Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Elucidation of polyethylene glycol adsorption at the solid-H_2O(l) interfaces of anatase TiO_2(101) using Density Functional Theory and molecular dynamics simulations

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Section S1. AIMD simulations for $H_2O(l)_{1ML}{}^*$ on TiO_2(101)

We have performed the AIMD simulation for $H_2O(l)_{1ML}{}^*$ using TiO_2(101). All the snapshots at each picosecond (ps) shows 1 monolayer (ML) of H_2O*, occupying all the Ti_{5C} sites. The representative snapshot is provided in Fig. S1. Table S1 shows a comparison of $H_2O(l)_{1ML}{}^*$ and $H_2O(l)_{<1ML}{}^*$. The energy difference of these two structures is more than 1 eV, because properties of bulk liquid water (e.g. total number of the hydrogen bond and the water structure) are different. Therefore, a direct comparison is not appropriate for analyzing the adsorption free energy of PEG*.

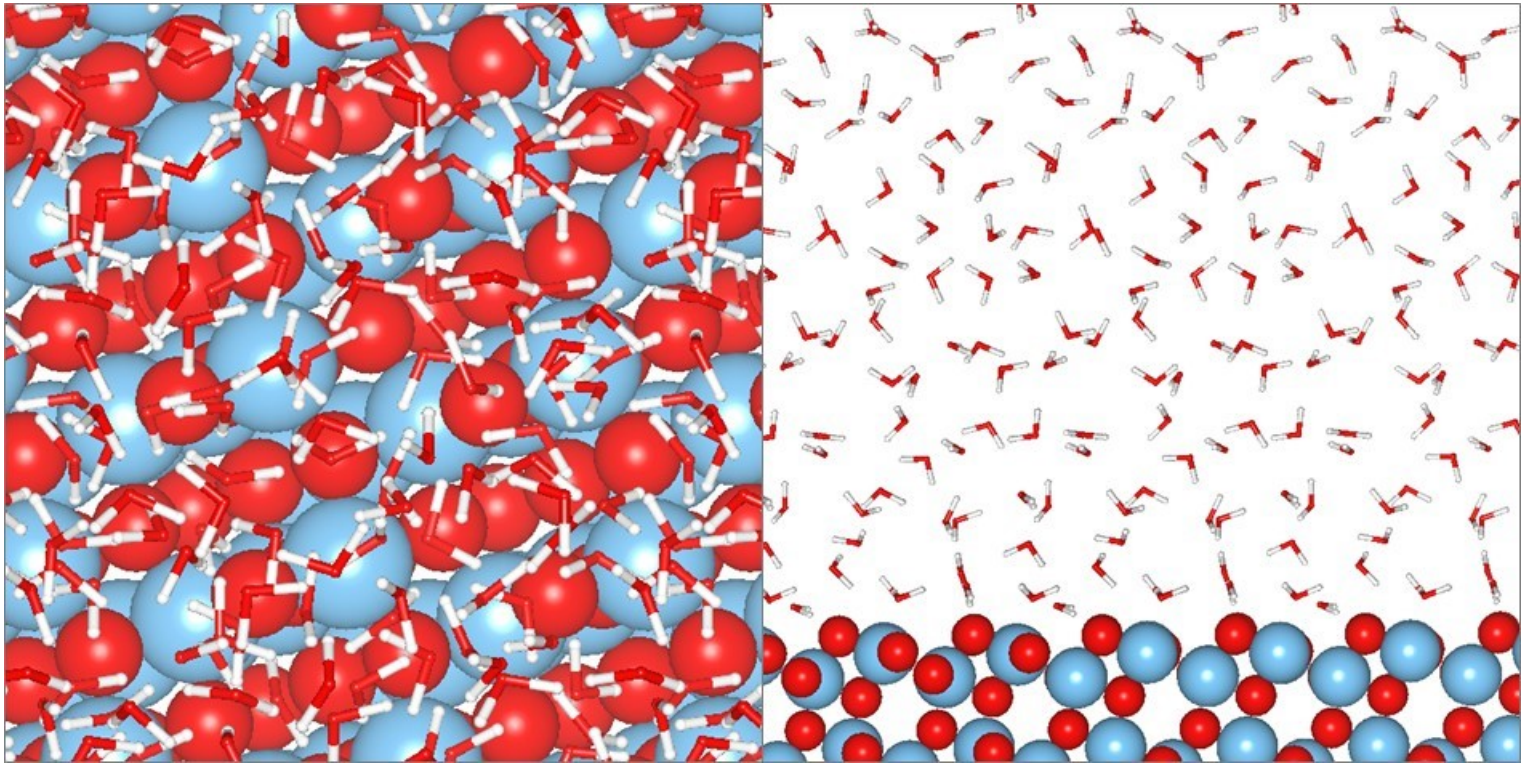

Fig. S1. Representative top and side views of the $H_2O(l)_{1ML}{}^*$ on the TiO_2(101) surface at 10 ps of the AIMD simulation. Water molecules are shown in a simplified form. Light blue, Ti; red, O; white, H.

Table S1. Comparison of $H_2O(l)_{1ML}{}^*$ and $H_2O(l)_{<1ML}{}^*$

ps	$H_2O(l)_{1ML}{}^*$			$H_2O(l)_{<1ML}{}^*$ [1]			$E_{DFT}{}_{H_2O(l)_{<1ML}{}^*} - E_{DFT}{}_{H_2O(l)_{1M}}$ (eV)
	E_{DFT} (eV)	Total number of the hydrogen bond in bulk liquid	$\theta_{H_2O^*}$ (ML)[2]	E_{DFT} (eV)	Total number of the hydrogen bond in bulk liquid	$\theta_{H_2O^*}$ (ML)[2]	
1	-1591.80	136	1.00	-1586.94	119	0.75	4.86
2	-1591.01	134	1.00	-1588.47	118	0.75	2.55
3	-1592.35	145	1.00	-1589.52	123	0.75	2.82
4	-1592.45	140	1.00	-1589.45	125	0.75	2.99
5	-1593.21	139	1.00	-1589.04	121	0.75	4.17
6	-1593.18	141	1.00	-1589.36	121	0.75	3.82
7	-1593.82	140	1.00	-1589.21	117	0.75	4.60
8	-1593.65	142	1.00	-1588.66	116	0.75	4.99
9	-1593.32	137	1.00	-1589.47	122	0.75	3.85
10	-1592.99	141	1.00	-1589.18	125	0.75	3.80
Average	-1592.78	139.50	1.00	-1588.93	120.70	0.75	3.85

[1] the corresponding water structure is obtained from the AIMD snapshots of 0.25 ML PEG-5*.

[2] the surface coverage of H_2O*.

Section S2. H_2O desorption energy ($\Delta G_{H_2O^* \rightarrow H_2O(l)}$)

When adsorbed H_2O is desorbed from the TiO_2 surface, it loses the adsorption energy while gains solvation energy. From the AIMD snapshots of $H_2O(l)_{1ML}{}^*$, we found that H_2O* has hydrogen bonds with water molecules and with the neighboring O_{2C} atom at the surface (Fig. S2). Thus, the energy of H_2O* is calculated based on this configuration using the single point calculations of the obtained AIMD snapshots.

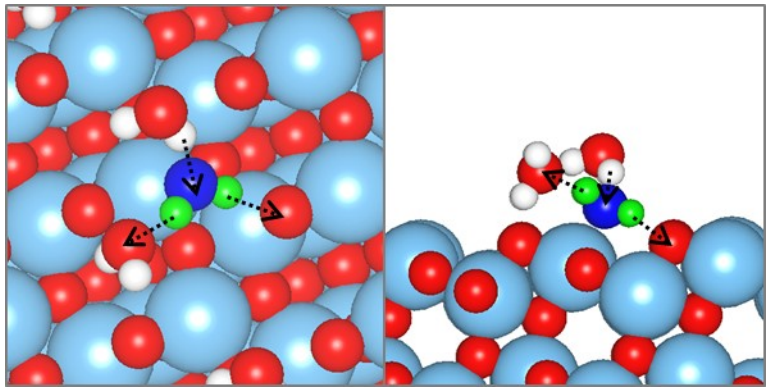

Fig. S2. Top and side views of H_2O^* on $TiO_2(101)$. The black arrows represent the hydrogen bonds. Light blue, Ti; red, O; blue, O of H_2O^*; light green, H of H_2O^*; white, H.

As for the $H_2O(l)$ solvation energy, we found that single $H_2O(l)$ in bulk liquid water has different number of hydrogen bonds. Thus, the water solvation energy was calculated for each case as provided in Table S2.

Table S2. Hydrogen bonds for single $H_2O(l)$ in ${H_2O(l)_{1ML}}^*$.

Number of hydrogen bond	Number of $H_2O(l)$ molecules that has corresponding hydrogen bonds	Solvation energy for single $H_2O(l)$ (eV)[1)]	Total solvation energy (eV)[2)]
5	2	-1.56	-3.12
4	16	-1.25	-19.97
3	19	-0.94	-17.79
2	22	-0.64	-13.73
1	10	-0.31	-3.12
Sum	69	-4.68	-57.73

[1)] Solvation energy (eV) = $E_{DFT}{}_{H_2O(l)_x{}^*} - E_{DFT}{}_{H_2O(l)_{x-1}{}^*} - E_{DFT}{}_{H_2O(g)}$ (x is the total number of $H_2O(l)$ molecules in the unit cell)

[2)] Total solvation energy (eV) = Solvation energy (eV) × the number of $H_2O(l)$ molecules that has corresponding hydrogen bonds.

The average solvation energy for $H_2O(l)$ ($E_{solvation}$) is the sum of total solvation energy (-57.73 eV) divided by the sum of the number of $H_2O(l)$ (69), which gives -0.84 eV/$H_2O(l)$. Thus, we can define the chemical potentials for H_2O^* and $H_2O(l)$ as follows:

$$\mu_{H_2O^*} = E_{DFT_{H_2O^*}} + ZPE_{H_2O^*} - T\Delta S_{H_2O^*} \quad \text{(S1)}$$

$$\mu_{H_2O(l)} = E_{DFT_{H2O(g)}} + ZPE_{H_2O(g)} - T\Delta S_{H_2O(g)} + E_{solvation} \quad \text{(S2)}$$

where E_{DFT}, ZPE, and ΔS are the DFT energy, zero-point energy, and entropy of the species, respectively. The entropy of H_2O(g) at the standard state was taken from the standard thermodynamic table,[S1] while the corresponding energy for H_2O* is calculated using the vibrational frequency based on frustrated translation and rotation.[S2] Putting Equations S1 and S2 in Equation 10 in the main text gives,

$$\Delta G_{H_2O^* \rightarrow H_2O(l)} = E_{DFT_{H2O(g)}} + ZPE_{H_2O(g)} - T\Delta S_{H_2O(g)} + E_{solvation} + E_{DFT*} - (E_{DFT_{H_2O^*}} + ZPE_{H_2O^*} - T\Delta S_{H_2O^*}) \quad \text{(S3)}$$

Consequently, a value for the desorption free energy for H_2O* on TiO_2(101) is 0.08 eV/H_2O. This indicates that the process is almost energetically neutral. The total number of adsorbed H_2O is 4/unit cell (1ML) at $^{H_2O(l)_{1ML}}{}^*$ based on our TiO_2 slab model (4 Ti_{5C} sites/unit cell) before PEG adsorption. Thus, the total number of desorbed H_2O molecules per unit cell (N) is determined by,

$$N \text{ (\#/unit cell)} = 4 - \text{the total number of } H_2O^* \text{ at } {}^{H_2O(l)_{<1ML}}{}^* \quad \text{(S4)}$$

Section S3. H_2O* dissociation and OH* formation on anatase TiO_2(101)

To confirm the OH* formation on TiO_2(101), we performed the kinetic barrier energy calculation for H_2O dissociation using the nudged elastic band (NEB) method.[S3] Fig. S3 (a) shows the H_2O* dissociation kinetic barriers in the presence of zero, single, and full liquid water on the TiO_2(101) slab where the coverage of PEG-5* is 0.75 ML. We found that the barrier energy increases with increasing the number of H_2O(l) because H_2O* dissociation requires more energy to break hydrogen bonding which is formed between water molecules. For example, in the presence of full liquid water, H_2O* on the surface forms hydrogen bonds with two H_2O(l) (Fig. S3 (b)), and the hydrogen bonds with these water molecules are broken during a H_2O* dissociation pathway. Therefore, the kinetic barrier energy under full liquid H_2O(l) (1.31 eV) is higher than the barrier from the situation where there is no (0.71 eV) or only single H_2O(l) (0.73 eV). Based on the harmonic transition state theory, the kinetic barrier of 1.31 eV is energetically insurmountable and therefore it could not generate

the observable rate at the room temperature. Therefore, the OH* formation is energetically unfavorable on anatase TiO_2(101) surface and is expected to form no or a very low surface coverage which may not impact on the PEG adsorption.

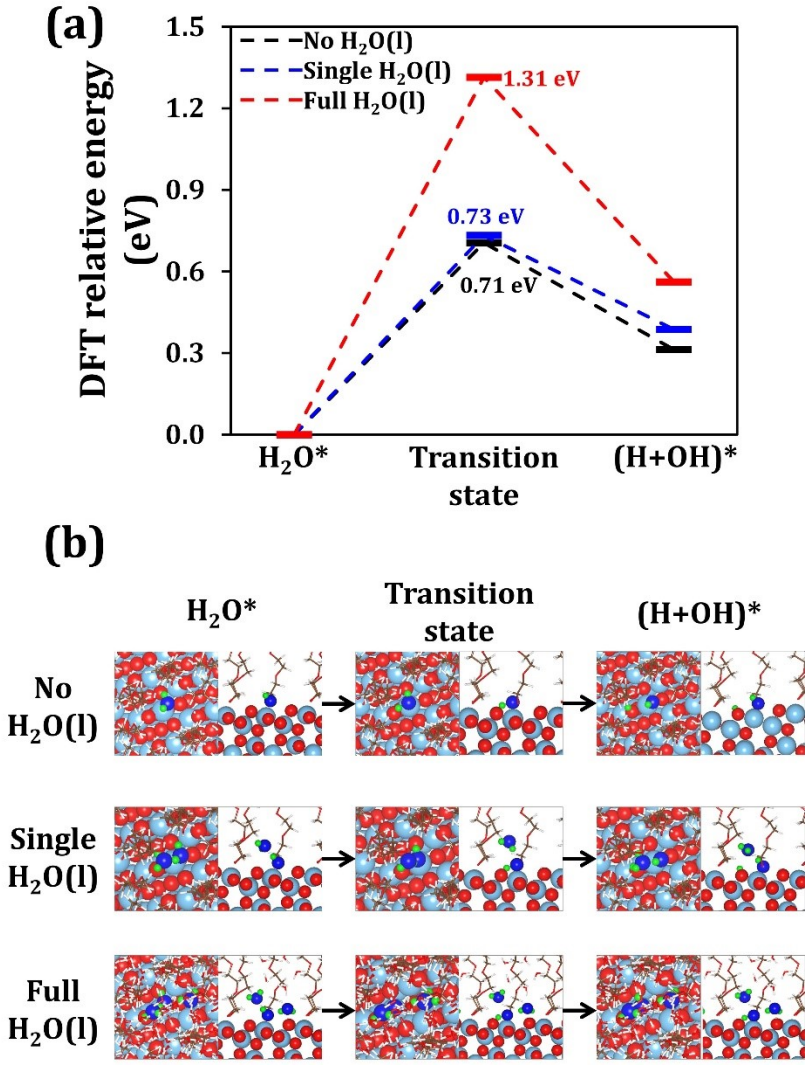

Fig. S3. (a) free energy diagrams for H_2O* dissociation on the anatase TiO_2(101) surface in the presence of PEG-5* (0.75 ML) and H_2O(l). The values shown in the plot are the kinetic barrier energies for H_2O* dissociation (the color index is the same as the plot). (b) Top and side views of H_2O* dissociation in the presence of PEG-5* (0.75 ML) and H_2O(l). The PEG-5* and bulk liquid water molecule are shown as simplified forms, while surface adsorbed H_2O (H_2O*) and surface adjacent H_2O(l) are described using blue (O) and light green (H) circles. Light blue, Ti; red, O; blue, O of H_2O* and surface adjacent H_2O(l); light green, H of H_2O* and surface adjacent H_2O(l); white, H of PEG*; brown, C of PEG*.

Section S4. AIMD simulation results for PEG-5*

Table S3. Data for 0.25 ML PEG-5* on TiO_2(101)

ps	$E_{DFT}{}_{(PEG/H_2O(l)<1ML)}$ (eV)	$E_{DFT}{}_{H_2O(l)<1ML}{}^{*}$ (eV)	$E_{DFT}{}_{PEG(g)}$ (undissociated) (eV)	$E_{DFT}{}_{PEG}{}^{*}$ (eV)	$E_{DFT}{}_{*}$ (slab) (eV)	$E_{DFT}{}_{PEG}$ (dissociated) (eV)[1)]	$E_{DFT}{}_{PEG(g)}$ (dissociated) (eV)[2)]	$E_{DFT}{}_{PEG\_head}{}^{*}{}_{(adsorption)}$ (eV)[3)]	$E_{DFT}{}_{PEG\_chain}{}^{*}{}_{(interaction)}$ (eV)[4)]
1	-1805.98	-1586.94	-212.28	-738.27	-524.07	-206.31	-206.27	-1.88	-0.04
2	-1807.58	-1588.47	-212.28	-738.36	-523.96	-206.42	-206.38	-2.08	-0.04
3	-1808.62	-1589.52	-212.28	-738.42	-524.13	-206.47	-206.45	-1.99	-0.02
4	-1808.79	-1589.45	-212.28	-738.38	-524.30	-206.46	-206.44	-1.77	-0.03
5	-1808.24	-1589.04	-212.28	-738.37	-524.37	-206.48	-206.45	-1.69	-0.02
6	-1808.50	-1589.36	-212.28	-738.47	-524.22	-206.52	-206.49	-1.93	-0.03
7	-1808.31	-1589.21	-212.28	-738.42	-524.41	-206.50	-206.47	-1.71	-0.03
8	-1808.26	-1588.66	-212.28	-738.44	-524.30	-206.51	-206.47	-1.82	-0.04
9	-1808.63	-1589.47	-212.28	-738.43	-524.30	-206.52	-206.49	-1.81	-0.03
10	-1808.73	-1589.18	-212.28	-738.34	-524.34	-206.46	-206.44	-1.70	-0.02
Average	-1808.16	-1588.93	-212.28	-738.39	-524.24	-206.47	-206.44	-1.84 ± 0.12	-0.03 ± 0.01

Table S3. continued

ps	$E_{DFT}{}_{PEG}{}^{*}{}_{(solvation)}$ (eV)[5)]	$\Delta H_{PEG}{}^{*}$ (eV)[6)]	$E_{DFT}{}_{PEG\_head}{}^{*}{}_{(adsorption)}$ /# of PEG (eV/PEG)[7)]	$E_{DFT}{}_{PEG\_chain}{}^{*}{}_{(interaction)}$ /# of monomer (eV/monomer)[8)]	$\#_{H-bond}$[9)]	$E_{DFT}{}_{PEG}{}^{*}{}_{(solvation)}$ /# of O in PEG* (eV/monomer)[10)]	$\theta_{PEG}{}^{*}$ (ML)[11)]	$\theta_{H_2O}{}^{*}$ (ML)[12)]	N[13)]
1	-4.84	-6.76	-1.88	-0.01	9	-0.81	0.25	0.75	1
2	-4.71	-6.83	-2.08	-0.01	9	-0.78	0.25	0.75	1
3	-4.81	-6.81	-1.99	-0.01	10	-0.80	0.25	0.75	1
4	-5.26	-7.05	-1.77	-0.01	9	-0.88	0.25	0.75	1
5	-5.21	-6.92	-1.69	-0.01	10	-0.87	0.25	0.75	1
6	-4.89	-6.86	-1.93	-0.01	8	-0.82	0.25	0.75	1
7	-5.08	-6.81	-1.71	-0.01	10	-0.85	0.25	0.75	1
8	-5.46	-7.32	-1.82	-0.01	10	-0.91	0.25	0.75	1
9	-5.03	-6.88	-1.81	-0.01	9	-0.84	0.25	0.75	1
10	-5.54	-7.26	-1.70	-0.01	11	-0.92	0.25	0.75	1

Average	-5.08 ± 0.27	-6.95 ± 0.19	-1.84	-0.01	9.50	-0.85	0.25	0.75	1

1) Single point calculation for dissociated PEG where the structure and unit cell are from $E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*}$

2) Single point calculation for dissociated PEG where the structure is from $E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*}$ in a large unit cell (no interactions between PEG)

3) $$E_{DFT}{}_{PEG\_head^*(adsorption)} = E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*} - E_{DFT}{}_{H_2O(l)<1ML^*} - E_{DFT}{}_{PEG(g)}(undissociated) - \Delta E_{DFT}{}_{PEG\_chain^*(interaction)}$$

4) $$E_{DFT}{}_{PEG\_chain^*(interaction)} = E_{DFT}{}_{PEG}(dissociated) - the\ total\ number\ of\ dissociated\ PEG^*\ in\ the\ unit\ cell \times E_{DFT}{}_{PEG(g)}(dissociated)$$

5) $$E_{DFT}{}_{PEG^*(solvation)} = E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*} - E_{DFT}{}_{H_2O(l)<1ML^*} - E_{DFT}{}_{PEG^*} + E_{DFT}{}_{*}$$

6) $$\Delta H_{PEG^*} = E_{DFT}{}_{PEG\_head^*(adsorption)} + E_{DFT}{}_{PEG\_chain^*(interaction)} + E_{DFT}{}_{PEG^*(solvation)}$$

7) $$\frac{E_{DFT}{}_{PEG_{head}{}^*(adsorption)}}{\#\ of\ PEG^*} = \frac{E_{DFT}{}_{PEG\_head^*(adsorption)}}{the\ total\ number\ of\ PEG^*\ in\ the\ unit\ cell}$$

8) $$\frac{E_{DFT}{}_{PEG_{chain}{}^*(interaction)}}{\#\ of\ monomer} = \frac{E_{DFT}{}_{PEG\_chain^*(interaction)}}{the\ total\ number\ of\ the\ PEG^*\ monomer\ in\ the\ unit\ cell}$$

9) the total hydrogen bond number between PEG* and surrounding H_2O(l) molecules

10) $$\frac{E_{DFT}{}_{PEG^*(solvation)}}{\#\ of\ O\ in\ PEG^*} = \frac{E_{DFT}{}_{PEG^*(solvation)}}{the\ total\ number\ of\ the\ oxygen\ atom\ in\ PEG^*\ in\ the\ unit\ cell}$$

11) the surface coverage of PEG* in the unit cell

12) the surface coverage of H_2O* in the unit cell

13) the total number of desorbed H_2O/unit cell during PEG adsorption

Table S4. Data for 0.50 ML PEG-5* on TiO_2(101)

ps	$E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)}$ (eV)	$E_{DFT}{}_{H_2O(l)<1ML^*}$ (eV)	$E_{DFT}{}_{PEG(g)}$ (undissociated) (eV)	$E_{DFT}{}_{PEG^*}$ (eV)	$E_{DFT}{}_{*}$ (slab) (eV)	$E_{DFT}{}_{PEG}$ (dissociated) (eV)[1)]	$E_{DFT}{}_{PEG(g)}$ (dissociated) (eV)[2)]	$E_{DFT}{}_{PEG\_head^*(adsorption)}$ (eV)[3)]	$E_{DFT}{}_{PEG\_chain^*(interaction)}$ (eV)[4)]
1	-1769.15	-1331.65	-212.28	-952.18	-523.05	-413.25	-206.35	-4.01	-0.56
2	-1770.36	-1332.38	-212.28	-952.05	-523.31	-413.16	-206.26	-3.53	-0.63
3	-1770.70	-1332.17	-212.28	-951.85	-523.06	-413.02	-206.45	-4.10	-0.12
4	-1769.36	-1331.19	-212.28	-952.24	-523.33	-413.31	-206.37	-3.78	-0.57
5	-1770.65	-1333.62	-212.28	-952.26	-522.78	-413.30	-206.40	-4.43	-0.49
6	-1770.49	-1333.09	-212.28	-952.04	-522.85	-413.31	-206.25	-3.82	-0.80
7	-1770.96	-1332.99	-212.28	-952.15	-523.14	-413.45	-206.35	-3.70	-0.74
8	-1771.07	-1333.32	-212.28	-952.36	-523.25	-413.54	-206.41	-3.83	-0.71
9	-1771.05	-1333.72	-212.28	-952.54	-523.27	-413.64	-206.47	-3.99	-0.71

10	-1771.31	-1333.84	-212.28	-952.49	-523.25	-413.59	-206.45	-3.98	-0.69
Average	-1770.51	-1332.80	-212.28	-952.22	-523.13	-413.36	-206.38	-3.92 ± 0.23	-0.60 ± 0.18

Table S4. continued

ps	$E_{DFT}{}_{PEG^*(solvation)}$ (eV)[5]	ΔH_{PEG^*} (eV)[6]	$E_{DFT}{}_{PEG\_head^*(adsorption)}$ /# of PEG (eV/PEG)[7]	$E_{DFT}{}_{PEG\_chain^*(interaction)}$ /# of monomer (eV/monomer)[8]	$\#_{H-bond}$[9]	$E_{DFT}{}_{PEG^*(solvation)}$ /# of O in PEG* (eV/monomer)[10]	θ_{PEG^*} (ML)[11]	$\theta_{H_2O^*}$ (ML)[12]	N[13]
1	-8.36	-12.93	-2.00	-0.06	17	-0.70	0.50	0.50	2
2	-9.25	-13.41	-1.77	-0.06	18	-0.77	0.50	0.50	2
3	-9.73	-13.96	-2.05	-0.01	20	-0.81	0.50	0.50	2
4	-9.25	-13.60	-1.89	-0.06	17	-0.77	0.50	0.50	2
5	-7.54	-12.46	-2.21	-0.05	15	-0.63	0.50	0.50	2
6	-8.21	-12.83	-1.91	-0.08	17	-0.68	0.50	0.50	2
7	-8.96	-13.40	-1.85	-0.07	18	-0.75	0.50	0.50	2
8	-8.63	-13.18	-1.92	-0.07	18	-0.72	0.50	0.50	2
9	-8.06	-12.76	-2.00	-0.07	16	-0.67	0.50	0.50	2
10	-8.23	-12.90	-1.99	-0.07	16	-0.69	0.50	0.50	2
Average	-8.62 ± 0.63	-13.14 ± 0.43	-1.96	-0.06	17.20	-0.72	0.50	0.50	2.00

[1] Single point calculation for dissociated PEG where the structure and unit cell are from $E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*}$

[2] Single point calculation for dissociated PEG where the structure is from $E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*}$ in a large unit cell (no interactions between PEG)

[3] $$E_{DFT}{}_{PEG\_head^*(adsorption)} = E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*} - E_{DFT}{}_{H_2O(l)<1ML^*} - E_{DFT}{}_{PEG(g)}(undissociated) - \Delta E_{DFT}{}_{PEG\_chain^*(interaction)}$$

[4] $$E_{DFT}{}_{PEG\_chain^*(interaction)} = E_{DFT}{}_{PEG}(dissociated) - the\ total\ number\ of\ dissociated\ PEG^*\ in\ the\ unit\ cell \times E_{DFT}{}_{PEG(g)}(dissociated)$$

[5] $$E_{DFT}{}_{PEG^*(solvation)} = E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*} - E_{DFT}{}_{H_2O(l)<1ML^*} - E_{DFT}{}_{PEG^*} + E_{DFT}{}_{*}$$

[6] $$\Delta H_{PEG^*} = E_{DFT}{}_{PEG\_head^*(adsorption)} + E_{DFT}{}_{PEG\_chain^*(interaction)} + E_{DFT}{}_{PEG^*(solvation)}$$

[7] $$\frac{E_{DFT}{}_{PEG_{head}{}^*(adsorption)}}{\#\ of\ PEG^*} = \frac{E_{DFT}{}_{PEG\_head^*(adsorption)}}{the\ total\ number\ of\ PEG^*\ in\ the\ unit\ cell}$$

[8] $$\frac{E_{DFT}{}_{PEG_{chain}{}^*(interaction)}}{\#\ of\ monomer} = \frac{E_{DFT}{}_{PEG\_chain^*(interaction)}}{the\ total\ number\ of\ the\ PEG^*\ monomer\ in\ the\ unit\ cell}$$

[9] the total hydrogen bond number between PEG* and surrounding $H_2O(l)$ molecules

[10] $$\frac{E_{DFT}{}_{PEG^*(solvation)}}{\#\ of\ O\ in\ PEG^*} = \frac{E_{DFT}{}_{PEG^*(solvation)}}{the\ total\ number\ of\ the\ oxygen\ atom\ in\ PEG^*\ in\ the\ unit\ cell}$$

[11] the surface coverage of PEG* in the unit cell
[12] the surface coverage of H_2O* in the unit cell
[13] the total number of desorbed H_2O/unit cell during PEG adsorption

Table S5. Data for 0.75 ML PEG-5* on TiO_2(101)

ps	E_{DFT} $_{(PEG/H_2O(l)<1ML)}$ (eV)	E_{DFT} $_{H_2O(l)<1ML}{}^*$ (eV)	E_{DFT} $_{PEG(g)}$ (undissociated) (eV)	E_{DFT} $_{PEG}{}^*$ (eV)	E_{DFT} $_*$ (slab) (eV)	E_{DFT} $_{PEG}$ (dissociated) (eV)[1]	E_{DFT} $_{PEG(g)}$ (dissociated) (eV)[2]	E_{DFT} $_{PEG\_head}{}^*{}_{(adsorption)}$ (eV)[3]	E_{DFT} $_{PEG\_chain}{}^*{}_{(interaction)}$ (eV)[4]
1	-1836.97	-1182.47	-212.28	-1166.94	-521.80	-620.68	-206.36	-6.70	-1.59
2	-1835.99	-1182.31	-212.28	-1167.22	-521.95	-620.82	-206.17	-6.10	-2.32
3	-1837.11	-1182.99	-212.28	-1167.26	-521.99	-620.54	-206.25	-6.63	-1.80
4	-1838.33	-1184.46	-212.28	-1168.06	-522.03	-621.32	-206.43	-7.15	-2.03
5	-1837.96	-1184.13	-212.28	-1168.10	-521.94	-621.51	-206.45	-7.15	-2.16
6	-1837.80	-1183.25	-212.28	-1168.07	-521.91	-621.48	-206.55	-7.47	-1.83
7	-1837.92	-1183.60	-212.28	-1168.00	-521.82	-621.53	-206.49	-7.26	-2.07
8	-1838.59	-1184.11	-212.28	-1167.95	-521.98	-621.67	-206.48	-6.90	-2.23
9	-1838.79	-1184.97	-212.28	-1167.96	-521.67	-623.58	-206.52	-5.42	-4.03
10	-1838.88	-1184.90	-212.28	-1168.01	-521.66	-621.72	-206.58	-7.52	-1.99
Average	-1837.84	-1183.72	-212.28	-1167.76	-521.87	-621.49	-206.43	-6.83 ± 0.62	-2.21 ± 0.64

Table S5. continued

ps	E_{DFT} $_{PEG}{}^*{}_{(solvation)}$ (eV)[5]	ΔH $_{PEG}{}^*$ (eV)[6]	E_{DFT} $_{PEG\_head}{}^*{}_{(adsorption)}$ /# of PEG (eV/PEG)[7]	E_{DFT} $_{PEG\_chain}{}^*{}_{(interaction)}$ /# of monomer (eV/monomer)[8]	$\#_{H-bond}$[9]	E_{DFT} $_{PEG}{}^*{}_{(solvation)}$ /# of O in PEG* (eV/monomer)[10]	θ $_{PEG}{}^*$ (ML)[11]	θ $_{H_2O}{}^*$ (ML)[12]	N[13]
1	-9.36	-17.65	-2.23	-0.11	20	-0.52	0.75	0.25	3
2	-8.41	-16.83	-2.03	-0.15	19	-0.47	0.75	0.25	3
3	-8.86	-17.28	-2.21	-0.12	20	-0.49	0.75	0.25	3
4	-7.84	-17.02	-2.38	-0.14	15	-0.44	0.75	0.25	3
5	-7.66	-16.98	-2.38	-0.14	15	-0.43	0.75	0.25	3
6	-8.40	-17.70	-2.49	-0.12	17	-0.47	0.75	0.25	3
7	-8.14	-17.47	-2.42	-0.14	16	-0.45	0.75	0.25	3
8	-8.51	-17.63	-2.30	-0.15	16	-0.47	0.75	0.25	3
9	-7.53	-16.97	-1.81	-0.27	16	-0.42	0.75	0.25	3
10	-7.62	-17.13	-2.51	-0.13	15	-0.42	0.75	0.25	3
Average	-8.23 ± 0.56	-17.27 ± 0.31	-2.28	-0.15	16.90	-0.46	0.75	0.25	3.00

[1] Single point calculation for dissociated PEG where the structure and unit cell are from E_{DFT} $_{(PEG/H_2O(l)<1ML)}{}^*$

[2] Single point calculation for dissociated PEG where the structure is from E_{DFT} $_{(PEG/H_2O(l)<1ML)}{}^*$ in a large unit cell (no interactions between PEG)

[3] E_{DFT} $_{PEG\_head}{}^*{}_{(adsorption)} = E_{DFT}$ $_{(PEG/H_2O(l)<1ML)}{}^* - E_{DFT}$ $_{H_2O(l)<1ML}{}^* - E_{DFT_{PEG(g)}}(undissociated) - \Delta E_{DFT}$ $_{PEG\_chain}{}^*{}_{(interaction)}$

4) $E_{DFT_{PEG\_chain^*(interaction)}} = E_{DFT_{PEG}}(dissociated) - the\ total\ number\ of\ dissociated\ PEG^*\ in\ the\ unit\ cell \times E_{DFT_{PEG(g)}}(dissociated)$

5) $E_{DFT_{PEG^*(solvation)}} = E_{DFT_{(PEG/H_2O(l)<1ML)^*}} - E_{DFT_{H_2O(l)<1ML}{}^*} - E_{DFT_{PEG^*}} + E_{DFT_*}$

6) $\Delta H_{PEG^*} = E_{DFT_{PEG\_head^*(adsorption)}} + E_{DFT_{PEG\_chain^*(interaction)}} + E_{DFT_{PEG^*(solvation)}}$

7) $\frac{E_{DFT_{PEG_{head}{}^*(adsorption)}}}{\#\ of\ PEG^*} = \frac{E_{DFT_{PEG\_head^*(adsorption)}}}{the\ total\ number\ of\ PEG^*\ in\ the\ unit\ cell}$

8) $\frac{E_{DFT_{PEG_{chain}{}^*(interaction)}}}{\#\ of\ monomer} = \frac{E_{DFT_{PEG\_chain^*(interaction)}}}{the\ total\ number\ of\ the\ PEG^*\ monomer\ in\ the\ unit\ cell}$

9) the total hydrogen bond number between PEG* and surrounding $H_2O(l)$ molecules

10) $\frac{E_{DFT_{PEG^*(solvation)}}}{\#\ of\ O\ in\ PEG^*} = \frac{E_{DFT_{PEG^*(solvation)}}}{the\ total\ number\ of\ the\ oxygen\ atom\ in\ PEG^*\ in\ the\ unit\ cell}$

11) the surface coverage of PEG* in the unit cell

12) the surface coverage of H_2O* in the unit cell

13) the total number of desorbed H_2O/unit cell during PEG adsorption

Table S6. Data for 1.00 ML PEG-5* on TiO_2(101)

ps	$E_{DFT_{(PEG/H_2O(l)<1ML)^*}}$ (eV)	$E_{DFT_{H_2O(l)<1ML}{}^*}$ (eV)	$E_{DFT_{PEG(g)}}$ (undissociated) (eV)	$E_{DFT_{PEG^*}}$ (eV)	E_{DFT_*} (slab) (eV)	$E_{DFT_{PEG}}$ (dissociated) (eV)[1]	$E_{DFT_{PEG(g)}}$ (dissociated) (eV)[2]	$E_{DFT_{PEG\_head^*(adsorption)}}$ (eV)[3]	$E_{DFT_{PEG\_chain^*(interaction)}}$ (eV)[4]
1	-1888.53	-1022.83	-212.28	-1383.55	-522.03	-835.67	-212.15	-7.96	-4.44
2	-1889.34	-1023.66	-212.28	-1383.59	-521.88	-835.73	-212.30	-7.65	-4.93
3	-1889.55	-1023.89	-212.28	-1384.15	-522.16	-835.80	-212.34	-8.14	-4.71
4	-1889.23	-1023.31	-212.28	-1383.59	-521.81	-835.79	-212.29	-8.43	-4.21
5	-1889.01	-1022.78	-212.28	-1383.40	-521.48	-835.85	-212.31	-8.58	-4.20
6	-1889.71	-1022.99	-212.28	-1383.80	-521.81	-835.95	-212.24	-8.78	-4.06
7	-1889.36	-1022.67	-212.28	-1383.73	-521.85	-835.92	-212.13	-8.41	-4.34
8	-1889.37	-1023.16	-212.28	-1383.84	-521.93	-835.98	-212.19	-8.43	-4.34
9	-1890.06	-1023.69	-212.28	-1383.84	-521.86	-836.00	-212.25	-8.64	-4.20
10	-1889.66	-1023.92	-212.28	-1383.92	-521.91	-836.25	-212.25	-8.61	-4.27
Average	-1889.38	-1023.29	-212.28	-1383.74	-521.87	-835.90	-212.24	-8.36 ± 0.33	-4.37 ± 0.25

Table S6. continued

ps	$E_{DFT_{PEG^*(solvation)}}$ (eV)[5]	ΔH_{PEG^*} (eV)[6]	$E_{DFT_{PEG\_head^*(adsorption)}}$ /# of PEG (eV/PEG)[7]	$E_{DFT_{PEG\_chain^*(interaction)}}$ /# of monomer (eV/monomer)[8]	$\#_{H-bond}$[9]	$E_{DFT_{PEG^*(solvation)}}$ /# of O in PEG* (eV/monomer)[10]	θ_{PEG^*} (ML)[11]	$\theta_{H_2O^*}$ (ML)[12]	N[13]

1	-4.17	-16.56	-1.99	-0.22	13	-0.17	1.00	0.00	4
2	-3.96	-16.54	-1.91	-0.25	12	-0.16	1.00	0.00	4
3	-3.67	-16.52	-2.03	-0.24	11	-0.15	1.00	0.00	4
4	-4.14	-16.78	-2.11	-0.21	13	-0.17	1.00	0.00	4
5	-4.31	-17.09	-2.14	-0.21	12	-0.18	1.00	0.00	4
6	-4.74	-17.59	-2.20	-0.20	13	-0.20	1.00	0.00	4
7	-4.80	-17.55	-2.10	-0.22	13	-0.20	1.00	0.00	4
8	-4.31	-17.08	-2.11	-0.22	13	-0.18	1.00	0.00	4
9	-4.39	-17.24	-2.16	-0.21	13	-0.18	1.00	0.00	4
10	-3.74	-16.61	-2.15	-0.21	12	-0.16	1.00	0.00	4
Average	-4.22 ± 0.36	-16.96 ± 0.39	-2.09	-0.22	12.50	-0.18	1.00	0.00	4.00

1) Single point calculation for dissociated PEG where the structure and unit cell are from $E_{DFT_{\left(PEG/H_2O(l)<1ML\right)^*}}$

2) Single point calculation for dissociated PEG where the structure is from $E_{DFT_{\left(PEG/H_2O(l)<1ML\right)^*}}$ in a large unit cell (no interactions between PEG)

3) $$E_{DFT_{PEG\_head^*(adsorption)}} = E_{DFT_{\left(PEG/H_2O(l)<1ML\right)^*}} - E_{DFT_{H_2O(l)<1ML^*}} - E_{DFT_{PEG(g)}}(undissociated) - \Delta E_{DFT_{PEG\_chain^*(interaction)}}$$

4) $$E_{DFT_{PEG\_chain^*(interaction)}} = E_{DFT_{PEG}}(dissociated) - the\ total\ number\ of\ dissociated\ PEG^*\ in\ the\ unit\ cell \times E_{DFT_{PEG(g)}}(dissociated)$$

5) $$E_{DFT_{PEG^*(solvation)}} = E_{DFT_{\left(PEG/H_2O(l)<1ML\right)^*}} - E_{DFT_{H_2O(l)<1ML^*}} - E_{DFT_{PEG^*}} + E_{DFT_*}$$

6) $$\Delta H_{PEG^*} = E_{DFT_{PEG\_head^*(adsorption)}} + E_{DFT_{PEG\_chain^*(interaction)}} + E_{DFT_{PEG^*(solvation)}}$$

7) $$\frac{E_{DFT_{PEG_{head}^*(adsorption)}}}{\#\ of\ PEG^*} = \frac{E_{DFT_{PEG\_head^*(adsorption)}}}{the\ total\ number\ of\ PEG^*\ in\ the\ unit\ cell}$$

8) $$\frac{E_{DFT_{PEG_{chain}^*(interaction)}}}{\#\ of\ monomer} = \frac{E_{DFT_{PEG\_chain^*(interaction)}}}{the\ total\ number\ of\ the\ PEG^*\ monomer\ in\ the\ unit\ cell}$$

9) the total hydrogen bond number between PEG* and surrounding H_2O(l) molecules

10) $$\frac{E_{DFT_{PEG^*(solvation)}}}{\#\ of\ O\ in\ PEG^*} = \frac{E_{DFT_{PEG^*(solvation)}}}{the\ total\ number\ of\ the\ oxygen\ atom\ in\ PEG^*\ in\ the\ unit\ cell}$$

11) the surface coverage of PEG* in the unit cell

12) the surface coverage of H_2O* in the unit cell

13) the total number of desorbed H_2O/unit cell during PEG adsorption

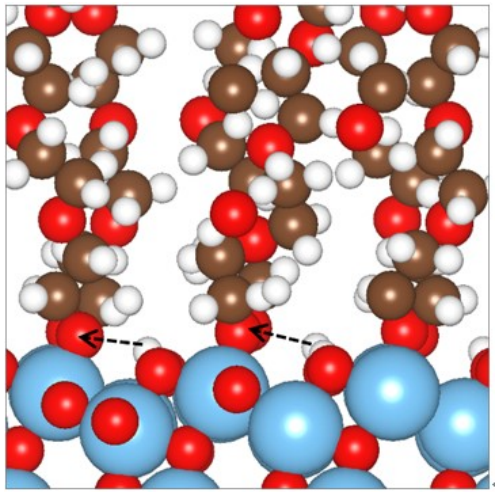

Fig. S4. Molecular configurations of PEG-5* on TiO_2(101) at 1.00 ML at 10 ps of AIMD simulation. The H_2O(l) molecules are deleted for a clarity. The dotted lines with arrows represent hydrogen bonding of the O species of PEG-5* with surface OH* of TiO_2(101).

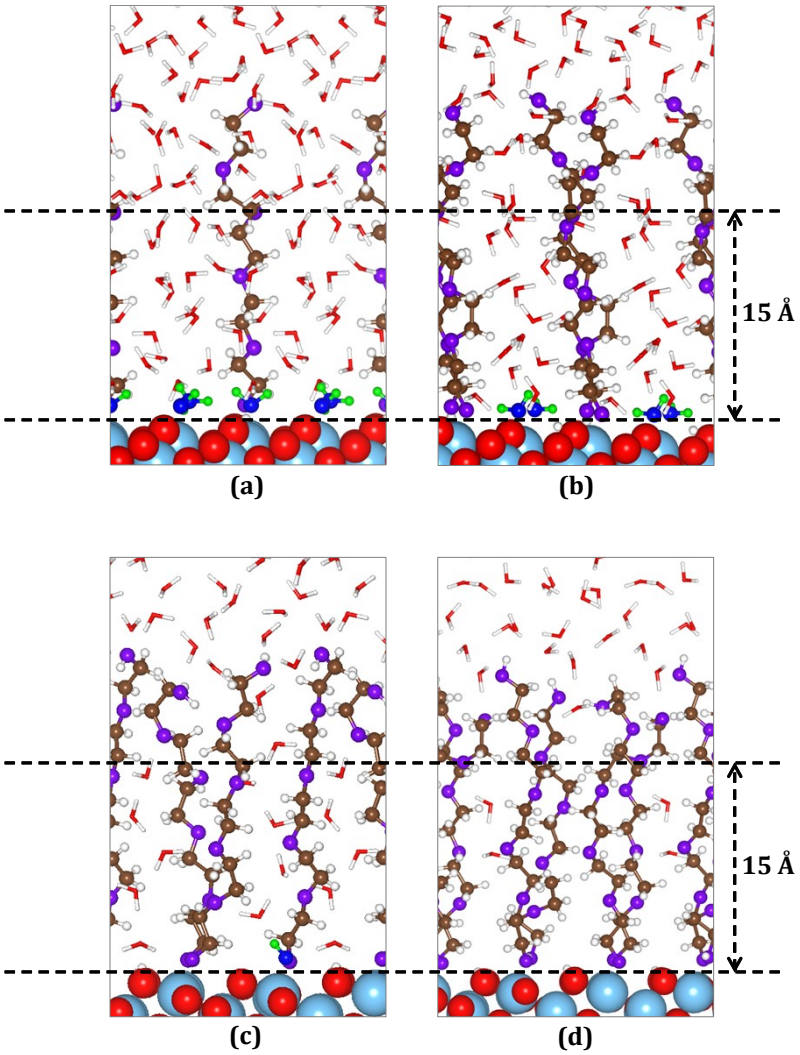

Fig. S5. Side views of the snapshots of $^{(PEG-5/H_2O(l)_{<1ML})^*}$ (10 ps) on TiO_2(101) where the PEG* coverage is (a) 0.25, (b) 0.50, (c) 0.75, and (d) 1.00 ML. The dotted lines represent a space up to 15 Å above the surface. Bulk liquid water molecules are described using a simplified form. Light blue, Ti; red, O; blue, O of H_2O*; light green, H of H_2O*; purple, O of PEG*; brown, C; white, H.

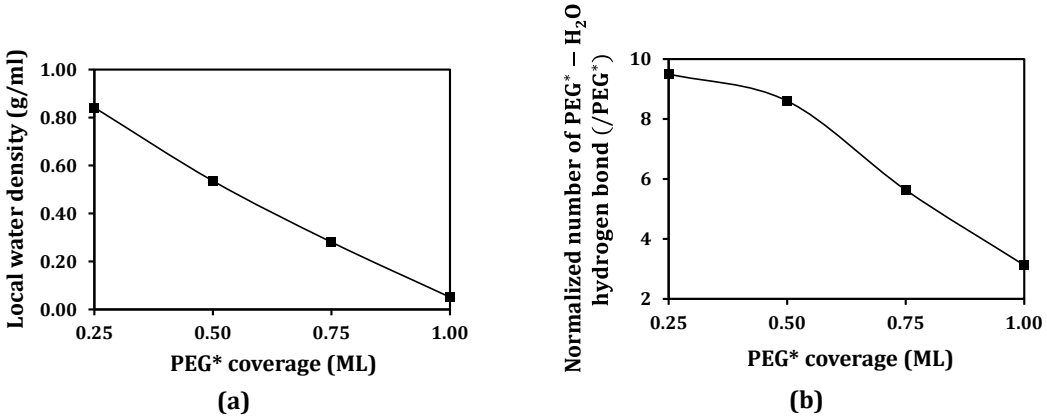

Fig. S6. PEG* coverage dependent of (a) the local H_2O density in space up to 15 Å from the surface and (b) normalized number of the PEG*–H_2O hydrogen bond.

Section S5. MD simulation results for PEG-3, PEG-5, PEG-10 and PEG-15 adsorption

Classical MD simulations for PEG-3, PEG-5, PEG-10 and PEG-15 adsorption on TiO_2(101) surface have been performed. Figs. S7-S9 are representative snapshots showing the brush type adsorption process of each polymer chain. Computed $^{T\Delta S}{}_{PEG^*}$ values are summarized in Fig. S10 and Table S7.

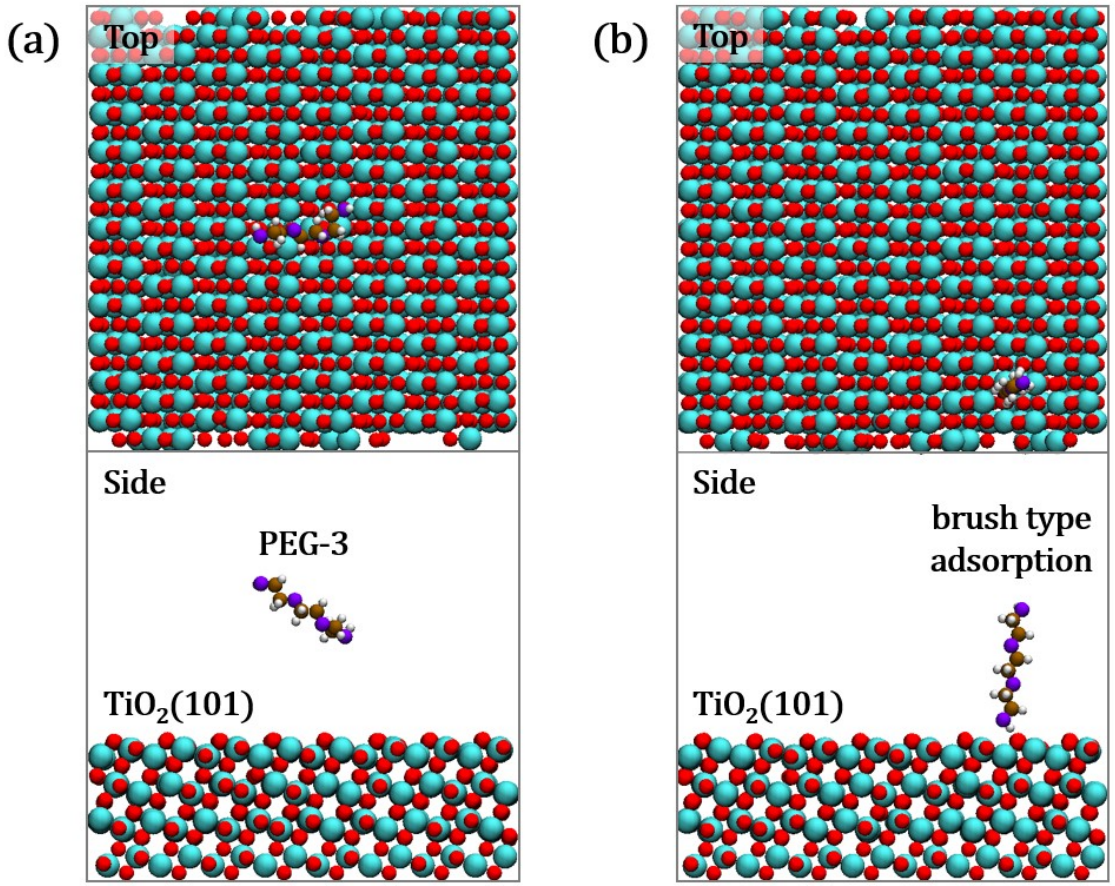

Fig. S7. Top and side views of PEG-3 adsorption on TiO_2(101) surface. (a) desorbed state and (b) adsorbed state.

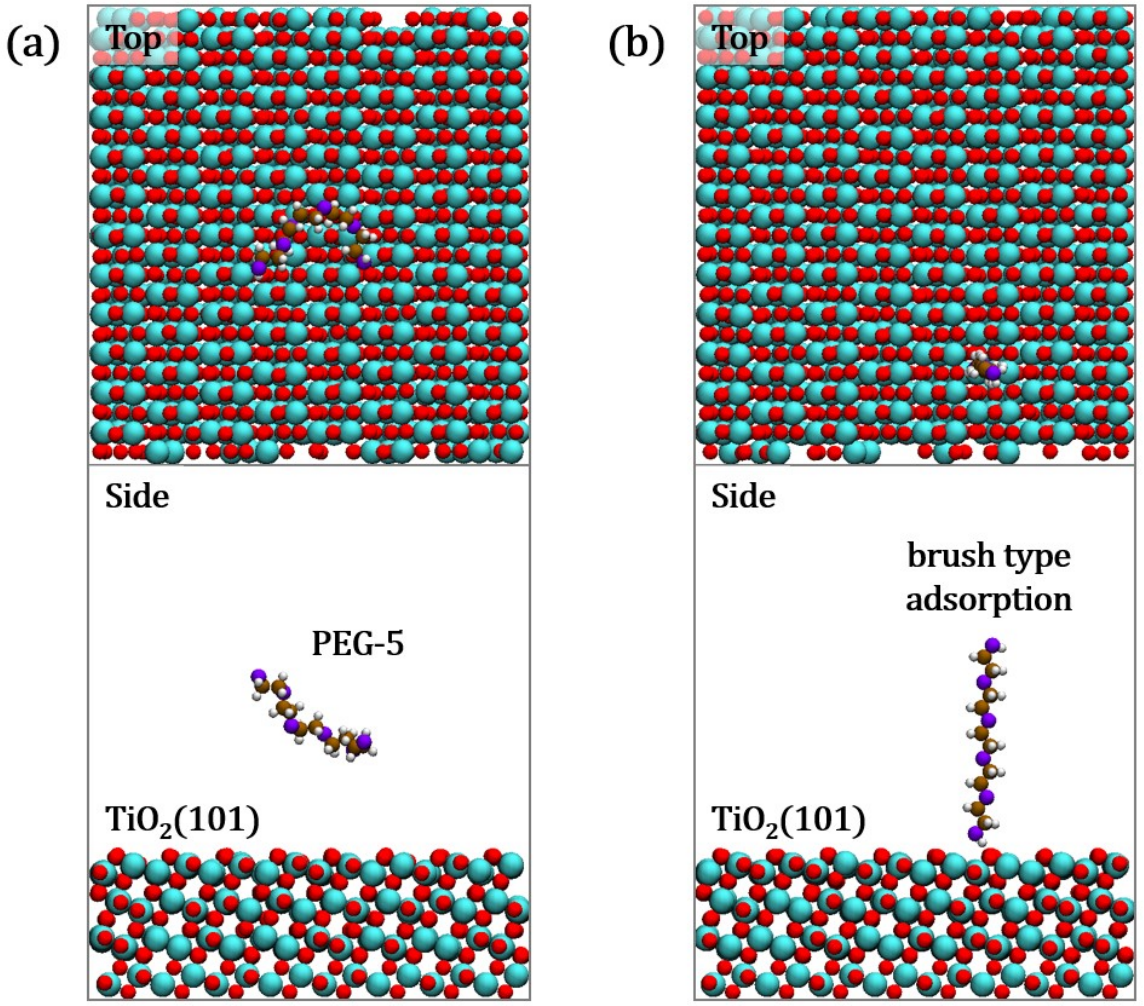

Fig. S8. Top and side views of PEG-5 adsorption on TiO_2(101) surface. (a) desorbed state and (b) adsorbed state.

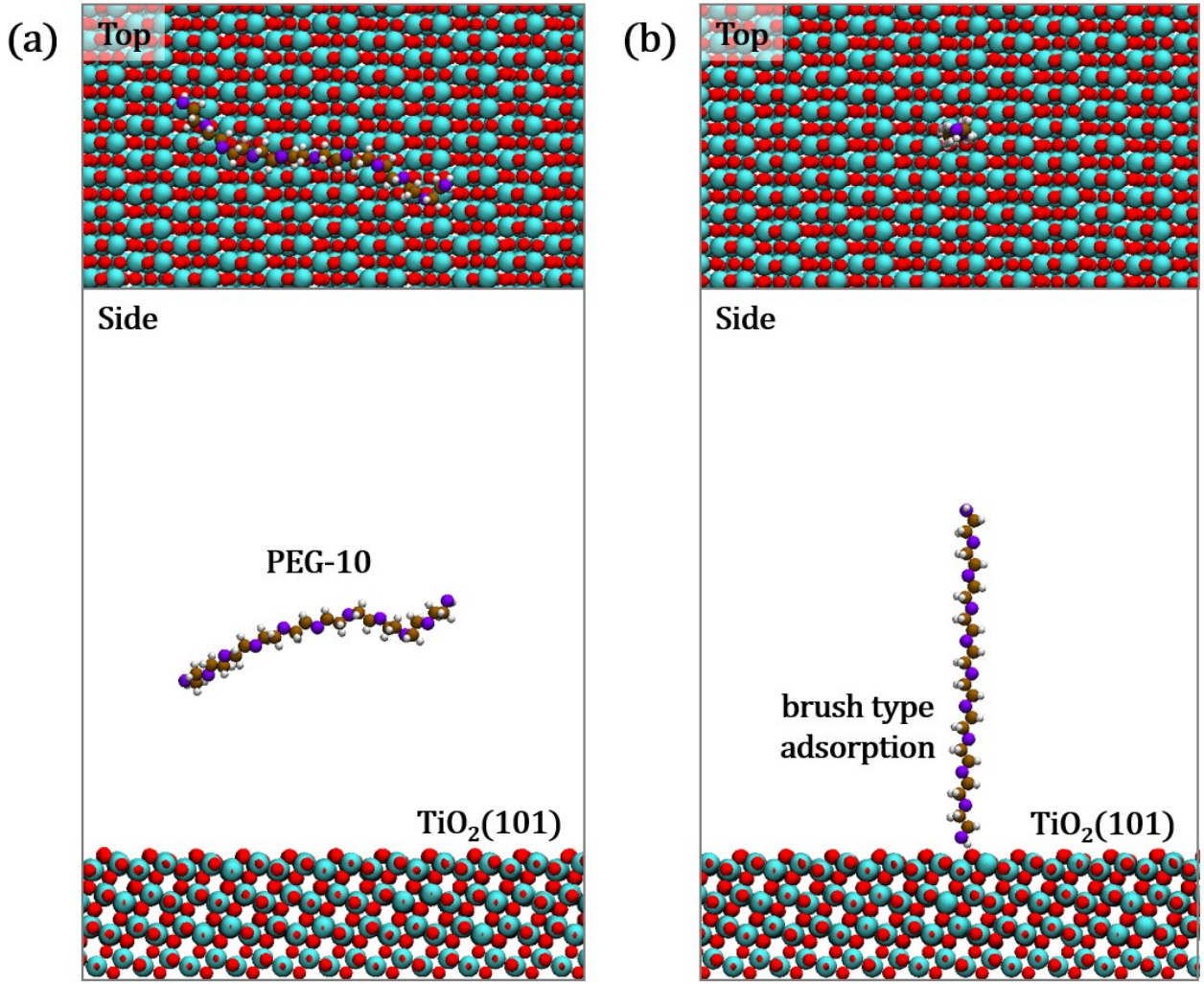

Fig. S9. Top and side views of PEG-10 adsorption on TiO_2(101) surface. (a) desorbed state and (b) adsorbed state.

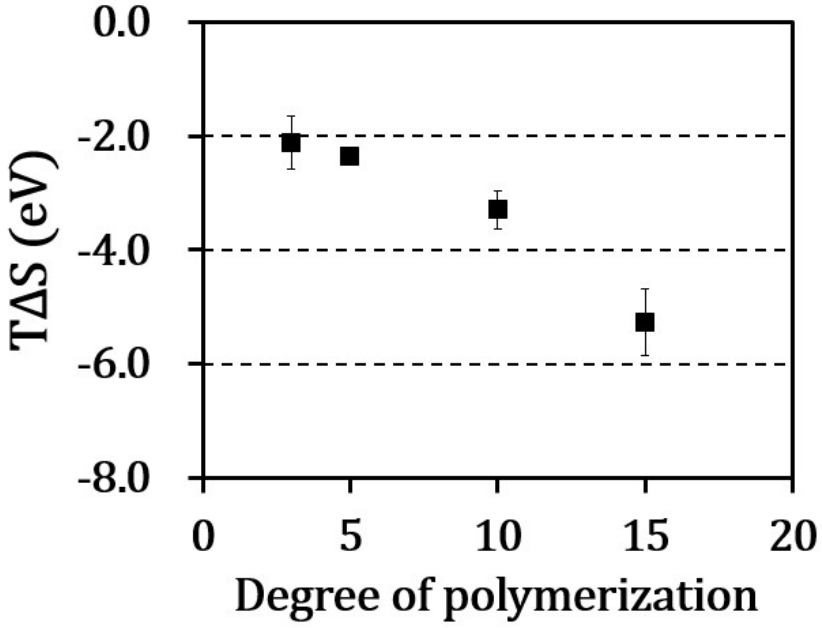

Fig. S10. $^{T\Delta S}{}_{PEG^*}$ values of PEG chain of varying degree of polymerization. Error bars corresponding to two standard deviations are drawn.

Table. S7. Estimated average and standard deviation of $^{T\Delta S}{}_{PEG^*}$ of PEG chain of varying degree of polymerization

Degree of polymerization	Average (eV)	Standard deviation (eV)
PEG-3	-2.12	0.24
PEG-5	-2.35	0.07
PEG-10	-3.29	0.17
PEG-15	-5.28	0.29

Section S6. ΔG_{ads} for PEG-5*

Table S8. Data for ΔG_{ads} of PEG-5* on TiO_2(101)

Coverage (ML)	E_{DFT} $_{PEG\_head^*(adsorption}$ (eV)[1]	E_{DFT} $_{PEG\_chain^*(interactio}$ (eV)[1]	E_{DFT} $_{PEG^*(solvation)}$ (eV)[1]	ΔH_{PEG^*} (eV)[1]	ΔZPE_{PEG^*} (eV)	$T\Delta S_{PEG^*}$ (eV)[2]	N[1,3]	H_2O^* desorption energy (eV/H_2O)[4]	Total H_2O^* desorption energy (eV)[5]	ΔG_{ads} (eV)[6]
0.25	-1.84	-0.03	-5.08	-6.95	0.17		1	0.08	0.08	-4.58
0.50	-3.92	-0.60	-8.62	-13.14	0.34		2	0.08	0.16	-8.41
0.75	-6.83	-2.21	-8.23	-17.27	0.50		3	0.08	0.24	-10.18
1.00	-8.36	-4.37	-4.22	-16.96	0.67		4	0.08	0.32	-7.50

$$\Delta H_{PEG^*} = E_{DFT\ PEG\_head^*(adsorption)} + E_{DFT\ PEG\_chain^*(interaction)} + E_{DFT\ PEG^*(solvation)}$$

[1] the values are from Tables S3-S6 in the SI /

[2] the values are from Section S4 in the SI.

[3] the total number of desorbed H_2O^*/unit cell during PEG adsorption

[4] the values are from Section S2 in the SI.

[5] Total H_2O^* desorption energy = $n \times$ H_2O^* desorption energy

[6] $\Delta G_{ads} = \Delta H_{PEG^*} + \Delta ZPE_{PEG^*} - \Delta S_{PEG^*} + Total\ H_2O^*\ desorption\ energy$

Table S9. Surface density of PEG-5* on the TiO_2(101) surfaces

PEG-5* coverage (ML)	Density of PEG-5* (/nm^2)
0.25	1.28
0.50	2.56
0.75	3.84
1.00	5.12

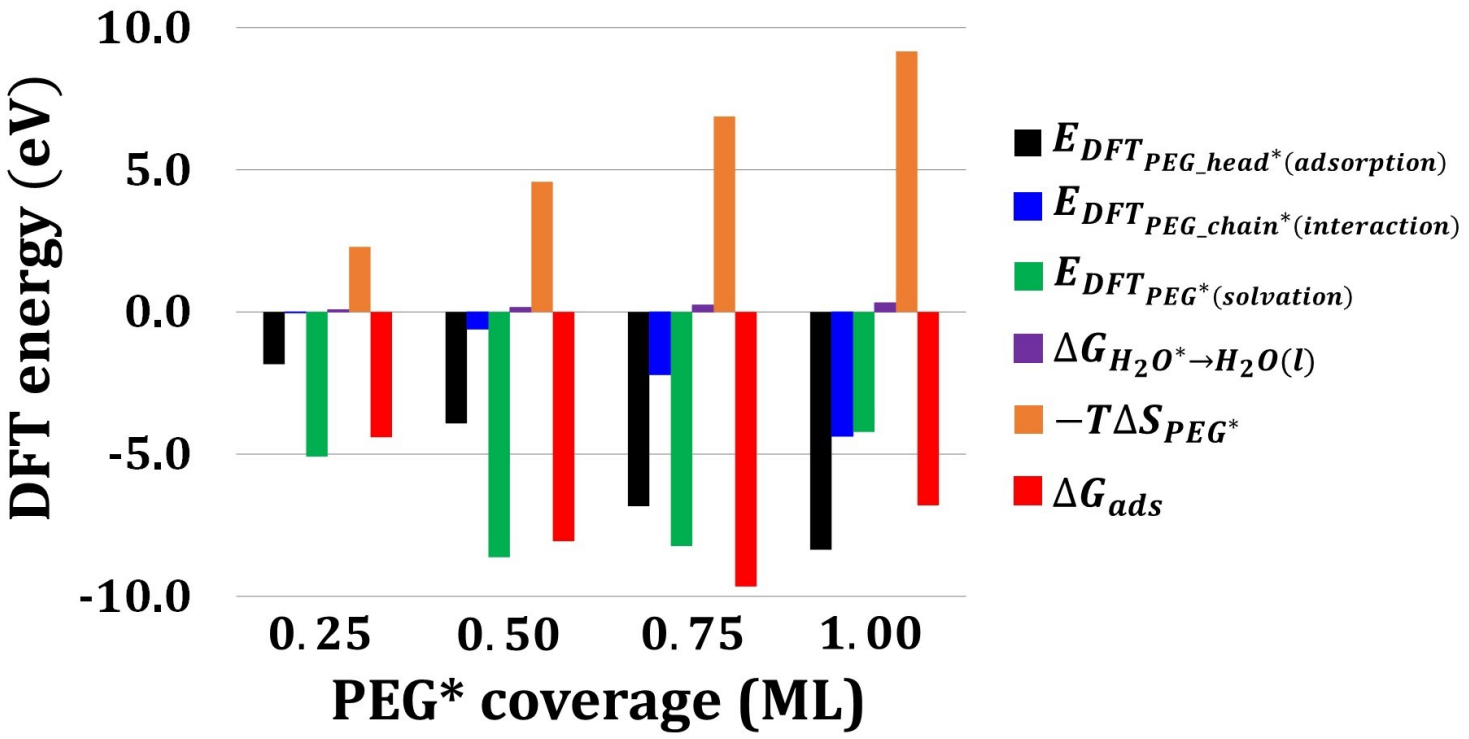

Fig. S11. Histograms for $E_{DFT_{PEG\_head^*(adsorption)}}$, $E_{DFT_{PEG\_chain^*(interaction)}}$, $E_{DFT_{PEG^*(solvation)}}$, $\Delta G_{H_2O^* \rightarrow H_2O(l)}$, $-T\Delta S_{PEG^*}$, and ΔG_{ads} of PEG-5* at different coverages.

Section S7. AIMD simulation results for PEG-3*, PEG-10*, and PEG-15*

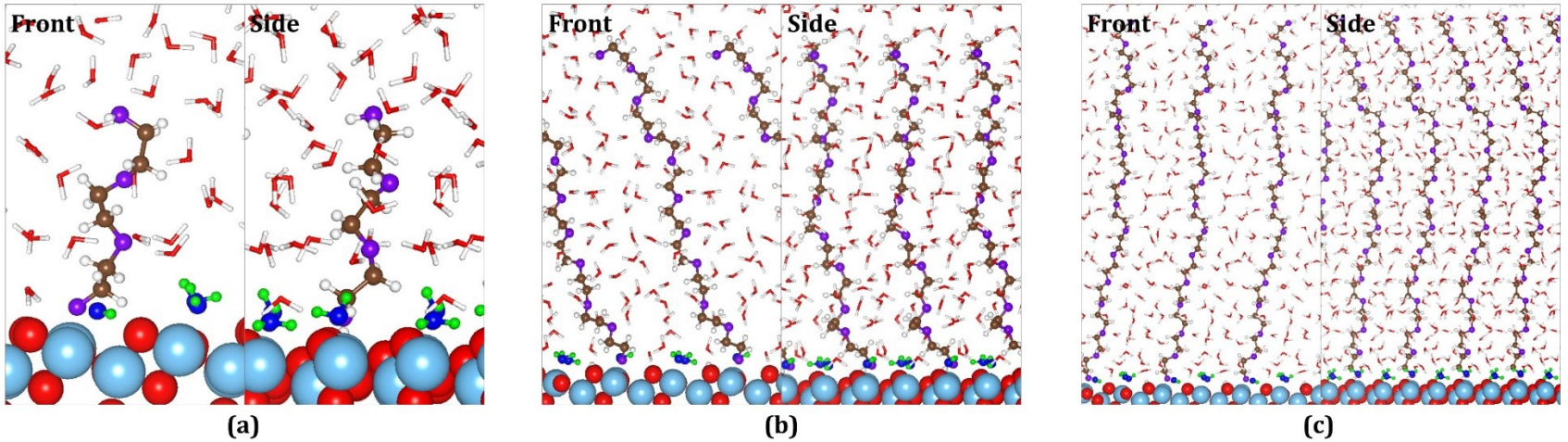

Fig. S12. Front and side views of the snapshots of $(PEG/H_2O(l)_{<1ML})^*$ (10 ps) on TiO_2(101). (a) PEG-3*, (b) PEG-10*, and (c) PEG-15*. The bulk liquid water is shown as a simplified. Light blue, Ti; red, O; blue, O of H_2O*; light green, H of H_2O*; purple, O of PEG*; brown, C; white, H.

Table S10. Data for 0.25 ML PEG-3* on TiO_2(101)

ps	$E_{DFT}{}_{(PEG/H_2O(l)<1ML)}$ (eV)	$E_{DFT}{}_{H_2O(l)<1ML}{}^*$ (eV)	$E_{DFT}{}_{PEG(g)}$ (undissociated) (eV)	$E_{DFT}{}_{PEG}{}^*$ (eV)	$E_{DFT}{}_*$ (slab) (eV)	$E_{DFT}{}_{PEG}$ (dissociated) (eV)[1)]	$E_{DFT}{}_{PEG(g)}$ (dissociated) (eV)[2)]	$E_{DFT}{}_{PEG\_head}{}^*{}_{(adsorption)}$ (eV)[3)]	$E_{DFT}{}_{PEG\_chain}{}^*{}_{(interaction)}$ (eV)[4)]
1	-1506.64	-1368.36	-133.03	-659.28	-524.27	-127.12	-127.10	-1.97	-0.01
2	-1506.56	-1368.06	-133.03	-659.46	-524.37	-127.10	-127.08	-2.05	-0.02
3	-1506.53	-1368.13	-133.03	-659.63	-524.29	-127.17	-127.14	-2.29	-0.02
4	-1506.84	-1368.48	-133.03	-659.80	-524.56	-127.12	-127.10	-2.19	-0.02
5	-1507.42	-1368.72	-133.03	-659.59	-524.63	-127.08	-127.06	-1.91	-0.02
6	-1507.38	-1369.16	-133.03	-659.64	-524.36	-127.10	-127.11	-2.25	0.01
7	-1507.31	-1369.07	-133.03	-659.34	-524.58	-126.93	-126.92	-1.73	-0.01
8	-1507.23	-1368.83	-133.03	-659.70	-524.20	-127.11	-127.09	-2.45	-0.02
9	-1507.27	-1368.97	-133.03	-659.54	-524.49	-127.06	-127.05	-2.01	-0.02
10	-1507.18	-1368.85	-133.03	-659.63	-524.54	-127.06	-126.95	-1.96	-0.10
Average	-1507.04	-1368.66	-133.03	-659.56	-524.43	-127.08	-127.06	-2.08 ± 0.20	-0.02 ± 0.03

Table S10. continued

ps	$E_{DFT}{}_{PEG}{}^*{}_{(solvation)}$ (eV)[5)]	$\Delta H_{PEG}{}^*$ (eV)[6)]	$E_{DFT}{}_{PEG\_head}{}^*{}_{(adsorption)}$ /# of PEG (eV/PEG)[7)]	$E_{DFT}{}_{PEG\_chain}{}^*{}_{(interaction)}$ /# of monomer (eV/monomer)[8)]	$\#_{H-bond}$[9)]	$E_{DFT}{}_{PEG}{}^*{}_{(solvation)}$ /# of O in PEG* (eV/monomer)[10)]	$\theta_{PEG}{}^*$ (ML)[11)]	$\theta_{H_2O}{}^*$ (ML)[12)]	N[13)]

1	-3.28	-5.26	-1.97	0.00	6	-0.82	0.25	0.75	1
2	-3.40	-5.47	-2.05	-0.01	7	-0.85	0.25	0.75	1
3	-3.05	-5.37	-2.29	-0.01	5	-0.76	0.25	0.75	1
4	-3.12	-5.33	-2.19	-0.01	5	-0.78	0.25	0.75	1
5	-3.74	-5.67	-1.91	-0.01	7	-0.94	0.25	0.75	1
6	-2.95	-5.19	-2.25	0.00	5	-0.74	0.25	0.75	1
7	-3.47	-5.21	-1.73	0.00	6	-0.87	0.25	0.75	1
8	-2.90	-5.37	-2.45	-0.01	5	-0.73	0.25	0.75	1
9	-3.25	-5.27	-2.01	-0.01	6	-0.81	0.25	0.75	1
10	-3.24	-5.30	-1.96	-0.03	6	-0.81	0.25	0.75	1
Average	-3.24 ± 0.24	-5.34 ± 0.13	-2.08	-0.01	5.80	-0.81	0.25	0.75	1.00

1) Single point calculation for dissociated PEG where the structure and unit cell are from $E_{DFT_{(PEG/H_2O(l)<1ML)^*}}$

2) Single point calculation for dissociated PEG where the structure is from $E_{DFT_{(PEG/H_2O(l)<1ML)^*}}$ in a large unit cell (no interactions between PEG)

3) $$E_{DFT_{PEG\_head^*(adsorption)}} = E_{DFT_{(PEG/H_2O(l)<1ML)^*}} - E_{DFT_{H_2O(l)<1ML^*}} - E_{DFT_{PEG(g)}}(undissociated) - \Delta E_{DFT_{PEG\_chain^*(interaction)}}$$

4) $$E_{DFT_{PEG\_chain^*(interaction)}} = E_{DFT_{PEG}}(dissociated) - the\ total\ number\ of\ dissociated\ PEG^*\ in\ the\ unit\ cell \times E_{DFT_{PEG(g)}}(dissociated)$$

5) $$E_{DFT_{PEG^*(solvation)}} = E_{DFT_{(PEG/H_2O(l)<1ML)^*}} - E_{DFT_{H_2O(l)<1ML^*}} - E_{DFT_{PEG^*}} + E_{DFT_*}$$

6) $$\Delta H_{PEG^*} = E_{DFT_{PEG\_head^*(adsorption)}} + E_{DFT_{PEG\_chain^*(interaction)}} + E_{DFT_{PEG^*(solvation)}}$$

7) $$\frac{E_{DFT_{PEG_{head}^*(adsorption)}}}{\#\ of\ PEG^*} = \frac{E_{DFT_{PEG\_head^*(adsorption)}}}{the\ total\ number\ of\ PEG^*\ in\ the\ unit\ cell}$$

8) $$\frac{E_{DFT_{PEG_{chain}^*(interaction)}}}{\#\ of\ monomer} = \frac{E_{DFT_{PEG\_chain^*(interaction)}}}{the\ total\ number\ of\ the\ PEG^*\ monomer\ in\ the\ unit\ cell}$$

9) the total hydrogen bond number between PEG* and surrounding H_2O(l) molecules

10) $$\frac{E_{DFT_{PEG^*(solvation)}}}{\#\ of\ O\ in\ PEG^*} = \frac{E_{DFT_{PEG^*(solvation)}}}{the\ total\ number\ of\ the\ oxygen\ atom\ in\ PEG^*\ in\ the\ unit\ cell}$$

11) the surface coverage of PEG* in the unit cell

12) the surface coverage of H_2O* in the unit cell

13) the total number of desorbed H_2O/unit cell during PEG adsorption

Table S11. Data for 0.25 ML PEG-10* on TiO_2(101)

ps	$E_{DFT}{}_{(PEG/H_2O(l)<1ML)^*}$ (eV)	$E_{DFT}{}_{H_2O(l)<1ML^*}$ (eV)	$E_{DFT}{}_{PEG(g)}$ (undissociated) (eV)	$E_{DFT}{}_{PEG^*}$ (eV)	$E_{DFT}{}_{*}$ (slab) (eV)	$E_{DFT}{}_{PEG}$ (dissociated) (eV)[1]	$E_{DFT}{}_{PEG(g)}$ (dissociated) (eV)[2]	$E_{DFT}{}_{PEG\_head^*(adsorption)}$ (eV)[3]	$E_{DFT}{}_{PEG\_chain^*(interaction)}$ (eV)[4]
1	-2463.75	-2042.25	-410.45	-937.18	-524.36	-404.76	-404.66	-2.27	-0.10
2	-2463.76	-2042.59	-410.45	-937.44	-524.61	-404.85	-404.76	-2.30	-0.09
3	-2465.23	-2043.20	-410.45	-937.41	-524.81	-404.79	-404.64	-2.00	-0.15
4	-2465.23	-2041.91	-410.45	-937.44	-524.83	-404.85	-404.66	-1.96	-0.20
5	-2465.14	-2042.94	-410.45	-937.26	-524.65	-404.74	-404.63	-2.05	-0.11
6	-2465.09	-2043.09	-410.45	-937.31	-524.77	-404.74	-404.62	-1.98	-0.11
7	-2464.50	-2042.28	-410.45	-937.28	-524.75	-404.71	-404.62	-2.00	-0.09
8	-2465.32	-2043.81	-410.45	-937.23	-524.61	-404.75	-404.65	-2.07	-0.10
9	-2465.81	-2044.26	-410.45	-937.21	-524.66	-404.74	-404.62	-1.99	-0.12
10	-2465.26	-2043.70	-410.45	-937.43	-524.81	-404.79	-404.67	-2.05	-0.12
Average	-2464.91	-2043.00	-410.45	-937.32	-524.69	-404.77	-404.65	-2.07 ± 0.11	-0.12 ± 0.03

Table S11. continued

ps	$E_{DFT}{}_{PEG^*(solvation)}$ (eV)[5]	ΔH_{PEG^*} (eV)[6]	$E_{DFT}{}_{PEG\_head^*(adsorption)}$ /# of PEG (eV/PEG)[7]	$E_{DFT}{}_{PEG\_chain^*(interaction)}$ /# of monomer (eV/monomer)[8]	$\#_{H-bond}$[9]	$E_{DFT}{}_{PEG^*(solvation)}$ /# of O in PEG* (eV/monomer)[10]	θ_{PEG^*} (ML)[11]	$\theta_{H_2O^*}$ (ML)[12]	N[13]
1	-8.68	-11.05	-2.27	-0.01	15	-0.79	0.25	0.75	1
2	-8.33	-10.72	-2.30	-0.01	16	-0.76	0.25	0.75	1
3	-9.43	-11.59	-2.00	-0.02	15	-0.86	0.25	0.75	1
4	-10.71	-12.87	-1.96	-0.02	16	-0.97	0.25	0.75	1
5	-9.58	-11.75	-2.05	-0.01	15	-0.87	0.25	0.75	1
6	-9.45	-11.55	-1.98	-0.01	15	-0.86	0.25	0.75	1
7	-9.67	-11.77	-2.00	-0.01	14	-0.88	0.25	0.75	1
8	-8.89	-11.06	-2.07	-0.01	12	-0.81	0.25	0.75	1
9	-9.00	-11.10	-1.99	-0.01	13	-0.82	0.25	0.75	1
10	-8.94	-11.11	-2.05	-0.01	13	-0.81	0.25	0.75	1
Average	-9.27 ± 0.63	-11.46 ± 0.58	-2.07	-0.01	14.40	-0.84	0.25	0.75	1.00

[1] Single point calculation for dissociated PEG where the structure and unit cell are from $E_{DFT}{}_{(PEG/H_2O(l)<1ML)^*}$

[2] Single point calculation for dissociated PEG where the structure is from $E_{DFT}{}_{(PEG/H_2O(l)<1ML)^*}$ in a large unit cell (no interactions between PEG)

[3] $E_{DFT}{}_{PEG\_head^*(adsorption)} = E_{DFT}{}_{(PEG/H_2O(l)<1ML)^*} - E_{DFT}{}_{H_2O(l)<1ML^*} - E_{DFT}{}_{PEG(g)}(undissociated) - \Delta E_{DFT}{}_{PEG\_chain^*(interaction)}$

[4] $E_{DFT}{}_{PEG\_chain^*(interaction)} = E_{DFT}{}_{PEG}(dissociated) - the\ total\ number\ of\ dissociated\ PEG^*\ in\ the\ unit\ cell \times E_{DFT}{}_{PEG(g)}(dissociated)$

[5] $E_{DFT}{}_{PEG^*(solvation)} = E_{DFT}{}_{(PEG/H_2O(l)<1ML)^*} - E_{DFT}{}_{H_2O(l)<1ML^*} - E_{DFT}{}_{PEG^*} + E_{DFT}{}_{*}$

[6] $\Delta H_{PEG^*} = E_{DFT}{}_{PEG\_head^*(adsorption)} + E_{DFT}{}_{PEG\_chain^*(interaction)} + E_{DFT}{}_{PEG^*(solvation)}$

$$\frac{E_{DFT}{}_{PEG_{head}{}^{*}(adsorption)}}{\#\ of\ PEG^{*}} = \frac{E_{DFT}{}_{PEG\_head^{*}(adsorption)}}{the\ total\ number\ of\ PEG^{*}\ in\ the\ unit\ cell}$$ 7)

$$\frac{E_{DFT}{}_{PEG_{chain}{}^{*}(interaction)}}{\#\ of\ monomer} = \frac{E_{DFT}{}_{PEG\_chain^{*}(interaction)}}{the\ total\ number\ of\ the\ PEG^{*}\ monomer\ in\ the\ unit\ cell}$$ 8)

9) the total hydrogen bond number between PEG* and surrounding H_2O(l) molecules

$$\frac{E_{DFT}{}_{PEG^{*}(solvation)}}{\#\ of\ O\ in\ PEG^{*}} = \frac{E_{DFT}{}_{PEG^{*}(solvation)}}{the\ total\ number\ of\ the\ oxygen\ atom\ in\ PEG^{*}\ in\ the\ unit\ cell}$$ 10)

11) the surface coverage of PEG* in the unit cell

12) the surface coverage of H_2O* in the unit cell

13) the total number of desorbed H_2O/unit cell during PEG adsorption

Table S12. Data for 0.25 ML PEG-15* on TiO_2(101)

ps	$E_{DFT}{}_{(PEG/H_2O(l)<1ML)}$ (eV)	$E_{DFT}{}_{H_2O(l)<1ML}{}^{*}$ (eV)	$E_{DFT}{}_{PEG(g)}$ (undissociated) (eV)	$E_{DFT}{}_{PEG^{*}}$ (eV)	$E_{DFT}{}_{*}$ (slab) (eV)	$E_{DFT}{}_{PEG}$ (dissociated) (eV)[1]	$E_{DFT}{}_{PEG(g)}$ (dissociated) (eV)[2]	$E_{DFT}{}_{PEG\_head^{*}(adsorption)}$ (eV)[3]	$E_{DFT}{}_{PEG\_chain^{*}(interaction)}$ (eV)[4]
1	-3088.16	-2464.39	-608.68	-1135.29	-524.68	-602.57	-602.41	-1.77	-0.16
2	-3090.94	-2468.54	-608.68	-1135.15	-524.71	-602.53	-602.42	-1.64	-0.12
3	-3090.71	-2467.12	-608.68	-1135.77	-524.86	-602.95	-602.82	-2.09	-0.14
4	-3091.52	-2468.84	-608.68	-1135.64	-524.69	-602.85	-602.73	-2.15	-0.12
5	-3090.95	-2467.75	-608.68	-1135.70	-524.49	-603.15	-602.99	-2.37	-0.17
6	-3090.80	-2468.01	-608.68	-1135.67	-524.78	-602.99	-602.76	-1.97	-0.23
7	-3092.03	-2469.03	-608.68	-1135.75	-524.87	-603.07	-602.96	-2.09	-0.11
8	-3092.21	-2469.39	-608.68	-1135.95	-524.91	-603.21	-603.06	-2.21	-0.15
9	-3091.44	-2468.11	-608.68	-1135.67	-524.59	-603.03	-602.90	-2.26	-0.14
10	-3090.82	-2468.24	-608.68	-1135.71	-524.93	-602.97	-602.84	-1.97	-0.13
Average	-3090.96	-2467.94	-608.68	-1135.63	-524.75	-602.93	-602.79	-2.05 ± 0.21	-0.15 ± 0.03

Table S12. continued

ps	$E_{DFT}{}_{PEG^{*}(solvation)}$ (eV)[5]	$\Delta H_{PEG^{*}}$ (eV)[6]	$E_{DFT}{}_{PEG\_head^{*}(adsorption)}$ /# of PEG (eV/PEG)[7]	$E_{DFT}{}_{PEG\_chain^{*}(interaction)}$ /# of monomer (eV/monomer)[8]	$\#_{H-bond}$[9]	$E_{DFT}{}_{PEG^{*}(solvation)}$ /# of O in PEG* (eV/monomer)[10]	$\theta_{PEG^{*}}$ (ML)[11]	$\theta_{H_2O^{*}}$ (ML)[12]	N[13]
1	-13.17	-15.10	-1.77	-0.01	21	-0.82	0.25	0.75	1
2	-11.97	-13.72	-1.64	-0.01	19	-0.75	0.25	0.75	1
3	-12.68	-14.91	-2.09	-0.01	22	-0.79	0.25	0.75	1
4	-11.74	-14.01	-2.15	-0.01	18	-0.73	0.25	0.75	1
5	-11.99	-14.52	-2.37	-0.01	18	-0.75	0.25	0.75	1
6	-11.91	-14.11	-1.97	-0.02	18	-0.74	0.25	0.75	1
7	-12.12	-14.32	-2.09	-0.01	17	-0.76	0.25	0.75	1

8	-11.77	-14.14	-2.21	-0.01	18	-0.74	0.25	0.75	1
9	-12.25	-14.65	-2.26	-0.01	21	-0.77	0.25	0.75	1
10	-11.80	-13.90	-1.97	-0.01	16	-0.74	0.25	0.75	1
Average	-12.14 ± 0.43	-14.34 ± 0.42	-2.05	-0.01	18.80	-0.76	0.25	0.75	1.00

[1] Single point calculation for dissociated PEG where the structure and unit cell are from $E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*}$

[2] Single point calculation for dissociated PEG where the structure is from $E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*}$ in a large unit cell (no interactions between PEG)

[3] $$E_{DFT}{}_{PEG\_head^*(adsorption)} = E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*} - E_{DFT}{}_{H_2O(l)<1ML^*} - E_{DFT}{}_{PEG(g)}(undissociated) - \Delta E_{DFT}{}_{PEG\_chain^*(interaction)}$$

[4] $$E_{DFT}{}_{PEG\_chain^*(interaction)} = E_{DFT}{}_{PEG}(dissociated) - the\ total\ number\ of\ dissociated\ PEG^*\ in\ the\ unit\ cell \times E_{DFT}{}_{PEG(g)}(dissociated)$$

[5] $$E_{DFT}{}_{PEG^*(solvation)} = E_{DFT}{}_{\left(PEG/H_2O(l)<1ML\right)^*} - E_{DFT}{}_{H_2O(l)<1ML^*} - E_{DFT}{}_{PEG^*} + E_{DFT}{}_{*}$$

[6] $$\Delta H_{PEG^*} = E_{DFT}{}_{PEG\_head^*(adsorption)} + E_{DFT}{}_{PEG\_chain^*(interaction)} + E_{DFT}{}_{PEG^*(solvation)}$$

[7] $$\frac{E_{DFT}{}_{PEG_{head}{}^*(adsorption)}}{\#\ of\ PEG^*} = \frac{E_{DFT}{}_{PEG\_head^*(adsorption)}}{the\ total\ number\ of\ PEG^*\ in\ the\ unit\ cell}$$

[8] $$\frac{E_{DFT}{}_{PEG_{chain}{}^*(interaction)}}{\#\ of\ monomer} = \frac{E_{DFT}{}_{PEG\_chain^*(interaction)}}{the\ total\ number\ of\ the\ PEG^*\ monomer\ in\ the\ unit\ cell}$$

[9] the total hydrogen bond number between PEG* and surrounding H_2O(l) molecules

[10] $$\frac{E_{DFT}{}_{PEG^*(solvation)}}{\#\ of\ O\ in\ PEG^*} = \frac{E_{DFT}{}_{PEG^*(solvation)}}{the\ total\ number\ of\ the\ oxygen\ atom\ in\ PEG^*\ in\ the\ unit\ cell}$$

[11] the surface coverage of PEG* in the unit cell

[12] the surface coverage of H_2O* in the unit cell

[13] the total number of desorbed H_2O/unit cell during PEG adsorption

Section S8. ΔG_{ads} for PEG-3*, PEG-5*, PEG-10*, and PEG-15*

Table S13. Data for ΔG_{ads} of PEG-3* on TiO_2(101)

Coverage (ML)	# of PEG* (#/unit cell)	# of PEG* monomer (#/unit cell)	# of oxygen atom in PEG* (#/unit cell)	$E_{DFT}{}_{PEG\_head^*(adsorption)}$ (eV)	$E_{DFT}{}_{PEG\_chain^*(interaction}$ (eV)	$E_{DFT}{}_{PEG^*(solvation)}$ (eV)	ΔH_{PEG^*} (eV)	ΔZPE_{PEG^*} (eV)	$T\Delta S_{PEG^*}$ (eV)
0.05	0.20	0.60	0.80	-0.52	-0.02	-0.62	-1.16	0.00	-0.50

0.10	0.40	1.20	1.60	-0.94	-0.02	-1.30	-2.27	-0.01	-1.00
0.15	0.60	1.80	2.40	-1.29	-0.02	-2.01	-3.32	-0.01	-1.50
0.20	0.80	2.40	3.20	-1.61	-0.02	-2.71	-4.34	-0.01	-2.00
0.25	1.00	3.00	4.00	-1.92	-0.03	-3.39	-5.34	-0.02	-2.51
0.30	1.20	3.60	4.80	-2.24	-0.05	-4.02	-6.31	-0.02	-3.01
0.35	1.40	4.20	5.60	-2.59	-0.09	-4.58	-7.27	-0.02	-3.51
0.40	1.60	4.80	6.40	-2.98	-0.16	-5.07	-8.21	-0.03	-4.01
0.45	1.80	5.40	7.20	-3.43	-0.25	-5.46	-9.13	-0.03	-4.51
0.50	2.00	6.00	8.00	-3.92	-0.36	-5.75	-10.03	-0.03	-5.01
0.55	2.20	6.60	8.80	-4.46	-0.50	-5.92	-10.88	-0.04	-5.51
0.60	2.40	7.20	9.60	-5.03	-0.67	-5.99	-11.69	-0.04	-6.01
0.65	2.60	7.80	10.40	-5.63	-0.87	-5.93	-12.43	-0.04	-6.52
0.70	2.80	8.40	11.20	-6.24	-1.09	-5.77	-13.09	-0.04	-7.02
0.75	3.00	9.00	12.00	-6.83	-1.32	-5.49	-13.64	-0.05	-7.52
0.80	3.20	9.60	12.80	-7.37	-1.58	-5.11	-14.06	-0.05	-8.02
0.85	3.40	10.20	13.60	-7.84	-1.84	-4.64	-14.32	-0.05	-8.52
0.90	3.60	10.80	14.40	-8.19	-2.11	-4.09	-14.38	-0.06	-9.02
0.95	3.80	11.40	15.20	-8.38	-2.37	-3.47	-14.22	-0.06	-9.52
1.00	4.00	12.00	16.00	-8.36	-2.62	-2.81	-13.80	-0.06	-10.02

Table S13. continued

Coverage (ML)	N	H_2O^* desorption energy (eV/H_2O)	Total H_2O^* desorption energy (eV)	ΔG_{ads} (eV)
0.05	0.20	0.08	0.02	-0.65
0.10	0.40	0.08	0.03	-1.24
0.15	0.60	0.08	0.05	-1.78
0.20	0.80	0.08	0.06	-2.29
0.25	1.00	0.08	0.08	-2.77
0.30	1.20	0.08	0.10	-3.23
0.35	1.40	0.08	0.11	-3.67
0.40	1.60	0.08	0.13	-4.10
0.45	1.80	0.08	0.14	-4.51
0.50	2.00	0.08	0.16	-4.89
0.55	2.20	0.08	0.18	-5.23
0.60	2.40	0.08	0.19	-5.52
0.65	2.60	0.08	0.21	-5.75
0.70	2.80	0.08	0.22	-5.89
0.75	3.00	0.08	0.24	-5.93
0.80	3.20	0.08	0.26	-5.83
0.85	3.40	0.08	0.27	-5.58
0.90	3.60	0.08	0.29	-5.13
0.95	3.80	0.08	0.30	-4.46
1.00	4.00	0.08	0.32	-3.52

Table S14. Data for ΔG_{ads} of PEG-5* on TiO_2(101)

Coverage (ML)	# of PEG* (#/unit cell)	# of PEG* monomer (#/unit cell)	# of oxygen atom in PEG* (#/unit cell)	$E_{DFT\ PEG\_head^*(adsorption)}$ (eV)	$E_{DFT\ PEG\_chain^*(interaction}$ (eV)	$E_{DFT\ PEG^*(solvation)}$ (eV)	ΔH_{PEG^*} (eV)	ΔZPE_{PEG^*} (eV)	$T\Delta S_{PEG^*}$ (eV)
0.05	0.20	2.00	2.20	-0.52	-0.06	-1.71	-2.30	-0.01	-0.92
0.10	0.40	4.00	4.40	-0.94	-0.08	-3.58	-4.60	-0.01	-1.84
0.15	0.60	6.00	6.60	-1.29	-0.07	-5.52	-6.89	-0.02	-2.76
0.20	0.80	8.00	8.80	-1.61	-0.07	-7.45	-9.14	-0.02	-3.68
0.25	1.00	10.00	11.00	-1.92	-0.10	-9.32	-11.34	-0.03	-4.60
0.30	1.20	12.00	13.20	-2.24	-0.18	-11.05	-13.47	-0.03	-5.52
0.35	1.40	14.00	15.40	-2.59	-0.32	-12.61	-15.52	-0.04	-6.44
0.40	1.60	16.00	17.60	-2.98	-0.53	-13.94	-17.45	-0.04	-7.36
0.45	1.80	18.00	19.80	-3.43	-0.82	-15.02	-19.27	-0.05	-8.28
0.50	2.00	20.00	22.00	-3.92	-1.21	-15.81	-20.93	-0.05	-9.20
0.55	2.20	22.00	24.20	-4.46	-1.68	-16.29	-22.43	-0.06	-10.12
0.60	2.40	24.00	26.40	-5.03	-2.24	-16.46	-23.74	-0.06	-11.04
0.65	2.60	26.00	28.60	-5.63	-2.89	-16.32	-24.84	-0.07	-11.96
0.70	2.80	28.00	30.80	-6.24	-3.62	-15.85	-25.71	-0.08	-12.88
0.75	3.00	30.00	33.00	-6.83	-4.41	-15.09	-26.33	-0.08	-13.80
0.80	3.20	32.00	35.20	-7.37	-5.26	-14.05	-26.68	-0.09	-14.72
0.85	3.40	34.00	37.40	-7.84	-6.13	-12.75	-26.72	-0.09	-15.64
0.90	3.60	36.00	39.60	-8.19	-7.03	-11.24	-26.45	-0.10	-16.56
0.95	3.80	38.00	41.80	-8.38	-7.90	-9.55	-25.83	-0.10	-17.48
1.00	4.00	40.00	44.00	-8.36	-8.74	-7.74	-24.85	-0.11	-18.40

Table S14. continued

Coverage (ML)	N	H_2O^* desorption energy (eV/H_2O)	Total H_2O^* desorption energy (eV)	ΔG_{ads} (eV)
0.05	0.20	0.08	0.02	-1.37
0.10	0.40	0.08	0.03	-2.74
0.15	0.60	0.08	0.05	-4.09
0.20	0.80	0.08	0.06	-5.41
0.25	1.00	0.08	0.08	-6.69
0.30	1.20	0.08	0.10	-7.89
0.35	1.40	0.08	0.11	-9.00
0.40	1.60	0.08	0.13	-10.01
0.45	1.80	0.08	0.14	-10.89
0.50	2.00	0.08	0.16	-11.62
0.55	2.20	0.08	0.18	-12.19
0.60	2.40	0.08	0.19	-12.57
0.65	2.60	0.08	0.21	-12.74
0.70	2.80	0.08	0.22	-12.68

0.75	3.00	0.08	0.24	-12.37
0.80	3.20	0.08	0.26	-11.79
0.85	3.40	0.08	0.27	-10.90
0.90	3.60	0.08	0.29	-9.70
0.95	3.80	0.08	0.30	-8.15
1.00	4.00	0.08	0.32	-6.23

Table S15. Data for ΔG_{ads} of PEG-10* on TiO_2(101)

Coverage (ML)	# of PEG* (#/unit cell)	# of PEG* monomer (#/unit cell)	# of oxygen atom in PEG* (#/unit cell)	$E_{DFT\ PEG\_head^*(adsorption)}$ (eV)	$E_{DFT\ PEG\_chain^*(interaction}$ (eV)	$E_{DFT\ PEG^*(solvation)}$ (eV)	ΔH_{PEG^*} (eV)	ΔZPE_{PEG^*} (eV)	$T\Delta S_{PEG^*}$ (eV)
0.05	0.20	2.00	2.20	-0.52	-0.06	-1.71	-2.30	-0.01	-0.64
0.10	0.40	4.00	4.40	-0.94	-0.08	-3.58	-4.60	-0.01	-1.27
0.15	0.60	6.00	6.60	-1.29	-0.07	-5.52	-6.89	-0.02	-1.91
0.20	0.80	8.00	8.80	-1.61	-0.07	-7.45	-9.14	-0.02	-2.55
0.25	1.00	10.00	11.00	-1.92	-0.10	-9.32	-11.34	-0.03	-3.19
0.30	1.20	12.00	13.20	-2.24	-0.18	-11.05	-13.47	-0.03	-3.82
0.35	1.40	14.00	15.40	-2.59	-0.32	-12.61	-15.52	-0.04	-4.46
0.40	1.60	16.00	17.60	-2.98	-0.53	-13.94	-17.45	-0.04	-5.10
0.45	1.80	18.00	19.80	-3.43	-0.82	-15.02	-19.27	-0.05	-5.74
0.50	2.00	20.00	22.00	-3.92	-1.21	-15.81	-20.93	-0.05	-6.37
0.55	2.20	22.00	24.20	-4.46	-1.68	-16.29	-22.43	-0.06	-7.01
0.60	2.40	24.00	26.40	-5.03	-2.24	-16.46	-23.74	-0.06	-7.65
0.65	2.60	26.00	28.60	-5.63	-2.89	-16.32	-24.84	-0.07	-8.29
0.70	2.80	28.00	30.80	-6.24	-3.62	-15.85	-25.71	-0.08	-8.92
0.75	3.00	30.00	33.00	-6.83	-4.41	-15.09	-26.33	-0.08	-9.56
0.80	3.20	32.00	35.20	-7.37	-5.26	-14.05	-26.68	-0.09	-10.20
0.85	3.40	34.00	37.40	-7.84	-6.13	-12.75	-26.72	-0.09	-10.84
0.90	3.60	36.00	39.60	-8.19	-7.03	-11.24	-26.45	-0.10	-11.47
0.95	3.80	38.00	41.80	-8.38	-7.90	-9.55	-25.83	-0.10	-12.11
1.00	4.00	40.00	44.00	-8.36	-8.74	-7.74	-24.85	-0.11	-12.75

Table S15. continued

Coverage (ML)	N	H_2O^* desorption energy (eV/H_2O)	Total H_2O^* desorption energy (eV)	ΔG_{ads} (eV)
0.05	0.20	0.08	0.02	-1.65
0.10	0.40	0.08	0.03	-3.30
0.15	0.60	0.08	0.05	-4.94
0.20	0.80	0.08	0.06	-6.55
0.25	1.00	0.08	0.08	-8.10
0.30	1.20	0.08	0.10	-9.58
0.35	1.40	0.08	0.11	-10.98

0.40	1.60	0.08	0.13	-12.27
0.45	1.80	0.08	0.14	-13.43
0.50	2.00	0.08	0.16	-14.45
0.55	2.20	0.08	0.18	-15.30
0.60	2.40	0.08	0.19	-15.96
0.65	2.60	0.08	0.21	-16.42
0.70	2.80	0.08	0.22	-16.64
0.75	3.00	0.08	0.24	-16.61
0.80	3.20	0.08	0.26	-16.31
0.85	3.40	0.08	0.27	-15.71
0.90	3.60	0.08	0.29	-14.79
0.95	3.80	0.08	0.30	-13.52
1.00	4.00	0.08	0.32	-11.88

Table S16. Data for ΔG_{ads} of PEG-15* on TiO_2(101)

Coverage (ML)	# of PEG* (#/unit cell)	# of PEG* monomer (#/unit cell)	# of oxygen atom in PEG* (#/unit cell)	$E_{DFT\ PEG\_head^*(adsorption)}$ (eV)	$E_{DFT\ PEG\_chain^*(interaction}$ (eV)	$E_{DFT\ PEG^*(solvation)}$ (eV)	ΔH_{PEG^*} (eV)	ΔZPE_{PEG^*} (eV)	$T\Delta S_{PEG^*}$ (eV)
0.05	0.20	3.00	3.20	-0.52	-0.10	-2.49	-3.11	-0.02	-1.15
0.10	0.40	6.00	6.40	-0.94	-0.12	-5.21	-6.27	-0.05	-2.30
0.15	0.60	9.00	9.60	-1.29	-0.11	-8.03	-9.43	-0.07	-3.45
0.20	0.80	12.00	12.80	-1.61	-0.11	-10.84	-12.56	-0.09	-4.60
0.25	1.00	15.00	16.00	-1.92	-0.16	-13.55	-15.63	-0.11	-5.75
0.30	1.20	18.00	19.20	-2.24	-0.27	-16.08	-18.59	-0.14	-6.90
0.35	1.40	21.00	22.40	-2.59	-0.47	-18.34	-21.41	-0.16	-8.05
0.40	1.60	24.00	25.60	-2.98	-0.79	-20.28	-24.05	-0.18	-9.20
0.45	1.80	27.00	28.80	-3.43	-1.23	-21.84	-26.50	-0.20	-10.35
0.50	2.00	30.00	32.00	-3.92	-1.81	-22.99	-28.72	-0.23	-11.50
0.55	2.20	33.00	35.20	-4.46	-2.52	-23.70	-30.67	-0.25	-12.65
0.60	2.40	36.00	38.40	-5.03	-3.37	-23.95	-32.34	-0.27	-13.80
0.65	2.60	39.00	41.60	-5.63	-4.34	-23.73	-33.70	-0.29	-14.95
0.70	2.80	42.00	44.80	-6.24	-5.43	-23.06	-34.73	-0.32	-16.10
0.75	3.00	45.00	48.00	-6.83	-6.62	-21.95	-35.40	-0.34	-17.25
0.80	3.20	48.00	51.20	-7.37	-7.89	-20.43	-35.69	-0.36	-18.40
0.85	3.40	51.00	54.40	-7.84	-9.20	-18.55	-35.59	-0.38	-19.55
0.90	3.60	54.00	57.60	-8.19	-10.54	-16.34	-35.07	-0.41	-20.70
0.95	3.80	57.00	60.80	-8.38	-11.86	-13.89	-34.12	-0.43	-21.85
1.00	4.00	60.00	64.00	-8.36	-13.12	-11.26	-32.74	-0.45	-23.00

Table S16. continued

Coverage (ML)	N	H_2O^* desorption energy (eV/H_2O)	Total H_2O^* desorption energy (eV)	ΔG_{ads} (eV)

0.05	0.20	0.08	0.02	-1.97
0.10	0.40	0.08	0.03	-3.98
0.15	0.60	0.08	0.05	-6.00
0.20	0.80	0.08	0.06	-7.99
0.25	1.00	0.08	0.08	-9.91
0.30	1.20	0.08	0.10	-11.73
0.35	1.40	0.08	0.11	-13.40
0.40	1.60	0.08	0.13	-14.91
0.45	1.80	0.08	0.14	-16.21
0.50	2.00	0.08	0.16	-17.29
0.55	2.20	0.08	0.18	-18.10
0.60	2.40	0.08	0.19	-18.63
0.65	2.60	0.08	0.21	-18.84
0.70	2.80	0.08	0.22	-18.72
0.75	3.00	0.08	0.24	-18.25
0.80	3.20	0.08	0.26	-17.40
0.85	3.40	0.08	0.27	-16.15
0.90	3.60	0.08	0.29	-14.49
0.95	3.80	0.08	0.30	-12.40
1.00	4.00	0.08	0.32	-9.87

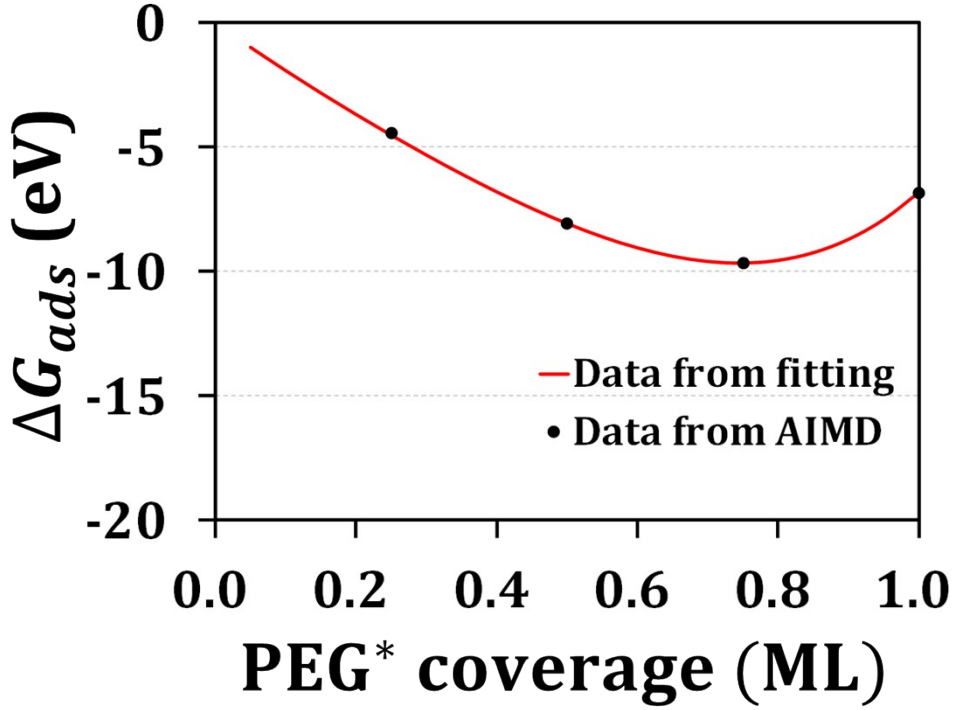

Fig. S13. Coverage-dependent $^{\Delta G_{ads}}$ for PEG-5* on TiO_2(101). The black dots represent the data points from Fig. 11 in the main text, while the red line is the data obtained using the fitting lines in Fig. 4 in the main text.

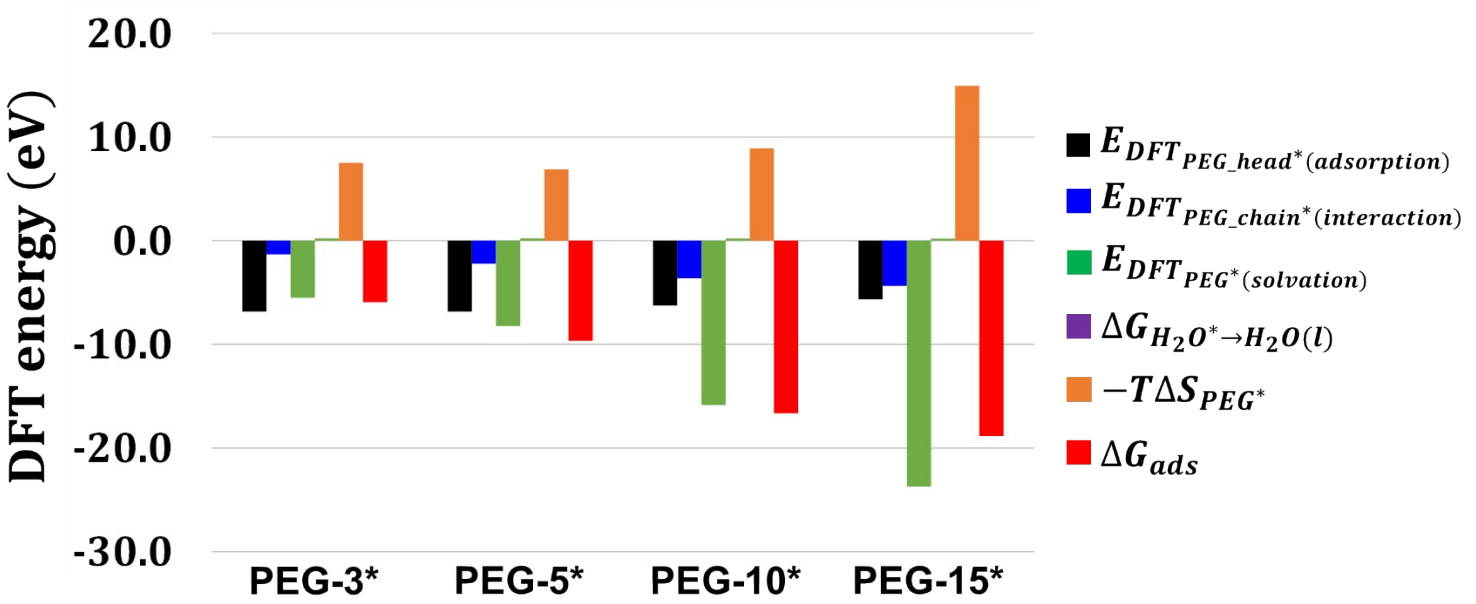

Fig. S14. Histograms for $E_{DFT_{PEG\_head^*(adsorption)}}$, $E_{DFT_{PEG\_chain^*(interaction)}}$, $E_{DFT_{PEG^*(solvation)}}$, $\Delta G_{H_2O^* \rightarrow H_2O(l)}$, $-T\Delta S_{PEG^*}$, and ΔG_{ads} of PEG-3*, PEG-5*, PEG-10*, and PEG-15* at each saturated coverage.

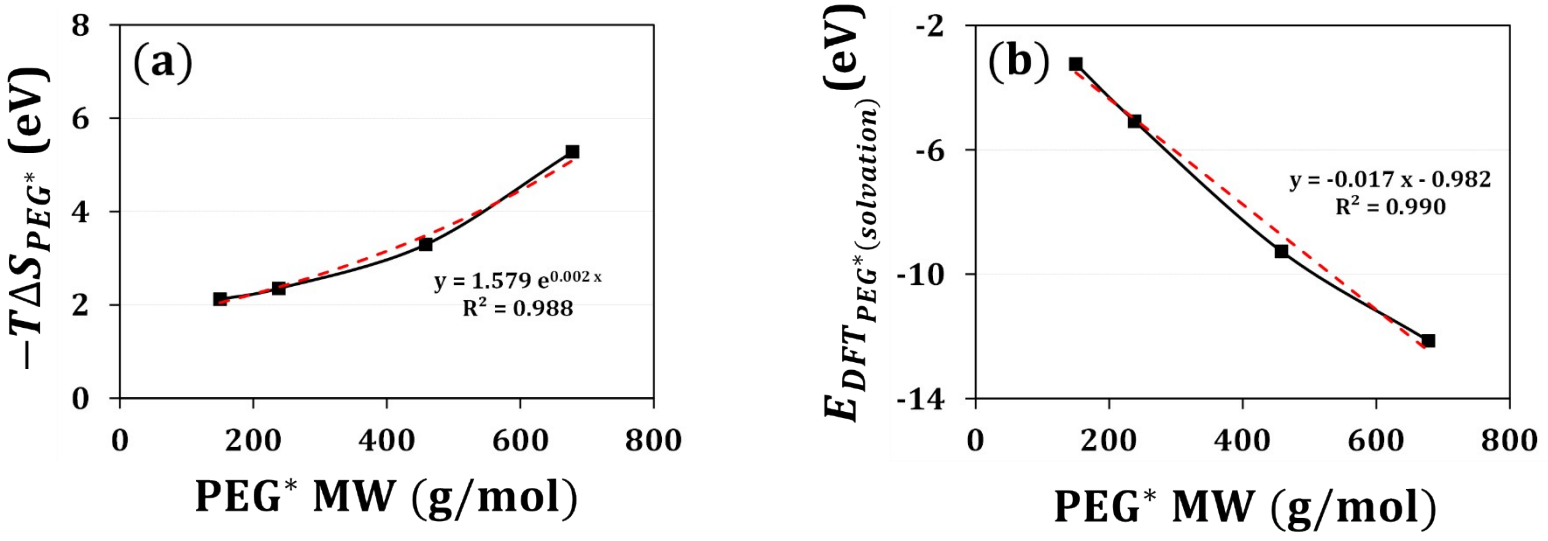

Fig. S15. PEG* MW-dependent (a) $-T\Delta S_{PEG^*}$ and (b) $E_{DFT_{PEG^*(solvation)}}$. The red dotted lines represent the trend lines.

References

S1. M. W. Chase, C. A. Davies, J. R. Downey, D. J. Frurip, R. A. McDonald and A. N. Syverud, *J. Phys. Chem. Ref. Data, Suppl.*, 1985, **14**, 1-926.

S2. Y. A. Zhu, D. Chen, X. G. Zhou and W. K. Yuan, *Catal. Today*, 2009, **148**, 260-267.

S3. G. Henkelman, B. P. Uberuaga and H. Jónsson, *J. Chem. Phys.*, 2000, **113**, 9901-9904.