Supporting Information

Molecular investigation of evaporation of biodroplets containing single strand DNA on graphene surface

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Accompanying Files:

S5.2. Movie of how to interact ssd$(A)_6$ homopolymer in a bio-droplet for less than a nanosecond.

S5.4. Movie of how to interact ssd$(C)_6$ homopolymer in a bio-droplet for less than a nanosecond.

S5.6. Movie of how to interact ssd$(G)_6$ homopolymer in a bio-droplet for less than a nanosecond.

S5.8. Movie of how to interact ssd$(T)_6$ homopolymer in a bio-droplet for less than a nanosecond.

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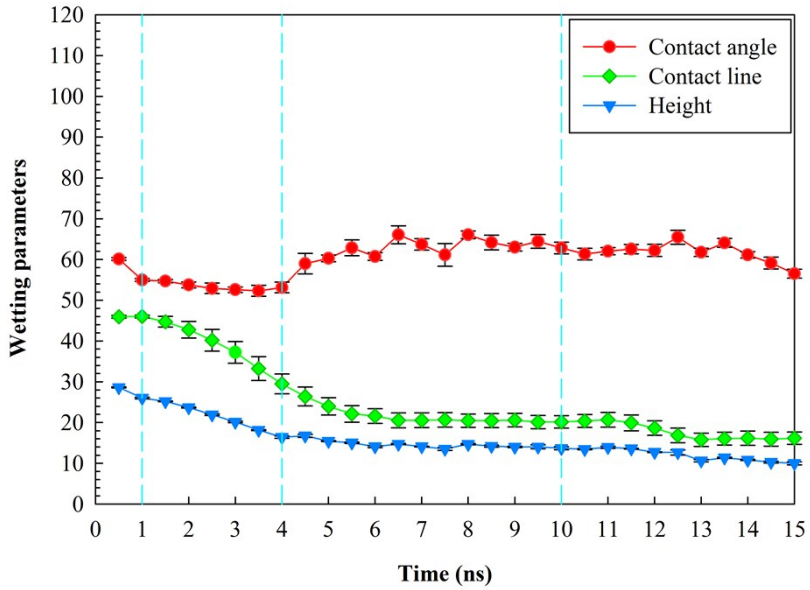
S1. Wetting parameters

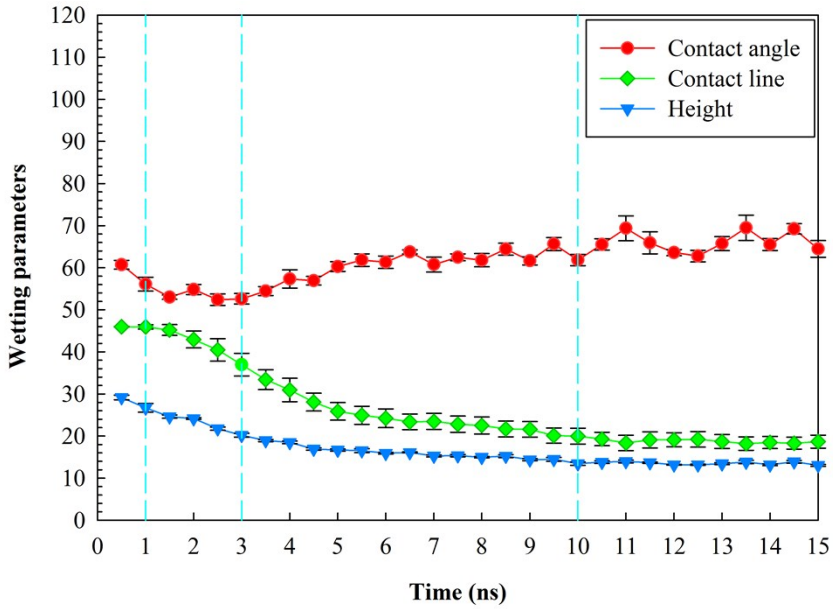
In this analysis, the drop has been considered as the part of a sphere. The contact angle can be calculated using the drop diameter (d) and drop height (h) geometrically. This method generates reasonable results where droplets are very small. Wetting is one of the physical properties of the system, which result from the interaction between the substrate and fluid. In fact, it is the result of the interaction between the solid-liquid, the liquid-gas and the solid-gas, and changes of substrate wettability display the variation in the present forces in the interaction between droplet and substrate. Therefore, the study of the contact angle during evaporation can be useful in interpreting the interaction of water droplet containing a single strand DNA with the substrate. Equation (1) is used to calculate the contact angle, which is one of the methods to determine the contact angle and has widely applied in the analysis of sessile droplet profiles.

$$\frac{\theta}{2} = tan^{-1}\left(\frac{h}{d}\right) \qquad (1)$$

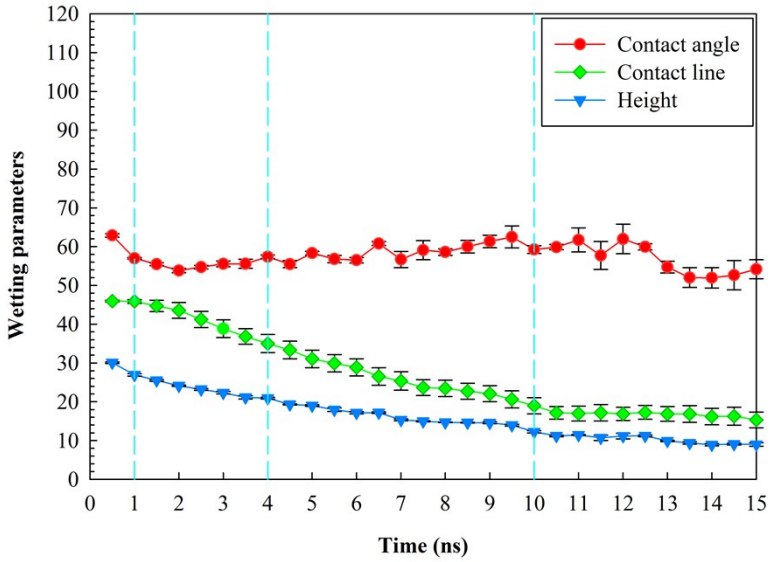
The wettability parameters include contact angle, contact line and drop height for single strand DNA with 6 nucleotides (a) adenine (b) cytosine (c) guanine (d) thymine is shown in Figures S1.1, S1.2, S1.3 and S1.4. As shown in these Figures, the time interval for each of the diagrams is divided into three parts. Each of these intervals refers to the different behaviors of the wettability parameters. The above interval is named steps 1 to 3.



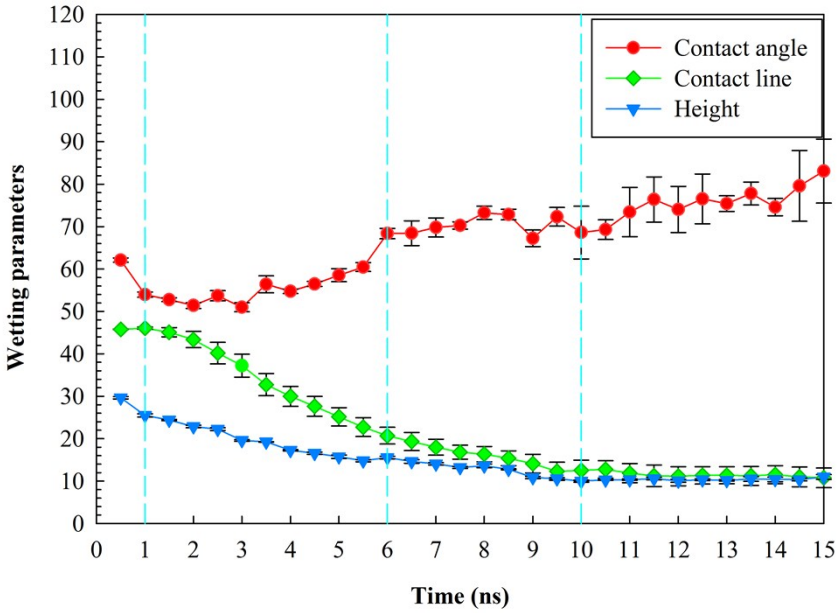
S1. 1. Wettability parameters including contact angle (°), contact line (Å), and the height of droplet (Å) for adenine single strand DNA.



S1.2. Wettability parameters including contact angle (°), contact line (Å), and the height of droplet (Å) for cytosine single strand DNA.



S1.3. Wettability parameters including contact angle (°), contact line (Å), and the height of droplet (Å) for guanine single strand DNA.



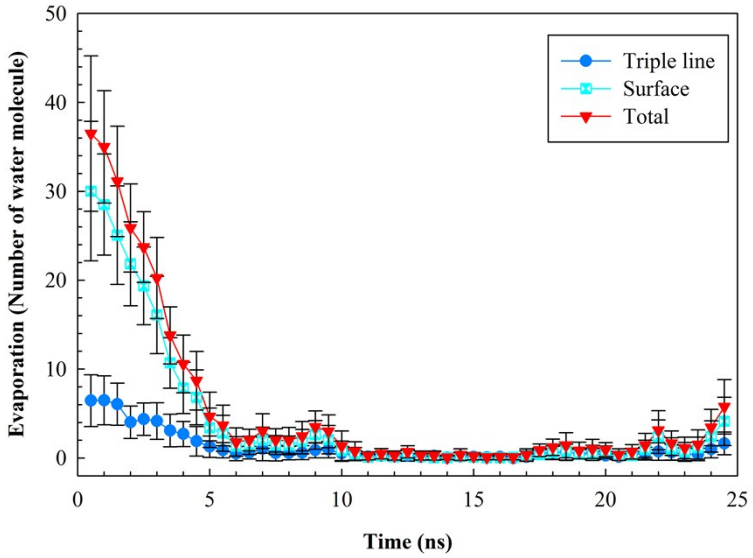
S1.4. Wettability parameters including contact angle (°), contact line (Å), and the height of droplet (Å) for thymine single strand DNA.

According to figures S1.1, S1.2, S1.3 and S1.4, in step 1, for all biodroplets, the contact angle is reduced by about 50 to 55 degrees, while the contact line and drop height are

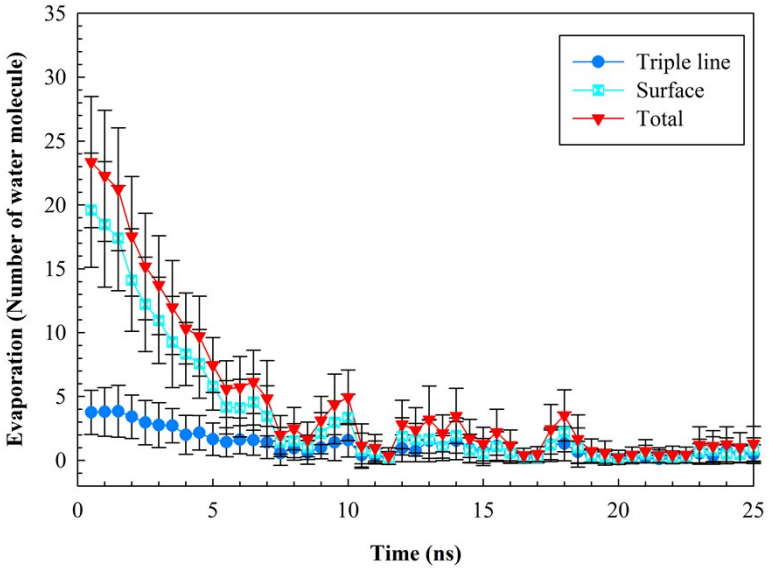
fixed and decreased respectively. The reduction of the contact angle for cytosine and guanine single-stranded continues up to 1.5 ns and shows more pining than adenine and thymine single strand. In step (2), the contact angle of the thymine biodroplet has an increasing trend. While in other biodroplets, the mode of the contact angle is constant and shows the equilibration in this step. The constant contact angle mode had been reported in the hydrophobic substrates and we have observed this result for all of the biodroplets except for thymine. The contact line is decreased for every four biodroplets. The contact line of guanine is decreased with a slight slope and contact line of thymine is decreased with a sharp slope compared to other single strands. As step 3 in figures 2-4, a great difference between the biodroplets is observed. In the case of a biodroplet containing adenine single strand, the contact angle is almost constant, but the contact line is decreased with a very gentle gradient slope. The height of droplet is decreased with a very slight slope. In the case of a biodroplet containing guanine single strand, the contact line and height is decreased in the range of 10 ns and the contact angle is increased. After this time, the contact angle, contact line, and height are almost constant. In the case of biodroplet containing cytosine single strand, contact angle, contact line with different slope is increased and decreased respectively, and height is almost constant. In the case of a biodroplet containing cytosine single strand, the contact angle is increased, while contact line and height is decreased by a gentle slope.

S2. The number of evaporated water molecules

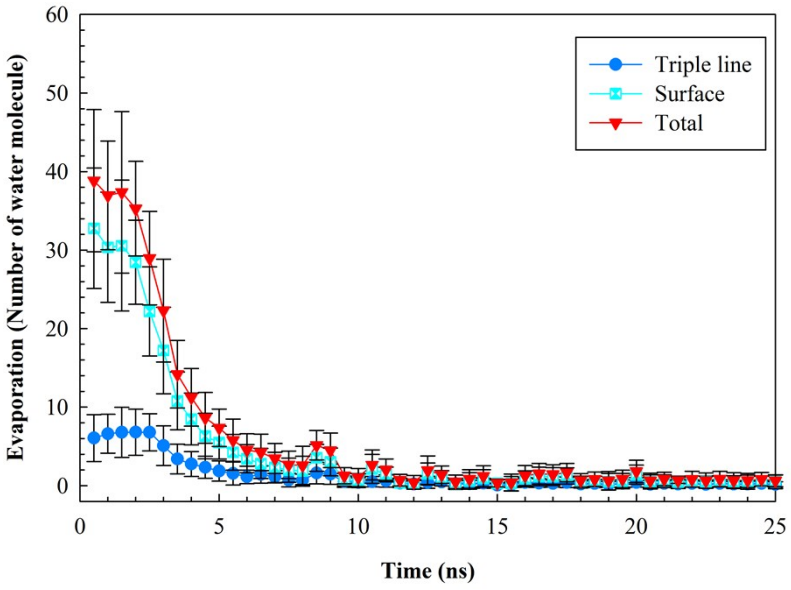
Figures S2.1, S2.2 and S2.3 show the number of evaporated water molecules from the surface and the triple point and sum of them in the biodroplet containing single strand of cytosine, guanine and thymine respectively.



S2.1. Number of evaporated molecule from the surface, triple point, and sum of them in the biodroplet containing single strand of cytosine.



S2.2. Number of evaporated molecule from the surface, triple point, and sum of them in the biodroplet containing single strand of guanine.

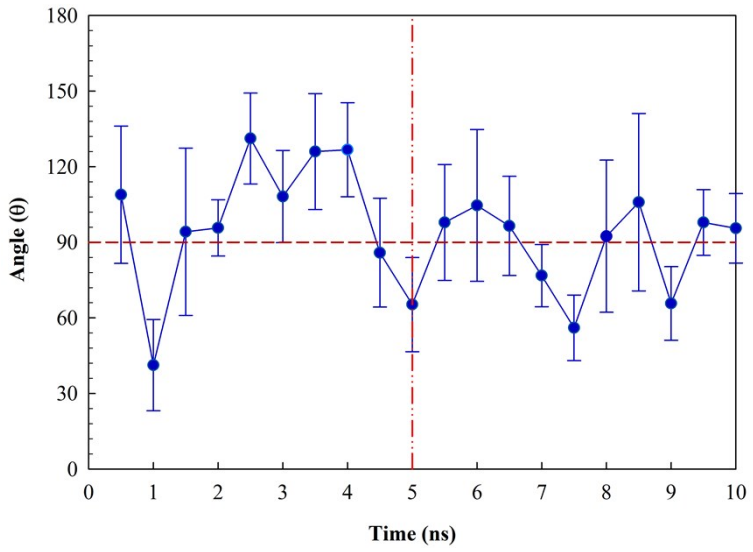


S2.3. Number of evaporated molecule from the surface, triple point, and sum of them in the biodroplets containing single strand of thymine.

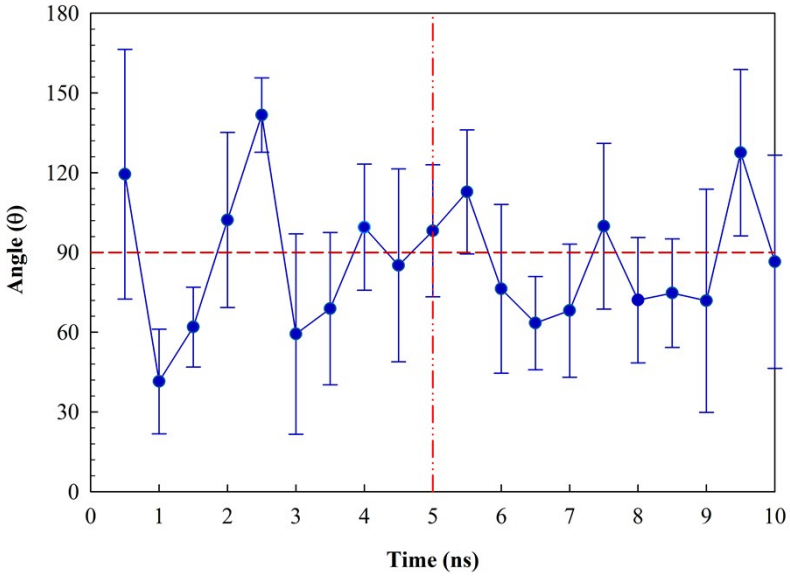
Plots of the number of evaporated water molecules show that the rate of evaporation for adenine, cytosine, and thymine has been higher than guanine. In step 1, the evaporation of water molecules from the triple point in the biodroplets of cytosine and guanine has a constant trend, while adenine and thymine show an increasing trend. But during this time, the evaporation of water molecules from the surface has a decreasing trend in all biodroplets. In step 2, the evaporation of water molecules in biodroplets of adenine, cytosine, and guanine shows a decreasing trend from both the surface and the triple point. The slope of evaporation descending diagram from the triple point for guanine is less than other biodroplets, and the rest of the biodroplets show approximately the same slope for evaporation diagram from the triple point. But the evaporation from the triple point of thymine biodroplets shows an increasing trend until 2 ns, and then evaporation has a decreasing trend to the end. The evaporation of thymine biodroplets from the surface also has a decreasing trend. Evaporation is not observed in step 3 because most of the water molecules evaporate before 5 ns and few water molecules remain.

S3. Angular orientation ssDNA on the graphene sheet

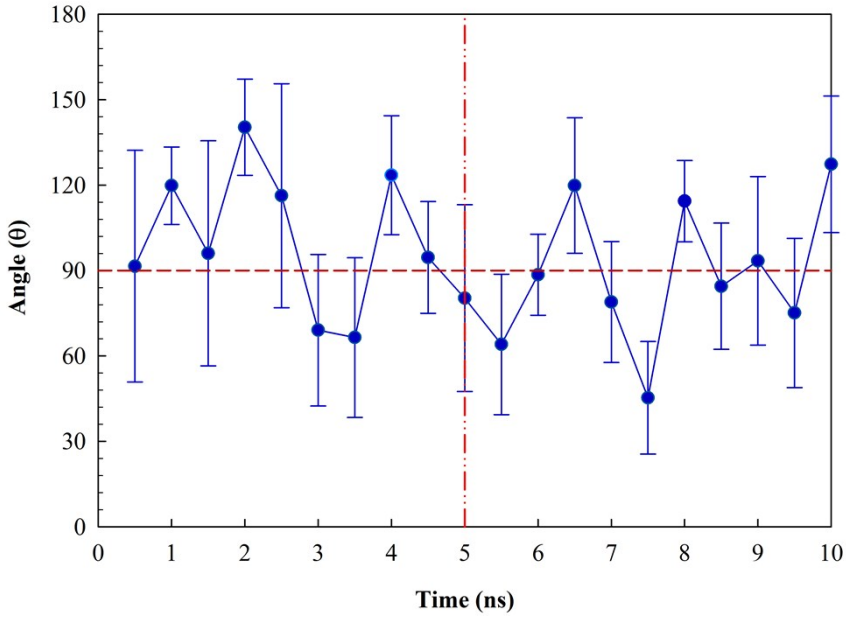
To study how single strands DNA placed on graphene, at first their angular orientation with the graphene sheet is considered. A schematic of this angle is shown in main text. This angle is the space between the line which connects two points in the farthest points on a single strand DNA with 6 bases and the line which passes through the center of mass of the droplet and the single strand DNA with 6 bases. This angle shows the orientation of single strand relative to the droplet. The zero angle shows that the single strand is perpendicular to the graphene sheet and corresponds to the center of mass of the droplet. The angle of 90 degrees indicates the parallel state and corresponds to the center of mass of the droplet. Angle with less than 90 degrees corresponds to the unparalleled state of single strand DNA relative to the graphene sheet and away from the center of the mass of the droplet, and greater than 90 degrees angle corresponds to the parallel structure but away from the center of the mass of the droplet. Figures S3.1, S3.2, S3.3 and S3.4 show the angular orientation of single strands in the droplet during evaporation. Since the evaporation of most water molecules takes place before 10 ns, just this time period was considered.



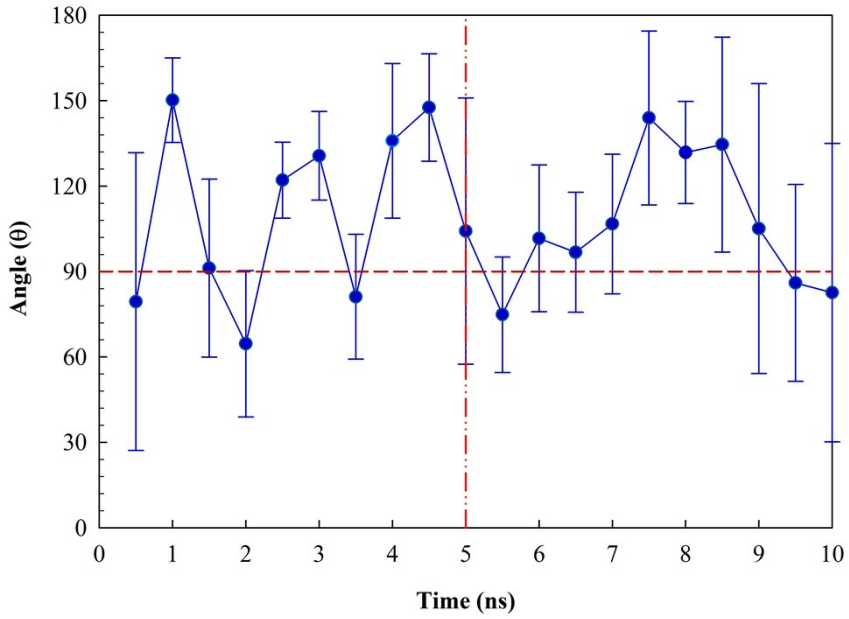
S3.1. Orientation changes of ssd$(A)_6$ related to graphene during the time.



S3.2. Orientation changes of ssd$(C)_6$ related to graphene during the time.



S3.3. Orientation changes of ssd$(G)_6$ related to graphene during the time.

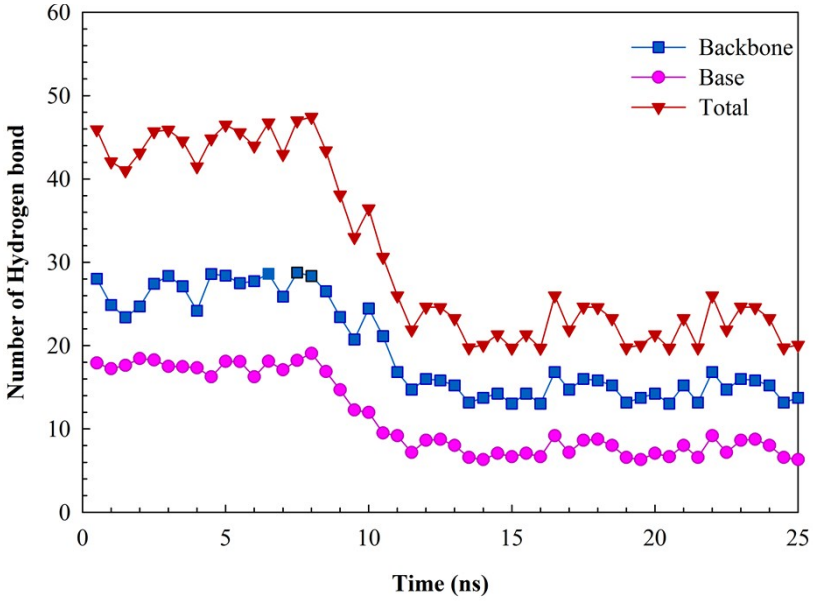


S3.4. Orientation changes of ssd$(T)_6$ related to graphene during the time.

Figures S3.1, S3.2, S3.3 and S3.4 show cytosine single strand is more parallel than the other single strands compared to the graphene sheet, and it spends more time in the center of the droplet during evaporation. Thymine is farther from the center of the droplet and more unparalleled related to graphene than the other single strands. During the evaporation, adenine and guanine single strand are almost parallel and in the center of the droplet. Another point is that adenine and cytosine sit parallel related to graphene at 1 ns, while guanine and thymine need 1.5 ns to become parallel related to graphene.

S4. The number of hydrogen bonds between water molecules with active sites in backbones and bases of ssDNA in the biodroplets

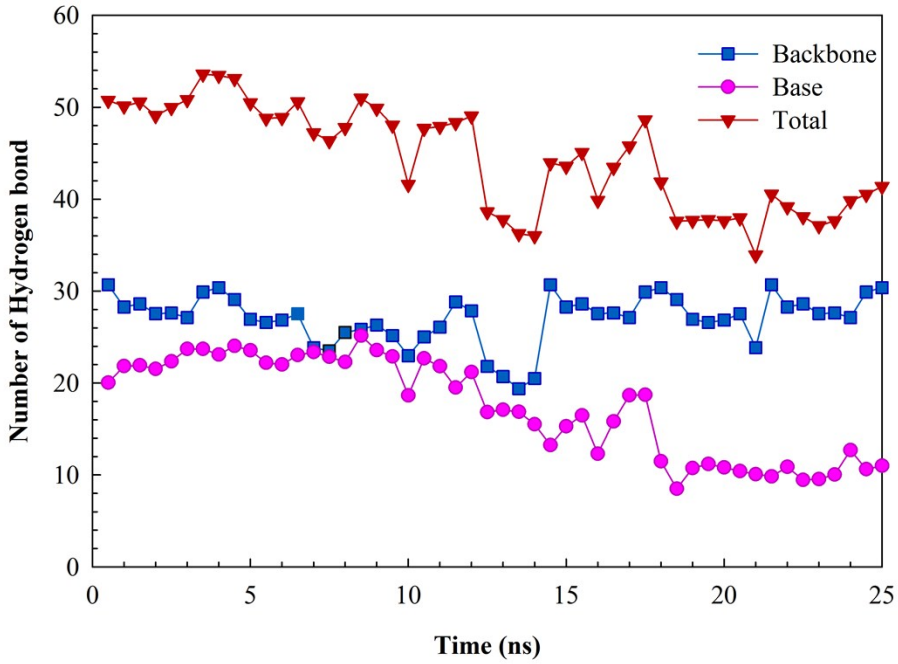
Figures S4.1, S4.2 and S4.3 show the number of hydrogen bonds between water molecules with active sites in backbone and bases in the biodroplets containing single strand of cytosine, guanine, and thymine over time, respectively. To calculate the hydrogen bond between the active sites of each base with water, a cut-off distance for donor-acceptor is 2.5-3.5 Å and an angle between donor-acceptor is greater than 125°. To obtain hydrogen bond between backbones of the single strand with water molecules, this bond is related to the oxygen atoms which connected to backbone phosphorus and hydrogen atoms of water. The distance between oxygen-hydrogen of water is smaller than 2.45 Å and the angle between the oxygen-hydrogen-oxygen of water is larger than 140 °. According to the number of water hydrogen bonds with active sites in backbones and bases in these Figures, the mechanism of the single strand placing on graphene is found.



S4.1. Changes in number of hydrogen bond between water molecules with active sites of backbone, bases, and sum of them in the cytosine single strand versus time.

According to this figure, hydrogen bond of single strand DNA with 6 cytosine bases is decreased before 1.5 ns, which is related to the formation of the hydrogen bond between backbone and water molecules. The hydrogen bond between active sites of the base with

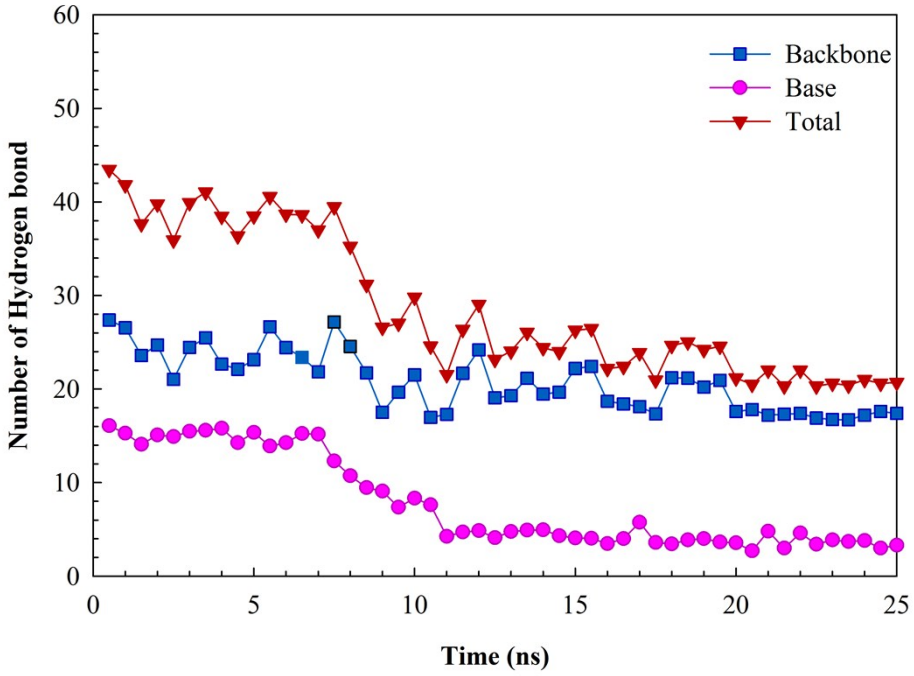
water molecules is constant until 8 ns, which indicates the orientation of cytosine single strand and high immobility. The hydrogen bond between water and single strand is increased immediately after 1.5 ns and is almost constant until 8 ns. However, cytosine has fewer active sites for hydrogen bond than adenine but because of its low tendency for internal hydrogen bond, the number of hydrogen bonds forms with water is more than the single strand of adenine, and then is decreased with steep slope by reducing the number of water molecules.



S4.2. Changes in number of hydrogen bond between water molecules with active sites of backbone, bases, and sum of them in the guanine single strand versus time.

Regarding Fig. S4.2 the number of the hydrogen bond between guanine single strand and water is higher than other single strands. Also, unlike other single strands, the hydrogen bond of single strand DNA with 6 guanine base and water is constant before 1.5 ns, since the hydrogen bond between backbone and water molecules is decreased during placing on the graphene. While the hydrogen bond between the base and water molecules is increased because of the presence of many active sites on each guanine base, lead to single strand is placed on graphene slower than other single strands. In the 1.5-12 ns which most of the

water molecules evaporate, the number of hydrogen bonds does not change significantly. This suggests that the above single strand sits on the graphene in such a way that its active sites are always accessible for water molecules, and then to the end of evaporation this diagram is decreased with a steep slope and all rings sit on graphene during this time interval, because of the dramatic decreasing in the number of water molecules.



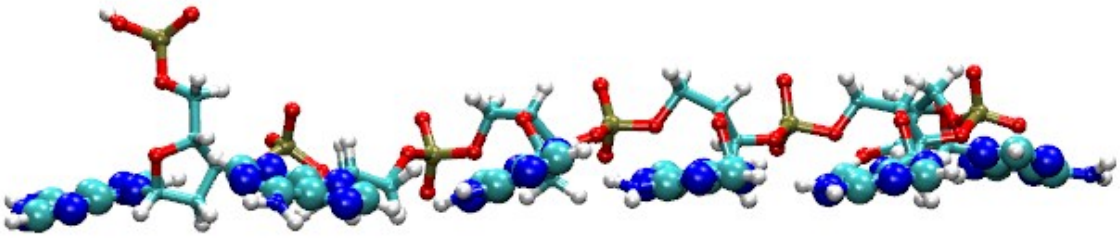
S4.3. Changes in number of hydrogen bond between water molecules with active sites of backbone, bases, and sum of them in the thymine single strand versus time.

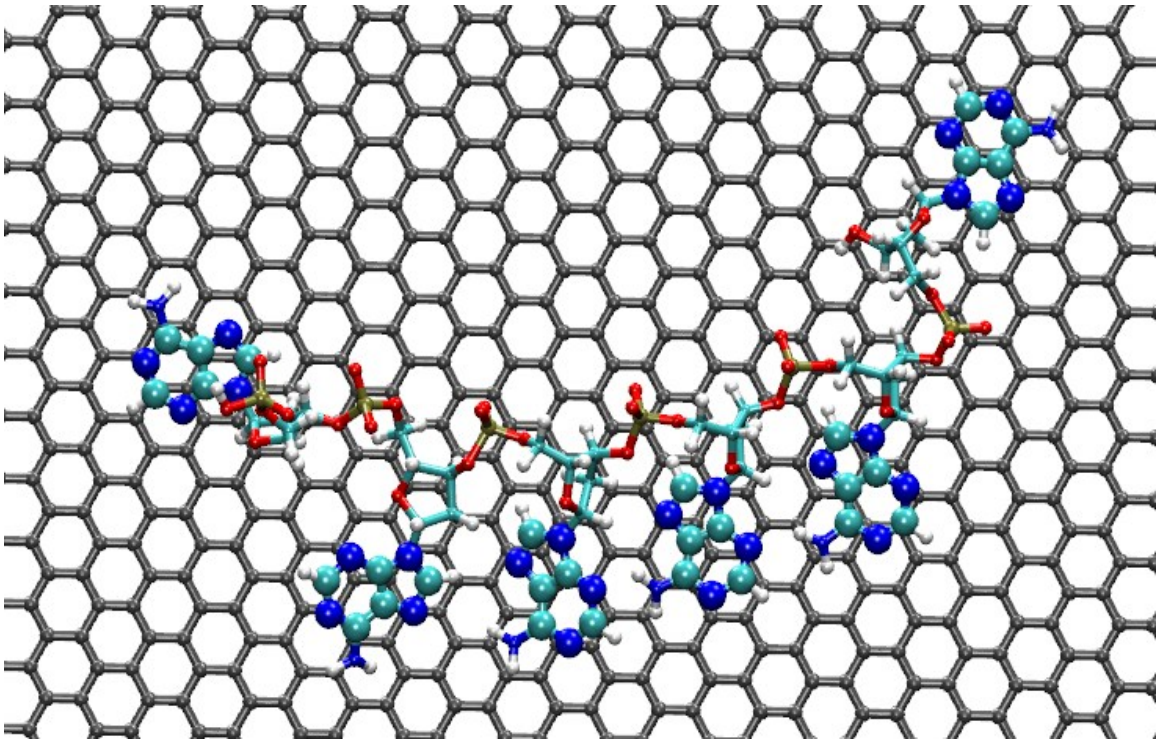
According to Fig. S4.3, the number of the hydrogen bond between the thymine single strand and water is less than the other single strands. As a result, the smallest change in the number of hydrogen bond affects the orientation of the single strand. The hydrogen bond between water and single strand DNA with 6 thymine base until 1.5 ns is decreased, which arise from the reduction of the hydrogen bond between the backbone and water molecules and the hydrogen bond between active sites of base and water molecules. The low tendency of thymine to create the π-π stacking bond with graphene also is decreased

when active sites participate in the hydrogen bond. Consequently, when the water molecules are going through the droplet surface, they pull this strand to the surface of the droplet. Most of the water molecules evaporate in 1.5 ns to 7 ns, the number of the hydrogen bond between base-water and backbone-water shows fluctuations which indicate a weak π-π stacking bond between the base and graphene. Then, due to the dramatic decrease in the number of water molecules to the end of evaporation, the slope of the plot related to the number of the hydrogen bond between base-water is decreased sharply, while the slope of the plot related to the number of the hydrogen bond between backbone-water is decreased very slightly. In this time, all the rings are parallel to graphene.

S5. Snapshot and movie

The snapshot of adenine single strand in 1 ns is shown in Fig. S5.1. It was observed in this figure that all bases of the single strand are almost parallel to the graphene sheet after half a nanosecond.



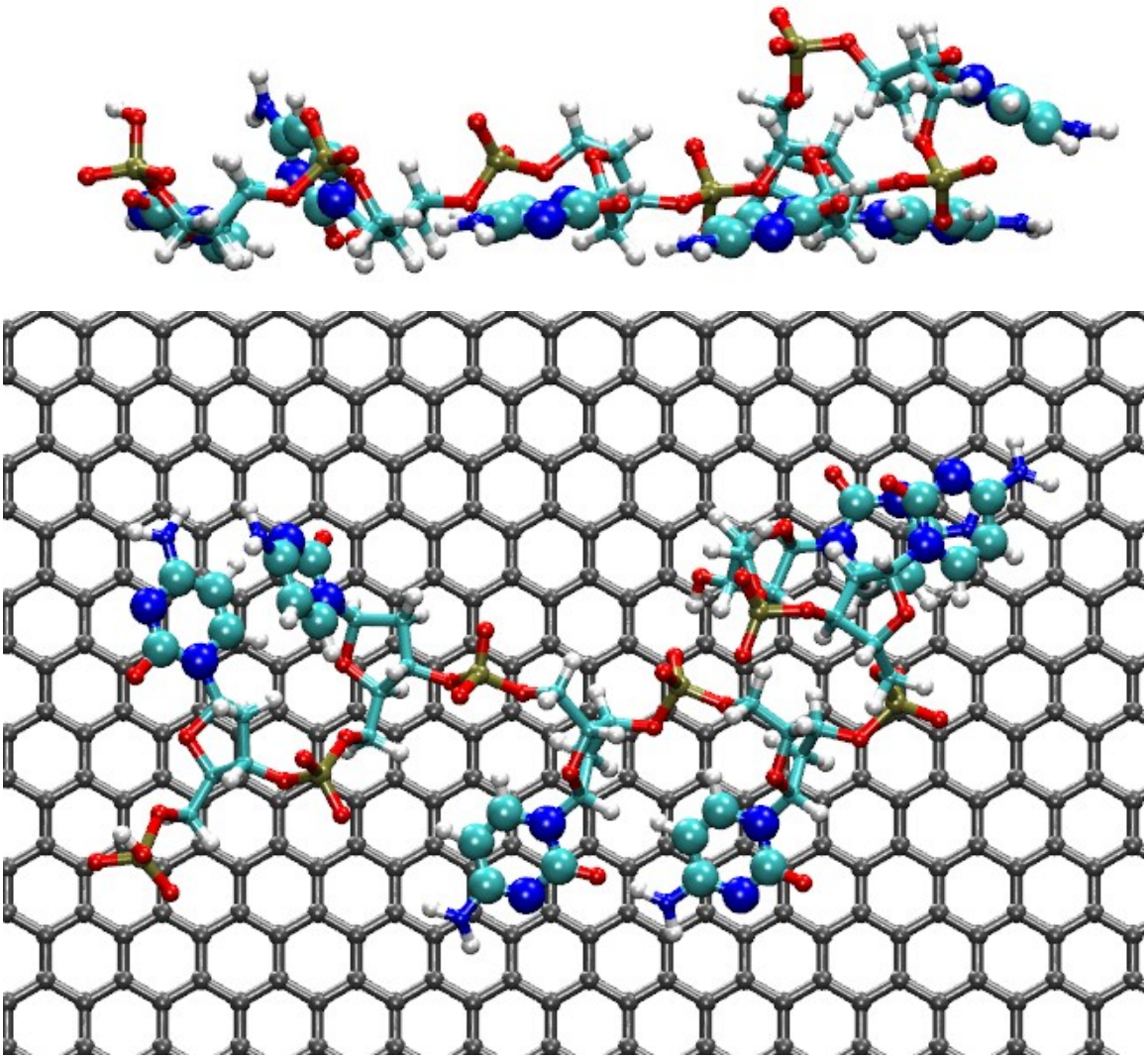


S5.1. Snapshot of adenine single strand before 1 ns a) side view, and b) top view.

S5.2. Movie of how to interact a ssd$(A)_6$ homopolymer in a bio-droplet for less than a nanosecond

You can find it in the accompanying files.

Figure S5.3 shows a single strand with 6 cytosine bases at 2 ns. The second base is far from the graphene until the end of the simulation and does not interact with graphene, and there is no internal hydrogen bond observed between the bases except the base number 2 with side bases.

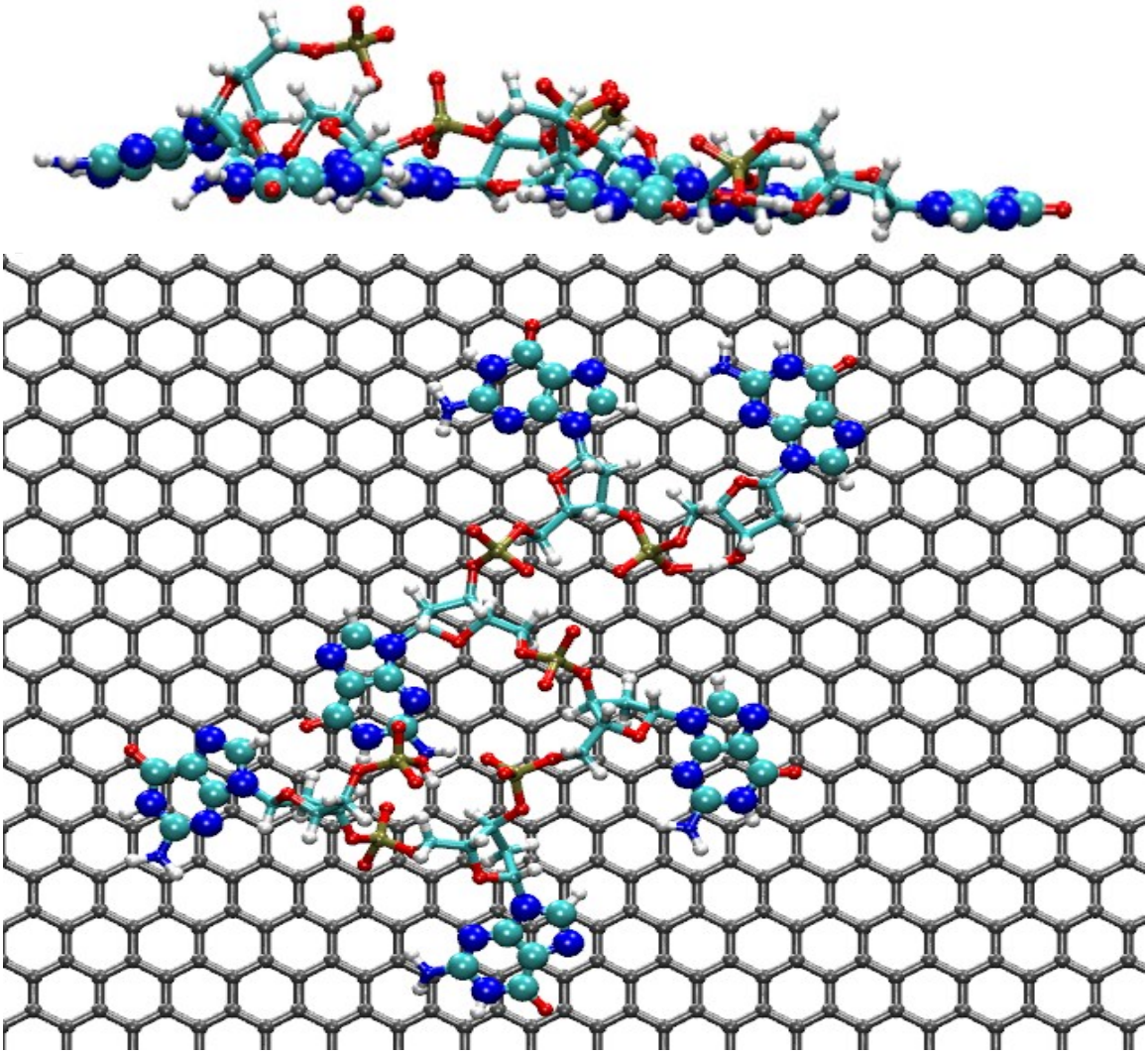


S5.3. Snapshot of cytosine single strand in 2 ns a) side view, and b) top view.

S5.4. Movie of a bio-droplet containing ssd$(C)_6$ homopolymer less than a nanosecond

You can find it in the accompany files.

After 8 ns, the fourth base forms π-π stacking bond with graphene due to a decrease in the number of water molecules, resulting in all bases form π-π stacking bond with graphene and increasing in the internal hydrogen bond. Figure S5.5 displays the snapshot of the conformation of this structure at the 10 ns.



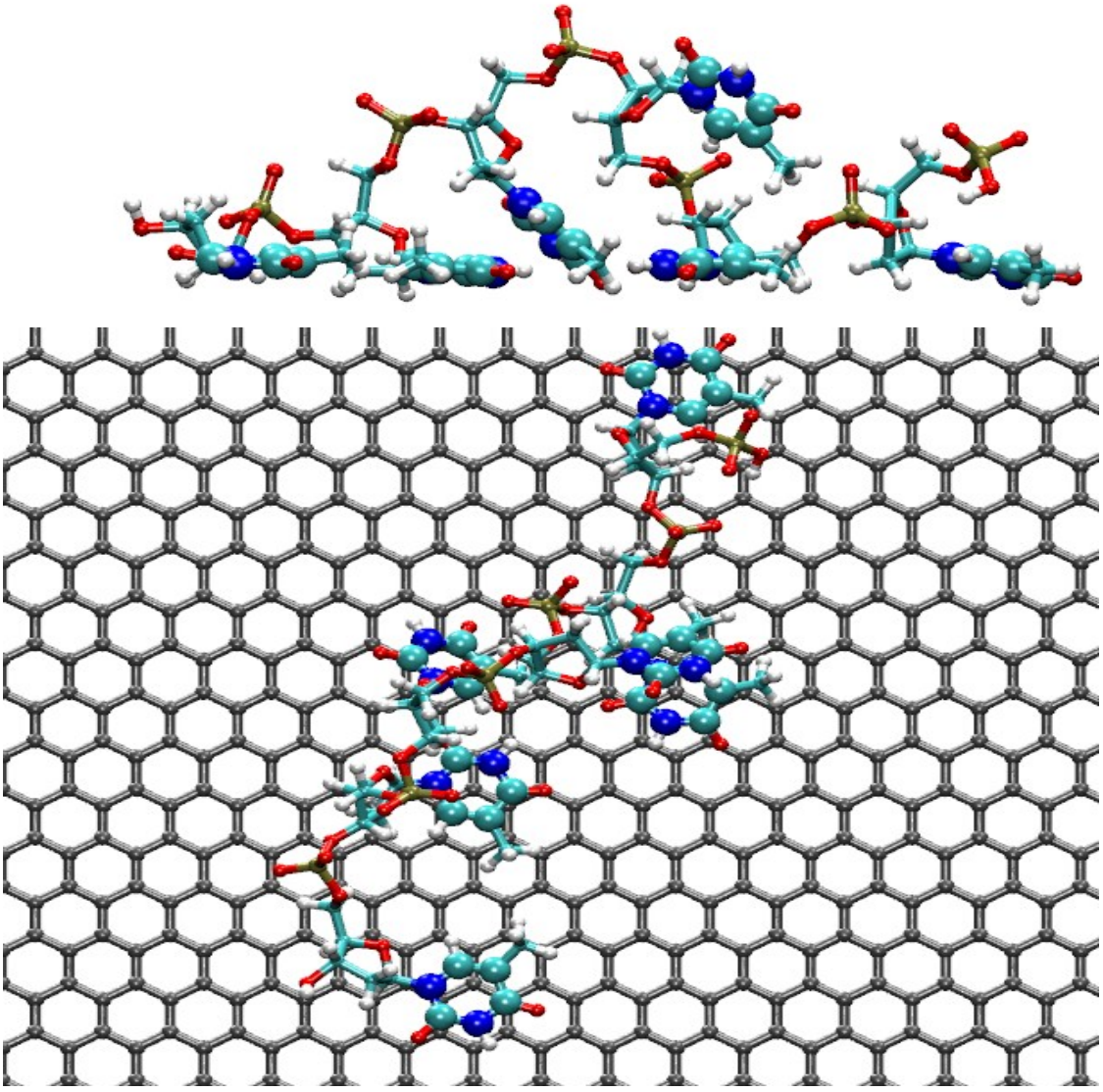
S5.5. Snapshot of guanine single strand in 10 ns a) side view, and b) top view.

S5.6. Movie of a how to interact ssd$(G)_6$ homopolymer in a bio-droplet for less than a nanosecond

You can find it in the accompany files.

Because the weakness of the π-π stacking bond between bases with graphene, the presence of hydrogen bonds between the single strand and water, the presence of internal π-π stacking bonds and moreover the current related water evaporation, external

movement of droplet for thymine bases is observed which leads to placing of thymine single strand on graphene by delayed. Only four of the six bases interact with graphene until 1 ns, which is illustrated in the snapshot of thymine single strand in Fig. S5.7.



S5.7. Snapshot of thymine single strand in 1 ns a) side view, and b) top view

S5.8. Movie of a how to interact ssd$(T)_6$ homopolymer in a bio-droplet for less than a nanosecond

You can find it in the accompany files.

S6. Detailed LJ and charge parameters

S6.1. Table of Lennard Jones parameters

Atom type	σ(Å)[a]	ε(kcal/mol)[a]	Atom type	σ(Å)[a]	ε(kcal/mol)[a]	Atom type	σ(Å)[a]	ε(kcal/mol)[a]	Atom type	σ(Å)[a]	ε(kcal/mol)[a]
	A			C			G			T	
HT	0.400	0.046	HT	0.400	0.046	HT	0.400	0.046	HT	0.400	0.046
CA	3.550	0.070	CA	3.550	0.070	CA	3.550	0.070	CA	3.550	0.070
OT	3.151	0.1521	OT	3.151	0.152	OT	3.151	0.152	OT	3.151	0.152
HN1	0.400	0.046	HN1	0.400	0.046	HN1	0.400	0.046	HN2	0.400	0.046
HN3	1.960	0.046	HN3	1.960	0.046	HN2	0.400	0.046	HN3	1.960	0.046
HN4	0.400	0.046	HN4	0.400	0.046	HN3	1.960	0.046	HN4	0.400	0.046
HN5	0.400	0.046	HN5	0.400	0.046	HN4	0.400	0.046	HN5	0.400	0.046
HN7	2.352	0.022	HN7	2.352	0.022	HN5	0.400	0.046	HN7	2.352	0.022
HN8	2.388	0.028	HN8	2.388	0.028	HN7	2.352	0.022	HN8	2.388	0.028
CN2	3.385	0.100	CN1	3.385	0.100	HN8	2.388	0.028	HN9	2.388	0.024
CN4	3.385	0.075	CN2	3.385	0.100	CN1	3.385	0.100	CN1	3.385	0.100
CN5	3.385	0.075	CN3	3.385	0.090	CN2	3.385	0.100	CN1T	3.385	0.100
CN7	4.054	0.020	CN7	4.054	0.020	CN4	3.385	0.075	CN3	3.385	0.090
CN7B	4.054	0.020	CN7B	4.054	0.020	CN5	3.385	0.075	CN3T	3.385	0.090
CN8	3.581	0.056	CN8	3.581	0.056	CN5G	3.385	0.075	CN7	4.054	0.020
CN8B	3.581	0.056	CN8B	3.581	0.056	CN7	4.054	0.020	CN7B	4.054	0.020
NN1	3.296	0.200	NN1	3.296	0.200	CN7B	4.054	0.020	CN8	3.581	0.056
NN2	3.296	0.200	NN2	3.296	0.200	CN8	3.581	0.056	CN8B	3.581	0.056
NN3A	3.296	0.200	NN3	3.296	0.200	CN8B	3.581	0.056	CN9	3.635	0.078
NN4	3.296	0.200	ON1C	3.029	0.120	NN1	3.296	0.200	NN2B	3.296	0.200
ON2	3.154	0.152	ON2	3.154	0.152	NN2B	3.296	0.200	NN2U	3.296	0.200
ON3	3.029	0.120	ON3	3.029	0.120	NN2G	3.296	0.200	ON1	3.029	0.120
ON4	3.154	0.152	ON4	3.154	0.152	NN3G	3.296	0.200	ON2	3.154	0.152
ON5	3.154	0.152	ON5	3.154	0.152	NN4	3.296	0.200	ON3	3.029	0.120
ON6	3.154	0.152	ON6	3.154	0.152	ON1	3.029	0.120	ON4	3.154	0.152
P	3.831	0.585	P	3.831	0.585	ON2	3.154	0.152	ON5	3.154	0.152
SOD	2.430	0.047	SOD	2.430	0.047	ON3	3.029	0.120	ON6	3.154	0.152
						ON4	3.154	0.152	P	3.831	0.585
						ON5	3.154	0.152	SOD	2.430	0.047
						ON6	3.154	0.152			

P	3.831	0.585
SOD	2.430	0.047

[a] Combination rule: $\sigma_{12} = (\sigma_1 + \sigma_2)/2$; $\varepsilon_{12} = \sqrt{\varepsilon_1} * \varepsilon_2$.

S6.2. Table of charge of atom types

Atom type	charge	Atom type	charge	Atom type	charge	Atom type	charge
A		C		G		T	
P	1.50	P	1.500	P	1.500	P	1.500
ON3	-0.82	ON3	-0.820	ON3	-0.820	ON3	-0.820
ON3	-0.82	ON3	-0.820	ON3	-0.820	ON3	-0.820
ON2	-0.62	ON2	-0.620	ON2	-0.620	ON2	-0.620
ON4	-0.68	ON4	-0.680	ON4	-0.680	ON4	-0.680
HN4	0.34	HN4	0.340	HN4	0.340	HN4	0.340
CN8B	-0.08	CN8B	-0.080	CN8B	-0.080	CN8B	-0.080
HN8	0.09	HN8	0.090	HN8	0.090	HN8	0.090
HN8	0.09	HN8	0.090	HN8	0.090	HN8	0.090
CN7	0.16	CN7B	0.160	CN7	0.160	CN7	0.160
HN7	0.09	HN7	0.090	HN7	0.090	HN7	0.090
ON6	-0.50	ON6	-0.500	ON6	-0.500	ON6	-0.500
CN7B	0.16	CN7	0.160	CN7B	0.160	CN7B	0.160
HN7	0.09	HN7	0.090	HN7	0.090	HN7	0.090
NN2	-0.05	NN2	-0.130	NN2B	-0.020	NN2B	-0.340
CN5	0.28	CN3	0.050	CN5	0.260	CN3	0.170
NN4	-0.71	HN3	0.170	NN1	-0.680	HN3	0.170
CN4	0.34	CN3	-0.130	HN1	0.320	CN1T	0.510
HN3	0.12	HN3	0.070	HN1	0.350	ON1	-0.410
NN3A	-0.74	CN1	0.520	NN3G	-0.740	NN2U	-0.460
CN4	0.50	ON1C	-0.490	CN2	0.750	HN2	0.360
HN3	0.13	NN3	-0.660	NN2G	-0.340	CN1	0.500
NN3A	-0.75	CN2	0.650	HN2	0.260	ON1	-0.450
CN5	0.43	NN1	-0.750	CN1	0.540	CN3T	-0.150
CN2	0.46	HN1	0.370	ON1	-0.510	CN9	-0.110
NN1	-0.77	HN1	0.330	CN5G	0.000	HN9	0.070
HN1	0.38	CN8	-0.180	NN4	-0.600	HN9	0.070
HN1	0.38	HN8	0.090	CN4	0.250	HN9	0.070
CN8	-0.18	HN8	0.090	HN3	0.160	CN8	-0.180
HN8	0.09	CN7	0.010	CN8	-0.180	HN8	0.090
HN8	0.09	HN7	0.090	HN8	0.090	HN8	0.090
CN7	0.01	ON2	-0.570	HN8	0.090	CN7	0.010
HN7	0.09			CN7	0.010	HN7	0.090

ON2	-0.57	HN7	0.090	ON2	-0.570
		ON2	-0.570		