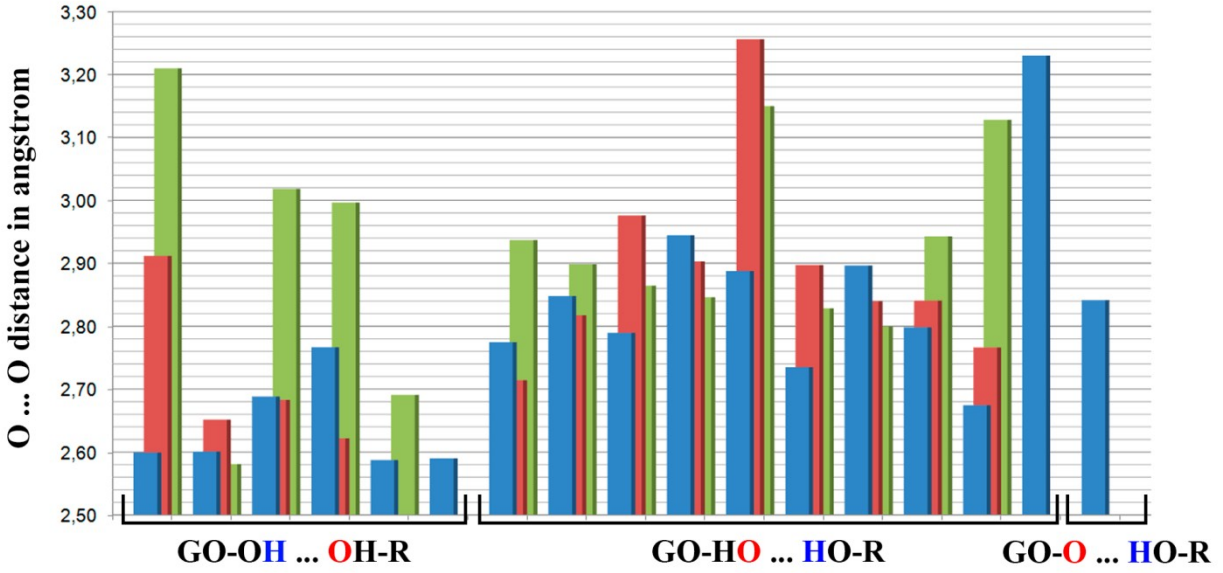

Figure S5. Distribution of the O ... O distances between the atoms of the GO and atoms of the solvent molecules involved in H-bonding. Blue, red and green columns correspond to water, methanol and ethanol molecules, respectively.

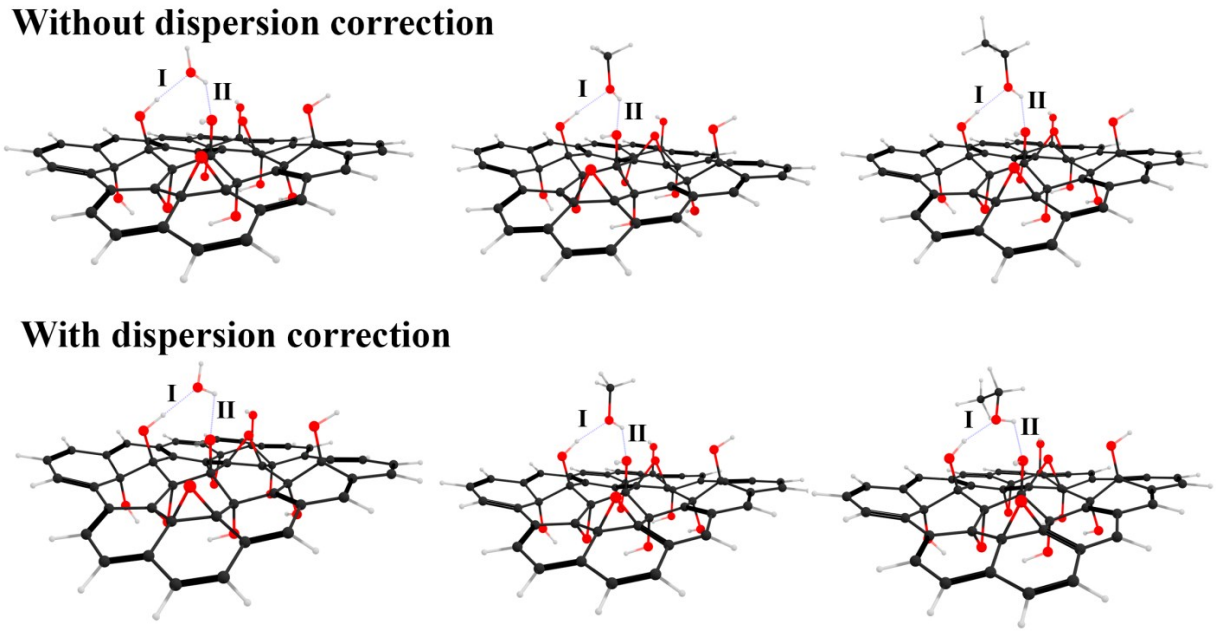

Figure S6. The GO solvate structures optimized with and without Grimme dispersion correction. Structural and topological parameters for the type I and II hydrogen bonds are listed in **Table S1.**

Table S7. Structural and topological parameters of type **I** and **II** hydrogen bonds between GO and water, methanol and ethanol molecules with and without Grimme dispersion correction

Bond	H...O distance, Å	Angle O..HO, °	ρ(r), a.u.	$\nabla^2\rho(r)$, a.u.	v(r), a.u.	E, kcal·mol^{-1}
GO-water						
B3LYP/6-31G(d) without Grimme's correction						
I	1.80461	169.24	0.038689	0.109944	-0.033242	10.43
II	1.89604	146.20	0.029402	0.094604	-0.025836	8.11
wB97XD/6-31G(d) with Grimme's correction						
I	1.78676	179.99	0.037301	0.119988	-0.033181	10.41
II	2.10462	124.80	0.029554	0.097464	-0.027346	8.58
GO-methanol						
B3LYP/6-31G(d) without Grimme's correction						
I	1.80837	169.42	0.037803	0.108763	-0.032216	10.11
II	1.90753	145.36	0.029048	0.093477	-0.025546	8.02
wB97XD/6-31G(d) with Grimme's correction						
I	1.78804	166.40	0.038690	0.117139	-0.033884	10.63
II	1.90387	144.20	0.029169	0.095709	-0.026172	8.21
GO-ethanol						
B3LYP/6-31G(d) without Grimme's correction						
I	1.80693	170.34	0.037996	0.109005	-0.032315	10.14
II	1.91775	144.635	0.028379	0.091538	-0.024960	7.83
wB97XD/6-31G(d) with Grimme's correction						
I	1.74160	165.80	0.036652	0.103031	-0.030652	9.62
II	2.01956	128.61	0.020996	0.080195	-0.020996	6.59

In addition, the calculations with Grimme dispersion correction implemented in the GAUSSIAN 09 package were performed. As this type of calculations are very time consuming we carried out the optimization at the wB97XD/6-31G(d) level of theory. For the same reason, we only considered interactions of single solvent molecule with the GO flake without taking into account implicit solvent effects. The analysis of these data allows us to conclude that for the present structures the dispersion correction does not influence the H-bonds energetical characteristics. Of course, the dispersion correction may play a significant role when the interactions between alcohol molecules and GO unoxidized areas are considered. The latter, however, constitute only a minor part of the GO surface while the major is covered by oxygen-containing groups capable of forming of H-bonds. Moreover, the authors of work [*A.V. Shishkina, V.V. Zhurov. A.I. Stash, M.V. Vener, A.A. Pinkerton and V.G. Tsirelson, Cryst. Growth Des., 2013, 13, 816−828*] showed that it is impossible to simultaneously estimate the strong and weak interactions when Grimme dispersion correction is taken into consideration.